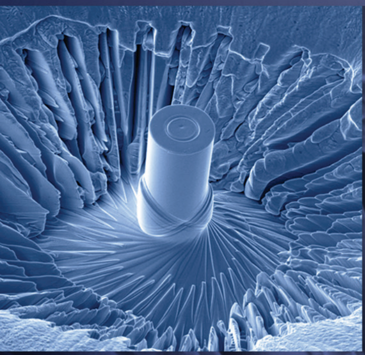
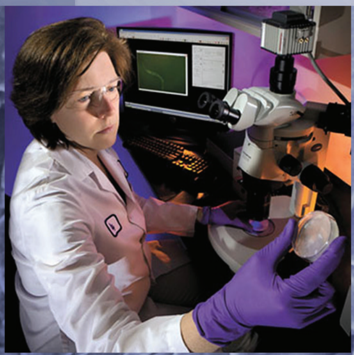
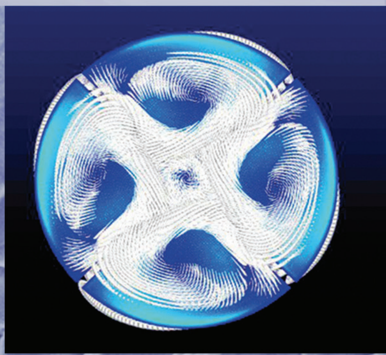
LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

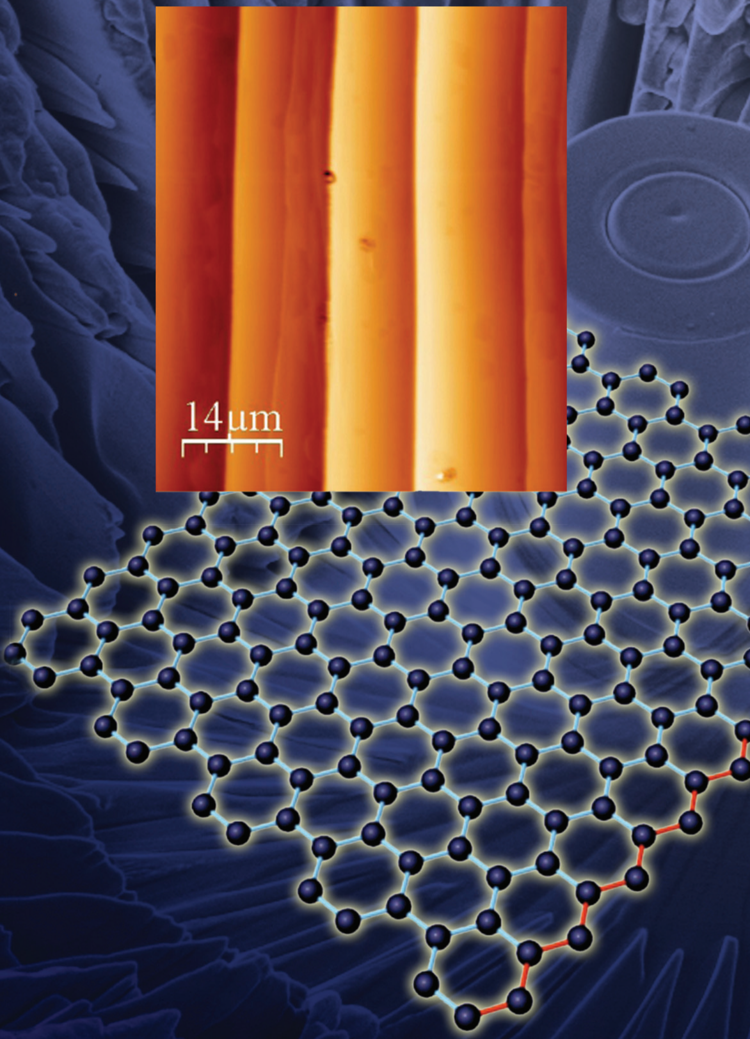
LDRD

ANNUAL REPORT 2010







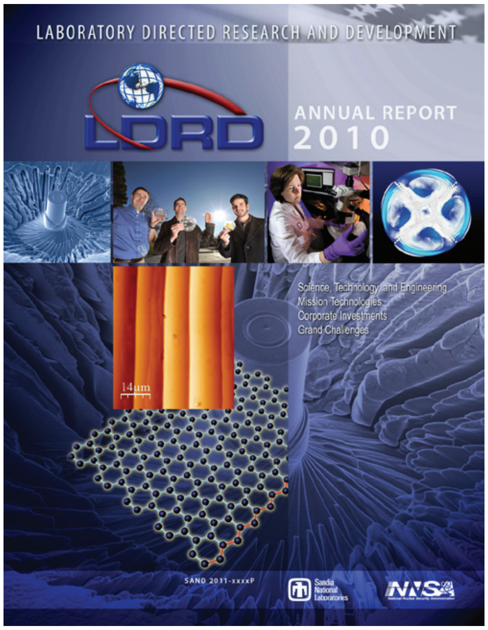


Science, Technology, and Engineering
Mission Technologies
Corporate Investments
Grand Challenges

SAND 2011-1924P

Sandia National Laboratories

NNSA National Nuclear Security Administration



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Cover photos:
Top Strip (left to right)
Left: Electron micrograph of a self ion irradiated Cu micropillar produced by focused ion beam milling; *left-center*: Sandians Murat Okandan, Greg Nielson, and Jose Luis Cruz-Campa hold samples containing arrays of microsolar cells only a few hundreds of micrometers in diameter; *right-center*: Cathy Branda examines specimens in her research to discover new systems for rapid detection of microorganisms; *right*: computational model of turbulent flow within contactor extraction device for nuclear waste reprocessing.

Lower Panel:
Superimposed on the Cu micropillar image is a micrograph (gold) of layered graphene sheets grown on silicon carbide and a drawing of the hexagonal bonding arrangement of the single layer of carbon atoms in graphene

Abstract

This report summarizes progress from the Laboratory Directed Research and Development (LDRD) program during fiscal year 2010. In addition to a programmatic and financial overview, the report includes progress reports from 432 individual R&D projects in 11 categories.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

SAND 2011-1924P
March 2011

LDRD Annual Report Staff:

Sandia National Laboratories

Hank Westrich
Sheri Martinez
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Donna Chavez

Contents

Sandia National Laboratories' FY 2010 Laboratory Directed Research and Development (LDRD) Program:

Discretionary Research and Development for the Future of the Labs!

J. Stephen Rottler , Vice President of Science, Technology, and Engineering and Chief Technology Officer

As authorized by Congress, the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories (SNL) is critical to maintaining the vitality of our Labs in mission-critical science and engineering (S&E) disciplines. As SNL's sole discretionary R&D program, LDRD enables our technical staff to pursue innovative, high-risk and potentially high-value research and development (R&D) for a range of difficult S&E challenges facing our nation. Through LDRD, the Labs can pursue game-changing S&E, develop the next generation of mission-critical capabilities, and seek innovative solutions for emerging technical surprises. In turn, innovation in each of these arenas is crucial to our overall mission of providing "exceptional service in the national interest."

Often described as the "seed corn" for SNL's future S&E capabilities development, the Lab's LDRD portfolio must be simultaneously at the forefront of science and engineering theory and practice and aligned with our Labs' national security missions. In addition, LDRD supports crosscutting R&D in nuclear, energy, and cyber security arenas to seek innovative technical solutions for these emerging S&E challenges facing our nation in the Twenty-First Century and beyond. These discretionary investments often provide benefits to multiple missions, frequently demonstrating a broader impact, unanticipated in the initial proposal. A robust peer-review process results in a 10-fold down-selection in the process of choosing funded projects from initially submitted ideas, resulting in the selection of only the highest quality R&D projects that are well-aligned with Sandia's national security missions. To maximize impact on national security, LDRD accomplishments are immediately leveraged by management who are actively engaged with direct programs.

The FY 2010 LDRD program sponsored 432 projects costing $156M. This annual report offers an overview of the LDRD projects that were ongoing in FY 2010, highlighting only a few examples to demonstrate the scope of LDRD investments. The program overview and project summaries provide a window into the program's S&E innovation and its potential for impact on national imperatives.

SANDIA FY 2010 PROGRAM OVERVIEW

PROGRAM PURPOSE

With the overarching goal of supporting the future missions of the Department of Energy/National Nuclear Security Administration (DOE/NNSA), the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories is advancing the frontiers of science and technology to enable and support our national security missions. Through pursuit of innovative, leading-edge science and engineering research and development (R&D), the LDRD program nurtures our core science and engineering capabilities and supports the development of staff technical expertise. With a budget of $156.0 M for the funding of 432 projects in FY 2010, the program has underwritten a myriad of high-risk science, technology, and engineering (ST&E), often in collaboration with scientists and engineers in academia, corporations and at other DOE laboratories. It has yielded outcomes contributing to nuclear, homeland, cyber, infrastructure, energy, climate, health, and intelligence security — in areas as diverse as nuclear weapons systems, novel sensor concepts and technologies, quantum science and technology, nanotechnology, metamaterials, computational modeling and simulation, carbon-neutral energy, molecular biology and biomedicine, and cognitive science. In turn, the outcomes of this research support DOE missions in nuclear security, energy security, environmental responsibility, and scientific discovery.

In supporting these national security missions, LDRD helps attract the best and brightest available scientists and engineers as new staff. This is an important component of the LDRD program in that it sustains Sandia's capabilities over the long term, the program serving as a training and mentoring vehicle to acclimate new staff to the research environment and to the unique responsibilities of advancing the frontier of national-security S&T. These staff members in turn, disseminate program outcomes through refereed publications and invited presentations — in numbers disproportionate to the size of the program — and their research has translated into numerous R&D 100 Awards (recognizing the nation's most innovative research and development) and laboratory patents. These outcomes form an important component underpinning our national and international ST&E leadership, while playing a key role in maintaining and enhancing our national security both at present and into the future.

It is the purpose of this annual report to summarize and delineate the spectrum of research supported by the Sandia LDRD program, presenting each project's purpose, outcomes, and significance in the context of both the Laboratories' mission and the broader national security context.

PROGRAM DESCRIPTION

ORGANIZATION: Responsibility for the Sandia LDRD program rests with the Sandia President, who delegates policy and process authority to the Chief Technology Officer (CTO). Reporting to the CTO, the LDRD Office is responsible for day-to-day program management, process development, final proposal review, monitoring of outcomes, reporting to the responsible NNSA entities, and when appropriate, conducting periodic operational program reviews for the purpose of recommending process amendments. To that end, the LDRD office conducted a web-based program survey of principal investigators (PIs) and project managers (PMs) in FY 2010, the results of which have engendered a series of recommendations to the CTO. Consequently, the program anticipates introducing procedural amendments to its project selection process for FY 2011 and FY 2012.

PROGRAM STRUCTURE: The detailed program structure, encompassing the 11 investment areas (IAs) organized under the four global categories or Program Areas of Sandia LDRD research investments is as follows (note that more-detailed descriptions of each IA, with summarized exemplary projects, can be found as sectional introductions within the body of this document, prior to the corpus of project reports for that particular IA; see pages 21, 97, 199, 249, 293, 396, 467, 515, 563, 576, and 604). Within the LDRD Mission Technologies Program Area, four of the 11 IAs support the four Sandia Mission Technology (MT) strategic management units (SMUs). Four IAs aim at conducting more-fundamental research under the aegis of the Science, Technology and Engineering Foundations (ST&E) Program Area; two IAs under the "Corporate Investments" Program Area are aimed at very high risk or university-collaborative research; and the eleventh IA (Grand Challenges) is multidisciplinary in scope. Newly initiated for FY 2010, an Early Career R&D LDRD program (described below) provides funding for LDRD projects that can fall within the scope of the 8 IAs in the MT and ST&E program areas.

PROGRAM AREA: Mission Technologies

Four Investment Areas:

- Defense Systems and Assessments — supporting the mission of the Department of defense (DoD) and the Intelligence community
- Nuclear Weapons — supporting the mission of the nuclear stockpile and the life extension program
- Energy, Resources, and Nonproliferation — supporting energy, water, climate, and global security missions
- Homeland Security — supporting the mission of the Department of Homeland Security (DHS)

PROGRAM AREA: Science, Technology, and Engineering Foundations

Four Investment Areas:

- Nanoscience to Microsystems — nanotechnology and microelectronics
- Enabling Predictive Simulation — engineering sciences, computational algorithm and hardware development
- New Directions — biological and cognitive science and technology
- Science of Extreme Environments — high-energy-density physics, radiation sciences, pulsed power, and fusion energy

PROGRAM AREA: Corporate Investments

Two Investment Areas:

- Strategic Partnerships — collaborative university R&D and partnering for advancing mutual ST&E capabilities
- Seniors' Council — novel, very high risk, high-impact R&D feasibility projects

PROGRAM AREA: Grand Challenges

Investment Area: Grand Challenges — broad-scope multidisciplinary projects addressing our nation's most-difficult problems

FUNDING PROCESS: The LDRD office coordinates with the director leads for each IA and the Senior Steering Committee (SSC), consisting of senior managers who represent each of the 11 investment areas delineated above. The IA directors and the SSC, with recommendations and direction from the LDRD office, helps develop policy to streamline the proposal evaluation processes and to encourage innovation and risk-taking in LDRD concept generation. Moreover, the IA directors and their management teams direct the crafting of the Call for Ideas. Each of the IA Calls elaborates that investment area's prioritized research interests, thereby providing a set of guidelines for technical staff in terms of the topics toward which research ideas should be directed in order to receive optimal consideration for funding. Once those staff ideas are submitted, the IA directors and their management teams direct reviews of those ideas, and subsequently, of full research proposals culled from those ideas that are both technically the most compelling and that best fit the parameters of the Call. The selected proposals are aligned with the overarching LDRD mandate that research proposals be leading-edge and entertain significant risk. Technical qualifications of staff composing a project's R&D team also factor into the decision about which projects will receive funding.

Subsequent to dissemination of the IA Calls, a web-based idea-submission process permits any regular employee to submit a 500-word idea (1000 words for a Grand Challenge idea). During FY 2010, 880 ideas were submitted, from which 184 were down-selected and invited to submit new (initial-funding) proposals. Generally, approximately half these proposals are approved for funding. In FY 2010, 88 new projects were funded, a final funding rate of 10% (88 of 880 ideas). To these 88 were added 151 late-start projects for a total new project count of 239 (included in this number were 21 "Early Career R&D," a new category of LDRD projects, as described below). These 239 newly funded projects were added to 193 continuing projects yielding a total of 432 LDRD projects funded for the fiscal year.

EARLY CAREER R&D (ECRD)

Initiated in FY 2010, the ECRD component of the LDRD program makes a maximum of $250 K of LDRD funding available to any Ph.D.-recipient staff member whose employment at Sandia commenced after October 1, 2010. ECRD is designed to smooth transition into the workforce, particularly for those individuals entering Sandia directly from a research-focused doctoral or postdoctoral program, enabling them to sustain that focus on creative activity, while simultaneously acclimating them to the national laboratory environment, with its dual focus on R&D and programmatic work. Applicants must submit a research proposal aligned with one of the Mission Technology or ST&E investment areas that clearly articulates a hypothesis and a research plan for testing that hypothesis. Initial response to this initiative has been large and overwhelmingly positive. (The LDRD Program Office is currently preparing a brochure delineating the research activities and experiences of the initial cohort of Early Career LDRD funding recipients.)

Given that the LDRD program is an essential component for attracting, sustaining, and developing world-class ST&E capabilities at Sandia, the ECRD also serves the function of increasing the attractiveness of a Sandia staff position. In addition to this new initiative, LDRD also serves as a valuable means of recruiting new talent through hiring postdoctoral staff and supporting graduate students, thereby leveraging complementary scientific capabilities through strategic collaborations with academia. In recent years, roughly 40% of LDRD projects engage in external collaborations with academia or industry. LDRD research is performed by a disproportionately large fraction (>40%) of young employees with less than 5 years service as well as over half of the postdoctoral staff. These statistics illustrate that the development of critical ST&E skills and leadership is strongly promoted by LDRD.

Budget: Since FY 2007, LDRD strategic investments have been based on a balanced portfolio principle of stable funding targets for major investment categories as well as the strategic intent of the LDRD portfolios. Illustrating the balanced portfolio principle, the breakdown of program investments for FY 2010 is shown in Figure 1.

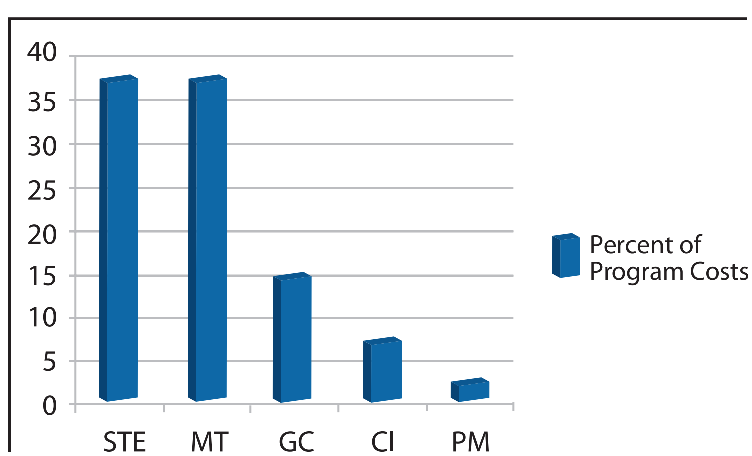


Figure 1. Investment portfolio breakdown for FY 2010 for the four Sandia LDRD program areas as a percentage of the total annual LDRD budget. STE: Science, Technology and Engineering Foundations; MT: Mission Technologies; GC: Grand Challenges; CI: Corporate Investments; PM: program management.

PORTFOLIO DESCRIPTION:

Project Size

Of the 432 projects active in FY 2010, 239 were newly funded, in their first year, while 193 were continuing in their second or third years. The FY 2010 project size, by budget, is shown in Figure 2.

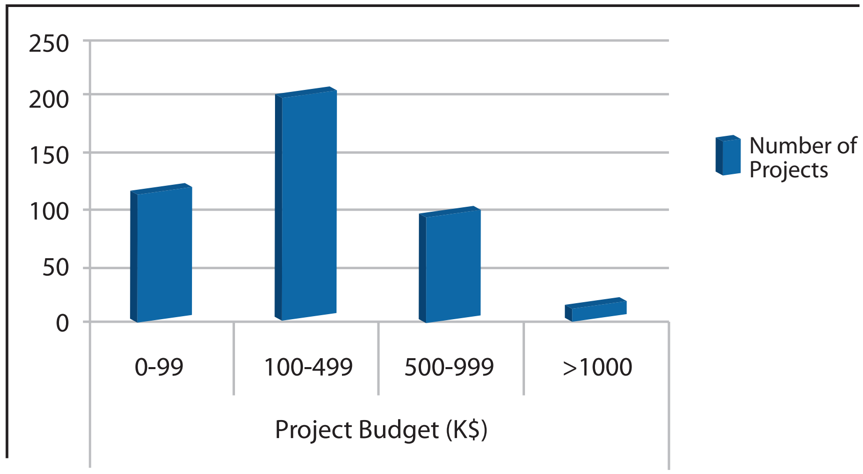


Figure 2. LDRD project size distribution, by budget: FY 2010

Project Strategic Intent Distribution

The LDRD program supports a range of R&D activities from fundamental research through proof-of-principle studies, and to a certain extent, even field demonstrations. In this context, each project is accorded a strategic designation of either Discover, Create, or Prove (D, C, or P). The intent of "**D**iscover" projects is the creation of new understanding or knowledge. "**C**reate" projects pursue the innovative application or combination of new or existing knowledge in a unique fashion, in order to create a novel solution to a problem, or to provide a revolutionary scientific, technological, or engineering advance. "**P**rove" projects pursue the validation of a prospective innovation or concept in a real-world environment, in a fashion that reduces any remaining unknowns and uncertainties. In addition to the balanced portfolio principle of stable funding targets for major investment categories (Figure 1), the program also attempts to maintain a balanced portfolio with respect to project strategic intent. This DCP balance for FY 2010, essentially unchanged from the prior two FYs, is shown in Figure 3.

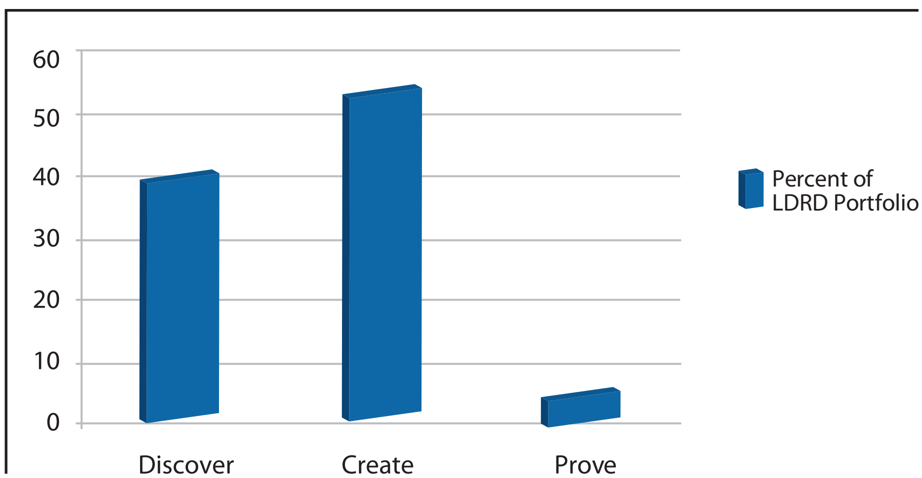


Figure 3. The DCP strategic intent for the FY 2010 LDRD portfolio

Technical Risk: Fundamental to creative innovation is some level of risk. The Sandia LDRD program has actively attempted to encourage risk-taking, by encouraging far-reaching project goals, while simultaneously requiring that risk-mitigation strategies be in place. Hence, for example, the program is flexible in permitting and, when relevant, encouraging project redirection, in order to maximize the potential for meaningful innovative outcomes. In July of 2010, the LDRD program office published a brochure entitled, *Risk, Challenge, and Reward in LDRD* (SAND 2010-3942P). By way of a dozen case studies, the brochure studied and analyzed the sources of technical risk within LDRD projects, the strategies employed for risk mitigation, and a variety of potential outcomes, when insurmountable roadblocks are confronted. This study indicated that Sandia LDRD principal investigators (PIs) employ risk-mitigation strategies at appropriate moments, are able to reconfigure and/or redirect project goals and activities to ensure positive, innovative outcomes, and are accepting of the understanding that, occasionally, and for a diversity of reasons, hypotheses can be disconfirmed by carefully conducted and validated experimental protocols — and that a hypothesis disconfirmed does indeed advance scientific knowledge by closing off fruitless research paths.

LDRD PROGRAM PERFORMANCE

LDRD creates and builds the core technologies that produce major scientific advancements and develop new capabilities through leading edge R&D. The long-range, forward-looking research anticipates solutions to mission challenges that are too risky for direct program funding, such as advanced architectures for high performance computing, novel electronics for space-based sensors, more efficient optoelectronic materials for solid state lighting, or innovative technologies for conversion of carbon dioxide to synthetic fuel. Approximately 10% of LDRD outcomes were featured in an LDRD Program Office publication, *Sandia LDRD 2010 Research Highlights* (SAND 2010-8330P).

The FY 2010 Sandia LDRD program grew in size over the previous year, proportional to an increase in the Labs' budget, and yielded a plethora of new scientific results. For example, over the past five years, over 50 percent of the labs' R&D 100 Awards (recognizing the nation's most innovative research and development), 20 percent of Sandia's refereed articles, and more than 40 percent of patents have roots in LDRD-supported efforts. This represents an extraordinary return on an 8 percent lab investment in R&D (Figure 4).

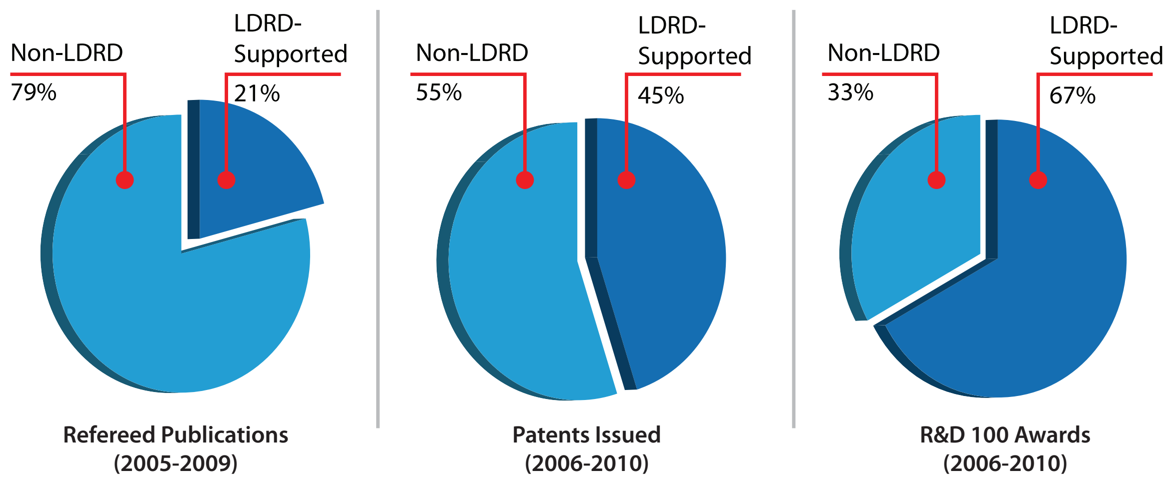


Figure 4. Performance measures

LDRD projects are a dominant part of the core of national laboratory innovation and vitality. In July 2010, R&D Magazine presented its "R&D 100" Awards to researchers who have developed the year's one hundred most outstanding advances in applied technologies. Sandia received five awards in 2010, two of which had deep roots in the LDRD program. These are as follows.

Multifunctional Optical Coatings: Involves the self-assembly of polymers to form nanostructured coatings with tailored properties, using commercially available polymers dispersed in common solvents, allowing easy and cost-effective routes to produce films through spin, dip, or spray coating in ambient conditions. These films possess physical properties approaching those of materials that are typically fabricated using expensive processes such as chemical vapor deposition and sputtering. Additionally, the chemical and physical properties of the self-assembled polymer films can be further tailored through a variety of near-ambient-condition processes.

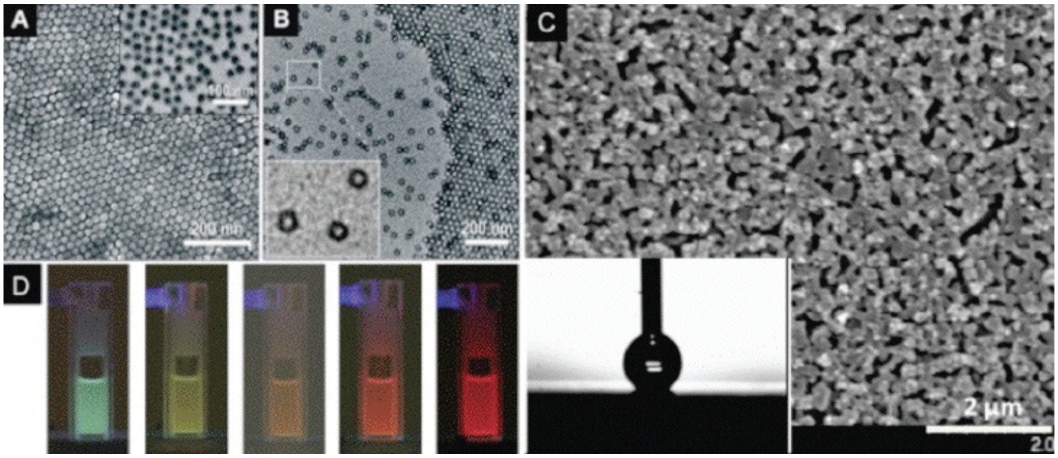


Figure 5. Micrographs of various self-assembled nanostructured optical coatings (A, B, and C) and photographs of hybrid organic/inorganic fluorescent nanoparticles in aqueous solutions (D).

Acoustic Wave Biosensors, Rapid Point-of-Care Medical Diagnostics *(joint entry with the University of New Mexico Health Sciences Center)* This innovative device is a handheld, battery-powered, portable detection system that is capable of multiplex identification of a wide range of medically relevant pathogens and their biomolecular signatures—viruses, bacteria, proteins, and DNA — at clinically relevant levels. This detection occurs within minutes, not hours, at the point of care, whether that care is in a physician's office, a hospital bed, or at the scene of a biodefense or biomedical emergency. The detection system employs Sandia's shear horizontal surface acoustic wave (SH-SAW) biosensor array functionalized with selective ligands — antibodies, peptides, or single-stranded DNA, depending on the application.

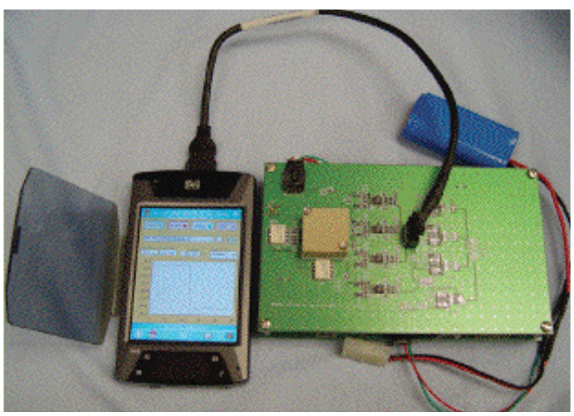


Figure 6. Acoustic wave biosensor with PDA controller (left) and rechargeable battery (blue, upper right). Sensor arrays fit in the tan enclosure on the green circuit board.

LDRD-related research accomplishments were also featured on the covers of peer-reviewed journals during FY 2010: for example, the November 2009 issue of the *Journal of Materials Chemistry* and the June 11, 2010 issue of *Physical Review Letters* (Figure 7).

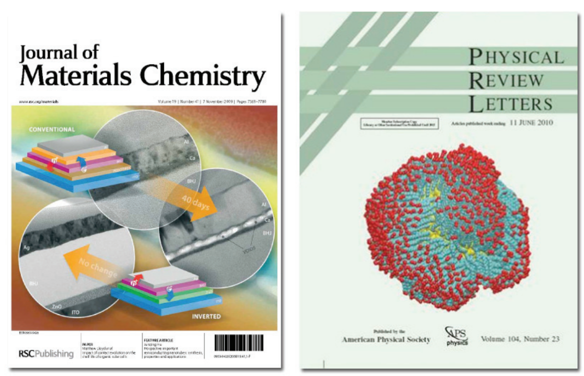


Figure 7. Journal Covers

These measures of program performance illustrate that the LDRD Program plays a crucial role in advancing the national security missions of Sandia National Laboratories. The breadth and depth of the program's contributions are more fully revealed by the project summaries contained in this annual report, which underline the contributions of the LDRD program to Sandia's overarching goal, first defined by President Harry S. Truman, of rendering "exceptional service in the national interest."

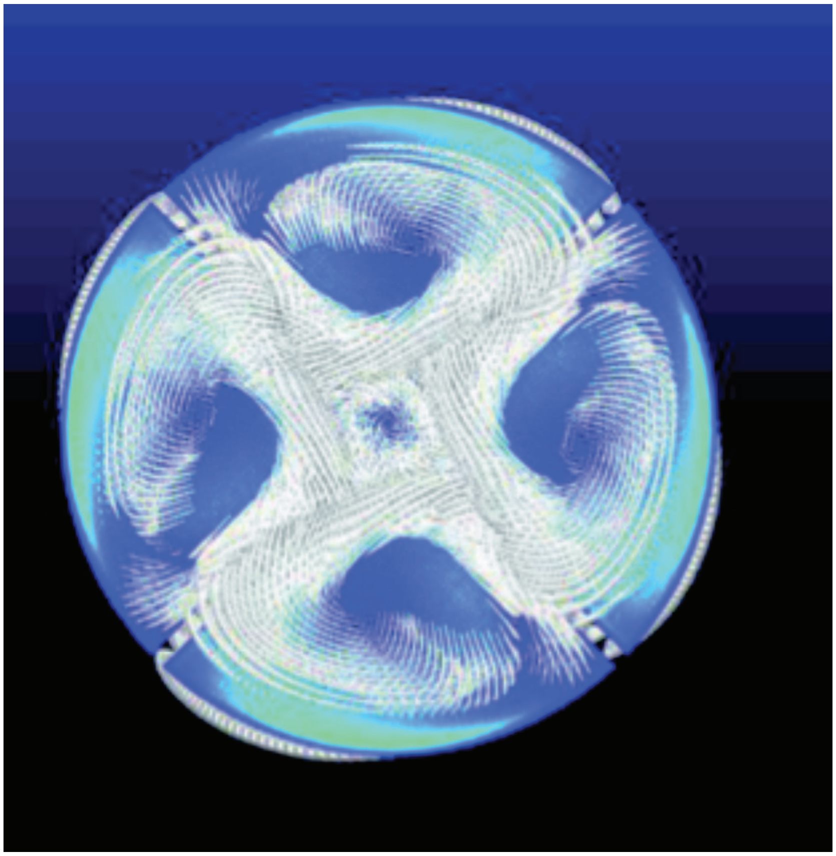
ENABLE PREDICTIVE SIMULATION INVESTMENT AREA

Computational modeling and simulation is the bailiwick of this investment area, funding research into computational activity that has the capability to both confirm and globalize experimental results, as well as to guide future experimentation and scientific intervention into national and global challenges. From predicting the course of epidemics, to models of material failure probabilities, to modeling water systems in semi-arid regions, to clarifying the properties of matter at the nanoscale, to new designs for computational memory, this IA's reach across Sandia's mission areas is quite extensive.

Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant-Scale

Project 141508

With the increased likelihood that nuclear energy will factor into the equation for energy production with a low-carbon footprint, models of nuclear reprocessing plants are needed to support nuclear materials accountancy, nonproliferation, plant design, and plant scale-up.



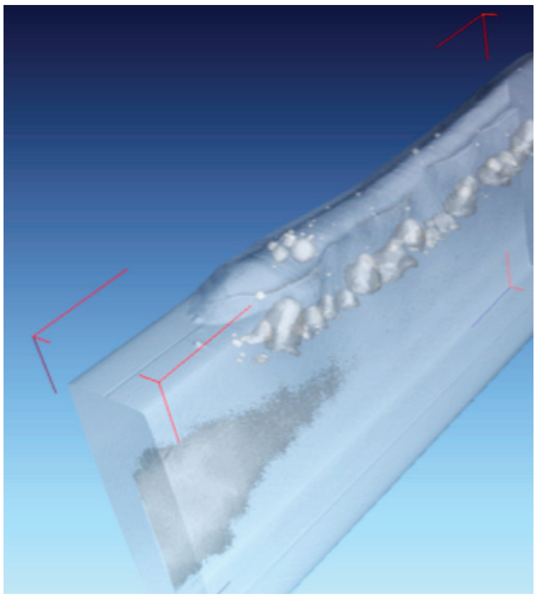
Model of turbulent flow within contactor extraction device.

This project is developing predictive capabilities targeting the design and monitoring of a next-generation nuclear fuel cycle to enable economical large-scale reprocessing with accurate material balances. In addition to plutonium/uranium extraction and separation models — which are being developed at several process scales, from single solution droplet to the contactor device in which extractions occur — plant "flow sheets" will be created using a novel, scalable network model that will allow coupling of massively parallel contactor models to simple models for other plant unit operations. This will be key to support nonproliferation activities including material accountancy, plant design, and diversion scenarios. Models will be validated through experiments at Sandia and in collaboration with Oak Ridge National Laboratory

Studies in High-Rate Solidification

Project 150638

The premise in this research is that the acquisition of 3-dimensional reconstructions of weld microstructures will provide more detailed characterization, which will, in turn, enhance the ability to develop predictive models of microstructural formation within a weld that influences its strength and other properties. To that end, the project is employing both microscopy of serial sections through welds and radiography with microcomputed tomography (similar to the process by which CT-scans are often used in medicine to image the three-dimensional structure of tissues and organs) to produce three-dimensional reconstructions of the grain microstructure and porosity within welds, parameters that are critical to assessing characteristics. By using the modeling capabilities in Sandia's Sierra software, a key connection is to utilize the experimental data to inform modeling initiatives, such that predictive capabilities will be greatly enhanced. In the future, this could possibly permit the establishment of better parameters for creating welds that would become more durable or would exhibit other prespecified characteristics. With the need to revitalize some of the nation's aging infrastructure, such initiatives represent an important step forward.



Three-dimensional reconstruction of weld properties.

ENABLE PREDICTIVE SIMULATION

Leveraging Multi-Way Linkages on Heterogeneous Data

117782
Year 3 of 3
Principal Investigator: T. G. Kolda

Project Purpose

This project's focus is the investigation and development of novel data analysis methods for heterogeneous data because recent experiences with Sandia intelligence analysts have revealed an emerging need to research analytic capabilities for large-scale, complex data sets. The goal is to be able to combine heterogeneous entities and multiple linkages (i.e., relationships) among them. We are developing a new class of algorithms, emphasizing scalability and robustness, for multi-way linkage dimensionality reduction that maps heterogeneous entities into a shared conceptual space. We measure the quality of the mapping according to how well "nearness" is maintained in the lower-dimensional conceptual space with respect to the multi-way links and various problem-dependent quality measures such as classification performance. Of important application interest, mapping the entities to conceptual space is fundamental to solving a variety of data analysis problems, including entity resolution and disambiguation, link prediction, and anomaly discovery.

Sandia is uniquely positioned to address these challenges because of our expertise in data and graph analysis, matrix and tensor methods, and high-performance computing. Our overarching goal is to develop robust and scalable methods for analyzing multi-way links on heterogeneous, inaccurate, and incomplete data from real-world applications. Although multi-way linkage analysis is of interest to us specifically because of its importance in the intelligence community, there are also applications to social network, bibliometric, critical infrastructure, and complex biological systems analysis. LDRD investment is enabling us to become established in this domain of large-scale, multi-linkage graph analysis.

Summary of Accomplishments

The goal was to investigate scalable and robust methods for multi-way data analysis. We developed a new optimization-based method called CPOPT for fitting a particular type of tensor factorization to data; CPOPT was compared against existing methods and found to be more accurate than any faster method and faster than any equally accurate method. We extended this method to computing tensor factorizations for problems with incomplete data; our results show that one can recover scientifically meaningful factorizations with large amounts of missing data (50% or more). The project has involved five members of the technical staff, two postdocs, and one summer intern. It has resulted in a total of 13 publications, two software releases, and over 30 presentations.

Significance

The project ties to Sandia's national security mission. Our goals of entity resolution/disambiguation, link prediction, and anomaly detection relate to problems of national security interest because they address data fusion across disparate data sources. Our technological aims are consistent with Sandia's and DOE's long history of support for the intelligence agencies. Other applications include social network, critical infrastructure, and complex biological system analyses. Several follow-on projects have already begun, with more potential projects in development.

Refereed Communications

D.M. Dunlavy, T.G. Kolda, and E. Acar, "Temporal Link Prediction Using Matrix and Tensor Factorizations," to be published in *ACM Transactions on Knowledge Discovery from Data*.

E. Acar, D.M. Dunlavy, and T.G. Kolda, "A Scalable Optimization Approach for Fitting Canonical Tensor Decompositions," to be published in the *Journal of Chemometrics*.

E. Acar, D.M. Dunlavy, T.G. Kolda, and M. Mørup, "Scalable Tensor Factorizations for Incomplete Data," to be published in *Chemometrics and Intelligent Laboratory Systems*.

Peridynamics as a Rigorous Coarse-Graining of Atomistics for Multiscale Materials Design

117783
Year 3 of 3
Principal Investigator: R. B. Lehoucq

Project Purpose

The goal of our project is to develop a coarse-graining of finite temperature molecular dynamics (MD) that successfully transitions from statistical mechanics to continuum mechanics. Our coarse-graining overcomes the intrinsic limitation of coupling atomistics with classical continuum mechanics via the FEM (finite element method), SPH (smoothed particle hydrodynamics), or MPM (material point method); namely, that classical continuum mechanics assumes a local force interaction that is incompatible with the nonlocal force model of atomistic methods. Therefore FEM, SPH, MPM inherit this limitation. This seemingly innocuous dichotomy has far-reaching consequences; for example, classical continuum mechanics cannot resolve the short wavelength behavior associated with atomistics. Other consequences include spurious forces, invalid phonon dispersion relationships, and irreconcilable descriptions/treatments of temperature.

We propose a statistically based coarse-graining of atomistics via peridynamics, and, hence, develop a first-of-a-kind mesoscopic capability to enable consistent, thermodynamically sound, atomistic-to-continuum (AtC) multiscale material simulation. Peridynamics (PD) is a micro-continuum theory that assumes nonlocal forces for describing long-range material interaction. The force interactions occurring at finite distances are naturally accounted for in PD. Moreover, PD's nonlocal force model is entirely consistent with those used by atomistics methods, in stark contrast to classical continuum mechanics. Hence, PD can be employed for mesoscopic phenomena that are beyond the realms of classical continuum mechanics and atomistic simulations, e.g., molecular dynamics and density functional theory (DFT). The latter two atomistic techniques are handicapped by the onerous length and time scales associated with simulating mesoscopic materials. Simulating such mesoscopic materials is likely to require, and greatly benefit from multiscale simulations coupling DFT, MD, PD, and explicit transient dynamic finite element methods FEM (e.g., Presto). The proposed work fills the gap needed to enable multiscale materials simulations.

Summary of Accomplishments

The project goal of establishing the theoretical basis for the coarse-graining MD into peridynamics was accomplished in two related approaches. The first approach derives the peridynamic balance of linear momentum and energy from the principles of statistical mechanics. The second approach represents interatomic potentials within peridynamics, or continulization (the process of replacing a discrete process with a continuous one) of molecular dynamics into peridynamics. Two instances of continulization are provided. The first is an upscaling of molecular dynamics into a high-order gradient theory, and then exploiting a relationship between peridynamics and a high-order gradient theory. The second instance of continulization represents an interatomic multibody potential as a peridynamic material, and then smooths the resulting heterogeneous peridynamic material model. The two coarse-graining approaches are synergistic.

The first approach, although of significant theoretical value, does not immediately lead to an expedient computational scheme. An important conclusion, however, is that the path from classical nonequilibrium statistical to classical continuum mechanics traverses the nonlocal continuum theory of peridynamics. A consequence is that peridynamics can augment, or replace, MD, and AtC coupling can be replaced by PtC coupling (peridynamics to classical continuum mechanics). Continulization is a practical application justifying the contention of the first approach that molecular dynamics can be coarse-grained into peridynamics. In contrast to classical continuum mechanics, peridynamics does capture the short-wavelength behavior associated with molecular dynamics without the need to assume the existence of higher-order derivatives associated with a high-order gradient theory. Moreover, continulization represents a sophisticated scheme for generating peridynamic material models by coarse-graining multibody interatomic potentials at the continuum level. Thermodynamic restrictions on peridynamic elastic materials was also determined by appealing to a Coleman-Noll like procedure. The restrictions ensure that the second law of thermodynamics is not violated.

Significance

Sandia/NNSA has a strong interest in science-based stockpile stewardship (advanced simulation and computing), developing nano- and microscale devices and designer materials for renewable energy production and storage. These three applications can significantly benefit from multiscale materials simulations at the mesoscopic level that incorporate first-principles techniques at the atomistic regime. This project will provide the research and tools to address this critical regime between the atomic and the continuum levels.

Refereed Communications

S.A. Silling and R.B. Lehoucq, “Peridynamic Theory of Solid Mechanics,” *Advances In Applied Mechanics*, vol. 44, pp. 73-168, 2010.

R.B. Lehoucq and A. Von Lilienfeld-Toal, “Translation of Walter Noll's 'Derivation of the Fundamental Equations of Continuum Thermodynamics from Statistical Mechanics,'” *Journal of Elasticity*, vol. 100, pp. 5-24, 2010.

S.A. Silling, “Linearized Theory of Peridynamic States,” *Journal of Elasticity*, vol. 99, pp. 85-111, 2010.

P. Seleson and M.L. Parks, “On the Role of the Influence Function in the Peridynamic Theory,” to be published in the *International Journal for Multiscale Computational Engineering*.

S.A. Silling, “A Coarsening Method for Linear Peridynamics,” to be published in the *International Journal for Multiscale Computational Engineering*.

Predicting Fracture in Brittle Micron-Scale Structures

117784
Year 3 of 3
Principal Investigator: E. D. Reedy Jr.

Project Purpose

Our goal is to develop a validated failure methodology that can be applied to micron-scale microelectromechanical systems (MEMS) made from polycrystalline silicon. The development of such a methodology is especially needed for MEMS structures that are subjected to high loads (e.g., a chevron thermal actuator, a bi-stable mechanism, etc.). This will require a detailed understanding of how the failure depends on flaw distributions, flaw geometry, material microstructure, and regions of intense stress gradients. One source of difficulty in developing such a failure analysis is a consequence of the fact that critical flaw size, grain size, and the region dominated by high stress gradients can all be on the same 100-nm length scale. Note that traditional Weibull statistics-based probabilistic failure modeling approaches are not applicable when flaws are not small compared to specimen dimensions or to the size of regions with high stress gradients.

In this project, we seek to understand how flaws and microstructure generate probabilistic strength distributions and how regions of high stress gradients affect such distributions. We are performing finite element analyses to determine the effect of crystal orientation, flaw geometry, etc., on predictions of specimen strength. One primary goal of the experimental effort is to develop novel on-chip and off-chip testing techniques that will allow us to test on the order of one-thousand nominally identical micron-scale tensile bars so as to define strength distribution tails. These techniques will be used to measure strength distributions of samples with and without stress concentrations (notches). Together, the computational and experimental results will direct the development of a methodology for predicting fracture of brittle micron-scale structures that does not explicitly model its microstructure and edge roughness.

Summary of Accomplishments

We used high-throughput test methods, developed during the previous years of this project, to measure the strength of SUMMiT V (Sandia ultraplanar multilevel MEMS technology V)(polycrystalline silicon tensile bars. Approximately 1300 nominally identical tensile bars were tested. One important finding is that measured tensile strength distributions display a strength threshold. This implies that the strength-controlling flaws produced by the SUMMiT V microfabrication process are all less than some maximum size. In addition to sidewall edge flaws, which are clearly linked to the measured variability in tensile strength, we investigated several other potential factors. These included variations in line width, stress inhomogeneity within a polycrystal, and variations in the apparent fracture toughness. None of these appear to be a dominate contributor to tensile strength variability. The dominant nature of sidewall flaws was further confirmed by an analysis that applied cohesive zone finite element results for blunted V-notches to actual atomic force microscopy images. This analysis predicted tensile strengths for the imaged sidewalls that fell within the range of measured tensile strengths. The existence of a maximum flaw size enables the use of a flaw tolerance fracture mechanics methodology for analyzing complex MEMS structures containing micron-scale stress concentrations. We used this approach to estimate a lower bound for the strength of a double edge-notch specimen that compared favorably with measured values.

Significance

High-performance micron-scale MEMS structures will be used in high-risk national security applications only if their structural integrity can be guaranteed. This is particularly true of micron-scale structures made of brittle polycrystalline silicon. A validated computational methodology for predicting fracture of brittle micron-scale structures can provide the confidence needed to enable their use in challenging applications. It can also aid in the design effort and guide processing improvements.

Refereed Communications

B.L. Boyce, "A Sequential Tensile Method for Rapid Characterization of Extreme-Value Behavior in Microfabricated Materials," *Experimental Mechanics*, vol. 50, pp. 993-997, 2010.

B.L. Boyce, J.Y. Huang, D.C. Miller, and M. Kennedy, "Deformation and Failure of Small Scale Structures," *JOM*, vol. 62, pp. 62-63, April 2010.

B.L. Boyce, M.J. Shaw, P. Lu, and M.T. Dugger, "Stronger Silicon for Microsystems," *Acta Materialia*, vol. 58, pp. 439-448, 2010.

A Light Weight Operating System for Multicore Capability Class Supercomputers

117785
Year 3 of 3
Principal Investigator: K. Pedretti

Project Purpose

Sandia has a long history of fielding capability supercomputers that are among the largest and most scalable in the world. One of the primary reasons for this success has been an in-house developed Light Weight Kernel (LWK) Operating System (OS) that embodies all of Sandia's experience in designing scalable systems. This project will perform the system software research and development necessary to extend this leadership to multi-core processors. Industry is focused on lower-end capacity machines and lacks sufficient commercial motivation to develop LWK OS technology for multi-core; however, our experience shows that this is an essential ingredient for successful capability supercomputers.

This project will investigate the complex memory hierarchies, advanced on-chip synchronization methods, enhanced hardware virtualization technology, and new programming models that are accompanying multi-core processors. To compensate for the expected significant drop in bytes-to-flop ratio, this project will seek out and invent new techniques for reducing per-core memory bandwidth requirements. The insight gained by exploring these topics will be incorporated into the LWK OS system that is developed.

In order to make LWK OS technology more accessible, the software developed by this project will be open-source and publicly available. The proprietary nature of existing LWK OS solutions, their lack of hardware support, and the inaccessibility of capability class testing platforms severely limits their scope. A goal of this project is to mitigate these issues and begin to build a LWK OS research community. If successful, expected benefits are increased proliferation of Sandia's LWK OS technology and increased system software innovation. These benefits would not be achievable using the current model of developing a proprietary LWK OS for each new capability supercomputer.

Summary of Accomplishments

We designed and developed the Kitten LWK OS. Kitten is a modern, open-source LWK platform that supports many-core processors (100s of cores), advanced intranode data movement (via SMARTMAP [Simple Mapping of Address Region Tables for Multicore Aware Programming]), current multithreaded programming models (via Linux user-space compatibility), commodity high-performance computing (HPC) networking (Infiniband), and full-featured guest operating systems (via the Palacios virtual machine monitor). The Kitten LWK has been downloaded hundreds of times, and there are several external researchers actively working to extend its capabilities. Several projects are leveraging the platform and we are positioning it as an ideal platform for conducting exascale supercomputer hardware/software co-design research. Kitten can be downloaded from http://software.sandia.gov/trac/kitten.

We invented the SMARTMAP virtual memory mapping technique for multicore processors. SMARTMAP significantly reduces intranode memory bandwidth requirements, a significant bottleneck on multicore processors. SMARTMAP was an important component of the 2009 "Catamount N-way Kernel" R&D100 award and we have applied for a patent.

We created a scalable virtualization environment for HPC. We teamed with separately funded researchers at Northwestern University and the University of New Mexico to incorporate their embeddable virtual machine monitor, called Palacios, into the Kitten LWK, and customize it for HPC workloads. Our solution is unique compared to other cloud/utility computing virtualization layers in that it is focused on HPC and takes advantage of the unique characteristics of the LWK environment to reduce virtualization overhead. We used the Kitten and Palacios combination to perform large-scale testing on up to 6,240 nodes of Red Storm Cray XT4 system using HPC micro-benchmarks and several real applications. The observed virtualization overhead of less than 5% demonstrated that it is feasible to run real, communication-intensive HPC applications in a virtualized environment at large scale.

Significance

Simulations and data analysis performed on capability supercomputers are critical components of DOE strategic goals in defense, energy, science, and environment. Specific examples include the nuclear weapons modeling necessary to maintain the stockpile, controlled-fusion reactor simulation, and climate modeling. This project will develop system software technology that is necessary to perform applications such as these on future petascale supercomputers made up of multicore processors.

Refereed Communications

K. Ferreira, P. Bridges, R. Brightwell, and K. Pedretti, “The Impact of System Design Parameters on Application Noise Sensitivity,” IEEE International Conference on Cluster Computing, Heraklion, Crete, Greece, September 2010.

J. Lange, K. Pedretti, T. Hudson, P. Dinda, Z. Cui, L. Xia, P. Bridges, A. Gocke, S. Jaconette, M. Levenhagen, and R. Brightwell, “Palacios and Kitten: New High Performance Operating Systems for Scalable Virtualized and Native Supercomputing,” IEEE International Parallel and Distributed Processing Symposium, Atlanta, GA, April 2010.

Enhanced Molecular Dynamics for Simulating Thermal and Charge Transport Phenomena in Metals and Semiconductors

117786
Year 3 of 3
Principal Investigator: R. E. Jones

Project Purpose

In modeling nonequilibrium thermal transport in solids, classical molecular dynamics (MD) has the primary strength of explicitly representing phonon modes and the defects that scatter phonons. On the other hand, electrons and their role in energy transport are missing. These effects are vital in applications such as laser processing of materials, synthesizing thermoelectric (TE) materials, and estimating heat transport in conducting nanotubes and nanowires. Predictive models of the phenomenology of the interactions between the charge carriers and the atoms represented in MD exist, albeit lacking the phonon-confinement, ballistic transport, defect and grain boundary scattering effects natural to MD. This project will greatly improve the state-of-the-art, consisting of a few attempts at adding electronic effects to MD, by fully coupling the thermal and electronic transport in a rational framework, extending the regimes of application with new models and rigorously treating defects. We have taken partial differential equation (PDE)-based models of the coupled electron-phonon system and represented the electron transport by finite elements (FE) and the phonon system with MD. By coupling classical MD to FE-based models of the missing physics, we are enabling the simulation of a broad range of physical phenomena from the rapid exchange of heat between the electron and phonon carriers in a lattice through current-induced thermal failure of nanowires. Our approach is intrinsically multiscale and multiphysics. Furthermore, the tight coupling between the MD and FE paradigms utilizes the inherent strengths of each. We will enable predictive simulation for applications such as nanowire lasers, components of integrated semiconductors circuits and superlattice thermoelectrics where the effects of nanosized structures and electronic transport are equally important. Moreover, in the process of developing the methods needed to address electronic transport effects in MD, we anticipate discovering novel means of describing and predicting coupled nanoscale transport.

Summary of Accomplishments

In this three year project we have developed new theory on the incoherent, coupled transport of energy via electrons and phonons, new algorithms for coupling molecular dynamics with finite-element based models of transport, and novel means of estimating transport coefficients from first principles, time-dependent density functional calculations. The work has been documented in a number of presentations and publications. Moreover, we have released working, validated simulation code to the general scientific community via an add-on package to Sandia's widely-used LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code. We expect this to generate new algorithms and applications in the national interest. We also have seen clear extensions to this work that have resulted in multiple follow-on projects based on the fundamental multiphysics and multiscale algorithms developed in this project.

Significance

High-efficiency thermoelectrics continue to be relevant to Sandia's missions and nanoscale powered devices are becoming increasingly so. The design of nanosized devices and simulating the relevant physics impact a wide range of DOE/NNSA applications including energy production, communication, and sensing applications. This project and the enabling simulation it develops will impact the design and understanding of the fundamental behavior of these devices.

Refereed Communications

R.E. Jones, J.A. Templeton, G.J. Wagner, D. Olmsted, and N.A. Modine, "Electron Transport Enhanced Molecular Dynamics for Metals and Semi-Metals," *International Journal for Numerical Methods in Engineering*, vol. 83, pp. 940–967, March 2010.

Solution Methods for Very Highly Integrated Circuits

117787
Year 3 of 3
Principal Investigator: H. K. Thornquist

Project Purpose

While advances in manufacturing enable the fabrication of integrated circuits containing tens-to-hundreds of millions of devices, time-sensitive modeling and simulation necessary to design these circuits poses a significant computational challenge. This is especially true for mixed-signal integrated circuits where detailed performance analyses are necessary for individual analog/digital circuit components and the full system. When the integrated circuit has millions of devices, performing a full system simulation is practically infeasible using currently available Electrical Design Automation (EDA) tools.

The proposed research addresses the computational difficulties introduced by these large nonlinear dynamical systems by using Model Order Reduction (MOR) to reduce the overall dynamical system size and generate specialized preconditioners that accelerate the underlying linear system solution computation. Some commercial EDA tools use linear MOR techniques for circuit interconnects, but robust methods for nonlinear MOR are nonexistent. Our goal is to develop robust nonlinear MOR techniques, as well as apply linear and nonlinear MOR techniques to individual devices or groups of devices in a circuit automatically using the circuit-level descriptions. While this approach effectively reduces the overall dynamical system size, efficient and scalable preconditioners are still vital to the feasibility of a full system simulation.

We will use information about the dynamical system behavior obtained by the MOR methods to pursue innovative, scalable preconditioning techniques for the reduced or full dynamical system. Success in this endeavor will provide capabilities for impacting the simulation of sensor systems and other circuit design challenges (e.g., parasitics, environmental/radiation effects). It would also potentially re-vector the EDA industry towards accurate, device-level simulation to help resolve nanoscale design challenges for the larger semiconductor industry.

Summary of Accomplishments

The progress made on this project has mainly addressed the research and development of linear and nonlinear model order reduction (MOR) techniques for generating broadly applicable macromodels. A thorough assessment of the current linear and linear time-varying MOR techniques has been performed and the methods are implemented in Myce, a Matlab circuit simulator written at Sandia. Current nonlinear MOR techniques have been assessed, but not fully implemented in Myce. So far, the nonlinear MOR assessment illustrates that the most robust approach was found in the piecewise-polynomial method and the most efficient was the empirical interpolation method.

In the assessment of the current linear and nonlinear time-varying MOR techniques, several deficiencies were identified as unique opportunities for us to impact the applicability of MOR to realistic science and engineering problems:

- The most promising linear MOR method, an optimal H2 approach, was extended to linear time-invariant systems in descriptor form by decoupling the differential algebraic equations into proper and improper portions and then applying the optimal H2 approach to the proper portion.

- Singular-value decomposition (SVD)-based methods, like the optimal H2 approach, have provable error bounds only in terms of the power difference between the original and reduced systems. A somewhat more useful notion of error can be measured in terms of peak amplitude. For this notion of error, we have developed a novel approach that uses L1 norm minimization for MOR.
- We have developed a new approach for linear time-varying (LTV) MOR that circumvents the larger dimension LTV transfer function and, if successful, would be a significant contribution to the MOR community.

Some progress has been made in the area of preconditioning: We have developed a specialized multigrid algorithm for solving linear systems generated by power grids or parasitic networks.

Significance

The proposed R&D will significantly impact the design of very-large mixed analog/digital circuits, including satellite Focal Plane Arrays and radiation-hardened application specific integrated circuits (ASICs) for nuclear weapons (NW) and other key national security applications as well as dynamical network problems like power distribution networks. Implementation of successful techniques will be available via Trilinos to other application areas, beyond circuit simulation, that are also of great importance to a variety of DOE and other federal agencies.

Refereed Communications

K.R. Santarelli, “A Framework for Reduced Order Modeling With Mixed Moment Matching and Peak Error Objectives," to be published in the *SIAM Journal on Scientific Computing*.

Scalable Solutions for Processing and Searching Very Large Document Collections

117788
Year 3 of 3
Principal Investigator: D. Dunlavy

Project Purpose

Intelligence analysts have a large data problem. They answer questions of national security under extreme time pressure, and current tools cannot handle the volume of data they must consider. In addition, they explore data iteratively by testing various "what-if" scenarios. As a result, quick turnaround time for processing, searching, and exploring large document collections is critical. No end-to-end scalable visual text analysis capabilities exist today, and this prevents analysts from exploring, annotating, and analyzing existing petascale document collections. The goal of this work is a suite of independent, scalable capabilities to process and search large document collections for use in data analysis and visualization — software that can efficiently leverage parallel algorithms. We will develop exact and conceptual searching methods as well as relevance feedback methods (i.e., active learning methods) for reducing uncertainty inherent in text analysis. Our end-to-end system will serve two purposes: (1) as a production capability, and (2) as an environment for rapid prototyping of algorithms. Initial uses of this new system will include application of existing methods to new problem areas and the development of hybrid algorithms that combine new and existing algorithms in novel ways.

LDRD investment in this project is crucial at this stage of development due to the risk involved (as the first end-to-end fully parallel data and execution text analysis and visualization pipeline) and the need for deeper understanding of the issues and challenges related to coupling text analysis, visualization, and user feedback methods for use in large-scale data analysis.

Summary of Accomplishments

In the final year of the project, we accomplished the following tasks:

1. Completed development scalable text analysis pipeline architecture (ParaText) in which all components could utilize resources in parallel on either a distributed memory or multithreaded environment. This was released as a capability within the Titan open source information visualization framework.
2. Open source release of the HEMLOCK toolkit for heterogeneous ensemble modeling for data classification problems.
3. Development of TextView, a software tool for visually comparing text analysis models generated using Latent Semantic Analysis and Latent Dirichlet Allocation, two modeling methods available in the ParaText software.
4. Collaboration with the research group developing the Linguistica software tool for linguistic analysis of text corpora. The morpheme analysis capabilities from the Linguistica tool are now available from within the Titan framework.
5. Demonstration of strong scalability of the ParaText system on Sandia's Thunderbird cluster using up to 512 processors. This work was published in the *Proceedings of the ACM Symposium on High Performance Distributed Computing*.

Significance

The volume of textual data is increasing exponentially and analysis tools are critical to understanding the vast collection of human knowledge and current events. The capabilities developed in this project will provide intelligence analysts with the most efficient text processing capabilities available, significantly reducing turnaround time associated with data exploration, hypothesis testing, and collaborative analysis, speeding analysis and detection of national security threats.

Refereed Communications

D.M. Dunlavy, T.M. Shead, and E.T. Stanton, "ParaText: Scalable Text Modeling and Analysis," published in *Proceedings of the 2010 ACM International Symposium on High Performance Distributed Computing,* New York, NY, June 2010.

Scaling I/O for High Performance Commodity Clusters

117789
Year 3 of 3
Principal Investigator: B. A. Allan

Project Purpose

While machine capabilities grow, file system advancement is falling far behind. Specialized distributed parallel file systems are developed outside of the Linux mainstream. Although the Linux mainstream distributed file system, NFS (network file system), is slowly being improved in functionality, the bulk of the effort is aimed at improving random input/output (I/O) for business applications rather than streaming I/O of high performance computing (HPC) applications. Recent benchmarking efforts show that less than 15% of the available bandwidth is utilized for streaming NFS writes, even though the same tests achieved 90% or more for reads.

We identify two strategies to optimize streaming writes on the client side. First, re-implement the Linux NFS client to be procedure-based, multithreaded and asynchronous. The NFS client can then perform network I/O simultaneously with the application data writing on multicore machines. Second, improve the behavior of the Linux virtual file system (VFS) and virtual machine manager to increase overlapping of application and network I/O. We will collaborate and consult with the Linux NFS, kernel, and network researchers in designing, testing, and building community support for changes to the Linux NFS that will enable open-source systems to achieve high streaming write throughput required by HPC applications. We propose to study the new algorithms on HPC clusters not commonly available in the NFS and kernel developer communities, to demonstrate changes to the NFS implementation to remove the bottleneck in NFS writes, and to build community advocacy for having these HPC-favorable changes migrated into the Linux mainstream.

Summary of Accomplishments

To diagnose the issues preventing good utilization, we worked up a set of baseline measurements and then instrumented the Linux kernel to ascertain throughput at various key points. This work showed two key points of the issue: first, that the Linux NFS stack, with or without bypass-enabled transports such as NFS/RDMA (remote direct memory access) was only capable of 600 MB/s (out of a potential 1.2 GB/s); second, that the NFS/RDMA transport was only preregistering small payloads for each remote direct memory access operation.

We corrected the identified issues, resulting in an improvement from ~320 MB/s to 425 MB/s. To correct the issues we, first, modified the Linux kernel NFS/RDMA transport to attempt payloads twice as large as previously and, second, profiled the kernel that identified the memory copies between user-space and memory-space as the prime contributor in the inherent limitation identified in the diagnostic phase. The NFS/RDMA transport changes improved performance in all cases. Elimination of the memory copies required application changes and, so, only improved applications realized this benefit.

We propagated our changes by working with the maintainers of the affected source codes. We developed a “supermon” reader called “FTQ-IO.” The supermon changes have been made available to the maintainers at Hewlett-Packard and IBM has requested the FTQ-IO reader.

We have reported via submission of a paper titled “On Scaling I/O for Commodity Clusters” to *Cluster ‘09*, a peer reviewed conference.

We analyzed the current performance of pNFS (NFS v4.1 open-source prototype implementations), PVFS, and Lustre on streaming write benchmarks. We identified a protocol-independent Linux kernel bottleneck that prevents single-process compute nodes from achieving more than 50% of the available network hardware bandwidth for streaming writes on high-speed interconnects. We published the benchmark results as a Sandia technical report.

Significance

This work is relevant to the goal of nuclear weapons stewardship, and supports the strategy of developing capabilities needed for long-term stewardship in the future. Many scientific applications perform periodic streaming writes for either check-pointing or storing intermediate results. These applications will benefit from the overall performance gain if we eliminate the NFS write bottlenecks on the client, yielding more-timely simulation results as we scale to larger machines. The results indicate that changes to fundamental buffer management and process scheduling in the Linux kernel are needed if saturating Linux compute-node network links is to be achieved.

Surface Rheology and Interface Stability

117790
Year 3 of 3
Principal Investigator: L. A. Mondy

Project Purpose

We experimentally investigated the surface rheological properties of surfactant solutions, as well as the stability of foams made with these solutions, to extend our physical knowledge of multiphase flows and guide the development of constitutive models for the mechanical behavior of interfaces. Interfacial properties are distinct from bulk properties on either side of the boundary, are not well understood, and are difficult to predict. Although interfacial properties have been studied for some time, the complexities of interactions among surfactant molecules, adsorption characteristics, dependence on the geometry of the interface, and the inherent multiscale nature of interfaces mean that much interfacial physics remains a mystery. We established unique laboratory capabilities by coupling information obtained using shear and dilatational interfacial stress rheometers with optical trapping and manipulation of microparticles (a novel micro-interfacial rheometer) to provide cutting-edge experimental discovery necessary to extend current computational models. Gathering data with multiple techniques was shown to be a necessity in many cases, as each technique had different limitations and sensitivities. Newly developed constitutive models were incorporated into Sandia's multiphysics codes; however, the computations proved difficult to converge. Suggestions for improvements to the implementation were made. Currently, no commercially available code can include surface rheological effects; therefore, when completed, this work will result in a unique capability for Sandia. Finally, the new experimental techniques can provide future measurements important to other computational capability development in progress, such as the ability to predict interactions between emulsifying agents used in foam processes or nanoparticle interactions in suspensions, where the physics is dominated by the thin films of the continuous phase.

Summary of Accomplishments

We developed a mature laboratory at Sandia to measure interfacial rheology, using home-built, commercially available, and customized commercial tools. An interfacial shear rheometer (KSV ISR-400) was modified and the software improved to increase sensitivity and reliability. Another shear rheometer, a TA Instruments AR-G2, was equipped with a Du Nouy ring, bicone geometry, and a double wall ring. These interfacial attachments were compared to each other and to the ISR. The best results with the AR-G2 were obtained with the Du Nouy ring. A micro-interfacial rheometer (MIR) was developed in house to obtain the much higher sensitivity given by a smaller probe. However, we found it difficult to apply this technique for highly elastic surfaces. Interfaces also exhibit dilatational rheology when the interface changes area, such as occurs when bubbles grow or shrink. To measure this rheological response we developed a surface dilatational rheometer in which changes in surface tension with surface area are measured during the oscillation of the volume of a pendant drop or bubble. All instruments were tested with various surfactant solutions to determine the limitations of each. In addition, foamability and foam stability were tested and compared with the rheology data. We found that there was no clear correlation of surface rheology with foaming/defoaming with different types of surfactants, but, within a family of surfactants, rheology could predict the foam stability. Diffusion of surfactants to the interface and the behavior of polyelectrolytes, were two subjects studied with the new equipment. Finally, surface rheological terms were added to a finite element Navier-Stokes solver and preliminary testing of the code completed. We provided recommendations for improved implementation. When completed, we plan to use the computations to better interpret the experimental data and account for the effects of the underlying bulk fluid.

Significance

This work will improve Sandia's core capability in modeling and simulation of fluid flow and complex coupled phenomena, allowing Sandia to become a leader in modeling interfacial rheology. Benefits will include better understanding of materials and processes dominated by interfacial effects, ranging from foaming and defoaming strategies in energy and environmental management programs to innovative microfluidic processes to create particle-doped membranes and other advanced materials. This work will have an immediate impact on the ability to develop work for others programs based on interest already shown by companies (e.g., Proctor & Gamble). The new laboratory will give us the ability to better characterize emulsions and foams in nuclear weapon development, including potential new polymeric foams for encapsulation and ceramics processed from emulsions for thermal battery applications. We expect immediate impact for potential oil recovery, environmental restoration, nanotechnology and microfluidics applications that may occur in the future.

"Equation-Free" Simulation Methods for Multiple Timescale Diffusion Processes in Solids

130732
Year 2 of 3
Principal Investigator: G. J. Wagner

Project Purpose

The purpose of this project is to develop a set of algorithms and computational tools, based on an "equation-free" multiscale modeling approach, in order to allow predictive simulation of long-timescale diffusion phemonena important in the synthesis, performance, and aging of materials. Traditional molecular dynamics (MD) simulation is not tractable for most of these problems because of the long timescales involved. To make progress, we can note that the quantities most of interest to a modeler can be described at a much coarser level than the atomic scale. One method that takes advantage of this fact is the so-called equation-free approach, which uses microscale computations, like MD simulations, as a set of numerical experiments from which can be distilled macroscale information, such as time derivatives of coarse-scale variables. We propose to use equation-free methods to extend the timescale in atomistic simulations to that necessary to accurate simulate and predict diffusion processes. However, an equation-free method that uses MD for its fine-scale simulations is likely to fail for problems driven by rare events, like atom hopping in diffusion, since MD cannot capture enough events in a short amount of time to be statistically relevant. The key innovation in our project is to use extended timescale methods, like Kinetic Monte Carlo (KMC) and Temperature Accelerated Dynamics (TAD), for the fine-scale computations that inform the continuum-level evolution in an equation-free approach; these methods themselves have their own size and timescale limitations that can be overcome by our novel combination of approaches. This project, if successful, will fill an important gap in Sandia's ability to perform atomic scale simulation of material stability and nanoscale transport over long times, phenomena that are vital to modeling aging of the nuclear stockpile as well as to the synthesis and performance optimization of nanostructured materials.

Summary of Accomplishments

The first major goal of our project is to develop extended timescale methods for surface diffusion using equation-free projective integration (EFPI). The keys to this method are the identification of a set of coarse-scale variables that parameterize the system, and the development of interscale operators that map between the coarse and fine descriptions. We have developed these interscale operators for surface diffusion, and found that it is necessary to include statistical information about the surface fluctuations in the coarse parameterization through the use of spatial correlation functions. It is also important to carefully delineate between fast and slow variables in the system. Using this method we have demonstrated 20× speed-ups for 2D surface diffusion models. We have recently extended our interscale operators for efficient use in 3D, and are applying this technique to the full 3D diffusion problem.

The second major goal of the project is to implement and study extended-timescale molecular dynamics methods, such as TAD, and use them as microscale simulators in EFPI simulations of interlayer diffusion of unlike metals. As a step toward full implementation of TAD in the Sandia molecular dynamics code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), we have implemented two components of the algorithm that are important tools in their own right: Parallel Replica Dynamics that uses multiple independent replicas of the system to detect and propagate rare events; and Nudged Elastic Band, a method for finding energy barriers and transition states. Finally, we have developed interscale operators for bulk diffusion problems using a simulated annealing technique, in which a microscale configuration is randomly modified so as to minimize the difference between the current and desired coarse parameterizations. This very general approach should have application as a coarse-to-fine operator in EFPI simulation of a wide variety of problems.

Significance

This project will provide a new capability to perform atomic scale simulation of material stability and nanoscale transport over long times, phenomena that are vital to modeling aging of the nuclear stockpile. The tools we develop will have application to the predictive simulation of the synthesis, performance, and aging of nanostructured materials, allowing modelers to bridge multiple scales and perform predictive simulation of a number of phenomena important to Sandia. The high-performance materials whose design, study, and optimization are enhanced by the methods developed in this project will benefit a range of Sandia missions, including engineered nuclear weapons systems and emerging energy technologies.

Refereed Communications

G.J. Wagner, X. Zhou, and S.J. Plimpton, “Equation-Free Accelerated Simulations of the Morphological Relaxation of Crystal Surfaces,” *International Journal for Multiscale Computational Engineering*, vol. 8, pp. 423-439, 2010.

Bayesian Data Assimilation for Stochastic Multiscale Models of Transport in Porous Media

130734
Year 2 of 3
Principal Investigator: J. Ray

Project Purpose

The project seeks to develop Bayesian techniques to infer multiscale coupling in heterogeneous physical processes by conditioning on observations. The fundamental difficulty in multiscale problems arises from the indeterminacy in extrapolating from fine-scale models to coarser levels. Simultaneously, coarse-scale models are unable to provide sufficiently resolved inputs to fine-scale models. Our core hypothesis is that physical variables affected by multiscale processes may be represented as multiscale random fields, with interscale dependencies modeled as conditional probabilities. Thereafter, on the availability of static and dynamic (system response) observations, the inference of the parameters of the multiscale random fields (and those necessary for defining the conditional probabilities) completes the specification of the multiscale coupling. However, this specification is mathematically difficult at realistic resolutions, given the high dimensionality of the problem. Reduced-order representations of multiscale random fields and efficient means of updating/exploring posterior probabilities form the bulk of the methodological research for this project. Although our techniques are general, we will demonstrate them on problems of porous media transport that are found in CO_2 sequestration, fuel cells, nuclear waste, etc. In FY 2009 we addressed the problem of inferring permeability from multiscale static and dynamic observations. Our preliminary efforts at inferring permeability fields show significant challenges in exploring the joint posterior probability, due to slow mixing of the Markov Chain Monte Carlo (MCMC) method. In the rest of FY 2009 and much of FY 2010, we explored means of improving the efficiency of the approach. Techniques being considered include low-dimensional representation using Karhunen-Loeve bases as well as the employment of multiscale/multilevel random fields so that data may be assimilated at a resolution where it was measured. Replacement of the forward model with an approximate surrogate will also be considered in certain cases.

Summary of Accomplishments

Over the last year, we have devised a statistical technique to estimate a multiscale field in a spatial domain from sparse and indirect observations. The technique is designed for fields that contain a range of length scales, only some of which can be fully resolved on the global computational mesh. Observations consist of static measurements that provide detailed information in a very localized region, and dynamic measurements of the response of the medium that are indirectly informative on a range of scales in the domain. In doing so, we integrate concepts from multiscale random field models, their low-order representations, and spatial statistics to pose and solve a Bayesian inference problem for the properties of interest. The inference procedure fully quantifies uncertainty arising from limited data, observational error, and subgrid modeling.

The technique was used to infer a 2D permeability field with a large dynamic range. We approximated it as a binary medium, consisting of a low-permeability matrix with small, unresolved high-permeability embedded inclusions. The proportion (volume fraction) of the inclusions varied in space and the effective permeability of the medium is a nonlinear (and discontinuous, due to percolation effects) function of the volume fraction and inclusion size. Observations consisted of permeability measurements over a few grid-blocks/sub-domains and tracer breakthrough times at a few observation points. The objects of inference were the volume-fraction field, an average size of the inclusions, and the permeability field, conditioned on the data. A novel development enabling such an inference was the creation of a probabilistic subgrid model that estimated the effect of the unresolved scales as a function of both coarse- and fine-scale quantities. Other advances were methodological, and increased the efficiency of inference.

The key accomplishments of this project are 1) development of parallel MCMC samplers, 2) development of Ensemble Kalman Filters (EnKF)-based technology for problems of inference, 3) experience with and demonstration of the use of Karhunen-Loeve expansions in large inferential problems, and 4) development of statistical subgrid models to represent unresolved physics/structures and their use in a problem of inference.

Significance

The project connects to DOE's ongoing research efforts in CO_2 sequestration, environmental remediation of dense non-aqueous phase liquid contaminated sites and transport-reaction coupling in fuel cells. This project is consistent with Sandia's DoD mission space in areas of transport and decontamination of chemical warfare agents and toxic industrial chemicals in porous/construction media. Inference techniques developed here will also apply to multiscale network models anticipated for control-systems purposes in next generation electric (green) grid research.

The first two accomplishments, above (parallel MCMC samplers and EnKF-based technology) are algorithmic and can be applied to any problem (of an inferential nature) of interest to Sandia. While both have been in practice for some time, they are new to Sandia, and will be critical as we transition to new problems of an environmental/climate nature. In this regard, the EnKF methods will be used in estimating CO_2 emissions from sparse observations, within the context of a new project. We are also applying them in estimating the permeability of binary-like media e.g., fractured media, that arise in CO_2 sequestration and environmental decontamination/remediation problems. The third, the use of truncated KL expansions as a convenient reduced-order model for high-dimensional fields can find use in the development of surrogate models, traditionally performed with Gaussian Process models (e.g., as part of advanced simulation and computing uncertainty quantification work in DOE/NNSA), in the inference of 2D/3D fields, and in matrix completion problems of many kinds. The last, development of simple, statistically based subgrid models, can be used in representing random porous media, ranging from geological strata to ageing explosives, when estimating their characteristics from data. We have obtained follow-up funding based on the results developed in this project.

Computational Mechanics for Geosystems Management to Support the Energy and Natural Resources Mission

130739
Year 2 of 3
Principal Investigator: C. M. Stone

Project Purpose

US energy needs include more economical extraction of fossil fuels, increasing recoverable reserves, protection of water resources, reduction of the impact of fossil fuels on climate change, mining nuclear fuel sources with minimal environmental impact, and technologies for safe disposal of energy wastes. Long-term solutions to these needs will require the ability to simulate, model, and predict behavior of subsurface systems including complex, heterogeneous mineral and porous rock thermo-chemo-mechanical behavior as well as the interactions with multiphase pore fluids and microbial activity. Accordingly, we are developing a coupled thermal, hydrological, mechanical, chemistry (THMC) simulation capability for massively parallel applications. Key research issues to be addressed are related to phase appearance/disappearance, geologic heterogeneity and other subgrid phenomena, robust solvers for fully coupled systems, and methods to deal with disparate time and length scales for the coupled multiphysics. An additional research issue is to develop/implement geomaterial constitutive models that directly utilize the coupling between porous flow, chemistry, and mechanics. To solve these complex issues, this project integrates research in numerical mathematics and algorithms for chemically reactive multiphase systems with computer science research in adaptive coupled solution control and framework architecture. The resulting coupled THMC code would be unmatched by any commercial or proprietary software. The new software would allow for multiphysics modeling on spatial/temporal scales not currently available. This development will impact Sandia's ability to respond to immediate national needs for energy security and solutions to global climate change. This project will promote further collaborations with industry, universities (including a collaboration with the University of Texas at Austin's Center for Subsurface Modeling), and other national labs on reactive transport modeling of deforming geomaterials.

Summary of Accomplishments

We have completed the project milestones listed for late FY 2009 and through the third quarter of FY 2010. We have demonstrated several multiphase flow (nonisothermal water/air with real thermodynamics, phase appearance/disappearance) benchmark problems, including a heat pipe problem that verifies implementation of evaporation/condensation, capillary pressure, binary gas diffusion and dry out (liquid phase disappearance). We have also implemented a two-phase, compressible or incompressible, immiscible flow system, as the initial step towards modeling carbon management problems. We have successfully solved a two-phase flow international benchmark problem involving injection of supercritical CO_2 into a brine aquifer intersected by a leaky well. We have also modeled several variations of a multiphysics waste repository problem in clay, which coupled THMC processes into one 10,000-year simulation. Important physics observed include a dry-out region near the heat-producing waste package with subsequent re-wetting as the repository cools and fluid wicks back into the previously dried clay near the waste canisters. We have also implemented a capability for modeling heterogeneous materials and are applying this capability to investigate the impact of heterogeneous permeability on CO_2 leakage. We developed a novel strategy for coupling capillary pressure across material interfaces, allowing for a true jump in saturation across the interface; commonly used methods average across the interface. We have also developed an algorithm for implementing phase appearance and disappearance for general fluid mixtures. The Chemeq chemistry package has been linked with the porous flow enabling its use for chemically reactive flow problems. Documentation includes a journal paper, a SAND report, a conference paper in conjunction with a conference presentation; technical presentations have been made to other national labs (e.g., National Energy Technology Laboratory); and an invitation to present a short course tutorial on multiphysics coupling at an international repository science meeting.

Significance

The accomplishments from this project enable Sandia to address many of the issues associated with protecting our economic and national security by assisting in the development of a diverse energy portfolio. In particular, the simulation software developed in this project enables Sandia to address the wide range of multiphysics and multiscale issues associated with the entire energy cycle from in situ fuel extraction to waste disposal. Our research and development accomplishments demonstrate a foundational capability to model heterogeneous subsurface geosystem problems involving coupled thermal, mechanical, chemical and multiphase flow physics on massively parallel computers. The progress to date provides the proof of concept that our techniques for coupling multiphysics modules are viable and generally applicable.

We have made significant progress toward integrating the coupled, multiphysics simulation software developed in this project to Sandia and (DOE) strategic goals of Energy, Science and the Environment. The simulation software has been used in several key Sandia energy projects, in particular, clay/shale and salt repository studies and CO_2 sequestration initiatives. This capability supports Sandia initiatives directed at establishing Sandia as the center for repository management and analysis (nuclear waste and compressed air energy storage), and energy security (CO_2 sequestration). This work has led to several new projects both at Sandia and external to Sandia, for example, new LDRD project on experiments and models for investigating clay/shale high-level waste repositories. Munitions/weapons safety will fund further development and validation of reactive transport to study hot gas channeling in the foam decomposition abnormal thermal environment. This work also led to a proposal to the DOE Office of Electricity for compressed air energy storage and to negotiations with the Southwest Partnership for Carbon Storage to apply the simulation capability to study coupled geomechanics effects associated with supercritical CO_2 injection in deep saline aquifers.

Refereed Communications

K.B. Nakshatrala and D.Z. Turner, “A Stabilized Mixed Formulation for Modified Darcy Equation,” to be published in the *International Journal of Engineering Science*.

Experimental Characterization of Energetic Material Dynamics for Multiphase Blast Simulation

130740
Year 2 of 3
Principal Investigator: S. J. Beresh

Project Purpose

Accurate simulation of energetic material detonation is crucial to a variety of national interests involving explosive devices, including vulnerability of weapons and structures to nearby explosions, blast mitigation, improvised explosive device (IED) protection, and enhanced blasts. Unfortunately, such predictive capability is limited by a lack of knowledge of the underlying phenomena of the earliest stages of the blast, where the particle dynamics of the fragmented materials within the gas expansion products are pivotal to understanding the continuing reaction. The complication is that, at the explosion's onset, the particles are densely packed within the expanding flow, whereas our knowledge of the process is restricted to dilute concentrations. One of the great challenges is that the opacity of the flow due to the large particle density prevents usage of common fluid dynamics diagnostics, and instead requires the development of unconventional measurement approaches.

We propose to fill this knowledge gap by constructing an unprecedented multiphase shock tube that can drive a shock front into a particle/gas mixture of a selected fill fraction, then measure the motion of the densely packed particles within the expanding gas. To penetrate the dense flow and provide measurement of the particle velocities, we seek to exploit measurement concepts previously utilized for multiphase flows and high-energy physics and adapt them to the uncommon difficulties of the present problem. No such experimental technology presently exists. The most promising approaches use x-ray sources, or potentially strong incoherent visible light, in concert with specifically designed tracer particles. Finally, while velocity measurements are of the greatest value, the lack of knowledge of this flow field is so profound that even delivery of simpler measurements such as shock speeds and pressure histories would represent a valuable contribution. By providing crucial new physical data, we can boost the level of fidelity in algorithms used to simulate blasts in national security applications.

Summary of Accomplishments

The principal activity has been devoted to the development of the multiphase shock tube. This novel facility can be conceptually divided into the shock tube itself to initiate a planar shock wave traveling through a duct, and the particle-laden test section to study the shock interaction with the dense particle/air mixture. A Mach-2.3 shock tube has been built in accordance with the design constraints identified during the project's first year, with the first shot achieved in April 2010. To make it a multiphase shock tube, the particle curtain developed during the first year to serve as a dense particle suspension scheme must be incorporated into the tube; this hardware is being fabricated at the time of this writing, with delivery scheduled for late April. Once the particle curtain has become operational within the shock tube during the 3rd quarter of FY 2010, this will complete one of the project's two primary goals, the development of a multiphase shock tube; no other testing facility like it exists in the world.

In concert with the development of the multiphase shock tube, we are developing a particle velocimetry diagnostic that can function despite the opacity of the flow. This approach involves seeding a particle curtain composed primarily of weakly attenuating particles with a small fraction of tracer particles, that when backlit with x-rays, will form readily identifiable shadow images. Two frames in rapid succession can track the motion of the shadow images using cross-correlation algorithms. We have successfully tested this approach using an x-ray source to illuminate a test cell representative of the multiphase shock tube flow. Similar x-ray sources are available within the center for use in the shock tube during this project, and a plan currently is being developed for their relocation and operation in conjunction with the shock tube.

Significance

Although explosives researchers have, for many decades, futilely sought gas dynamics data in densely packed shock-driven two-phase flows, more recent improvements in energetic materials and, most particularly, growth in nonintrusive measurement capabilities make this field currently ripe for further development. Even partial success in the current project would provide a unique capability within the broader national establishment and be of significant service to the explosives community. A consequential improvement to blast simulation is unlikely to occur without improving the physical understanding of the reaction regime immediately following detonation. Because of the almost complete lack of knowledge of such complex flow physics, both at Sandia and throughout the scientific community, the provision of even limited data would be a great boon to modeling and simulation efforts used to support both explosive design and vulnerability assessment. Such improvements would benefit core Sandia responsibilities regarding vulnerability of weapons and structures to nearby explosions, facilities protection, and blast mitigation. Furthermore, given that Sandia is involved in other research initiatives covering such explosive topics as enhanced blasts, structure-coupled blasts, IED protection, and thermobaric explosives, an infusion of new data is of direct and wide-ranging importance. Potential also exists to port newly developed diagnostics to related explosive tests and field-scale validation activities. Thus, this research effort is of great interest to Sandia's defense programs, and additionally to the broader national defense establishment.

Nanomanufacturing: Nanostructured Materials Made Layer-by-Layer

130741
Year 2 of 3
Principal Investigator: P. R. Schunk

Project Purpose

Large-scale, high-throughput production of nanostructured materials (i.e., nanomanufacturing) is crucial to national security and a strategic area in manufacturing, with markets projected to exceed $1 trillion by 2015. Nanomanufacturing is still in its infancy; process/product developments are costly and only touch on potential opportunities enabled by growing nanoscience discoveries. Interestingly, the greatest promise for high-volume manufacturing lies in age-old coating and imprinting operations. For materials with tailored nm-scale structure, imprinting/embossing must be achieved at high speeds (roll-to-roll) and/or over large areas (batch operation) with feature sizes less than 100 nm. Dispersion coatings with nanoparticles (NPs) can also tailor structure through self- or directed-assembly. Layering films structured with these processes has tremendous potential for efficient manufacturing of microelectronics, photovoltaics and other nanostructured materials. This project is aimed at expediting benchtop-to-manufacturing scaleup through modeling and simulation; project success is critical for broadening Sandia's advanced simulation and computing class software for impact in nanoengineering. Connecting machine design variables to design parameters (e.g., feature size/structure) is challenging due to a large range of relevant length/time scales. Computational models of coating and imprinting operations have been invaluable to manufacturing; application to nanomanufacturing is topical, uncharted and ripe for scientific breakthroughs. In this project's first two years, research and development has led to innovations in finite-element technology, subgrid physics models, experimental discoveries, and unprecedented multiscale analysis, leading to heightened interest and even additional funds from private industry.

Summary of Accomplishments

Subtasks of this project are directed at representative suboperations of a commercially viable manufacturing processes known as SFIL (step-and-flash imprint lithography). Specifically, the fundamental unit operations are: coating (spraying), imprinting, solidification, embossing/releasing, and directed nanoparticle assembly. We now address significant accomplishments in turn.

- Imprinting model development and discovery: 1) Single-feature fill models (2D and 3D) with SIERRA application Aria were accomplished to ascertain parametric sensitivity of filling extent to applied pressure and liquid volume. Imprinting model development at the atomistic scale was also developed to address adhesion and atomistic friction effects at nanoscales . 2) Advanced unique stacked lubrication and porous/structure shell models were implemented in GOMA to address multiple feature filling . 3) We successfully validated fluid/structural/porous flow shell model with realistic parameters of a model SFIL configuration, with dynamics predicted for filling trillions of features of a square inch with hundreds of spray drops. We are awaiting experimental validation data
- Embossing/Releasing model research and development: 1) We accomplished single and multiple feature model development for release at the atomistic level using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) and polymethylmethacrylate. Coarse-grained atomistic friction models to feed continuum level simulations . 2) Single and multiple (hundreds) feature release models were developed in the continuum with PRESTO. 3) Coarse-grained PRESTO release models were successfully transitioned to an "effective toughness" model, and verified against direct numerical simulations.
- Experimental discovery on imprinting with nanoparticles: We demonstrated that an external pressure can be

utilized to direct nanoparticle assembly and to fabricate new nanoparticle architectures without relying on these specific interactions. This mechanical compression process opens up a new pathway to the engineering and fabrication of nanoparticle.

Significance

Breakthrough-technologies for safe, affordable, abundant energy require volume production. Whether it is photovoltaic, thermoelectric, or photosynthesis technology, nanotechnology discoveries are stymied by lack of a viable manufacturing approach. This project expands Sandia and DOE's existing nanotechnology thrusts in these areas into the manufacturing sector and increases the return-on-investment in nanoscience; current DOE programs are not addressing manufacturing to our knowledge.

Within Sandia and with respect to DoD, benefits from the computational technology are numerous. Already, we have applied the shell technology to a Naval rail-gun program with success. We have proposed with several S&T organizations the use of the computational technology to address and even explore forces and mechanics at the nanoscale and to survey alternate methods to produced patterned layers at the nanoscale. Exemplary applications central to Sandia's mission space are interface materials for weapons components, electrode and active-layer materials for energy storage (battery) and conversion (fuel cell) devices, and patterned substrates for optical transmission control and other lithographic needs.

Optimization of Large-Scale Heterogeneous System-of-Systems Models

130742
Year 2 of 3
Principal Investigator: J. D. Siirola

Project Purpose

A major challenge for decision-makers is the analysis of national-scale man-made systems that are composed of interacting subsystems. Effective integration of subsystem models is difficult; there are many discrete system parameters to analyze, and there are fundamental modeling uncertainties that complicate an analysis.

This project is developing methods to effectively analyze heterogeneous system of systems (HSoS) models that have emerged as a promising approach for describing complex man-made systems. An HSoS model is a heterogeneous assembly of system models that can operate as a single integrated system whose behavior reflects the interactions of the constituent system models. HSoS models can leverage system domain expertise in a modular fashion, so diverse aspects of man-made systems can be integrated into an HSoS model (e.g., economics, climate, human behavior).

We are developing efficient optimization techniques that can address modeling uncertainties in the analysis of large-scale man-made systems. Our goal is to deliver a differentiating capability in the form of peer-reviewed publications and software that can analyze large-scale HSoS models, including the following:

1. Multi-stage stochastic optimization with recourse to model human decision-making given uncertain information about the future
2. Risk management to identify system parameters that are insensitive to data uncertainties
3. Multicriteria optimization to assess tradeoffs between performance criteria
4. Model analysis techniques to identify critical modeling uncertainties and quantify model confidence

The simulation cost of large HSoS models makes black-box optimization prohibitively expensive. Thus, these optimization techniques will exploit mathematical structure to enable global analysis of mixed-continuous decision spaces. Prototypical HSoS applications will be used to motivate and evaluate these optimization techniques, including analysis of future energy infrastructure and multiplatform intelligence collection systems. These applications will illustrate decision-support capabilities to assess the impact of new technologies, identify system bottlenecks, evaluate policy choices, and design future systems.

Summary of Accomplishments

- We extended Progressive Hedging (PH) solver in PySP (Python-based Stochastic Programming) to a) support minimization of the conditional value at risk measure, b) compute confidence intervals on the value of final solution, c) support scenario clustering scalable parallel optimization, d) devise a generic infrastructure for parallelizing PH on clusters and massively parallel computers, and e) include a linearization of the quadratic equations used by PH.
- We have applied PH to multistage resource allocation and sensor placement problems, and we are collaborating with researchers at Lawrence Livermore National Laboratory on a test case using a nuclear weapons-related enterprise planning application.

- We developed collaborations with academic groups at the University of California, Davis, Universidad de Chile, North Carolina State University (NCSU), Texas A&M University, and Iowa State University to use our Coopr (computational infrastructure for operations research) software in a variety of optimization applications. We have also integrated Coopr into the Computational Infrastructure for Operations Research (COIN-OR) project, an initiative to spur the development of open-source software for the operations research community.
- We began collaborating with researchers at NCSU related to work with energy economic models. We have identified diversity analysis methods for this application that can be applied to single-objective and multi-objective formulations.
- We identified candidate mixed-variable surrogate modeling approaches and prototype implementations, and we identified possible roles for surrogates in mixed-integer and/or stochastic programming algorithms.
- We continued to extend the COLIN optimization interface library, which provides an extensible framework for hybrid optimization. These extensions support our development of multi-objective optimizers for uncertain objectives.
- Project members gave 11 presentations at international conferences, including one keynote address. Two conference papers were published. Three other journal articles were submitted.
- We prepared software releases for several packages: PyUtilib 3.0-3.2 Coopr 2.3; UTILIB 4.1; FAST 2.1-2.5; PageMarkup 0.1-0.2; TicketModerator 0.3-0.5. There have been over 1000 unique downloads and checkouts of software packages supported by this project in the past year.

Significance

Many Sandia and DOE programmatic thrusts that concern the analysis of complex man-made systems, and national infrastructure models are being used to inform government policy, assess risks, and evaluate system interdependencies. Complex systems analysis is highlighted in numerous investment areas. These optimization methods can analyze models for the Sandia Water-Energy Nexus, DOE Hydrogen Program, the National Energy Modeling System, and related problems for the Environmental Protection Agency, the Defense Threat Reduction Agency, DoD and DHS.

System-Directed Resilience for Exascale Platforms

130743
Year 2 of 3
Principal Investigator: R. E. Riesen

Project Purpose

Resilience on massively parallel processing systems has traditionally been the responsibility of the application, with the primary tool being application-directed checkpoints. However, as systems continue to increase in size and complexity, the viability of application-directed checkpoint as a sole solution decreases. Recent studies performed at Sandia projected that as systems grow beyond 100,000 components, a combination of factors lead to checkpoint overheads in excess of 50%. In this project, we will investigate alternative approaches for applications running on capability-class systems to support resilience. The goal is to provide efficient, application-transparent resilience through coordinated use of system resources. The primary R&D topics focus around the problem of continuous computing in the event of a component failure. A preliminary list of required new capabilities include, but are not limited to the following.

- Application quiescence: the ability to suspend CPU, network, and storage services used by an individual application without interfering with the progress of other applications;
- efficient state management: the ability to identify, extract, and manage application state in a transparent, efficient, and non-intrusive way; and
- fault recovery: the ability to transparently replace a failed component without restarting the entire application.

Summary of Accomplishments

A large portion of effort and time this year was devoted to explore redundant computing. Our poster presentation at Supercomputing 2009 generated considerable interest and led to a contract with North Carolina State University to use and enhance our library source code to investigate silent data corruption and develop methods to detect and correct such errors. We presented some of our early work at Los Alamos Computer Science Institute workshop on fault tolerance. This led to a collaboration with Oak Ridge National Laboratory on a proposal to the DOE Office of Science for work that would build directly on outcomes of our LDRD project work. Our paper was accepted at the workshop on Fault-Tolerance for High Performance Computing at Extreme Scale, part of the 40th Annual Institute of Electrical and Electronics Engineers/ International Federation for Information Processing International Conference on Dependable Systems and Networks, and we have four more papers in submission, two to *Supercomputing*, and one each to *Cluster* and *EuroMPI*. The simulator, which allows us to explore redundant computing, has been released as open source software and is available for download from Sandia's web site. Another contract with the University of New Mexico will enhance this simulator to explore alternative checkpoint/restart methods and make the timing and bandwidth constraints of creating a checkpoint more realistic.

We are currently working on refining our memory characterization work and exploring the role new architectural features, such as graphic processing units and multicore processors, play in creating and managing checkpoints. Overall we made very good progress toward a formalized understanding of redundant computing for extreme-scale systems.

Significance

This project is relevant to Sandia's Science, Technology, and Engineering mission. If successful, it will have a direct impact on applications in virtually all areas of advanced computing.

Refereed Communications

R. Brightwell, K. Ferreira, and R. Riesen, "Transparent Redundant Computing with MPI," EuroMPI 2010, Stuttgart, Germany, September 2010.

R. Riesen, K. Ferreira, and J. Stearley, "See Applications Run and Throughput Jump: The Case for Redundant Computing in HPC," First International Workshop on Fault-Tolerance for HPC at Extreme Scale (FTXS 2010) in conjunction with The 40th Annual IEEE/IFIP International Conference on Dependable Systems and Networks (DSN 2010), Chicago, IL, June 2010.

An Internet Emulation System to Enable Predictive Simulation of Nation-Scale Internet Behavior

141505
Year 1 of 3
Principal Investigator: R. G. Minnich

Project Purpose

We propose a three-part project aimed to construct an emulation platform that will allow us to model, analyze and predict the behavior of nation-scale networks.

Recent vulnerabilities in network architectures/protocols have caused intense interest in the development of a national capability to simulate very large networks to better understand problems with existing networks and to develop more secure technologies. However, simulations lack the fidelity of testbeds of network hardware and testbeds cannot scale to the sizes required. Virtualization helps scale testbeds beyond what can be physically implemented. Using virtual machines (VMs), users analyze large networks by copying and instantiating machines onto virtual testbeds. Since VMs run the same binaries as physical machines, VM testbeds have higher fidelity than simulations.

Although VM-based testbeds scale better than physical testbeds, they are limited by the underlying VM technology. Off-the-shelf VMs (e.g., QEMU, VMware, and Dynamips) allow < 25 VM instances to run per physical host. For large-scale analyses (e.g., to determine protection strategies for nationwide networks), we require 100–1000 VMs per physical node.

Using recent advances in lightweight virtualization, we propose to develop VMs capable of scaling to 100s–1000s of emulated nodes per processor, enabling simulation/emulation of millions of nodes. We will investigate methods to configure and collect data from emulations employing millions of VMs on high-performance computing (HPC) clusters.

Summary of Accomplishments

- We have developed a prototype botnet — “sandbot” — based on the sand pile model. We have run that botnet on 25,000 VMs on the “Talon” cluster, as well as on 500,000 VMs on the Lawrence Livermore National Laboratory (LLNL) Hyperion cluster. We have a movie of the 50,000 node run that we showed at the *SuperComputing 2009* conference, and it shows the emergent behavior of even this trivially simple algorithm when run at large scale.
- We have developed tools for visualizing the actions of botnets containing a million virtual machines.
- The data collection software (pushmon) is working very well. We gathered 5 Gbytes of data from pushmon on one run and the effect on the systems was not measurable; this was a 14 byte heartbeat per host over 500,000 hosts, at an aggregate rate of 1/3 Mbyte/second. This may seem low, but one must consider that it represents ½ million packets per second, which if managed as individual packets and writes to a file server, would probably disable it. By comparison, other monitoring systems measure at 10-minute intervals and far lower aggregate data rates.
- We have set up a data analysis system at LLNL and are beginning to map out the data analysis tasks.
- We have developed new software (VMatic) which allows us to configure and start up one million or more virtual machines with a very minimal configuration file — 20 lines in the case of the 1000-node

Hyperion cluster. This is the first application of what we are calling Computational Configuration, i.e. the configuration data is created by computing it from a set of formulas, rather than enumerating it in a file. This software allowed us to spin up 500,000 VMs on Hyperion in 3 minutes. No other software comes close to this kind of performance.

Significance

Our proposed work will support the mission of DHS Objectives 3.2 and 3.3 ("Ensure Continuity of Government Communications and Operations" and "Improving Cyber Security"). Our project also supports the US strategy articulated in response to the Comprehensive National Cyber Initiative by supporting cyber threat analysis, by supporting the prototyping of sophisticated defensive systems and furthering cyber science and technology research and development.

Effects of Morphology on Ion Transport in Ionomers for Energy Storage

141506
Year 1 of 3
Principal Investigator: A. Frischknecht

Project Purpose

Polymer electrolytes are essential elements of current and next-generation energy storage applications. An important class of polymer electrolytes is ionomers, in which one of the ions is covalently bound to the polymer backbone. Ionomers are currently used in fuel cells, and show extraordinary promise as solid electrolytes in batteries for transportation and portable-power applications. Solid electrolytes are desirable for a variety of reasons. A primary one is safety: the lack of solvent leads to fewer electrochemical reactions (i.e., with the electrodes) and the absence of flammable liquids. Solvent-free electrolytes allow for less packaging and easier manufacture. Single-ion conductors such as ionomers also have the advantage of higher efficiency (high lithium transference numbers), since the anions are bound to the polymer backbone and the current is primarily due to the cations. However, present ionomeric materials do not have sufficiently high conductivities. Ion transport mechanisms in ionomers and their relation to molecular structure are poorly understood, although it is known that ion transport is coupled to polymeric motion and to the nanoscale morphology of ionic aggregates that self-assemble in the polymer matrix. We propose to develop and use a suite of multiscale models and tools to investigate the ionic structure/morphology and to predict their effects on ion transport in ionomers. Modeling charged polymers is challenging, and to date, there have been no multiscale models of ionomer properties. In this project, we will develop a method for propagating information from the quantum and atomistic scales, through the mesoscale and up to the continuum level, incorporating the necessary chemistry and physics to accurately predict the behavior and properties of ionomeric materials. The ability to model these materials will enable the design and synthesis of new ionomers that could lead to sizeable improvements in battery safety and performance essential for electrified vehicles.

Summary of Accomplishments

Work in the first part of the project has focused on starting our efforts at all scales of modeling. We are implementing changes to codes to enable modeling of ionomers, as well as performing initial calculations and simulations of ionomers in order to explore appropriate methods and to determine what will be needed for predictive models of these materials. The ab initio work to date has focused on the model system of Li^+ ions in water, in order to determine how much of the solvation environment must be included to obtain a converged calculation for properties such as the Li chemical shift. We have used solid state ^1H and ^{13}C magic angle spinning nuclear magnetic resonance (NMR) spectroscopy to characterize a set of Zn-neutralized ionomer membranes (obtained from the University of Pennsylvania). The NMR reveals that the changes in PE-AA poly(ethylene-co-acrylic acid) structure and dynamics imposed by these carboxylic acid defects are distinct from simple polyethylene (PE) membranes. To simulate morphology, we have performed a series of molecular dynamics simulations of coarse-grained models of these ionomers, varying the number of neutral sites between charged groups, the size of the counterions, and the dielectric constant of the system. We find different morphologies of the ionic aggregates depending on the model parameters, with trends that match x-ray scattering data. We are currently preparing a manuscript about this work. Initial work using fluids density functional theory has been devoted to improvements to the code, including implementing an improved description of charged polymers. At the continuum level, we are in the process of designing additions to Cantera, the constitutive modeling code that we have used to build a successful 1D thermal battery model, that will incorporate ion transport mechanisms believed to be important in ionomers into a transport object within the code.

Significance

The success of this project could have a significant impact on Sandia's missions in predictive simulation and electrical energy storage. The proposed work could enable the design of better ionomers for lithium ion batteries, leading to smaller, safer, and more efficient batteries for vehicles. This project will establish Sandia in the area of predictive simulation of polyelectrolytes, and will position us to have impact on future energy solutions and energy security for DOE and the nation.

Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant-Scale

141508
Year 1 of 3
Principal Investigator: R. R. Rao

Project Purpose

Nuclear waste reprocessing and nonproliferation models are needed to support the renaissance in nuclear energy; a proven technology without a carbon footprint. Our aim is to develop predictive capabilities targeting the design and monitoring of a next-generation nuclear fuel cycle to enable economic large-scale reprocessing with highly accurate material balances to mitigate public concerns regarding waste disposal and proliferation. Models will advance the state-of-the-art at four length-scales: droplet, contactor, column, and plant.

The Pu/U extraction process model will be developed in SIERRA Mechanics at the droplet and contactor-scales, using a continuous and discontinuous finite element modeling (CDFEM) representation of the interfacial mass transport that occurs in the turbulent emulsion. Mass transport predictions will be based on non-ideal thermodynamics provided by Cantera, replacing the current empirical ones. Predicted distributions of radionuclides will be used in SCEPTRE to determine criticality constraints and maximum contactor size. Column-scale models, based on droplet population balances from the high-fidelity simulations, will be developed to investigate contactor placements and coupling. Plant flow sheets for reprocessing will be created using a novel, scalable network model developed under the Office of Advanced Scientific Computing Research (ASCR) that will allow coupling of massively parallel contactor models to simple equilibrium models for other plant unit operations. The plant models will be critical to support nonproliferation activities including material accountancy, plant design, detector placement, and diversion scenarios. Models will be validated through experimental work at Sandia, and the Oak Ridge National Laboratory (ORNL) pilot plant.

This work will allow Sandia to leverage its existing expertise in turbulent reacting flow, concentrated solution thermodynamics, level set technology, neutronics, network modeling, and uncertainty quantification, developed under the advanced simulation and computing initiative and ASCR, to address separations while producing publishable work in several areas and producing novel capabilities.

Summary of Accomplishments

- The project consists of four tasks: 1) experimental validation, 2) fluid and transport modeling, 3) thermodynamics, and 4) plant-scale modeling. We have made significant progress on all four tasks. We have designed and fabricated a microfluidic device to examine mass transport in a single droplet. This was fabricated in glass to allow for experiments with concentrated nitric acid. We have utilized a nonradioactive model system based on the lanthanide europium, which will serve as an analog for uranium. A commercial contactor has been purchased for full-scale validation. Experiments are underway using a simple model system.
- The CDFEM algorithm has been tested and improved based on several mesoscale problems including a droplet in a shear flow and a stagnant bubble. This work will be documented in a journal article in preparation. The coupling between CDFEM and the turbulence models in SIERRA is being advanced via a new hybrid finite element method that allows us to use turbulence models in the same Galerkin framework and element space used for the CDFEM. Testing is underway of the turbulence models in a contactor geometry.

- Thermodynamic modeling of tri-butyl phosphate-water-nitric acid-uranium systems, including activity coefficient and transport properties, has been undertaken and implemented into Cantera for future coupling to SIERRA. We have developed a transport formalism for this coupling and this has resulted in an implementation plan.
- A section of the material accountancy model has been translated into network units suitable for implementation into the ASCR network tool. These units will provide the building blocks for the translation of the entire Separations and Safeguards Performance Model to meet the FY 2010 milestone. A contract has been placed with Yale University to develop a population-balance approach to contactor modeling suitable for implementation in the network tool. This approach will advance our unit operations for plant-modeling.

Significance

Sandia has pioneered the field of surety by designing technology-based safety and security systems for nuclear weapons, and extending surety to commercial nuclear facilities for the Nuclear Regulatory Commission. We propose to develop technologies to ensure surety of nuclear waste reprocessing facilities by drawing on our engineering and computational science expertise, 12 years of ASC SIERRA Mechanics code development, and over 60 years of surety engineering. This work will support DOE missions in nuclear energy and nonproliferation, as well as renewable, carbon-free, energy. Improvements to SIERRA for turbulent multiphase flow will also support the nuclear weapons program directly. Outcomes for this project include the following: 1) new methods of solving multiphysics simulation by incorporating detailed thermodynamics with transport in a massively parallel framework to enable first-principles prediction of emulsion formation, advancing the state-of-the-art; 2) numerical models to support design and development of a nuclear waste reprocessing facility in the US; 3) plant-scale modeling capability to support collaborations with the oil and chemical industry; 4) high performance computing separations models for liquid-liquid extraction. Outputs include new capabilities in SIERRA mechanics to enable the solution of previously unsolvable problems, as well as publications in the open literature including journals and conference presentations. We intend to publish material from the droplet-scale validation studies, the contactor-scale experiments, the CDFEM verification work, the thermodynamic modeling of actinide separations, and the population balance models of the mixing zone in the contactor.

This work could attract cooperative research and development agreements with industry partners. This project is an initial investment that can be applied to many other related unit operations and plant models in the emerging alternative energy field, such as CO_2 scrubbing or algal separations. Our existing expertise in turbulent reacting flow, level set technology, and nuclear waste disposal will be brought to address the separations science area, a natural growth area for these applications.

Predictive Multiscale Modeling of Thermal Abuse in Transportation Batteries

141509
Year 1 of 3
Principal Investigator: R. P. Muller

Project Purpose

Transition from fossil-fueled to electrified vehicles depends on developing economical, reliable batteries with high energy densities and long life. Safety, preventing premature or catastrophic failure, is of paramount importance in battery design. The largest gaps in our technical understanding of the safe operation of electrical energy storage devices involve the fundamental mechanisms, energetics, and inefficiencies of complex processes that occur during battery operation that can lead to thermal runaway: charge transfer, charge carrier and ion transport, both in the bulk and at various interfaces, and morphological and phase transitions associated with Li-ion transport between cathode and anode. We will develop a comprehensive predictive capability for thermal management and the onset of thermal runaway in transportation-based secondary Li-ion batteries, rooted in a first-principles description of the governing atomistic processes at the electrode-electrolyte interface, propagating chemical information through multiple scales to a continuum-scale description of thermal transport and failure capable of addressing a variety of operational and thermal excursion conditions. The development of such a comprehensive model will enable scientists and engineers to identify and address potential safety and stability issues of new battery designs prior to experimental realization. This development will constitute a unique capability, and will be of great significance within Sandia, for the DOE and DoD, and for its current and future commercial partners.

Summary of Accomplishments

During the first year of this project, we have made significant progress toward our overall project goals, and have met the milestones to date. At the cell level, we have investigated existing empirical models for thermal runaway in Li-ion batteries. We have developed an improved model for fitting existing experimental calorimetry data to differential equation form. We have begun the work of describing the chemical reactions that the electrolyte molecules undergo with the anodes and cathodes. We have computed Li-ion diffusion rates through the cathode and the electrolyte materials. And we have developed a version of the Cantera chemical reaction code on top of the Trilinos parallel math libraries to provide a scalable capability for simulating thermal runaway in batteries.

A key element of our work is the development of new simulation capabilities. One effort focuses on modeling chemical reactions occurring at electrode/electrolyte interfaces. Toward this goal, we designed the necessary interfaces between SeqQuest and Tramonto, and are implementing release versions that will be the foundation for the integration. We have begun preliminary integration work under the LIME (lightweight integrating multiphysics environment) framework, a part of Trilinos.

A second effort seeks to model the growth of the solid electrolyte interphase protecting the battery anode. Toward this goal, we have implemented a kinetic Monte Carlo technique to model growth of the organic and inorganic components of this layer.

We have actively pursued identifying relevant data for model validation. We have begun work on identifying and ranking phenomena relevant to thermal abuse in Li-ion batteries. We have also begun collaboration with the University of Florida to provide additional validation data, using impedance spectroscopy at elevated temperatures.

Significance

Advances in batteries are driven by improvements in the materials that comprise them. Materials changes require a complete experimental characterization to ensure the batteries remain safe; such a characterization is time consuming and expensive. By developing a method that will enable a first-principles correlation of basic materials properties to thermal runaway and associated safety problems, we expect to largely overcome this costly empirical characterization. This will reduce the expense and the time required to develop new battery chemistries.

We are in the process of creating a predictive modeling capability for the safety of transportation batteries, validated against the results from the Sandia battery testing laboratory. Coupling Sandia's abuse experiment and test capabilities with our ability to predict and understand test results through predictive simulation will further assert and maintain Sandia's leadership in this area. These strengths will be particularly valuable to Sandia with the national focus on renewable energy and green transportation.

During the first year we have made meaningful strides toward achieving this goal. We have begun to develop new modeling capabilities, and have made significant progress in understanding the relevant published data. During the course of the year, we have received a great deal of interest in potential collaboration from industry and other laboratories. We have briefed the United States Advanced Battery Consortium, LLC, Freedom Car Board of Directors about our work. We have met with several researchers from General Motors on multiple occasions. We have helped the DOE/EERE (Division of Energy Efficiency and Renewable Energy) develop a new related research program for the Computer Aided Engineering of Batteries (CAEBAT), resulting in additional funded research from the DOE/EERE CAEBAT program, and that has also given us many opportunities to release the ultimate results and capabilities generated by this project when they are available.

Risk Assessment of Climate Systems for National Security

141510
Year 1 of 3
Principal Investigator: G. A. Backus

Project Purpose

The purpose of this work is to develop analytical methods to quantify the integrated risk from climate change. The physical risk requires a better understanding of the climate change uncertainty. We are developing the uncertainty quantification (UQ) methods to sample and characterize this, despite the large computational expense of climate simulations. There is also a need to quantify the validity in using climate models for such assessments. We are extending PCMM (Predictive Capability Maturity Model) to serve this function. Climate change affects socioeconomic conditions largely though hydrological intermediation. Further, rapidly changing conditions in the Arctic have the potential of significant ramifications for hydrological and socioeconomic conditions. We are developing new hydrological simulations to accommodate permafrost, land movement, and biomass progression for use in the US Community Earth System Model (CESM). Further, we are developing the simulation of the linkage between hydrological condition and socioeconomic activity. Additionally, we are using simulations of the Arctic to determine the realizability of (unexpected) emergent phenomena, using the ice-free Arctic as a test case.

Summary of Accomplishments

The following is a list of accomplishments.

- Linked Dakota to the Community Climate System Model (CCSM) and are currently running UQ analyses. Red Sky simulations are still running with results over the next month.
- Prototyped methods for underrepresented phenomena (clouds).
- Prototyped methods for underrepresented phenomena (tail-distribution parameters).
- Are running CCSM for emergent phenomena (ice free-Arctic).
- Initial report on new PCMM metrics for climate models.
- Development and testing of 1D hydrology model for use with CCSM in Arctic analyses; next year's work will extend this to 3D plus ground movement.
- Developed interface for linking hydrological impact to socioeconomic impacts; have screened countries mostly like to be at greatest risk from the various physical effects from climate change.
- Have developed new methods to understand the impact of cloud formation on climate uncertainty by developing detailed models of cloud formation dynamics.

Significance

This effort further develops the foundational capabilities Sandia requires for its participation in existing DOE Office of Science efforts, including the pending NNSA climate impact effort. Our intelligence community, DHS, and defense agencies have all expressed concerns directly to Sandia about the impacts of climate change and the need for Sandia to extend its national security assessment capabilities into the realm of climate change. In accordance with these goals, this effort improves high-resolution climate modeling methods of critical importance to predictive science, develops advanced spatially and temporally resolved methods to enable discovery of phenomena, and develops new computational and statistical approaches for optimization, verification, validation, and uncertainty quantification necessary for regional predictions to enable national security assessments.

Streaming Data Analysis for Cyber Security

141511
Year 1 of 3
Principal Investigator: S. J. Plimpton

Project Purpose

A ubiquitous task in cyber security is monitoring network traffic, looking for anomalies that indicate incoming attacks, intruders or malware already inside a local network, or data exfiltration. Monitoring typically involves data collection and post-processing of archived log files using manually updated filters along with human inspection and judgment. While effective, this approach has limitations: timely responses may be impossible, analyses may be inaccurate or incomplete because data exceeds storage capabilities, and rapidly evolving strategies may be undetectable.

These issues can potentially be addressed by modeling and analyzing the stream of network traffic in real time, as it is captured. This is challenging due to the large volume of data, limited computational power in monitoring hardware, and a lack of mathematical definitions of interesting events and algorithms to detect them in streaming data.

We propose to develop new streaming algorithms and software to overcome these challenges and enable the power of post-processing methods — which employ graph-based algorithms and classification techniques — to be applied in real time.

This project aligns with several national and Sandia goals. It also addresses three of this year's five focus areas: formulation of mathematical models, codification of new methodologies, and development of platforms/architectures/frameworks for enabling predictive simulation.

Summary of Accomplishments

In the first year of this project, we have worked to detect and capture interesting "events" in network packet flows. We are working to analyze and classify these events and their associated data in a post-processing fashion, with the goal of eventually enabling real-time flagging of potentially damaging events and intrusions.

Significance

Sandia has made a strategic decision to emphasize cyber security. This project can contribute to two specific. The first is to become a "model laboratory" for DOE in information security, going beyond basic compliance. Having the tools at our disposal that this project should create is a step in that direction. Second, the report discusses a "super-defense" strategy for cyber security. The software produced by this project could be part of that solution.

The benefits of the proposed work are practical, programmatic, and scientific. Our streaming algorithms on data collection hardware will enable Sandia (and others) to protect network and sensitive data. Our collection of algorithms will be novel technology that Sandia can use to form partnerships in the intelligence community. More broadly, processing streaming data is a computational challenge gaining importance in many fields of security and science. For example, in financial transaction software, what we are attempting to do is termed "complex event detection." Cloud computing is also beginning to grapple with streaming algorithms, due to the immense volumes of data it can process. Success in this project would enable Sandia to become a leader in this emerging area.

As far as possible, given the sensitive use of this kind of software, we will publish our algorithmic work in the open literature. We also plan collaborations with academics working in the more general area of streaming algorithms.

Distinguishing Documents by Parts-of-Speech Dynamics

149045
Year 1 of 1
Principal Investigator: S. A. Mitchell

Project Purpose

We propose a sentence mining technique that exploits both the distribution and the order of parts-of-speech (POS, as defined by the Penn Treebank) in sentences in English language documents. The research is focused on discovering meaningful sentence dynamics (grammar) signatures. If successful, it would be possible to discover "call-to-action" framing documents hidden within a corpus of mostly expository documents, even if the documents were all on the same topic and used the same vocabulary. This distinguishes the proposed work from ongoing activities in topic identification, which analyzes the bag of words in documents using linear algebra. While the rules of grammar are specified a priori by linguists, this would be the first known computational approach to discovering and characterizing actual, observed English grammar.

Distinguishing framing vs. expository documents within unknown topics is the most important problem of this type, but this project would start with an easier problem with readily available data. We seek to distinguish opinion vs. exposition, in particular, distinguishing Netflix "positive" and "negative" movie reviews from abstracts from a groundwater science journal, without exploiting topic and word differences. Our preliminary work shows that the cosine similarity of the subsequences of POS is able to distinguish between abstracts and Netflix; and also between 1) actual sentences and 2) the same sentences reversed and 3) the same sentences with their POS randomly permuted. It appears that subsequence lengths between 2 and 5, especially 3, are better differentiators than simply the frequency of POS (i.e., subsequence length 1).

From preliminary work, we have figures that contrast the cosine similarity for subsequence length 1,2,3,4,5, among 100 scientific abstract sentences, the same sentences backwards, and the same sentences randomly permuted; also between 100 scientific abstract sentences and 100 "negative" and 100 "positive" movie reviews.

Summary of Accomplishments

We proposed a sentence mining technique that exploited both the distribution and the order of parts-of-speech (POS) in sentences in English language documents. The ultimate goal was to be able to discover "call-to-action" framing documents hidden within a corpus of mostly expository documents, even if the documents were all on the same topic and used the same vocabulary. Using POS was novel. We also took a novel approach to analyzing POS. We used the hypothesis that English follows a dynamical system and the POS are trajectories from one state to another. We analyzed the sequences of POS using support vector machines and the cycles of POS using computational homology. We discovered that the POS constituted a very weak signal and did not support our hypothesis well. Our original goal appeared to be unobtainable with our original approach.

We turned our attention to study an aspect of a more traditional approach to distinguishing documents. Latent Dirichlet Allocation turns documents into bags-of-words, then into mixture-model points. A distance function is used to cluster groups of points to discover relatedness between documents. We performed a geometric and algebraic analysis of the most popular distance functions and made some significant and surprising discoveries. We showed that several popular distances, chi-squared, Jensen-Shannon divergence, and the square of the Hellinger distance were nearly equivalent — in terms of functional forms after transformations, factorizations, and series expansions, and in terms of the shape and proximity of constant-value contours. A single one-dimensional family of curves describes their relationship, even for high dimensional data. We see that clustering results will be the same, except where the data points' coordinate value ratios are higher than about 5. This is somewhat surprising given that their original functional forms look quite different. Cosine similarity is the square of the Euclidean distance, and a similar geometric relationship is shown with Hellinger and another cosine.

Significance

This work supports text analysis, important for nonproliferation, cyber security, and other data-centric security missions.

The potential for the part-of-speech work was that it could eventually lead to finding unknown social movements within unknown topics, for the above missions. Eventually we may be able to distinguish:

1. Fluent vs. non-fluent English
2. Machine vs. human generated
3. Opinion vs. narrative, exposition, or enumeration
4. Framing vs. narrative, exposition, or enumeration
5. Framing vs. opinion

The distance-function work addresses the same problem, but with a non-topological approach. Additionally, it addresses the broader question of, “how do we know we have the ‘right’ clustering?” At Sandia we cluster data daily, putting points into groups, for cyber, nonproliferation etc. The clustering obtained depends on the choices we make along the way, and there are many. Do we even know how these choices change the answer? One of the fundamental choices is how to measure how close two data points are to each other. This new geometric comparison of the most popular distance functions for a certain model shows that many of the functions are very similar, but with sharp differences in certain areas. So far the results regarding these distances have been surprising to the local community.

Development of a Quantum Chemistry Application within a Scale-Free Computing Model

149046
Year 1 of 1
Principal Investigator: J. P. Kenny

Project Purpose

Current programming models for high-performance computing are fault-intolerant and use global operations. Those properties are unsustainable as computers scale to millions of CPUs; instead, one must recognize that these systems will be hierarchical in structure, prone to constant faults, and global operations will be infeasible.

The FAST-OS HARE project is introducing a scale-free computing model to address these issues. This model is hierarchical and fault-tolerant by design, allows for the clean overlap of computation and communication, reducing the network load, does not require check-pointing, and avoids the complexity of many high performance computing (HPC) runtimes. Development of an algorithm within this model requires a change in focus from imperative programming to a data-centric approach.

Quantum chemistry (QC) algorithms, in particular electronic structure methods, are an ideal test bed for this computing model. These methods describe the distribution of electrons in a molecule, which determine the properties of the molecule. The computational cost of these methods is high, scaling quartically or higher in the size of the molecule, which is the reason QC applications are major users of HPC resources. The complexity of these algorithms means that message passing interface alone is insufficient to achieve parallel scaling; QC developers have been forced to use alternative approaches to achieve scalability and would be receptive to radical shifts in the programming paradigm.

Initial work in adapting the simplest QC method, Hartree-Fock, to this the new programming model indicates that the approach is beneficial for QC applications. However, the advantages to being able to scale to exascale computers are greatest for the computationally most expensive algorithms; within QC these are the high-accuracy coupled-cluster methods. This project investigated how such science applications can be constructed with scale free, data-centric programming models to enable extreme-scale performance.

Summary of Accomplishments

We developed a scale-free implementation of the matrix multiply kernel, a critical step in many science applications such as the coupled cluster quantum chemistry method. Practical realization of this required development of prototype generic interfaces for data-centric computing and automated problem decomposition. The implementation of the matrix multiply kernel demonstrated the efficacy of these interfaces, guiding development of new runtime systems and applications for extreme-scale parallel computers. These interfaces and kernel provide important building blocks for continuing design and simulation of applications and hardware for extreme scale.

Significance

Computation at the largest scales is an enabling technology across DOE's mission areas and the national security mission, as a whole. This project investigated the next step in developing algorithms for the forthcoming high-performance computers, by providing an exascale-class algorithm for an important application and demonstrating the viability of the programming model. This work is particularly crosscutting: it involved research both into the computer science of the problem as well as focusing on a quantum chemistry application and involved significant staff collaboration.

Peer-to-Peer Architectures for Exascale Computing

149048
Year 1 of 1
Principal Investigator: J. Mayo

Project Purpose

The goal of this research was to investigate the potential for employing dynamic, decentralized software architectures to achieve reliability in future high-performance computing platforms. These architectures, inspired by peer-to-peer (P2P) networks such as botnets that already scale to millions of unreliable nodes, hold promise for enabling scientific applications to run usefully on next-generation exascale platforms ($\sim 10^{18}$ operations per second). Traditional parallel programming techniques suffer rapid deterioration of performance scaling with growing platform size, as the work of coping with increasingly frequent failures dominates over useful computation. This project aimed to study the dynamics of P2P networks in the context of a design for exascale systems and applications. We sought to obtain theoretical insight into the stability and large-scale behavior of candidate architectures, and to work toward leveraging Sandia's Emulytics platform to test promising candidates in a realistic (ultimately $\geq 10^7$ nodes) setting.

Summary of Accomplishments

We developed a simulation framework, as well as a preliminary implementation in a large-scale emulation environment, for exploration of "fault-oblivious computing" approaches. We designed a general architecture that allows effective failure management and, under some conditions, fault obliviousness in exascale computing scenarios. Our studies suggested that such an architecture, in which failures are treated as ubiquitous and their effects are considered as simply another controllable source of error in a scientific computation, can remove obstacles to exascale computing for certain applications. Our primary example applications were drawn from linear algebra: a Jacobi relaxation solver for the heat equation, and the closely related technique of value iteration in optimization.

Significance

High-performance computing (HPC) is at the heart of both nuclear weapons and energy programs and research. DOE intends to remain at the forefront of HPC, and the next generation of computers will require a considerably more robust approach to system and application software. This project contributes to providing the robustness necessary to make these next-generation computers practical. Recovering from failures with sufficient accuracy using local data, and avoiding the need for global check-pointing and the resulting slowdown, would remove a major obstacle to exascale computing. This work has leveraged, and will continue to inform LDRD Project 141505 and related efforts. We will draw on these insights in its HPC mission work. The robustness of large networks is an aspect of complex systems and also applies to Sandia's cyber-security mission, suggesting other relevant opportunities.

Natural Materials for Carbon Capture

149205
Year 1 of 1
Principal Investigator: R. T. Cygan

Project Purpose

Naturally occurring clay minerals provide a distinctive material for carbon capture and carbon dioxide sequestration. In particular, swelling clay minerals, such as the smectite variety, possess an aluminosilicate structure that is controlled by low-charge layers that easily expand to accommodate water molecules and, potentially, carbon dioxide. The interlayer of smectite clays also includes counterbalancing cations such as sodium that balance the negative layer charge. Recent experimental studies have demonstrated the efficacy of intercalating carbon dioxide in the interlayer of layered clays but little is known about the molecular mechanisms of the process and the extent of carbon capture as a function of clay charge and structure. In economic terms, clay minerals are a common natural resource and are proverbially "dirt cheap." Clay minerals are an attractive alternative to more complex materials that often require significant chemical functionalization to ensure acceptable carbon capture performance. Such materials could have a distinct advantage in that they can be used once and buried, saving the cost of regenerative energy, CO_2 compression, and subsurface injection. Molecular dynamics simulations will be performed at Sandia to better assess the molecular interactions associated with incorporation of the CO_2 in the interlayer of montmorillonite clay, and to simulate vibrational spectra to help validate the models with experimental observation. This computational chemistry project will provide proof of concept that our predictive simulation tools can meet future research needs of the National Energy Technology Laboratory (NETL) and provide the foundation to expand Sandia's role in carbon management in partnership with NETL.

Summary of Accomplishments

We have completed a series of molecular dynamics simulations to better assess the molecular interactions associated with incorporation of the CO_2 in the interlayer of montmorillonite, and to simulate vibrational spectra to help validate the models with experimental observation. We first extended several published three-site potential models of CO_2 to derive a set of accurate interaction parameters that are compatible with the widely-used CLAYFF (Clay Force Field). The extended set of interaction parameters permits full flexibility of the molecule allowing bond stretching and bond bending. Comparison of experimental and theoretical data with our molecular dynamics simulations of gaseous and liquid CO_2 confirms the accuracy of the new force field. Based on the experimental evidence for CO_2 intercalation in montmorillonite clay, provided by NETL, we developed a conceptual model for the intercalated structure and performed a series of molecular dynamics simulations. Power spectra were derived from the equilibrated atomic and velocity trajectories that allowed the isolation of signal from key components of the molecular model. Normal model analysis of optimized structures of CO_2 and Na-CO_2 derived from density functional calculations are in general agreement with the findings of the classical results obtained from the molecular dynamics simulations. Our dynamics results indicate that, once intercalated into the clay the bending motion of CO_2 at approximately 667 cm^{-1} is blue-shifted and split. The asymmetric stretch of CO_2 at 2350 cm^{-1} exhibits a smaller blue shift, however it is consistent with the experimental findings of NETL. This computational chemistry investigation provides a proof of concept that molecular simulation methods have the capability and accuracy to predict the mechanisms associated with CO_2 capture in complex natural materials.

Significance

This project emphasizes the fundamental behavior of gaseous, liquid, and supercritical carbon dioxide and clay-intercalated carbon dioxide. It provides a theoretical foundation for evaluating the mechanisms of carbon capture and sequestration, and confirms the ability of an economically attractive and naturally occurring mineral to capture carbon dioxide. The technical collaboration with NETL supports the development of a long-term technical partnership. Furthermore, the state-of-the-art molecular simulations support efforts to develop tools and methods for the accurate modeling of complex systems.

Molecular Modeling in Support of CO_2 Sequestration and Enhanced Oil Recovery

149209
Year 1 of 1
Principal Investigator: L. Criscenti

Project Purpose

CO_2 sequestration in sedimentary basins has been proposed to store excess atmospheric CO_2. Suitable formations for sequestration will be over 800 m deep, where high pressures will maintain a CO_2 density that decreases CO_2 buoyancy with respect to water and oil. The relationships between the simple fluid phases (CO_2, water and oil) that coexist in a basin are established. However, the interactions between these fluids and the surrounding rock matrix are not well studied and impact CO_2 mobility. The "wettability" of minerals to H_2O, CO_2, and hydrocarbons affects the distribution, transport and fate of these fluids in sedimentary basins. For example, CO_2 adsorption to the rock matrix may enhance CO_2 sequestration; however, if the aqueous solutions and petroleum fluids have greater affinity for the mineral surfaces, CO_2 may migrate through fractures towards the surface. Changes in CO_2 viscosity, water concentration, and ionic species in the CO_2 fluid from the basin environment through the caprock will play a role in CO_2 migration. We will investigate CO_2 mobility in reservoir and caprock systems by studying the relative adsorption of H_2O, CO_2, and heptane to key sedimentary minerals as a function of temperature and pressure using molecular dynamics simulations. This investigation will also provide guidelines for the use of CO_2 in enhanced oil recovery.

Summary of Accomplishments

We used molecular dynamics simulations to examine the wettability of minerals to different fluid phases. Large-scale molecular dynamics simulations involving between 100,000 and 200,000 atoms were conducted to establish a dynamic equilibrium between a drop of liquid water, water vapor, and kaolinite surfaces. These calculations were performed using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), a parallel-processing molecular dynamics code and the CLAYFF (Clay Force Field) both developed at Sandia. The water drops consisted of at least 1700 molecules. Simulations were performed for five nanoseconds. Two approaches were tested to extract contact angle information from simulation trajectories. Contact angles were determined on both the siloxane and gibbsite surfaces of kaolinite. The contact angle calculated for the siloxane surface is approximately 110º, and compares well with calculated contact angles for silica reported in the literature. The contact angle determined for the gibbsite surface is approximately 13º and compares favorably to reported experimental results. As expected, the siloxane surface is calculated to be hydrophobic and the gibbsite surface hydrophilic. We have developed a post-processing algorithm to calculate contact angles from molecular dynamics trajectories, and it can be used to investigate the interaction of other fluids such as heptane and carbon dioxide with solid surfaces. This technique should prove useful to investigate the relative wettability of different minerals with subsurface fluids including supercritical CO_2.

Significance

Using Sandia-developed computational tools, we established a methodology for calculating contact angles directly from classical molecular dynamics simulation output. We developed post-processing codes to implement two different algorithms for calculating contact angles. We successfully compared our calculated contact angles for water on both hydrophilic and hydrophobic surfaces to reported experimental and calculated results in the literature. Our research will feed into the CO_2 management thrust area where the relative wettability of mineral surfaces with respect to different fluids including oil and supercritical carbon dioxide is critical knowledge required for developing approaches for CO_2 sequestration and enhanced oil recovery (EOR). This research prepares us to tie modeling efforts to experimental studies that are getting underway in various

Sandia programs including the University of Texas (UT)-Sandia Energy Frontier Research Center, and Basic Energy Sciences. The goal of this research is to provide the capability of using molecular simulation as a tool to understand macroscopic fluid-mineral interactions in porous media in order to provide guidance for managing underground systems for CO_2 sequestration and EOR.

Nanocrystal-Enabled Solid-State Bonding

149210
Year 1 of 1
Principal Investigator: E. A. Holm

Project Purpose

Virtually all engineering components are comprised of materials that have been joined together. While joining technology has advanced, there are still critical applications where the joining solutions create unacceptable problems such as thermal stress-induced cracking, phase transformations, and thermal component damage. These problems are exacerbated by joining dissimilar materials or complex shapes, and bonding processes that occur late in assembly. Many of these problems occur because bonding temperatures and pressures are quite high. For example, welding and brazing use solidification of molten materials to form the joint, potentially leading to thermal stress generation and profound microstructural changes.

Nanocrystalline metals may allow us to dramatically lower the temperatures and pressures required for solid-state diffusion bonding between metals and ceramics. Recent work has demonstrated the efficacy of this approach in the copper-silver system. At this point, it is unclear how to explain or predict this phenomenon. One model for describing solid-state bonding with metal nanoparticles would be based on sintering theory. We propose a set of model bonding experiments between copper plates using silver and gold nanoparticles with a range of temperatures and pressures to be compared with sintering simulations of the same. The outcomes of this study would be the following: 1) an evaluation of sintering theory as a predictive tool for nanocrystal-enabled diffusion bonding, 2) a determination of the sensitivity of this process to the size of nanoparticles, and 3) a recommendation for the future potential of this approach. If successful, this project will create much fundamental, exciting science, in particular, regarding the prediction of sintering behavior in nanoscale materials. In addition, this project will lay the foundations for technology that could benefit a number of key programs at Sandia (nuclear weapons [NW] and defense systems and assessments) for which low-temperature, low-pressure diffusion bonding is a potential breakthrough technology.

Summary of Accomplishments

We performed a preliminary set of sintering experiments to examine nanocrystal-enabled diffusion bonding (NEDB) in Ag-on-Ag and Cu-on-Cu using Ag nanoparticles. The experimental test matrix included the effects of material system, temperature, pressure, and particle size. The nanoparticle compacts were bonded between plates using a customized hot press, tested in shear, and examined postmortem using microscopy techniques. NEDB was found to be a feasible mechanism for low-temperature, low-pressure, solid-state bonding of like materials, creating bonded interfaces that were able to support substantial loads. The maximum supported shear strength varied substantially within sample cohorts due to variation in bonded area; however, systematic variation with fabrication conditions was also observed. Mesoscale sintering simulations were performed in order to understand whether sintering models can aid in understanding the NEDB process. A pressure-assisted sintering model was incorporated into the SPPARKS kinetic Monte Carlo sintering code. Results reproduce most of the qualitative behavior observed in experiments, indicating that simulation can augment experiments during the development of the NEDB process. Because NEDB offers a promising route to low-temperature, low-pressure, solid-state bonding, we recommend further research and development with a goal of devising new NEDB bonding processes to support relevant agencies.

Significance

Nanocrystal-enabled solid-state joining would provide a complete jump in bonding technology available at Sandia. DOE and other federal agencies would eagerly welcome these advances.

Mechanical Properties of Self-Lubricating, Nanocrystalline Metal Films

149214
Year 1 of 1
Principal Investigator: C. C. Battaile

Project Purpose

Recent research at Sandia has shown that bare metal surfaces can, under certain conditions, form self-lubricating tribofilms as they wear. The available evidence suggests that this is due to the refinement of the microstructure near the contact surface, and that the mechanism is diffusion-mediated grain boundary sliding in the ultrafine-grained material that forms there. If this is true, the tribofilm should be mechanically softer than the original, parent material. However, because 1) the film is only about 500-nm deep, 2) its surface is relatively rough, and 3) polishing would destroy the film, nanoindentation is not viable as the sole approach to ascertaining the film's mechanical properties. Instead, we used a focused ion beam to create cylindrical nanopillars of approximately 250-nm diameter and 500-nm tall, and we used a nanoindenter to compress the pillars in order to characterize their mechanical properties.

Summary of Accomplishments

The specimens tested in this study represent the smallest pillars ever created at Sandia. The results indicate that the material in the wear tracks is more than twice as soft as unworn material, and this provides potential evidence of an "inverse Hall-Petch" phenomenon in nanocrystalline nickel.

Significance

Tribology and wear is responsible for a variety of aging, failure, and reliability issues in a wide range of applications, from microelectromechanical systems to electrical contacts. This work not only elucidates the basic mechanisms of self-lubrication in metals, to aid in the design of next-generation wear-resistant materials, but also contributes to the science of strength in ultrafine-scale structures and the development of future models thereof.

The Integration of Process Monitoring and Data Authentication for Safeguards

149283
Year 1 of 1
Principal Investigator: B. B. Cipiti

Project Purpose

The development of advanced safeguards concepts, approaches, and assessment methodologies to enhance the effectiveness, efficiency, and credibility of international safeguards is a key objective for the DOE/NNSA. Development of facility-specific safeguards approaches, such as process monitoring, is recognized as a need in this area. Data authentication is critical to ensure data security and authenticity. This project seeks to integrate and model both elements using the Sandia Separations and Safeguards Performance Model (SSPM) to provide a predictive simulation tool for advanced safeguards design. The SSPM is a transient model of a reprocessing plant that is used as a tool for safeguards design and analysis. The advantage of such a tool is that it will provide predictive results of novel process monitoring concepts without requiring expensive experimental work. The incorporation of process monitoring data in the model can be tested under various diversion scenarios to determine any potential improvements to diversion detection. Data authentication, typically performed on discrete pieces of equipment and not viewed from a systems level, can also be incorporated into the model. This will be the first time that such modeling has been attempted. This project will lay the groundwork to advance this area of modeling and simulation. The end goal of the work is an exemplary scenario that will build Sandia's reputation in the areas of process monitoring, authentication, and modeling and simulation with the intent of seeking additional work in these areas.

Summary of Accomplishments

Process monitoring measurements were added into the Separations and Safeguards Performance Model (SSPM) to provide the capability to use the SSPM as a tool for advanced safeguards analyses. Algorithms were added to perform bulk material balances for all vessels in the plant and to correlate that data with traditional plutonium accountancy data. Alarm conditions and thresholds were set while taking into account bias correction. The final product is a reprocessing plant model capable of performing diversion scenarios analyses using advanced process monitoring systems. We found that the process monitoring data was able to drastically improve the timeliness of detecting diversion events.

Significance

This project builds upon Sandia's capabilities in process monitoring and authentication. It will provide the demonstrable example needed to further expand our work in process monitoring. Further, this work will provide a mechanism to train new staff members in this area.

Lagrangian Shock Modeling in Highly Deformable Materials with Remeshing

149479
Year 1 of 1
Principal Investigator: A. S. Gullerud

Project Purpose

This project focuses on developing new approaches for modeling mild shocks in a Lagrangian finite element framework for highly deformable materials. Recent research at Sandia has led to the development of a remeshing approach for Lagrangian explicit transient dynamic analyses within the Sierra suite of codes. This approach employs nodal-based tetrahedral (tet) elements, which store values at their nodes, and a remeshing technique that attempts to preserve node locations. This pairing significantly reduces the amount of variable remapping that is needed, and thus holds the promise of significantly reducing the error caused by the remeshing process. This approach has been successful for low-velocity events; however, scenarios that include very high velocity impacts and/or energetic loadings require proper modeling of shock phenomena. Previous tetrahedral element formulations have been shown to behave poorly in the shock regime, and preserving accuracy during remeshing becomes much more difficult when dealing with the energy terms that proper shock modeling requires. These effects are clearly demonstrated when the current remeshing capabilities are used for problems undergoing high-rate or energetic loadings. This project will characterize the existing issues with the nodal-based tetrahedral elements in the shock regime, and seek new stabilization strategies to improve the overall response. Furthermore, it will include a detailed study of the effect of remeshing on key parameters, and provide new approaches that reduce the error involved with mesh changes.

Summary of Accomplishments

Thorough testing of the nodal-based tet under a variety of loading scenarios has demonstrated that the element has serious deficiencies in its ability to capture pressure fields effectively. This is particularly apparent in situations where shear is an important part of the deformation field. In some cases, global deformation metrics can appear to be of good quality, but the local solution within the body is still problematic. The analyses demonstrate that the connectivity of the nodal-based tet mesh is a key factor in the pressure response — changes in the regularity of the mesh typically cause corresponding changes in pressure. Using a “cross-triangle” meshing strategy appears to give a good quality pressure field for the nodal-based tet, but at a large computational expense. These difficulties bring into question the solution quality that results from using remeshing on these elements. Changes in connectivity affect the solution, thus remeshing affects the solution in unexpected ways. In summary, the deficiencies of the element need to be addressed before they can be used in problems where the pressure fields are important (such as the shock regime), and analyses that currently depend on nodal-based tets and accompanying remeshing need to be investigated closely to see if these deficiencies significantly affect the solution.

Significance

Simulations that could be positively affected by a working nodal-based tet element with remeshing include modeling of weapons storage facilities, transportation systems, safety and security of the energy infrastructure, spaced-based assets under environmental and adversarial threats, missile defense applications, penetration modeling, and other abnormal and hostile threat situations. Unfortunately, follow-on work is required to correct the problems identified in this work before it can be used for these areas. Current analyses that rely on the nodal-based tets with or without remeshing need to carefully reexamine their work to assess whether or not the deficiencies are strongly affecting the quality of the results.

Systems Analysis Tools for Next-Generation Grid Planning, Operations, and Control

149520
Year 1 of 1
Principal Investigator: J. Watson

Project Purpose

The success of evolving an advanced, reliable power grid from the current infrastructure hinges on two key factors. From an operational perspective, it is critical to manage the large fluctuations in supply associated with technologies such as solar and wind. Thermal or hydro plants, or posited short-term storage devices, are the primary control mechanisms. From a planning perspective, management of uncertainties is the critical factor in cost and security-constrained system design, including projected renewable efficiencies, fuel costs, demands, and water availability. The long-term planning and operations scheduling processes are — especially at a national scale — extremely challenging operations research optimization problems, while real-time management of fluctuations in renewable power sources is a key issue in control theory. The objective of this project is to leverage already developed algorithmic tools to conclusively demonstrate the potential to solve these national-scale planning, operations scheduling, and operations control problems. Further, the multiple timescales involved must be ultimately bridged, potentially leading to a novel fusion of operations research and control-theoretic paradigms.

Summary of Accomplishments

We developed two key stochastic mixed-integer optimization models. The first addresses long-term grid generation expansion, i.e., the question of what new generators to build, of which type, and in which year, to satisfy projected demand given uncertainty in fuel prices. The second addresses unit commitment, i.e., the day-to-day question of which generators to turn on, when, and at what output level. Both models are expressed in Sandia's Coopr mathematical modeling framework, and solved used the Coopr PySP (Python for Stochastic Programming) solver library. We demonstrated the applicability of Sandia's solver technology for stochastic mixed-integer programs to address these critical energy operational and planning problems, the foundational models in grid operations and planning. The generation expansion work was performed in conjunction with researchers at Iowa State University, while the unit commitment problem was performed in conjunction with researchers at Argonne National Laboratory. We were able to tailor our solvers to quickly identify near-optimal solutions to these problems, via parallel algorithmic decomposition strategies. Finally, we developed and tested techniques for quantifying the robustness of the solutions obtained. Stochastic programs are generally solved by sampling from the universe of scenarios. Consequently, the related questions of "do we have enough samples?" and "how far might we be from optimal?" must be addressed. Our techniques indicate that for generation expansion, thousands of scenarios are sufficient to obtain solutions that are provably — in the statistical sense — within 1% of optimal. In contrast, for unit commitment, scalability remains a major challenge, where optimality gap estimates exceed 10 to 20 percent given the number of scenarios we can address computationally (on the order of 100).

Significance

This work is focused on ensuring that new energy technologies will be able to be assimilated into the current grid with high confidence, at minimal cost, while addressing security and reliability concerns. Successfully achieving this goal is crucial to the energy, military, and economic security of the US.

We have demonstrated the utility of stochastic mixed-integer programming, expressed via Sandia's Coopr mathematical modeling software, to solve core grid operations and planning problems. We have scalable solver results for grid generation expansion. For unit commitment, solver scalability is, at worst, consistent (and is better in many cases) with the state of the art in the literature, but further advances are required to solve industrial-scale problem instances.

Our results regarding the computation of solution robustness is novel in several regards. First, these techniques have not been previously applied to problems in the electrical grid domain. Consequently, researchers have proceeded without answer to the questions of whether a sufficient number of scenarios were being used, and without a metric for the optimality gap. Without a confidence interval on the optimality gap, which quantifies solution robustness, solutions are of very limited use to decision-makers; the down-side risk is far too large. Second, these techniques rigorously motivate — in the case of unit commitment — the need for both significantly larger numbers of scenarios and, as a consequence, high-performance computing. The latter is ultimately required to address scalability, as problem difficulty is proportional to the number of scenarios considered. High-performance computing is generally ignored in the electrical industry. Our results provide a rigorous, quantitative answer (in the form of a specific computational answer to a key operational problem) to the question of "what is the need for high-performance computing?"

The baseline studies focus on stochastic mixed-integer optimization problems in which the objective is to minimize expected cost. An alternative metric that emphasizes mitigation of down-side risk is known as conditional value-at-risk (CVaR). We have replicated our computational studies on both the generation expansion and unit commitment problems considering the CVaR optimization objective. The solver scalability results hold for this risk-aware metric. However, given a fixed number of scenarios, solution robustness is significantly impacted. Specifically, the confidence interval width on the optimality gap for these problems is significantly (an order of magnitude) larger when considering the CVaR optimization metric. Intuitively, this is expected behavior, as more samples are required to identify high-cost "tail" scenarios. The result further emphasizes the need for scalable stochastic programming solvers because the number of scenarios required to obtain robust solutions for risk-oriented optimization metrics is significant (further motivating the need for high-performance computing solutions).

Parallel Octree-Based Hexahedral Mesh Generation for Eularian to Lagrangian Conversion

149521
Year 1 of 1
Principal Investigator: S. J. Owen

Project Purpose

Computational simulation must often be performed on domains where materials are represented as scalar quantities or volume fractions at cell centers of an octree-based grid. Common examples include biomedical, geotechnical or shock physics calculations where interface boundaries are represented only as discrete statistical approximations. Accurate simulation that utilizes this data can require a Lagrangian hexahedral finite element mesh with hundreds of millions or even billions of degrees of freedom.

Previous work in the literature has explored methods for generating an octree-based hexahedral mesh from volume fraction data, however these methods can lack element quality or fail to adequately resolve the domain. In addition, none have focused on the specific shock physics problems that are relevant to advanced simulation and computing codes such as CTH and Alegra. More important, existing methods have not yet been proposed for extending these techniques to parallel domains where massive numbers of degrees of freedom are required.

Summary of Accomplishments

This work has demonstrated new procedures and methods for generating both hexahedral and tetrahedral meshes from volume fraction data defined on a Cartesian grid. We recognize that, with the limited resources for this project, there are many areas left to explore. We would anticipate that the results of such research would move this technology towards a tool that can be robustly used for coupling Eulerian and Lagrangian codes. We do, however, offer that these methods improve on existing techniques proposed in the literature, particularly as they apply to parallel mesh generation using overlay grid methods.

Significance

Shock physics and high-speed impact phenomena as characterized by the advanced simulation and computing Eulerian codes provide important insights into weapons effects, armor/anti-armor interactions, warhead design, high-explosive initiation physics and weapon safety issues. These codes can be limited by the effectiveness of the Eulerian grid. Lagrangian hexahedral meshes developed on a massive scale will help extend the application of these insights to help answer questions important to DOE’s national security mission.

Effective Programming Tools and Techniques for the New Graph Architecture HPC Machines

149655
Year 1 of 3
Principal Investigator: D. Dechev

Project Purpose

Large graph problems that arise in complex network analysis, data mining, computational biology, and national security applications have sparked the development of new types of high performance architectures and codes. These codes involve very large numbers of threads and much greater sharing of information among processors than traditional scientific computing approaches, posing much greater concurrency challenges. Unfortunately, concurrent programming for shared memory multithreaded applications is nontrivial because of the numerous hazards including race conditions, deadlocks, livelocks, and order violations. Such errors are hard to reproduce, often lead to unpredictable real-time behavior, and are notoriously difficult to debug. The use of mutual exclusion, the most common synchronization technique for shared data, can lead to significant overhead, high complexity, and reduced parallelism in addition to the aforementioned safety risks. Even for conventional multicore systems and datasets of modest size, the use of mutual exclusion can cause convoying effects that, in turn, can seriously affect the application's performance. According to a number of studies at NASA Ames, the current development and validation techniques are prohibitively expensive for problems of such complexity. We propose to address this highly challenging problem by creating a software framework for safe and efficient concurrent synchronization for massively multithreaded shared-memory programs. This approach will be based on the application of lock-free synchronization, a new alternative to mutual exclusion for designing scalable data objects. In our previous work we have shown that lock-free synchronization eliminates whole classes of concurrency hazards while delivering performance improvements for many scenarios by a large factor. Our goal is to create a portable and generic software platform that will greatly assist domain scientists who are not experts in concurrency theory and formal methods produce highly efficient and correct high-performance computing (HPC) code for solving large graph analysis problems.

Summary of Accomplishments

Since the start of the project in April 2010, we have accomplished the following:

1. We performed a survey of the most recent multicore programming techniques.
2. We implemented a number of non-blocking techniques published in the literature including linked-lists, hash tables, and vectors and performed a range of experiments.
3. We studied the new C++ standard — "C++0x" — and in particular, its features related to providing a new memory model, support for concurrency, and automated garbage collection. We evaluated the possible impact of these new language features for the design of new programming models.
4. We initiated a study of the methodologies necessary to establish the correctness of a non-blocking algorithm, in particular by providing designs that are linearizable, meet the progress guarantees, and are also ABA-free. ABA is a fundamental problem in concurrent designs. (ABA is not an acronym and is a shortcut for stating that a value at a shared location can change from A to B and then back to A.)
5. We designed a generic solution to the ABA problem for lock-free descriptor-based designs and incorporated it in a lock-free vector implementation.
6. We wrote a paper on our approach for ABA avoidance: "Understanding and Effectively Preventing the ABA Problem in Lock-Free Descriptor-Based Designs," and presented it in May 2010 at the Institute of Electrical and Electronics Engineers International Symposium on Object/Component/Service-Oriented Real-Time Distributed Computing. (IEEE/ISORC) 2010 International Symposium in Carmona, Spain.

7. We prepared an extended journal version of our ISORC 2010 paper and submitted it to the Wiley journal, *Software: Practice and Experience* as an invited paper.
8. We performed a study regarding the role of source code rejuvenation and the possibility for lock-based to lock-free code transformation. We wrote a paper entitled "Support for the evolution of C++ Generic Functions," accepted for publication at the 3rd International Conference on Software Language Engineering.

Significance

The proposed work is of high relevance to the core mission of the advanced simulation and computing community, the intelligence community, the National Infrastructure Simulation and Analysis Center (NISAC), as well as the efforts in the area of Enabling Predictive Simulation. Our approach will deliver high performance and increased safety for future HPC platforms and will provide an alternative to the current prohibitively expensive and hazardous coding techniques for concurrent programming. Our research will eliminate many bottlenecks and provide better performance for advanced simulations.

QMU as an Approach to Strengthening the Predictive Capabilities of Complex Models

149819
Year 1 of 1
Principal Investigator: G. A. Gray

Project Purpose

Quantification of margins and uncertainties (QMU) supports risk-informed decision-making, where risk refers to the likelihood of a system failing or not achieving performance requirements. To date, QMU has played an important role in the nuclear weapon life cycle for which formal requirements have been long established. However, as we move forward in designing the complex systems that will support our future national security infrastructure, requirements and acceptable margins for performance, resilience, and security are fuzzy, at best. Such systems include next-generation computer networks, transportation energy infrastructure, and physical security. Without requirements, we cannot hope to design cost-effective systems that will meet our national security needs.

Increasingly, significant effort is being put into developing modeling and simulation technology for predicting the behavior of complex infrastructure systems. Many of these systems include human factors and phenomena for which there is little or no data. It is our hypothesis that simulations can be used to guide the development of requirements and margins at system, subsystem, component, and constitutive levels. Thus, our goal is to develop a QMU framework that will work in conjunction with complex system simulations to provide a defensible basis for performance requirements. This includes the characterization of their associated uncertainties. We will pay particular attention to requirements for failure or for "bad consequences" that, due to lack of knowledge, cannot be defined in formal, mathematical terms or with fixed thresholds. This framework will be adaptable in order to accommodate improvements in models and understanding as data is collected over time.

Summary of Accomplishments

We have three accomplishments to note. First, we developed and implemented an algorithm for evaluating the expected risk of a decision as the basis for the optimal testing strategy. Moreover, the key limiting cases were analyzed to prove the effectiveness of this testing strategy. Second, we discovered the characteristics of the cyber infrastructure problem. This information was collected and considered in the context of needs for the development QMU-based tools. Third, we learned about existing uncertainty quantification methodologies for the quantification of model discrepancies. These were considered in the context of statistical models of cyber activity.

Significance

This work provides the foundation needed to provide a tractable yet rigorous risk-informed approach to defining system requirements in an environment where requirements for failure or for bad consequences cannot be defined in formal, mathematical terms or with fixed thresholds. These requirements are essential to the efficient design and improvement of many aspects of the nation's infrastructure security.

Stochastic Study of Microparticle Adhesion due to Capillary Condensation

150123
Year 1 of 3
Principal Investigator: J. A. Hubbard

Project Purpose

The fundamental issue for investigation in this project involves the conditions for microparticle adhesion and re-suspension in realistic ambient environments. While many researchers have measured microparticle adhesive forces, relatively few have studied adhesion due to capillary condensation at realistic relative humidities. Rather, most experiments are designed to eliminate this as a factor as it complicates analysis. This is a serious flaw because these forces can be significant in practical applications and have been shown to persist after long periods of drying. It is the hypothesis of this work that capillary adhesion forces on microparticles will be dominant, with respect to electrostatic and van der Waals forces, in many cases for which relative humidity is greater than 40% due to the combined effects of surface tension and capillary pressure. Complex particle and surface properties like morphology and wettability also cause real systems to display probabilistic behaviors due to random variations in properties occurring at the micro- through nanoscales. Current research emphasizes stochastic adhesion models to account for these effects rather than relying on analytical expressions derived under assumptions of ideal geometry and surface properties. This project's experimental work will be used to develop stochastic models of capillary adhesion required for prediction of aerosol microparticle fate with an emphasis on advancing computational modeling tools like GOMA (multi-physics finite element code) and LAMMPS (molecular dynamics code). The following problems relevant to Sandia missions will then be made more tractable: trace detection of CBRNE (chemical, biological, radiological, nuclear, and explosive materials), and predicting the effects of surface contamination in critical systems components (e.g., satellites).

Summary of Accomplishments

The first engineering challenge is to synthesize microparticle aggregates (1–10 micrometers) from primary particles (150–300 nanometers) suspended in solution. The concept is to create microparticles of uniform and structured surface morphology. An experimental apparatus for particle synthesis has been designed, constructed, and preliminary performance measurements are in progress. A Sono-Tek ultrasonic nozzle is used to generate large droplets containing primary particles. The solvent evaporates and the aggregates are fed into a sintering tube oven. At this time, thermal performance of the oven is being characterized for accurate control over the sintering process. Nozzle performance has also been characterized with a Malvern Spraytec Laser Diffraction instrument. Process parameters will be analyzed through Scanning Electron Microscopy (SEM) of synthesized particles.

In early July, a meeting was held with Molecular Imprints (MI), Austin, Texas, to establish our industrial collaboration. They agreed to contribute nanostructured test substrates for adhesion experiments. The nano-feature height for these materials is approximately 100–200 nanometers with equivalent inter-feature spacing. Surfaces of silica and an acrylate-etching polymer will be tested. Process Engineers at MI have also provided surface cleaning protocols and substrate preparation (e.g., cutting into test coupons) is ongoing at the Microsystems and Engineering Sciences Applications fabrication facility.

Particle detachment techniques have been analyzed and a collaboration formed with the microelectromechanical system vibration laboratory, to leverage existing experimental facilities. Their laser Doppler vibrometer will be used to make in-situ measurements of substrate dynamics during the detachment process. Surface accelerations, i.e., detachment forces, will be measured for substrates excited with contact transducers with frequencies up to 10 megahertz. A small mechanical shock device is also being designed to create larger accelerations (~10,000 g) that may be required to overcome adhesion.

Significance

This project will support DOE's strategic mission to strengthen scientific discovery and innovation in the physical sciences. Experiments will provide a validation data set for interfacial physical models to be developed in the future and ultimately enable predictive simulation of related problems. Our approach will be multidisciplinary, and collaborative with industry. Both of these characteristics are goals of the DOE to create the leverage needed to address the nation's security challenges. DHS missions (e.g., chemical, biological, radiation, nuclear detection) will also be supported through future application of knowledge gained here to protect our nation's citizens and infrastructure.

Cross-Domain Predictive Simulation Focusing on Energy Security

150252
Year 1 of 1
Principal Investigator: C. R. Lawton

Project Purpose

Energy security encompasses a collection of issues and characteristics cross-cutting numerous sciences and technology (S&T) domains, including energy technologies (e.g., fossil, solar, wind, nuclear) and national security domains (e.g., economic, environmental, political, defense, homeland security). The simulation models typically used to analyze the energy S&T domains and those that support analysis of the national security sectors are fundamentally different: models of energy S&T are governed by the highly deterministic, well understood "laws of physics" while models of national security sectors are governed by the highly uncertain, temporally dynamic "laws of experience."

Furthermore, the research, development, and engineering communities applying these analytical models traditionally work independently, resulting in highly stovepiped capabilities. What is necessary to adequately understand the energy security challenge of the future (and to enable predictive simulation capabilities that will help plan an optimal energy strategy) is a holistic view of energy security that brings together the analytical communities of the energy science and technologies and the national security sectors.

This project will focus on a specific subset of domains drawn from the energy science and technologies and national security sectors and bring together the related simulation communities and tools. Bringing the tools together will require significant R&D into heterogeneous modeling across many disparate sciences, specifically the merging of highly uncertain, abstract, temporally dynamic simulations with more deterministic, high fidelity, physics based models. We look to leverage Sandia's high performance computing assets, security principles expertise, and existing modeling capabilities performed in specific energy S&T domains and national security sectors. Focusing on a subset of the energy S&T and national security sectors will allow us to begin to explore this holistic view of energy security in a structured framework.

Summary of Accomplishments

This project is a small-scale demonstration of a modeling framework consisting of a holistic "systems" approach used to integrate normally independent modeling capabilities in order to support a new mathematical construct to benefit the DOE energy security mission.

We developed a conceptual model that provides a holistic view of the energy system across many complex, interdependent measures of performance and its relation to national security. The model allows for prediction of impact of future energy system performance and constraints on national security (e.g., economic measures). The model allows for an understanding of the energy system behavior and the bounds of required economic efficiencies of renewable energy systems through time.

The model is a "systems" level mathematical optimization formulation that relates energy supply and distribution market sectors with national security domains focusing on economic impact (business productivity). This was demonstrated through an example studying the relationship of energy security to the economics of an urban area. For demonstration purposes, we gathered real-world data based on an existing energy and economic system (based on real data collected based on the energy distribution system within Albuquerque and for a business market sector of Albuquerque).

Significance

Our goal is to bring together and organize Sandia's core strengths and capabilities around energy security and position Sandia as a national resource for energy security planning and decision-making. This project utilizes a holistic technical approach within which we can demonstrate the value of integrating normally independent simulation capabilities to support a new mathematical construct essential for Sandia to fully realize the goals of its energy security thrust.

The model provides a rigorous "systems engineering" structure/framework within which to evaluate the many complexities of energy security and those functional elements of the energy security system (and their interrelationships). The model can be leveraged for future systems engineering and systems analysis approaches to energy security and could be used as a mechanism to integrate disparate simulations that focus on very specific elements of energy security.

By focusing on a real-world example — the energy-distribution system in Albuquerque for a small business market sector — we were able to demonstrate how different energy security system measures of effectiveness interact, and the feasibility of data collection necessary to feed the mathematical optimization at a fidelity necessary to produce results that would help future decisions regarding investments in energy security.

Drying/Self-Assembly of Nanoparticle Suspensions

150631
Year 1 of 1
Principal Investigator: G. S. Grest

Project Purpose

The most feasible way to disperse particles in a bulk material or control their packing at a substrate is through fluidization in a carrier that can be processed with well-known techniques (e.g., spin, drip and spray coating, fiber drawing, casting). The next stage in the processing is often solidification involving drying by solvent evaporation. While there has been significant progress in the past few years in developing discrete element numerical methods to model dense nanoparticle dispersion/suspension rheology, which properly treat the hydrodynamic interactions of the solvent, these methods cannot at present account for the volume reduction of the suspension due to solvent evaporation. The goal of the present research is to develop and validate methods to remove solvent particles and volume, and hence solvent mass from the liquid/vapor interface of the suspension to account for volume reduction (solvent drying) effects in the current suite of discrete element methods.

Summary of Accomplishments

We have implemented, in the parallel molecular dynamics code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), a procedure to explicitly remove the solvent near the boundary in a manner consistent with the limit of very slow evaporation. Explicit atom molecular dynamics simulations for three model systems were carried out to validate the model. Simulations of solvent evaporation from a nanoparticle suspension are underway.

Significance

This work has a broad relevance of a predictive modeling methodology for nanomanfacturing, suspension rheology, and encapsulants. Research will strengthen our relationship with the nanocomposite manufacturing industry through the NanoParticle Flow Consortium.

Studies in High-Rate Solidification

150638
Year 1 of 3
Principal Investigator: J. D. Madison

Project Purpose

Investigation of the linkage between processing and resultant microstructures will be pursued through investigation of high-rate solidification events found in welds, brazes and solders. Simulation tools developed at Sandia, previously used to examine the effects of macrostructure on mechanical properties will be extended to evaluate a smaller length-scale. The presence, variability and distribution of microstructural features such as porosity will also be examined, among others, for determination of impact and effect on joint stability, integrity, and composition. These factors will also be related to process parameters such as weld speed, pulse rate, and/or material type. In all instances, microstructural three-dimensional reconstructions will be pursued along with microscale multiphysics simulations for the purposes of yielding process-influenced measures of variability and associate such variations with microstructural characteristics.

Summary of Accomplishments

We have:

- identified, selected and obtained weld materials of current interest and use for investigation
- designed a matrix of laser weld parameters to yield the full breadth of currently documented porosity types for examination
- performed direct radiography for planar inspection of characteristic porosities
- acquired microcomputed tomography of large and small-scale weld porosities in two samples for production of initial 3-dimensional datasets highlighting critical variation in joining process parameter effects on resultant microstructure.

Significance

Sandia is responsible for the quality of welds and brazes throughout the DOE/NNSA, with applications ranging from nuclear weapons and energy to waste storage and renewable energy. This work has direct applicability to life extension efforts in deep welds of precipitation hardened martensitic steels and the employing of nitrogen strengthened stainless steels. This work will also allow improvement in Sandia's ability to support welds and joinings throughout the entire DOE/NNSA complex with a greater emphasis on predictive capability as opposed to largely diagnostic expertise.

Structural Simulations of Nanomaterials Self-Assembled from Ionic Macrocycles

150639
Year 1 of 1
Principal Investigator: F. B. Van Swol

Project Purpose

Detailed information about the internal structures of nanomaterials can be crucial for understanding their function. In the case of the organic binary ionic solids developed at Sandia and being studied in this project, knowledge of the internal structure (i.e., the arrangement of the organic ions) is especially important because interactions between the organic ions control key properties of the materials such as light absorption, charge separation, and electron transfer. However, obtaining detailed structural information is problematic because direct structural characterization by conventional techniques such as x-ray crystallography is not feasible. The goal of this work is to develop a platform for predictive simulations of the structures of these new organic binary ionic materials using Monte Carlo and Brownian Dynamics methods. We propose to develop a new predictive simulations platform for modeling the structures of materials composed of organic ions. This will provide a new method for studying the structures of this class of ionic solids. The code and methods developed will also be applicable to a range of self-assembled ionic solids. In addition, the insights gained will aid in the design of new organic binary ionic solids at Sandia.

Summary of Accomplishments

To gain insights into the internal structures of binary ionic nanomaterials, we have developed a classical model of nonconvex charge-decorated particles that interact through short-ranged Yukawa potentials (a porphyrin ion was modeled as a block with spheres at the four corners representing the substituents on the macrocycle). Monte Carlo simulations of the self-assembled porphyrin nanostructures were undertaken using a structure derived from the crystal structure of the common synthetic porphyrin 5,10,15,20-tetraphenylporphyrin (H2TPP). Most of the porphyrins used in the experimental ionic self-assembly studies are variants of TPP with ionic groups located on the porphyrin macrocycle.

The self-assembly process of the oppositely charged porphyrins was investigated using two sets of starting structures: a) those with randomly oriented porphyrins (derived from extended NVT [number of molecules, volume, temperature]) runs of the ordered lattice structures at high temperatures), and b) ordered lattice structures, particularly a segregated structure. The goal was to investigate if it was possible to generate an ordered lattice from a randomly oriented structure or to transition between different lattice structures.

NVT studies of the random structures did not result in the formation of lattice structures, although a degree of local order was observed in some cases. In particular, portions of many simulations displayed ribbon-like structure with alternating oppositely charge porphyrins. NpT (number of molecules, pressure, temperature) studies beginning with a random structure also did not result in the formation of ordered lattices. The formation of a different and more stable lattice was observed when the segregated structure was used as a starting point in the NVT runs. The final structure showed the principal elements of the interleaved structure, usually with some slight slippage between layers. The energy of the final structure did not match that of the fully interleaved structure, presumably due to the fact that the simulation box contains several ordered regions separated by voids.

Significance

Many of the organic binary ionic nano- and micro-materials have potential applications in solar energy technologies, batteries, and supercapacitors that are relevant to the DOE energy mission. The ability to predict and engineer the electronic and optical properties of the organic binary ionic (such as oppositely charged porphyrins) materials might also benefit the DOE national security mission. We recognize that organic binary ionics are fundamentally different from common salts in that the ions are not simply limited to the elements in the periodic table, but instead can be tailored into complex shapes. For the case at hand, the ions are essentially planar macrocycles (a block with spheres at the four corners representing the substituents on the macrocycle). Now, the interplay between charges and shape is a new feature, not previously studied. This is why we have chosen to model these ionic systems in a sufficiently simplified way that allows one to generate fundamental understanding from the modeling, while maintaining the essential physics. This approach is computationally efficient, and entirely in line with current understanding of the behavior and structures of common salts, such as NaCl. Their solid structure is the result of the competition between oppositely charged and like-charged ions that gives rise to charge ordering (both in the solid and the liquid phase), which is of long range nature. We can demonstrated (e.g., with mixtures of non-additive hard spheres) that the long range ordering is not itself a consequence of the presence of long range Coulombic interactions, but stems from the aforementioned competition. Short-ranged Yukawa interactions also produce charge-ordering. We have demonstrated that the simplified model can be used to study self-assembly of ionic macrocycles, and the new capability enables predictive simulations. Specifically, one can now study the interplay between macrocycle shape and charge distributions, an interplay that appears to be critical to the understanding of nanomaterials of organic binary ionic solids.

Uncertainty Quantification of Cinematic Imaging for Development of Predictive Simulations of Turbulent Combustion

150641
Year 1 of 1
Principal Investigator: J. H. Frank

Project Purpose

Accurate simulations of turbulent flames are required for the development of advanced combustion technologies with high efficiency and low emissions. The development of high-fidelity numerical simulations of turbulent combustion and the associated submodels requires improved understanding of turbulence-chemistry interactions and detailed validation by experiments. The central goal of the proposed work is to enable quantitative measurements of the spatial and temporal evolution of turbulent flames in order to advance Sandia's predictive simulation capabilities. To date, model validation experiments have primarily used single-point measurements, which do not capture the full dynamics of turbulent flames. We are developing approaches for comparing large-eddy simulations with 2D and 3D laser-based imaging measurements of turbulent flames. Central to this effort is the development of a high-repetition-rate imaging capability for measuring the spatial and temporal evolution of turbulent flames. Recent advances in complementary metal oxide semiconductor (CMOS) detector technology and diode pumped solid-state lasers enable us to perform 2D laser-induced fluorescence (LIF) measurements of combustion intermediates in turbulent flames at rates on the order of 10 kHz. However, measurements with high-speed CMOS cameras are inherently noisier than those performed at lower repetition rates with charge-coupled device (CCD) cameras. In addition, evidence indicates that CMOS cameras can have nonlinear responses. These issues present a significant challenge for performing the quantitative measurements that are necessary for developing predictive simulations. We propose to combine detailed experimental characterization of high-speed CMOS cameras with uncertainty quantification analysis to design optimal noise filters and provide uncertainty estimates for high-speed imaging measurements. The results will establish the feasibility of coupling quantitative high-speed imaging measurements with numerical simulations of the temporal evolution of turbulent flames. This work will position our group to attract new funding from DOE to build a unique capability for tightly coupled computational and experimental research.

Summary of Accomplishments

We systematically quantified the noise characteristics and nonlinear response of intensified and unintensified high-speed CMOS cameras on a pixel by pixel basis. We learned that the detector nonlinearities, especially for the intensified camera were more significant than expected and presented additional challenges for interpreting inherently noisy imaging data. We performed 10-kHz cinematic OH (hydroxyl radical) LIF imaging measurements of the temporal evolution of turbulent jet flames with varying degrees of intermittent localized extinction and re-ignition. One of the important applications of this project is to enable quantitative cinematic imaging of extinction and re-ignition events. Measurements in steady laminar flames were also performed to provide initial tests of our data analysis methodology. The flames considered used dimethyl ether (DME) as a fuel. DME is one of the simpler oxygenated fuels, and thus represents a class of potential alternative fuels for practical combustion devices.

We developed a Bayesian methodology for inferring actual OH LIF signals based on the measured signals, using pixel-specific calibration curves and noise models. We employed Karhunen-Loeve expansions to obtain near-optimal basis for a reduced-order representation of the spatial distributions of the LIF signals.

We developed a locally adaptive wavelet de-noising method that takes advantage of the lack of spatial correlation in the noise between different rows of pixels on the CMOS detector. We tested these analysis and noise-reduction methods on OH LIF imaging measurements from the laminar and turbulent flames. We used 1D implementations of the algorithms to analyze individual rows of pixels within the OH LIF images. We demonstrated proof of concept for filtering and calibration methods that will enable the use of high-speed imaging for quantitative measurements of turbulent flame dynamics. We developed a roadmap for future extensions of this work to full 2D and possibly 3D (space and time) implementations.

Significance

This project addresses the DOE mission of energy security. It targets the critical need to develop computational and experimental capabilities that will enable predictive simulations of combustion phenomena using new fuel technologies. The development of these capabilities is urgently needed to underpin development of advanced combustion technologies for clean and efficient energy utilization and reduction of dependence on foreign energy sources.

The results of this project establish a foundation for using cinematic imaging of combustion dynamics for the development of predictive simulations of turbulent combustion. The results are expected to impact the international combustion research community, which has begun to adopt the use of high-speed intensified CMOS cameras without careful attention to treatment of the noise and nonlinearities of these detectors. Our accomplishments will directly impact the development of large eddy simulations in the Combustion Research Facility's Basic Energy Sciences research program. They will also likely impact DOE/Energy Efficiency and Renewable Energy funded research in engine combustion. The development of methods for measuring and modeling the temporal evolution of turbulent flames in internal combustion engines is particularly challenging.

Further advances in the methodology that we have developed could result in a broader impact of our work. Our approaches to analyzing imaging data from inherently noisy and nonlinear detectors could facilitate quantitative interpretation of imaging data in fields beyond combustion, such as geophysics, climate, and microscopy research.

An Extensible Framework for Specifying and Configuring Emulytics Testbeds

151172
Year 1 of 1
Principal Investigator: R. A. Ballance

Project Purpose

Emulytics involves modeling large, complex, and uncontrolled systems using smaller, simpler, managed, and instrumented systems. We are specifically interested in modeling cyber networks, their static and dynamic properties, and the services and infrastructures that depend upon their operation. Our ultimate goal is to enable modeling, simulating, analyzing, or predicting the behavior of cyber-based systems at any resolution, any depth, any scale, from small-scale targeted assessments up to 10^7 nodes, while deploying components having a fidelity appropriate to the domain of study and the question at hand.

Our project intends to provide the key infrastructure — specification languages, platform architecture, management and visualization tools — for creating and operating scientifically well-founded emulation laboratories for network research. The testbed being built must be "trusted" in the sense that users will have confidence that is it configured as specified, that the its configuration can be replicated at will, and that it is operating correctly. This work addresses the critical needs for rapidly configuring, managing, and effectively operating emulation laboratories with attention to scaling, integration of virtual and real components having varying degrees of fidelity, derivation of behavioral understanding, data analysis, network instrumentation, human interaction, and real-time situational awareness.

This research will create methods for describing, analyzing, and configuring an emulytic network via an analysis process as described in an invention disclosure. Our primary goal was to establish the viability of a high-level approach to configuring emulytic testbeds from experimental specifications. While some cyber-emulation systems exist (e.g., OPNET, EMULAB), none provide the scalability, depth, resolution, and usability properties necessary for the classes of cyber experimentation/analysis arising today. A crucial and innovative element is that the system will be designed to function with multiple high-performance computing (HPC) platforms, some of which were not designed to run these classes of cyber emulation problems.

Summary of Accomplishments

This project enabled us to develop a basic prototype for the experiment description, the description analyzer, and to lay the foundational groundwork for deploying a test onto the Black ICE cluster at Sandia. The work integrates research from programming language design and implementation, HPC system design and management, network security monitoring, automated system configuration, and high-availability, distributed telephony systems to sculpt a powerful environment for cyber-security experiments.

Key issues at each link in the chain of activities have been investigated. The description language was defined, and the core of an analyzer was written. Key techniques for configuring a hardware platform at small-scale have been demonstrated using Moab, xCat, and CFengine. Portions of the runtime mechanisms were developed in Erlang. However, the work to date provides only a roadmap to guide us toward a full-scale production capability.

Significance

Modeling, simulating, and analyzing cyber threats that target large-scale engineered and human-coupled computer networks is a domain of heightened national interest. Critical US infrastructures (power, water, communications, finance, medicine, and government itself) are becoming ever more interdependent, even as the sophistication and rate of attacks on their underlying information systems accelerate. Modeling and simulation within securely contained environments can help us better understand the threats and develop strategies and technologies to mitigate their blows. Our research addresses the critical needs for rapidly configuring, managing, and effectively operating emulation laboratories with attention to scaling, integration of virtual and real components having varying degrees of fidelity, derivation of behavioral understanding, data analysis, network instrumentation, human interaction, and real-time situational awareness.

This work aims to provide key advances for reliably constructing “emulation laboratories” for large-scale, vastly heterogeneous networked systems. Specifically, it is addressing the issues of automated construction and verified configuration of core testbed components. Those components will include a variety of operating systems, applications, and networking gear. The components themselves will also vary from highest fidelity to virtualized systems to emulated systems and simulated subsystems.

Scientific repeatability and the need to understand the ground truth underlying a particular emulative simulation means that any system designed to support emulytics must itself be trusted and must be independent from the systems under investigation. The system must support staged sequences of tests, as investigators hone in on the information and details needed to complete their studies. The design, deployment, and operation of a large-scale, scientifically grounded, emulative platform will drive R&D innovations in emulytic platforms, configuration management, rapid configuration and organization of large-scale computing environments including millions of virtual machines, data collection and analysis at near-Internet scale, instrumentation and event tracing across networks, algorithms for analyzing large-scale information-based data streams, and tool support for comprehending situational awareness.

A production large-scale emulytics platform will provide resources for Sandians and other researchers to test, evaluate, and train on their own systems, and to deploy and test new protocols and systems in a managed and contained cyber environment. Large-scale emulytic platforms will also generate large amounts of information that requires analysis, thereby making them a logical pairing with the informatics platforms now being investigated at Sandia. Emulytics and informatics are co-supporting technologies. Finally, this research and development thrust is providing new opportunities for Sandia personnel to grow, learn new tools, and become more effective at system, network and network-analysis, and cyber-security operations.

NANOSCIENCE TO MICROSYSTEMS INVESTMENT AREA

This investment area funds both fundamental and applied research into phenomena that arise from the distinctive properties of matter at the nanoscale (billionths of a meter), the scale of single atoms, small clusters of atoms, and small molecules, and of structures at the microscale (millionths of a meter). This includes both inorganic nanoparticle research and applications, for example, single atomic nanoparticles of metals such as gold, and also biological nanoparticles and nanomachines — and often, the combination of inorganic and biological, with bio-nanostructures sometimes providing models for developers to emulate.

Applications range from micromachines such as tiny heat engines and microelectromechnical systems (MEMs), to quantum cascade lasers to improved computer memories and new types of computing data structures (as in quantum computing), as well as nano- and microstructures showing novel optical and electromagnetic properties that tend not to be observed at larger scales. In addition to fundamental insights into the nature of materials and nanostructures, this IA ultimately offers solutions to problems in energy security, climate change, secure communications, cryptography, remote sensing and threat detection, and other arenas germane to national and global security.

Integrated Optical Phase Locked Loop (IO-PLL) for Attosecond Timing in Microwave Oscillators

Project 117822

Compact, low power, and high-performance microwave oscillators are nearly ubiquitous in microelectronics — in radar, global positioning systems (GPS), and various other communications devices. However, their use in systems requiring high-precision clocking and/or fine phase resolution tends to be limited by phase noise. An optoelectronic chip that could improve this situation by reaching the limits of phase noise and improve or remove other inherent noise sources would represent a significant step forward in this arena.

This project, a close collaboration with the Massachusetts Institute of Technology (MIT), has addressed this issue through a fundamental investigation into the limits of precision timing, with MIT performing benchtop experiments and Sandia focusing on developing an integrated chip-level solution that draws on the capabilities of Sandia's Microsystems and Engineering Sciences Applications facility (MESA) and the Center for Integrated Nanotechnologies (CINT). In developing a process compatible with the Microelectronics Development Laboratory that would integrate low-loss silicon waveguides and phase modulators with germanium detectors, the Sandia/MIT team has established a baseline process flow for integration of low-loss waveguides and fiber-to-chip coupling with silicon microphotonic modulators, and has demonstrated a new record in relative timing stability, better than any result from NIST. The goal is to ultimately create a chip-scale device to achieve sub-femtosecond timing resolution, an accomplishment that would represent a substantial inroad into that regime of phase-locking.

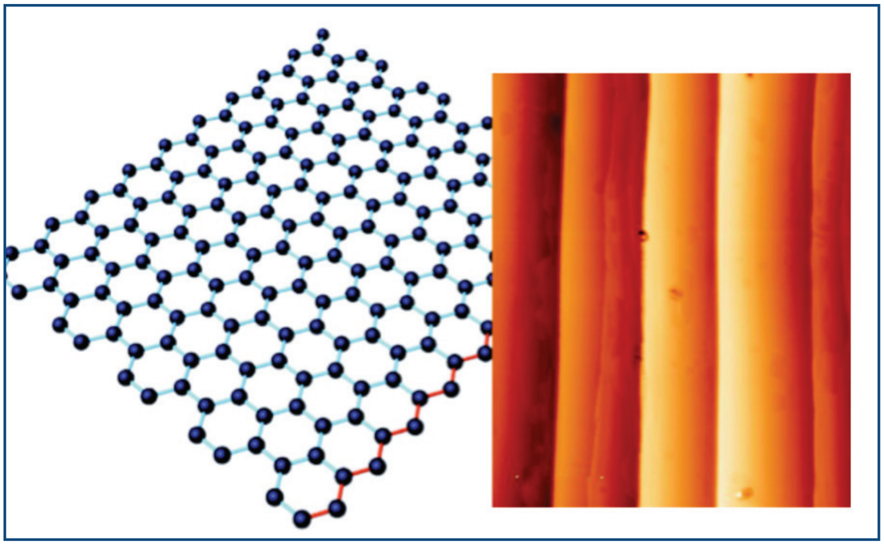
Image of the device engineered in this project

Enabling Graphene Nanoelectronics

Project 13077

A single layer of hexagonally bonded carbon atoms, graphene's high-performance electronic properties, its physical strength, potential for band gap manipulation and other properties make it a promising candidate as a novel semiconductor in nanoelectronics. However, techniques must be developed to reproducibly deposit and/or synthesize high-quality graphene onto wafer-scale areas. Given the paucity of fundamental knowledge about graphene formation and defects that may arise, the genesis of such large-area graphene sheets is a daunting proposition.

This project is pursuing multiple approaches to synthesize reduced-defect graphene sheets and transferring them to other surfaces, the goal to produce graphene with ever-higher carrier mobility, predicted to be as high as ~200,000 cm^2/Vsec because of quantum electrodynamic effects. The project has formed graphene by thermal decomposition of silicon carbide, and nucleated the vapor on different metals. In addition, the team has been successful in transferring graphene to glass substrates and characterizing properties using low energy electron microscopy (LEEM), Raman spectroscopy, and measurements of electronic transport, during which the integer quantum Hall effect was observed.



Graphene molecular structure (left) and micrograph of layered graphene sheets grown on silicon carbide (right).

NANOSCIENCE TO MICROSYSTEMS INVESTMENT AREA

Injection-Locked Composite Lasers for Millimeter-Wave Modulation

117819
Year 3 of 3
Principal Investigator: G. A. Vawter

Project Purpose

Since its invention, the diode laser has been hampered by limited frequency-modulation response resulting from nonlinear coupling of injected carriers with photons in the laser. This coupling has a relaxation resonance at 15–25 GHz, which limits the frequency response of laser modulation. Very recently, injection locking of small diode lasers has been observed to enhance the resonance frequency by a factor of two or more. However, the fundamental understanding of this frequency enhancement is not well developed. An opportunity and a need exist to more fully develop the theoretical basis of injection locking of strongly coupled laser cavities so as to enable development of high-performance microsystems that exploit injection locking.

We will develop a new theoretical and practical understanding of strongly coupled laser microsystems using combined theoretical work and a novel "photonic lab bench on a chip." This synergistic use of our leading-edge theoretical capability and a photonic microsystem purpose-built to create highly controlled laser cavity characteristics and intracavity coupling will lead to new science of coupled laser cavities and dramatic improvement of the modulation frequency. Shrinking the lab bench onto a photonic integrated circuit (PIC) requires that two primary obstacles be addressed, removal of the optical isolator and reduction of the timescale of interactions to only a few picoseconds. Accordingly, we will develop new theories for frequency- and time-dependent coupled laser systems on the scale of a photonic integrated circuit. We will further verify and extend this theory by building a photonic-lab-bench-on-a-chip which microscopically reproduces the laser characteristics and laser-to-laser coupling in order to observe regimes of stable, chaotic, and frequency-enhanced resonant oscillations. At the conclusion of this project, we expect to demonstrate world-record modulation frequencies for monolithic diode laser systems.

Summary of Accomplishments

We have developed a new theoretical and practical understanding of strongly coupled laser microsystems using combined theoretical work and a novel "photonic lab bench on a chip." Shrinking the lab bench onto a photonic integrated circuit (PIC) required that two primary obstacles be addressed, removal of the optical isolator and reduction of the time scale of interactions to only a few picoseconds. Accordingly, a theory capable of treating strongly coupled lasers and providing a rigorous description of outcoupling was developed. The resulting laser model provided an understanding of underlying physical mechanisms by tracing dynamical performance improvements to local spatial hole burning and dynamical bifurcations arising from the interaction between the nonlinear gain medium and coupled-cavity fields. Spatial hole burning allows fundamental and sideband optical fields to extract gain from different lasers, thus decreasing gain competition that would have inhibited the growth of modulation-generated sidebands.

We then verified this theory by building a photonic-lab-bench-on-a-chip which microscopically reproduces the laser characteristics and laser-to-laser coupling in order to observe regimes of stable, chaotic, and frequency-enhanced resonant oscillations. Using this chip we have demonstrated a ten-fold increase of the relaxation resonance frequency in a PIC composed of two coupled DBR (distributed Bragg reflector) lasers. This compact chip is compatible with further integration, enabling highly functional PICs to take advantage of the benefits of optical injection locking.

Additionally, mutual injection locking between the two lasers separated by an on-chip optical modulator has been demonstrated and the lock-band measured. The frequency response measurements show a five-fold increase in the device bandwidth compared to the modulator alone.

Significance

We have been successful in simulating and experimentally demonstrating that the modulation response enhancement from optical injection locking is possible even if the optical isolator between the master and slave lasers is removed. We accomplished this by developing composite coupled-mode theory capable of treating strongly coupled lasers and providing a rigorous description of outcoupling. This modeling provided a greater fundamental understanding of the physical mechanisms of device modulation under injection locking. The characterization of PICs designed according to the simulations verified the modulation enhancement attributed to optical injection locking in coupled-cavity devices. Additionally, more complex PICs incorporating an electro-absorption modulator demonstrated this enhancement without a low-frequency roll-off. Ultimately, we have demonstrated PICs with strongly coupled-cavities that have resonance frequencies tenfold that of a directly modulated laser and bandwidths five times that of a laser-modulator pair. We also demonstrated significant increase in the modulation efficiency under mutual injection. Due to their compact size, these devices have the potential to be important components of integrated photonics microsystems requiring extremely high bandwidths.

This work has demonstrated injection locking dynamics in a small PIC similar to large complex tabletop systems employing discrete lasers and isolators. The simplicity and compatibility with integration of the PIC make it an attractive building block in highly-functional PICs. These devices would be well suited for applications requiring a narrow frequency range modulation or amplification at high frequencies. We expect that improved engineering of the cavity spacing and coupling strengths will produce devices with the broadband response needed for many applications.

Nanopatterned Ferroelectrics for Ultrahigh-Density Rad-Hard Nonvolatile Memories

117820
Year 3 of 3
Principal Investigator: G. L. Brennecka

Project Purpose

Radiation-hard nonvolatile random access memory (NVRAM) is essential for many DOE and DoD integrated electronics applications, but novel fabrication approaches are necessary to achieve ultrahigh density of low-power memory types such as ferroelectric RAM (FERAM). This project aims to extend a patterning technique based upon directed self-assembly of diblock copolymers to be largely materials-independent, and therefore amenable to the fabrication of ultrahigh density FERAM, and to combine it with our advanced capabilities in nanoscale solution deposition of both simple and complex oxides. Further, we will investigate the phase and interface development involved in the fabrication and processing of nanoscale ferroelectrics in technologically relevant systems and perform a systematic study of thickness and lateral size effects on the ferroelectric behavior of such systems. This project envisions many potentially groundbreaking results, including extension of copolymer-based nanopatterning to arbitrary substrates through appropriate surface neutralization, transfer of such patterns to ferroelectric materials, lateral size-effect studies of discrete ferroelectric nanostructures in technologically relevant architectures, and in-situ and ex-situ characterization of the phase/interface development in such systems with unprecedented resolution. The potential benefits to Sandia are significant, but the high risk involved with achieving and integrating these leading-edge results are not appropriate for programmatic funding. In addition to the fundamental science of ferroelectric nanofeatures that we will explore and report to the broader scientific community, the material-independent nanopatterning platform that we are developing will give Sandia a flexible platform for further nanoscale studies not available anywhere else.

Summary of Accomplishments

We extended the directed self-assembly of block copolymer masks to non-Si/SiO_2 (indeed, to nearly any available material) for the first time and showed that this approach is compatible with not only vapor-phase deposition techniques, but also with much more chemically flexible solution deposition. In addition to the direct-patterning breakthrough, we have also developed the capability to deposit alternative oxide electrodes ($LaNiO_3$ and $SrRuO_3$) that may result in cleaner (i.e., less atomic disorder) interfaces with integrated ferroelectrics such as $Pb(Zr,Ti)O_3$ (PZT). We have even combined our best current practice assembly capabilities with these oxide electrodes to create self-assembled oxide nanocomposites. Our collaborations with the University of Florida on this project have resulted in the highest-known-resolution in-situ measurements of the phase development of integrated PZT films during thermal processing. We furthered development of our already highly advanced nanoscale chemical mapping capabilities and began investigation of alternate electrode adhesion layer stacks for improved reliability and robustness during thermal processing. We also carried out initial investigations on the effects of grain size on dynamic ferroelectric response.

Significance

Rad-hard NVRAM is crucial to many defense and surveillance applications. Currently available technologies for ultrahigh-density NVRAM draw significantly greater power than would be required for similarly sized FERAM, but there are two significant challenges currently limiting integrated FERAM from being fabricated below 100 nm: appropriate patterning and integration technologies and uncertainty about the scaling of ferroelectric performance at the extreme nanoscale.

The patterning approach developed here has enabled the formation of discrete patterned nanofeatures — ~20 nm in diameter — of nearly any material that is compatible with chemical solution and/or vapor-phase deposition techniques onto substrate layers of essentially any material, dramatically extending Sandia's nanofabrication capabilities. In concert, we have extended our characterization capabilities to allow analysis not only of the structure and morphology, but also of the chemical distribution and electrical properties of such patterned nanoscale features. Both this new chemically flexible nanofabrication platform and the associated nanoscale chemical analysis have the potential to be key capabilities for future projects. In addition, we have carried out the ultrahigh-resolution in-situ studies of crystallizing PZT-based thin films on technologically-relevant Pt/Si substrates, which, combined with the sub-5 nm chemical mapping technique developed through this project, shed tremendous new light on the phase sequence, interface development, and cation segregation, all of which occur during thermal processing of solution-derived PZT-based thin films.

Initial ferroelectric size effects and dynamic response studies have potential for great impact to the greater S&T community as well as direct relevance to Sandia's mission. The fabrication and analysis tools will (and in fact, already are in many cases) serve as enabling technologies for many future projects associated with nanoscale fabrication and/or integration.

Integrated Optical Phase Locked Loop (IO-PLL) for Attosecond Timing in Microwave Oscillators

117822
Year 3 of 3
Principal Investigator: A. L. Lentine

Project Purpose

Phase noise in traditional microwave oscillators limits or compromises their use in applications that require high precision clocking and/or fine phase resolution. To overcome the limitations of traditional microwave oscillators, we are locking a microwave oscillator to an integrated optical phase locked loop (IO-PLL). An optically referenced microwave oscillator represents a paradigm shift with the potential to move the clocking precision of a microwave oscillator from the femtosecond to the attosecond regime. This project is a collaboration between Sandia and the Massachusetts Institute of Technology (MIT), with MIT performing benchtop experiments and Sandia focusing on developing an integrated chip-level solution. Ultimately, our goal is to leverage the results generated by our Sandia-MIT team, and use the capabilities of the Microsystems and Engineering Sciences Applications (MESA) facility and the Center for Integrated Nanotechnologies (CINT) to integrate the required optical components onto an optoelectronic chip. It is important to emphasize that the goal of this work is not solely either integration or miniaturization. Chip-scale integration will enable fundamental limits of phase noise to be reached by removing 1/f and other noise sources inherent to bulk optic setups. Thus, via integration, we aim to achieve subfemtosecond timing resolution on a chip-scale device, a feat that to our knowledge has not been performed, in any form, large or small.

Summary of Accomplishments

- Accomplishment 1: We have demonstrated the smallest, highest-speed (10 Gb/s) and lowest-power resonant silicon amplitude modulators on record.
- Accomplishment 2: Our first silicon phase modulators have been designed and fabricated, and testing has been completed, yielding very low power for 2-π phase shift.
- Accomplishment 3: Our first IO-PLL loop has been designed and fabricated.
- Accomplishment 4: Our first germanium detectors have been designed and tested.
- Accomplishment 5: We have developed a process for fiber-attachment to our waveguides. Initial results demonstrate 3 dB fiber-to-chip coupling losses.
- Accomplishment 6: Our collaborators at MIT have performed a complete system characterization and analysis of fundamental timing errors in a voltage-controlled oscillator locked to a femtosecond pulse stream/optical phase detector. We have received a complete report detailing the fundamental timing errors from MIT. Further, MIT demonstrated a phase noise of –130 dB, 10Hz from the carrier leading to 6.8 fs relative timing stability over 10 hours (10^{-19}) between a pair of 10 GHz microwave oscillators, using their bench top optical phase locked loop. This represents a new record for radio-frequency extraction of timing stability from a mode-locked laser.
- Accomplishment 7: We presented an invited talk on our IO-PLL work at the Precise Time and Time Interval Meeting 2008, submitted several papers and gave other invited talks on silicon photonics technology developed under this project.

Significance

Given the universal need (e.g. radar, GPS, and communications) of compact, low-power, and high-performance oscillators, the national security impact of this project will be substantial. In addition, this project will enable Sandia to solidify its silicon photonics platform, explore fundamental limits of precision timing, and will promote a university collaboration with a leading scientific institution, MIT, thereby strengthening US scientific competitiveness at a DOE laboratory.

Refereed Communications

M.R. Watts, W.A. Zortman, D.C. Trotter, R.W. Young, and A.L. Lentine, “Low Voltage Compact Depletion Mode Silicon Mach-Zehnder Modulator,” *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 16, pp. 159-164, February 2010.

Four-Wave Mixing for Phase-Matching-Free Nonlinear Optics in Quantum Cascade Structures

117825
Year 3 of 3
Principal Investigator: W. W. Chow

Project Purpose

Problem: Nonlinear optics has the potential for efficient, high-temperature generation of coherent terahertz (THz) radiation. However, with present schemes, considerable effort must be spent satisfying phase matching conditions. At best, the need to phase match limits the interaction length, and therefore, the photon conversion efficiency.

This project involves an optically pumped, electrically biased quantum cascade (QC) scheme, where four-wave mixing (a nonlinear optical process) is automatically phase matched. The scheme also provides drive photon recycling, resulting in conversion efficiencies that exceed the fundamental limit for pure optical pumping (Manley-Rowe limit). With further development, the scheme can lead to efficient, high-temperature THz lasers. Besides exploring a novel way to generate THz radiation, there is significant science that should be explored. Four-wave mixing is being used successfully for new frequency generation in atomic and solid state systems. Replicating the results in a semiconductor system will be challenging because of intrinsic and extrinsic losses, such as carrier-carrier and carrier-phonon scatterings, and losses from the presence of impurities. We will need to explore how to mitigate the negative effects that these behaviors can cause.

Summary of Accomplishments

We have improved our understanding of quantum cascade laser (QCL) dynamics and optical nonlinearities. Through our work, we added significant capabilities to our modeling codes including adding electromagnetic field interactions with intersubband transitions, to enable temporal dynamics simulations. We introduced various ideas for new intersubband and mixed interband/intersubband devices, including a semiconductor photon recycling detector that could generate more than one electron per photon. The latter idea was spun-off into a separate project. We initiated a bandstructure optimization scheme that resulted in a publication and the inception of a new LDRD project to explore the unique capabilities of the code. We could not grow many of our desired designs due to issues beyond our control, and therefore, initiated the new capability at Sandia to grow the thin layers for quantum cascade type structures using metal organic chemical vapor deposition. In addition, we initiated theoretical exploration of semiconductor quantum optics, which allowed us to develop tools enabling the study of nonclassical-light devices, which could have applications in quantum computing or secure communication.

Significance

This research advances semiconductor quantum optics and QCL device engineering. The work improved Sandia's capabilities in terms of device growth, intersubband device modeling, ability to explore devices more systematically, and new tools for understanding and designing nonclassical-light devices. This will potentially impact future work in quantum computing, optical communication and cryptology, and solar energy harvesting.

Refereed Communications

A. Carmele, M. Richter, W.W. Chow, and A. Knorr, "Antibunching of Thermal Radiation by a Room-Temperature Phonon Bath: A Numerically Solvable Model for a Strongly Interacting Light-Matter-Reservoir System," *Physical Review Letters*, vol. 104, p. 156801, April 2010.

I. Waldmueller, M.C. Wanke, M. Lerttamrab, D.G. Allen, and W.W. Chow, "Inverse-Quantum-Engineering: A New Methodology for Designing Quantum Cascade Lasers," *IEEE Journal of Quantum Electronics*, vol. 46, pp. 1414-1420, 2010.

Z. Yang, A.Tauke-Pedretti, G A. Vawter, and W.W. Chow, "Mechanism for Modulation Response Improvement in Mutually Injection-Locked Semiconductor Lasers," to be published in the *IEEE Journal of Quantum Electronics*.

J. Kabuss, A. Carmele, M. Richter, W.W. Chow, and A. Knorr, "Inductive Equation of Motion Approach for a Semiconductor QD-QED: Coherence Induced Control of Photon Statistics," to be published in *Physica Status Solidi*.

D.G. Allen, T.W. Hargett, J.L. Reno, and M.C. Wanke, "Optical Bistability from Domain Formation in Terahertz Quantum Cascade Lasers," to be published in the *IEEE Journal of Selected Topics in Quantum Electronics*.

A Revolution in Micropower: The Catalytic Nanodiode

117827
Year 3 of 3
Principal Investigator: J. R. Creighton

Project Purpose

Micropower sources have numerous applications for microelectromechanical systems and microsensors. Microsensor systems are of interest for a variety of applications such as remote sensing of chemicals, radioactivity, or biological agents, in order to address issues related to the detection, location, and composition of weapons of mass destruction, as well as to assist in various nonproliferation efforts of DOE. Our ability to field useful, nano-enabled microsystems that capitalize on recent advances in sensor technology is severely limited by the energy density of available power sources.

In this project, we aimed to develop an alternative revolutionary source of micropower; the catalytic nanodiode (see http://pubs.acs.org/cen/news/83/i15/8315notw1.html). Like a fuel cell, this device utilizes a fuel and oxidizer, but, unlike a fuel cell, the fuel and oxidizer combine at the same surface (the catalyst) on the catalytic nanodiode. A sizable fraction of the chemical energy is, in principle, harvested via hot electrons that are created by the catalytic chemical reaction. These electrons are collected on the semiconductor side of the metal-semiconductor (Schottky) diode structure in the form of a “chemicurrent.” Unlike a fuel cell, there is not a second electrode, and the transport of other charged species (e.g., H^+) across an aqueous or solid media is not required. The fuel and oxidizer may be in the gaseous or liquid state. In this respect, the catalytic nanodiode is a simple, compact, and robust technology. This technology maps extremely well onto Sandia’s expertise in semiconductor device fabrication at the Microsystems and Engineering Sciences Applications facility, micropower applications, solid-state physics, and surface chemistry and catalysis. The goal of this project is to validate the concept, then use Sandia scientific and engineering expertise to significantly advance nanodiode technology. The final project goal was to demonstrate a functional catalytic nanodiode micropower device operating near room temperature (<50 °C) using a convenient fuel source (e.g., ethanol vapor).

Summary of Accomplishments

Our major accomplishments are as follows:

1. We built a novel mid-infrared pyrometer to unambiguously measure the platinum surface temperature during a chemical reaction. This pyrometer relies on the optical opacity of sapphire near 8 μm, and the semi-transparency of the nanometer thin film of platinum. The pyrometer also has a spatial resolution of ~2 mm needed to resolve the active Pt contact from the surrounding area. During typical experimental conditions the CO oxidation reaction generates a temperature rise of ~3 °C, which is orders of magnitude larger than the estimates in the existing literature. This temperature rise, together with the large GaN Seebeck coefficient, easily produces the observed chemical signal via the thermoelectric effect.
2. To supplement our experimental efforts we developed a complete 3D simulation of the thermal and chemical processes using Charon software. Steady-state simulations of reaction conditions demonstrated Pt temperature rises of 1–5 °C, in good agreement with the experimental results. The simulations also allowed us to investigate lateral temperature gradients within the nanodiode device, which are not easily probed experimentally.

In summary, we have discovered that all attributes of the chemical signal during reaction can be qualitatively and quantitatively explained by the reaction exothermicity and thermo-electrical properties of the diode; previous claims of a true chemicurrent are therefore erroneous.

Significance

DOE has several programs in sensors and long-term operations that must currently work with commercially available power sources. In most of these systems, batteries consume more than 95% of the system volume, due to the need for long duration. This revolutionary micropower source (if viable) would have enabled vast reductions in the size of fieldable systems for deployment into strategic weapons, nonproliferation technologies, national security defense systems, and space applications.

Unfortunately, our results demonstrate that previous researchers incorrectly interpreted their results. We have shown that the purported “chemicurrent” is in fact entirely due to a thermoelectric current generated by the chemical reaction exothermicity. Therefore the catalytic nanodiode appears to have no immediate future as a potential source of micropower.

Efficient Multi-Exciton Emission from Quantum Dots

117829
Year 3 of 3
Principal Investigator: T. S. Luk

Project Purpose

We propose to control the radiative processes of single or multiple excitons in quantum dots (QDs) by controlling the photonic density of states (PDOS) surrounding the QDs using photonic crystals (PCs). Enhancing the radiative rate can result in reducing the branching ratio to other nonradiative decay, especially Auger relaxation and heat producing processes, therefore controlling energy flow of quantum dot relaxation. Using this approach, energies of excitons and multi-excitons in quantum dots can be harvested through radiative emission processes rather than through charge separation and transfer.

We explored two approaches, both using large density of states enhancement at the emission wavelength of the radiative transition. The first method employs a nanocavity in the 2D PC with low loss and small volume to control PDOS. The second approach utilizes the band edge effect of photonic crystals. The main objective of this project is to enhance radiative emission properties of QD nanomaterials by factors of 10^3 to 10^4. Previous experimental efforts using colloidal QDs in 2D photonic systems demonstrated modest enhancement due to inability to incorporate QDs into the cavities with sufficiently low loss. For 3D PC systems, very little work has been performed because of the difficulties in fabricating high quality 3D PCs. This investigation will include both experimental, theoretical understanding of enhancement effects, as well as technological limits of this approach that enables efficient solar energy harvesting based on quantum dots and more-efficient light emitter devices. With this understanding, the groundwork will be laid to exploit QDs in light absorption and emission systems important to national security applications such as renewable energy, sensing, zero threshold lasing, and single photon sources.

Summary of Accomplishments

In this project, we demonstrated interfacial self-assembly and transfer as an approach to address a long-standing technology challenge: how to integrate colloidal light emitters (e.g., semiconductor QDs) with a nanophotonic structure in a manner that achieves good QD coupling with antinodes of the optical microcavity and avoids significant Q-factor degradation. This method enables us to measure large enhancement in PbS emission from a PC microcavity and waveguide.

We measured > 50 times enhancement in emission from lithographically produced photonic crystals with post-processing colloidal QD incorporation. Our analysis shows that the observed enhancement cannot be explained by the combined effects of Purcell enhancement and dielectric enhancement with microscopic local fields. We are still in the process of identifying other possible enhancement mechanisms.

Significance

This project entails controlling radiative behavior of nano and quantum systems. It is important to understand the fundamental mechanisms that enable enhanced emission. This project is an important milestone toward harvesting free and clean solar energy. It is also a steppingstone toward the development of a solar-pumped laser for satellite applications and a unique single photon source on-demand for secure quantum encryption and communication to ensure protection of national security interests.

Refereed Communications

S. Xiong, X. Miao, J. Spencer, C. Khripin, T.S. Luk, and C.J. Brinker, "Integration of a Close-Packed Quantum Dot Monolayer with a Photonic-Crystal Cavity Via Interfacial Self-Assembly and Transfer," *Small*, vol. 6, pp. 2126-2129, October 2010.

X. Miao, I. Brener, and T.S. Luk, "Nanocomposite Plasmonic Fluorescence Emitters With Core/Shell Configurations," *Journal of the Optical Society of America B*, vol. 27, pp. 1561-1570, July 2010.

Programmed Assembly of Nanoscale Three-Dimensional Networks of Inorganic Materials

117830
Year 3 of 3
Principal Investigator: D. Robinson

Project Purpose

Sandia and others have made great efforts toward the synthesis of nanowires and nanoparticles, with the hope that they will lead to electronic circuits beyond the limits of photolithography; that will produce new electronic and optical transducers, memory elements, and other devices that exploit quantum confinement effects; and will provide analytical devices that interface with single molecules or enzymes. While some methods are known for assembly of nanomaterials into ordered arrays, relatively little effort or progress has been made toward arbitrary and scalable arrangement of these materials into useful, rigid structures. By analogy, we have many lumber mills, and we can stack wood into piles, but we lack technologies that act as nails.

To build such structures, we use sequence-specific polymers to provide scaffolding for inorganic materials, in collaboration with the Molecular Foundry at Lawrence Berkeley National Laboratory. Branched nucleic acids are proving to be the best path to specific connectivity and long-range chirality. However, nucleic acid assemblies are stable under a narrow range of environmental conditions — a range in which inorganic nanomaterials tend to be unstable. To provide chemical stability, rigidity, and specific interactions with inorganic materials, we encapsulate inorganics and DNA in oligo (N-functional glycine)s, also known as peptoids. These polymers can have helical conformations stable under extreme conditions, and can confer stability to both nanoparticles and nucleic acids. They are sequence specific, allowing precise positioning of chemical functionality. In this project, we have focused on demonstration of a test system in which peptoid-stabilized nanomaterials are attached to a nucleic acid template in a programmed way, without binding in the wrong places or interfering with template assembly and structure.

Summary of Accomplishments

We designed short peptoids that stabilize gold nanoparticles under the conditions necessary to assemble and stabilize complex DNA nanostructures: high ionic strength buffers that contain both monovalent and divalent salt. Previous applications of gold nanoparticles to DNA have required omission of divalent salt, which can precipitate many particle formulations with as little as 1 mM magnesium ion. However, typically about 10 mM is needed to stabilize compactly folded DNA nanostructures. Another option is to encase the particle in a thick polymer shell, but this can defeat the purpose of the fine spatial resolution afforded by a DNA nanostructure, and can mask the chemical and physical functionality of the inorganic material.

The tunable functionality of peptoids allowed us to optimize the structure of small-molecule monolayer coatings for nanoparticles that stabilize particles in high-salt conditions, allow co-functionalization with measurable numbers of nucleic acids to permit binding to a DNA structure, and can be further functionalized after binding to DNA. The particles do not bind to other particles, surfaces, or DNA structures when not specifically designed to do so, a problem that has plagued other approaches. Peptoid-protected nanoparticles can withstand the elevated temperatures needed to assemble DNA nanostructures, and the particles or any excess peptoid do not interfere with the assembly process.

By changing the peptoid design, we can make versions that do interact with nucleic acids. These are a promising approach to protection of DNA nanostructures outside of the conditions in which they assemble, or in the presence of enzymes or intercalators that could damage them.

In the course of this work, we made useful contributions to the technology of peptoid synthesis, demonstrating new monomers and expanding knowledge of the properties of known monomers during synthesis, characterization, and application.

Significance

Sequence-specific polymers fill the final scaling gap in nanofabrication left by other forms of polymer-based lithography, reaching the ultimate practical limit of about 1 nm resolution, and allowing creation of three-dimensional structures. This will allow the ultimate scaling advances in electrical and optical circuits and of precise interfaces with biological structures of a similar scale. The most powerful version of this method uses DNA. The fact that it requires salty aqueous assembly conditions is both blessing and curse: a blessing because water is easy and safe to handle, but a curse because many nanoscale materials and electrical devices are not stable in the presence of water or salt. We have made progress on removing the curse by making the inorganic materials more stable in the presence of salty water, and the nucleic acids more stable once it is removed.

The use of peptoids bypasses many disadvantages that plague other attempts to overcome these problems. The simplicity, stability, and diverse chemical functionality of chiral oligo (N-substituted glycines) makes them a robust platform for rational and systematic development of inorganic materials templated by their assemblies. This provides the freedom to generate materials that are sophisticated enough to behave in specific, designed ways, while remaining simple enough to be predictable — a balance that has previously been absent. Our approach will eventually permit the synthesis of inorganic nanomaterials with an entirely new class of structure and functionality, as well as their integration into device structures that have otherwise been difficult or uneconomical to achieve. Templating through sequence-specific polymers is a fundamental approach to material synthesis that is likely to be to the 21^{st} century what photolithography was to the 20^{th}.

Stabilization of nanoparticles under biological conditions is likely to benefit medical therapeutic and diagnostic technologies that use nanoscale inorganic materials. Instability of these materials has been a major obstacle to their implementation in drug delivery, cancer cell targeting, and medical imaging.

Portions of this work were performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences, US Department of Energy, under Contract No. DE-AC02-05CH11231.

Templated Synthesis of Nanomaterials for Ultracapacitors

117832
Year 3 of 3
Principal Investigator: B. C. Bunker

Project Purpose

This project explored the extent to which nanoscale templates can be used to produce solution-derived nanocomposites for ultracapacitors. Ultracapacitors incorporate electroactive materials such as those found in batteries into electrolyte-filled electrical double layer capacitors to produce materials with exceptional capacitance, power and energy densities, charge/discharge rates, and reversible cycling capability. However, achieving the ultimate performance characteristics requires that materials for ultracapacitors be engineered at nanometer length scales to maximize electrode/electrolyte contact and minimize diffusion distances for charge-compensating carriers such as protons. The goal of this project was to combine electroactive oxides having the maximum charge storage capabilities with electroactive polymers having enhanced proton conductivities to produce hybrid nanocomposites that are ideal for preparing on-chip ultracapacitors.

The key to producing desired nano-architectures involved the use of low-temperature, solution-based processing on nanoscale templates, resulting in regular arrays of oxides, polymers, and electrolyte solutions distributed at length scales ranging from 1–150 nm. Two complementary strategies were used for preparing nanoscale architectures: 1) using self-assembled polymer precursors as templates for the solution deposition of a porous oxide matrix, and 2) using nanoporous oxides as templates for the in-situ polymerization of conducting polymers. In both cases, the compositions and architectures of the resulting nanocomposites were extensively characterized using techniques such as solid state nuclear magnetic resonance spectroscopy, transmission electron microscopy, and both x-ray and neutron scattering. Performance characteristics of the ultracapacitors were determined using cyclic voltammetry and electrochemical impedence spectroscopy. Correlations between charge storage characteristics and nanocomposite structures were developed to optimize ultracapacitor performance. Knowledge obtained on the template-based solution synthesis of oxide-polymer nanostructures for ultracapacitors will have a major impact on Sandia's core capabilities in self-assembled nanomaterials for other applications including batteries, fuel cells, solar collectors, and sensors.

Summary of Accomplishments

Major conclusions and accomplishments resulting from the project are the following:

1. Relatively inexpensive solution processing methods can be used to create nanoarchitectures for ultracapacitors, batteries, and capacitors with pore sizes ranging from less than one nanometer to over one micron.
2. Similar processing routes can be used to create intimate mixtures of electro-active materials, electron conductors, and ion conductors at nanometer length scales.
3. Templated solution growth methods can create materials that match or exceed the performance of the best materials reported in the literature.
4. In composites materials, combinations of relatively inexpensive components can match or exceed the performance of much more expensive single-component systems. Specific accomplishments include the following:
    - Template Development — We developed a range of nanoscale objects to serve as templates for the organization of solution-derived electroactive materials, including self-assembled surfactant arrays, sacrificial ZnO nanorods, and lithographically defined nanoporous carbon substrates.
    - Inorganic Nanomaterials — We produced electroactive oxides and hydroxides with nanoscale features via solution processing, including nanocrystalline $LiTiO_2$, $Ni/Ni(OH)_2$ nanorods, and RuO_2 with hierarchical nanoporosity.

- Conductive Polymers — New families of electroactive polymers were produced based on components including thiophenes, phenazenes, and quinoxalines. These polymers exhibited record capacitances, especially when deployed in nanoscale templates such as anodized alumina and our new nanocarbon electrodes.
- Multi-component Composites — We demonstrated new solution-based routes for making composites in which electroactive materials, electron conductors, and proton conductors were intimately mixed at the nanoscale. We demonstrated that these composites not only exhibit exceptional charge storage performance, but achieve this performance at low cost.
- Theory and Modeling — Mathematical models were developed to explain and predict the electrochemical performance of electrode materials based on both composition and nanoarchitecture. The models combine coupled processes of electron and ion transport, interfacial redox reactions, and electrolyte transport as confined within nanoporous structures.

Significance

The needs for enhanced materials for energy storage span a broad range of Sandia and DOE mission space, from basic research in energy storage to energy storage needs for transportation, the US power grid, responsive on-chip power devices, and a wide range of defense applications.

Refereed Communications

M.T. Brumbach, T.M. Alam, P.G. Kotula, B.B. McKenzie, and B.C. Bunker, "Nanostructured Ruthenium Oxide Electrodes via High-Temperature Molecular Templating for use in Electrochemical Capacitors," *ACS Applied Materials and Interfaces*, vol. 2, p. 778, March 2010.

M.T. Brumbach, T.M. Alam, R.H. Nilson, P.G. Kotula, B.B. McKenzie, R.G. Tissot, and B.C. Bunker, "Ruthenium Oxide-Niobium Hydroxide Composites for Pseudocapacitor Electrodes," to be published in *Materials Chemistry and Physics*.

M.E. Roberts, D.R. Wheeler, B.B. McKenzie, and B.C. Bunker, "High Specific Capacitance Conducting Polymer Supercapacitor Electrodes based on Poly(tris(thiophenylphenyl)amine)," *Journal of Materials Chemistry*, vol. 19, pp. 6977-6979, September 2009.

R. Polsky, X. Xiao, M.E. Roberts, D.B. Burckel, C.M. Washburn, T.L. Edwards, J.C. Harper, B.C. Bunker, S.M. Brozik, and D.R. Wheeler, "Electrochemical Polymerization of Bithiophene onto Lithographically Defined Porous Carbon Electrodes," to be published in *ACS Applied Materials and Interfaces.*

Anomalous Suppression of Fatigue and Wear Through Stable Nanodomains

117833
Year 3 of 3
Principal Investigator: B. Boyce

Project Purpose

Fatigue and wear are pervasive problems in engineering designs. There are numerous Sandia designs from nuclear weapon (NW) stronglink components to satellite flexures that have fatigue and/or friction/wear concerns. In this project, we propose to develop a revolutionary new class of nanotailored alloys that are impervious or strongly resistant to fatigue and have low friction with exceptional wear resistance. Our approach to reduce or eliminate a material's susceptibility to fatigue and sliding contact damage is by perturbing the requisite dislocation-length scales.

Our very encouraging preliminary work indicates that a new regime of behavior occurs when dislocation-mediated deformation is suppressed. As a specific example, our results suggest that persistent slip bands (PSBs), the cyclic-dislocation precursor to fatigue-crack initiation, can be suppressed by incorporating stable arrangements of dislocation-pinning obstacles at less than the required PSB length-scale. These experiments have shown that a Ni alloy with a sub-50 nm grain size will not fail at cyclic stresses of 1.5 GPa even after 10 M cycles: a 3000× enhancement compared to the best conventional alloys. The locking aspect is critical: other nanocrystalline (nc) metals suffer from stress-induced grain growth and commensurate loss of anomalous fatigue and frictional sliding contact properties. In another preliminary experiment, nc nickel was discovered to have anomalously low friction and noticeably absent metallic stick-slip behavior. However, the exceptional tribological behavior was lost after either excessive cycling or modest thermal exposure. We postulate that enhanced properties via length-scale suppression occur only when the nc structure is stabilized against thermally or mechanically induced evolution. To complement experimental investigation of these phenomena, we have implemented mesoscale grain evolution simulations to characterize microstructural regimes that are sufficiently resistant to anomalous grain formation and growth both during annealing and under strain. In parallel, a multiscale modeling approach evaluates length-scale dependent deformation-mechanism transitions for comparison to experimental results.

Summary of Accomplishments

Through this project, we have demonstrated that nanocrystalline metallic alloys impede traditional dislocation-mediated damage processes, resulting in exceptional fatigue, friction, and wear performance. The detailed results of this investigation have yielded nine journal articles.

Studying the fatigue and wear mechanisms of a new class of alloys through a combined experimental and modeling approach requires an integration of resources (financial, intellectual, and infrastructural) that is uncommon outside of the national laboratory environment. Through this effort, we have been able to tackle a set of seemingly "impossible" problems: including the first integration of dislocation dynamics theory into a polycrystalline finite element formulation, the development of a high-cycle fatigue test system for micron-scale thin films, and the "needle-in-a-haystack" problem of locating the nanoscale origins of the fatigue-crack initiation process. The project brought together diverse researchers with expertise ranging from experimental mechanics to grain-growth simulation, tribology, and electrodeposition.

Significance

Wear damage and fatigue crack formation are pervasive concerns in a wide range of Sandia designs from stronglinks to satellites. We have established a new class of metals with grain size <100 nm, in which cyclic damage mechanisms are suppressed, leading to truly exceptional fatigue and wear performance. Specifically, while the coefficient of friction of conventional alloys is invariably m >0.6, these nanocrystalline alloys exhibit m <0.3. In fatigue performance, conventional alloys loaded to stresses at or above their yield strength invariably fail after < 10^4 cycles, whereas these nanocrystalline alloys persist for >10^7 cycles. This new class of alloy provides design engineers with a new alternative for applications where cyclic damage is a significant reliability concern. These alloys are being evaluated by stronglink engineers to achieve improved performance and reliability. Beyond the game-changing properties available for future engineering designs, the research effort has also revealed key new insights into the metallurgical mechanisms associated with cyclic deformation. The discovery of cyclically driven room-temperature grain growth in nanocrystalline Ni alloys is causing scientists to rethink the current diffusional description of grain boundary motion, leading to significant investments from DOE-Basic Energy Sciences for further investigation.

Refereed Communications

H.A. Padilla, and B.L. Boyce, “A Review of Fatigue Behavior in Nanocrystalline Metals,” *Experimental Mechanics*, vol. 50, pp. 5-23, January 2010.

B.L. Boyce, J.Y. Huang, D.C. Miller, and M. Kennedy, “Deformation and Failure of Small-Scale Structures,” *JOM*, vol. 62, pp. 62-63, 2010.

Impact of Defects on the Electrical Transport, Optical Properties and Failure Mechanisms of GaN Nanowires

117834
Year 3 of 3
Principal Investigator: A. Armstrong

Project Purpose

GaN-based nanowires are attractive for applications requiring compact, high-current density devices such as ultraviolet laser arrays. Understanding GaN nanowire failure at high-current density is crucial to developing nanowire devices. Nanowire device failure is likely more complex than failures in thin films due to the prominence of surface effects and enhanced interaction among point defects. Understanding the impact of surfaces and point defects on nanowire thermal and electrical transport is the first step toward rational control and mitigation of device failure mechanisms. However, investigating defects in GaN nanowires is extremely challenging because conventional defect spectroscopy techniques are unsuitable for wide-bandgap nanostructures. Nevertheless, studying GaN nanowires is scientifically interesting because the combination of threading dislocation (TD)-free nanowire growth and large surface-to-volume ratio enables investigation of TD- and surface-related defects at a sensitivity beyond that achievable in thin films. For example, comparing electrical and thermal properties of nanowires before and after TD introduction directly measures the unresolved question of the influence of TDs on GaN properties in general. To understand nanowire breakdown, the influence of pre-existing and emergent defects during high current stress on nanowire properties has been investigated. Acute sensitivity of NW thermal conductivity to point-defect density is expected due to the lack of TD gettering sites, and enhanced phonon-surface scattering further inhibits thermal transport. Excess defect creation during Joule heating could further degrade thermal conductivity, producing a viscous cycle culminating in catastrophic breakdown. To investigate these issues, a unique combination of electron microscopy, scanning luminescence and photoconductivity implemented at the nanoscale has been used in concert with sophisticated molecular-dynamics calculations of surface and defect-mediated nanowire thermal transport. This project seeks to elucidate longstanding material science questions for GaN while addressing issues critical to realizing reliable GaN nanowire devices.

Summary of Accomplishments

A major accomplishment of this project was the development and use of defect spectroscopy for GaN nanowires, including the first application of deep level optical spectroscopy (DLOS). Using DLOS, we discovered that the defect spectrum of GaN nanowires is very similar to that of thin film GaN. This suggests that surface defects in GaN nanowires are effectively screened by the surface depletion field due to Fermi level pinning. Using nanoscale cathodoluminescence, we also found strong evidence for segregation of defects (likely the gallium vacancy) to the nanowire surface.

Molecular dynamics (MD) calculations of thermal conductivity were performed for GaN nanowires. An analytic model was developed to bridge the gap between tractable calculations of nanowires (~20 nm length) and actual nanowire device sizes (~2000 nm length). This model included surface and edge effects. It was found that NW thermal conductivity was significantly lower than that of thin films and that the diameter dependence on thermal conductivity becomes weak for diameters greater than ~ 70 nm.

Various methods were employed to measure the thermal conductivity of GaN nanowires experimentally. In one method, the energy and full-width at half-maximum of nanowire band edge luminescence was monitored to determined the nanowire temperature distribution as a function of electrical or optical excitation. Another method suspended a nanowire in thermal isolation and measured the temperature change as a function of input heat. For both cases, the nanowire thermal conductivities were much smaller than values reported for thin films, and also much small than calculated values. Since MD calculations include surface and edge effects but do not include phonon scattering by point defects, we concluded that nanowire thermal conductivity is significantly limited by both the former and the latter.

Significance

GaN nanowire properties, including increased radiative efficiency and enhanced surface sensitivity, make GaN-based nanowires devices candidates for solid-state lighting applications and compact chemical and biological sensors. Resolving the influence of defects on electrical and thermal transport in GaN nanowires will benefit efforts for enhanced sensing applications and energy conservation through advancement of solid-state lighting.

Refereed Communications

A. Armstrong, Q. Li, Y. Lin, A.A. Talin, and G.T. Wang, "GaN Nanowire Surface State Observed Using Deep Level Optical Spectroscopy," *Applied Physics Letters*, vol. 96, p. 163106-3, April 2010.

K.K. Mandadapu1, R.E. Jones, and P. Papadopoulos, "Generalization of the Homogeneous Nonequilibrium Molecular Dynamics Method for Calculating Thermal Conductivity to Multibody Potentials," *Physical Review E*, vol. 80, p. 047702, October 2009.

X.W. Zhou, R.E. Jones and S. Aubry, "Molecular Dynamics Prediction of Thermal Conductivity of GaN Films and Wires at Realistic Length Scales," *Physical Review B*, vol. 81, p. 155321, April 2010.

X.W. Zhou, R.E. Jones, and S. Aubry, "Analytical Law for Size Effects on Thermal Conductivity of Nanostructures," *Physical Review B*, vol. 81, p. 3304, February 2010.

Q. Li and G.T. Wang, "Spatial Distribution of Defect Luminescence in GaN Nanowires," *Nano Letters*, vol. 10, pp. 1554-1558, April 2010.

Energy Conversion using Chromophore-Functionalized Carbon Nanotubes

117835
Year 3 of 3
Principal Investigator: A. Vance

Project Purpose

The conversion of optical energy to electrical energy is a topic of great interest, with significant R&D invested in conventional materials such as silicon. Nanomaterials such as quantum dots and nanowires offer much promise for optical energy conversion, due to their unique electronic, optical, and mechanical properties. Among nanomaterials, carbon nanotubes are especially attractive for optoelectronics because all of the bandgaps in all carbon nanotubes are direct, and also because of the possibility of ballistic electronic transport. While photoresponse in individual carbon nanotubes has been demonstrated, these experiments were done at high light intensities (lasers). Furthermore, the spectral range of the optical absorption is limited by that of the nanotube. We propose to circumvent these issues by using chromophore-functionalized carbon nanotubes to generate a photoresponse at low-intensity optical radiation in targeted or broad regions of the optical spectrum. In FY 2009, we demonstrated nanoscale color photo detection using chromophore-nanotube hybrid devices [*Nano Letters*, 9, p.1028, 2009] and this work was featured in *Nature Photonics*, physicsworld.com, *Technology Review*, and *Spektrum der Wissenschaft*. We will expand upon these discoveries and use chromophore-nanotube hybrids to study energy conversion at the nanoscale and develop a fundamental understanding of their behavior. Throughout the life of this project, experiments and simulation will be closely linked. We will explore factors such as chromophore density, the role of electrical contacts, and time dependence of light-induced conductance changes. Carbon nanotube devices are clearly a popular area of research; however, there are few groups studying their use in generating a photoresponse from low-intensity optical energy. The ability to use light to modulate the conductance of carbon nanotube devices through minimally intrusive, noncovalent modification of the nanotubes could lead to significant advances in areas such as nanoscale electronics, solar energy and photodetectors.

Summary of Accomplishments

Through both experimental and theoretical studies, this work showed that single-walled nanotubes (SWNTs) can transduce the photoabsorption-induced isomerizations of nearby chromophores into electrical signals. By designing chromophores to absorb in a narrow window of the optical spectrum and applying them to SWNT-FETs (field-effect transistors), sensitive nanoscale color detectors were demonstrated. This system can be used to study fundamental properties of chromophore-nanotube hybrids and to probe molecular transitions. We expect that improvements in the signal transduction will lead to the ability to detect single molecular transformation events, and that molecular engineering can provide detection in other regions of the optical spectrum.

Significance

Chromophore-nanotube hybrids have the potential to become efficient, low-power and compact photo-sensors. Carbon nanotubes are compatible with existing semiconductor production processes and could be incorporated into flexible electronics. With wavelength-specific chromophores, device response could be tuned to wavelengths ranging from the ultraviolet to the near-infrared. Our initial work has already demonstrated the ability of devices consisting of chromophore-functionalized single nanotubes to detect visible light. To achieve the goal of utilizing chromophore-nanotube photodetectors as components of photosensors, a fundamental understanding of the science governing the properties of chromophore-nanotube hybrids is necessary. Our work helped establish new scientific approaches to rationally design and synthesize chromophores, discovered new techniques to functionalize carbon nanotubes, probed molecular transformations at the nanometer scale, and provided a quantitative link between experiment and ab initio modeling of chromophore-nanotube hybrids.

Studies of the Viscoelastic Properties of Water Confined Between Surfaces of Specified Chemical Nature

117837
Year 3 of 3
Principal Investigator: N. W. Moore

Project Purpose

The molecular origins of the no-slip boundary condition remains vitally important for understanding molecular transport in biological, environmental and energy-related processes, with broad technological implications. More generally, the viscoelastic properties of fluids in nanoconfinement or near surfaces are not well-understood. In particular, the transition between bulk fluidity and near-surface behavior has been determined for only a few cases. Our goals have been to develop a systematic understanding of the flow of fluid confined between surfaces of nanometer separation to allow fundamental improvements in the design of materials, as well as to understand chemical and structural change in the myriad of naturally occurring materials where water is involved. Our approach has been to combine novel experimental capabilities (e.g., Interfacial Force Microscopy) with a full range of theory (ab initio, continuum molecular dynamics) to develop a fundamental understanding of nanoconfined fluid flow over multiple length scales. Water is famously complicated and suitable computational methods for handling this are presently under broad and intense development. Similarly, experimental methods suitable for measuring the viscoelastic properties of a fluid film of only a few molecules in thickness are still in their infancy. Thus, the evaluation of theoretical and experimental methodologies is an integral and substantial part of the project. The potential impact of this effort extends to several important Sandia missions, including the flow behavior in microfluidics and desalination membranes as well as environmental “stiction” problems in microelectromechanical-device development.

Summary of Accomplishments

Our theoretical and experimental discoveries include insight into the orientation of water molecules on metal surfaces, the nucleation of water and alcohol vapors between surface asperities and their lubricity when confined inside nanopores, and the influence of vapor condensation and ion partitioning on nanoscale adhesion. Two accomplishments that attracted much positive attention from the popular press were the discovery of superplasticity in nanowires made of common salt (reported by *The New York Times*, National Public Radio, and others), and a review article on water-solid interactions written for *Physics Today*. Additionally, we have evaluated key theoretical and experimental methodologies, including interfacial force microscopy, leading to establishment of the limitations and capabilities of the techniques as pertains to nanorheology, as well as improved the methods for other work.

Significance

Water/material interface properties govern a broad array of vital natural and artificial processes, including a spectrum of technological issues from corrosion to desalination, energy storage and conversion, the stability of geological zones intended for carbon sequestration, and the efficiency and reliability of microfluidics and microelectromechanical systems/ nanoelectromechanical systems (MEMS/NEMS). For example, the way in which the first layer of water molecules arranges onto a hydrophilic surface influences the no-slip boundary condition with which every engineer is acquainted yet no one can understand. Importantly, how fluidity is altered by nanoconfinement, surface topography or electric fields is also largely unexplored, yet has important implications for the efficiency of electrocatalysis, for example. Thus, the improved fundamental understanding of water behavior within nanometers of surfaces remains a broadly important and, as yet, unanswered challenge. As such, this work addresses key fundamental nanoscience issues relevant for DOE.

Refereed Communications

P.J. Feibelman, “The First Wetting Layer on a Solid,” *Physics Today*, vol. 63, pp. 34-39, February 2010.

S. Nie, P.J. Feibelman, N.C. Bartelt, and K. Thurmer, “Pentagons and Heptagons in the First Water Layer on Pt(111),” *Physical Review Letters*, vol. 105, p. 026102, July 2010.

C.D. Lorenz, M. Chandross, and G.S. Grest, “Large Scale Molecular Dynamics Simulations of Vapor Phase Lubrication for MEMS,” to be published in the *Journal of Adhesion Science and Technology*.

N.W. Mooreand and J.E. Houston, “The Pull-off Force and the Work of Adhesion: New Challenges at the Nanoscale,” to be published in the *Journal of Adhesion Science and Technology.*

M.P. Goertz and N.W. Moore, “Mechanics of Soft Interfaces Studied with Displacement-controlled Scanning Probe Microscopy,” to be published in *Progress in Surface Science.*

Nanolithography by Combined Self-Assembly and Directed Assembly

120711
Year 3 of 3
Principal Investigator: D. L. Huber

Project Purpose

We will develop the scientific understanding required for a simple, inexpensive process to create nanometer-scale patterns. Current approaches to nanoscale patterning rely on expensive equipment, such as electron beam lithography and extreme UV lithography. Other approaches, e.g., scanning probe manipulation of nanomaterials, are sequential and not conducive to large-scale integration. To make nanoscale lithography more widely accessible and practical, alternate simple, inexpensive, and nonsequential (parallel) approaches are needed. Microphase separation in diblock copolymers has been demonstrated for lithography. However, it is expensive and difficult to synthesize diblock copolymers, and the resulting patterns are either uncontrolled, or require a predefined nanopattern made by expensive techniques. Our novel approach is to create micron-size patterns that will then direct the self-assembly of surface-bonded polymer blends to create nanoscale patterns. The micron-sized features will be lithographically defined by widely available soft lithography or standard UV lithography, and a mixed polymer monolayer synthesized within these features. Nanoscale phase separation of the mixed polymer layer will form parallel lines within the micron-sized lines. Molecular theory will be used to understand the nanoscale thermodynamics of the system, with predictions to guide experimental design. We will elucidate how polymeric parameters and microscale geometries control the nanoscale features.

Summary of Accomplishments

The result of this project has been a proof of concepts of an exciting new method to create controllable, nanoscale patterns in a rapid and repeatable way. The method has been demonstrated to be amenable to standard lithographic techniques and is therefore convenient in a research setting, but also commercially viable. Experimentally, we developed a method to conveniently pattern initiators, grow polymers on these features, then backfill unpatterned regions with initiators to grow an immiscible polymer. We have characterized the resulting phase separated nanomaterials, and have investigated approaches to annealing the polymers to allow patterns to form. A surprising result was that these polymers can yield patterns in a matter of seconds or minutes. This is a major benefit of this approach. The simulation efforts have applied Self Consistent Field Theory (SCFT) to study the phase behavior of a mixed brush system focusing on its lithographic application. Unlike some applications, for example, wetting and adhesion, in which only the gross composition of the uppermost layer is important, in applications such as templates for nanoscale structures, the long-range order of the microphase-separated structures and how it developed in depth is of importance. Thus, it requires full three-dimensional SCFT calculations, which have been widely successful in predicting microphases in block copolymer systems. We have developed new methods and codes to efficiently perform these challenging calculations. We were able to calculate the phase diagram in the melt condition as a function of composition and segregation force and compared it with the diblock copolymer system. These calculations are critical to guide experiments to develop a specific desired structure.

Significance

The understanding of nanoscale self-assembly gained from this project will be applicable to outcomes that impact national missions in energy and security. Applications include improved photovoltaics, nanoelectronic and nanophotonic devices, sensors, and nanofluidic systems. This project addresses several research areas outlined in the National Nanotechnology Initiative, in particular the design and synthesis of structured nanomaterials and in reliable, cost-effective nanomanufacturing.

Architecturally Controlled Nanocathode Materials for Improved Rechargeable Batteries

130767
Year 2 of 3
Principal Investigator: E. D. Spoerke

Project Purpose

Current rechargeable battery technologies are unable to meet the growing demands of electric or hybrid electric vehicles, clean energy harvest of renewable power sources, improvements in utility power grid efficiency, and power sources for our ubiquitous energy-hungry portable electronics. Concentrating on promising lithium ion technologies, we are working specifically to improve cathode materials, whose poor capacities continue to limit cell performance. We are working to take advantage of inexpensive, moderate voltage ceramic materials with high theoretical capacities (e.g., iron oxides). Our initial efforts have focused on developing a comprehensive, baseline understanding of the chemistry and properties of common iron oxides, most of which display high capacity, but at voltages too low for use as cathodes. Using these early studies to develop a detailed understanding the relationships between electrochemical activity and variables such as material phase, nanoscale morphology, and atomic doping, we expect to be able to engineer, in this project, the extension of high capacity voltage plateaus at moderate voltages. This alternative "capacity-based" approach will enable us to produce cathodes capable of attaining high energy densities while avoiding the host of serious, often dangerous, side-effects (e.g., electrolyte degradation, current collector corrosion, binder deterioration, and other deleterious side reactions) associated with higher voltage cathodes popular in current battery research. Efforts moving forward will continue to rely on an integrated, collaborative approach wherein atomistic modeling, designer chemical synthesis, and in situ crystallographic and electrochemical characterization will contribute to the exploration of both new regions of metal oxide phase space and new, nanoscale morphologies of active materials. By building on the theoretical and empirical data obtained to date and expanding on the synthetic capabilities and materials developed, we expect to reveal promising new insights and materials technologies for next-generation lithium ion cathode materials.

Summary of Accomplishments

Research in FY 2010 has focused on synthesizing and characterizing iron oxides capable of producing extended voltage plateaus above 1 volt (V). We have explored a number of different high-capacity oxides, the vast majority of which discharge at voltages too low to be useful for cathode development (below 1 V vs. lithium). Efforts to produce higher-voltage materials have focused on higher oxidation state materials, though these have proven either electrochemically inactive or synthetically unstable.

Evaluation of a promising lithiated precursor to these higher oxidation state materials, produced a modest, though non-cycling, plateau around 2 V. Molecular simulations indicated that the limited capacity of this system likely resulted from poor ionic mobility in a densely packed crystal lattice, but also suggested that disrupting the atomic packing with defects could dramatically improve Li-ion mobilities.

This insight led to some very promising results obtained from two iron oxide phases with lattice and defect structures capable of supporting both cationic doping and potentially significant Li-diffusion. Evaluation of these phases has revealed an electrochemical discharge plateau between 1.5–2 V with a capacity on the order of several hundred mAh/g. Perhaps just as important, these materials have shown promising cycling stability.

Extending the study of this promising phase, we have utilized custom alkoxide chemistries to produce nanoparticles of a select, electroactive iron oxide phase with varied nanoscale morphologies, creating a unique opportunity to evaluate the influence of small-scale morphology on an electroactive iron oxide phase.

In addition to the technical objectives of the project, we have produced several publications in preparation for submission to scientific journals and have also given several technical presentations. The project has also produced intellectual property, outlined in several invention disclosures currently in preparation.

Significance

This energy-related project on battery materials research seeks to develop new science and technology related to energy storage, an important national and global topic. Project success will provide valuable new insight into battery materials research with potentially significant impact on energy storage for transportation, capturing renewable energy, improving power grid efficiency, and powering both consumer and military portable electronics. This particular project stands to make a unique impact in the S&T community because it is focused on the use of iron oxides as electrode materials. These materials have been traditionally dismissed because of poor electrochemical performance, but our efforts are showing that engineering these oxides appropriately may make them viable electrochemical candidates that would be extremely attractive owing to their low cost and environmental friendliness.

Atomic Mechanisms Governing Interface Formation in Nanostructured, Phase-Separated Thermoelectric Alloys

130768
Year 2 of 2
Principal Investigator: D. L. Medlin

Project Purpose

Expanding the use of thermoelectric devices for waste heat recovery and more-efficient cooling will require new bulk materials with dramatically improved energy conversion efficiencies over the current state-of-the-art. The central materials challenge is to balance the competing requirements of high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. Overcoming this challenge is difficult because these properties are highly interrelated in traditional, single-phase, solid-solution alloys. However, recent work has shown that it is possible to decouple these transport properties by introducing nanometer-scale distributions of interfaces that, for instance, preferentially scatter phonons, reducing the thermal conductivity, or selectively filter low-energy charge carriers, enhancing the Seebeck coefficient. One promising route to introducing the necessary interfaces in bulk materials is to control the solid-state phase-separation processes in multiphase alloys to produce a nanometer-scale distribution of heterophase interfaces. In particular, recent work at the California Institute of Technology (Caltech) has demonstrated that the phase-decomposition in the Pb-Sb-Te system can be controlled to produce a bulk, self-assembled, layered material consisting of nanometer-scale lamellae of PbTe and Sb_2Te_3. Under this project, we are collaborating with those Caltech researchers to explore the atomic-scale mechanisms that govern this self-assembly process. Our goal is to understand the science underpinning these nanostructured thermoelectric alloys.

Summary of Accomplishments

We have investigated interfaces between the tetradymite structured compound, Sb_2Te_3, and two different rock-salt structured tellurides, PbTe and $AgSbTe_2$. These materials are synthesized through solid-state precipitation routes. We have established the specimen preparation protocols to reliably prepare specimens for microscopic analysis, and have analyzed the detailed interfacial structure of PbTe/ Sb_2Te_3 and $AgSbTe_2$/ Sb_2Te_3 interfaces using transmission electron microscopy. Our work has shown how misfit strain and phase transformations are connected to the interfacial line defects. These issues are important because local strain and interfacial defects likely affect the formation and morphological stability of the interfaces as well as their electronic and thermal transport properties. We also investigated the growth of silver telluride precipitates in lead-telluride thermoelectric materials. With suitable doping, enhanced *ZT* was demonstrated, resulting largely due to increased phonon scattering at the embedded Ag_2Te precipitates. Finally, we also explored more broadly the role of interfaces in nanostructured, bulk thermoelectrics by completing an invited review article on this subject.

Significance

Thermoelectrics have diverse energy conversion and cooling applications that span much of Sandia and DOE mission space. Existing and potential future applications include long-term, high-reliability power sources, localized cooling devices, low-temperature power scavenging, and high-temperature waste heat recovery.

Refereed Communications

Y. Pei, J. Lensch-Falk, E.S. Toberer, D.L. Medlin, and G.J. Snyder, “High Thermoelectric Performance in PbTe due to Large Nanoscale Ag_2Te Precipitates and La Doping,” *Advanced Functional Materials,* vol 21, p.241, 2011.

J. L. Lensch-Falk, J.D. Sugar, M.A. Hekmaty, and D.L. Medlin, ”Morphological Evolution of Ag_2Te Precipitates in Thermoelectric PbTe,” *Journal of Alloys and Compounds*, vol. 504, pp. 37-44, August 2010.

D.L. Medlin and J.D. Sugar, “Interfacial Defect Structure at Sb_2Te_3 Precipitates in the Thermoelectric Compound $AgSbTe_2$,” *Scripta Materialia*, vol. 62, pp. 379-382, November 2009.

D.L. Medlin and G.J. Snyder, “Interfaces in Bulk Thermoelectric Materials,” *Current Opinion in Colloid and Interface Science*, vol. 14, pp. 226-235, August 2009.

Bio-Inspired Nanocomposite Assemblies as Smart Skin Components

130769
Year 2 of 3
Principal Investigator: S. M. Brozik

Project Purpose

The Defense Threat Reduction Agency (DTRA) is interested in the development of sophisticated materials that can automatically detect and respond to chemical and biological threats without the need for human intervention. In living systems, cell membranes perform such functions on a routine basis, detecting threats, communicating with the interior of the cell, and triggering automatic responses such as the opening and closing of ion channels. The purpose of this project is to learn how to replicate simple threat detection and response functions within artificial membrane systems. The key attributes that we intend to explore to make such a “smart skin” include: 1) a lipid bilayer host matrix with sufficient mobility to allow components to reconfigure themselves in response to specific stimuli; 2) recognition sites that both adsorb “threats” and trigger membrane responses; 3) functionalized nanoparticles that can be reconfigured to reversibly switch the membrane between an open, permeable state and a closed, impermeable state; and 4) an underlying substrate that provides the stimuli for programming the membrane once threats are detected. The proposed work will provide the scientific underpinning for developing a wide range of responsive membrane-based nanocomposites for both homeland defense and energy applications.

Summary of Accomplishments

In FY 2010 we proposed to study the mechanism of insertion of particles into lipid bilayers and begin to develop functionalized particles that we could control assembly within bilayers electrochemically, through changes in pH, etc. Experimentally we have functionalized gold nanoparticles (NPs) with 11-mercaptoundecanoic acid, terpyradine lipoic acid, naphthalen-1-yl 5-(1,2-dithiolan-3-yl)pentanoate, and TTF-lipoic acid and have prepared lipids used to assemble bilayers. The model lipid bilayers were cationic dioleoyltrimethylammonium propane mixed with zwitterionic distearoylphosphatidylcholine or zwitterionic 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine at several compositions. Scanning probe microscopic methods were used to probe the surface charge localization and the electrostatic interaction between positively charged lipid bilayers and negatively charged Au NPs. The surface charges were distributed over the entire membrane surfaces through the molecular mixing and the mobility of the supported bilayers, but could be localized at the nanometer or molecular scale due to the formation of individual phases, domains, and networks. In order to develop a responsive system, we need to be able to control the assembly of the particles in the bilayers. Our initial work has resulted in the formation of nano-ring structures within bilayers through 2D coordination reaction. $ZrCl_4$ was introduced to coordinate Au NPs functionalized with a mixed monolayer of dodecanethiol and 11-mercaptoundecanoic acid in lipid bilayers. We are currently working on controlled assembly of the other functionalized Au-NPs mentioned above that we hope to reversibly interact by changing the oxidation potential of the electroactive group bound to the NPs. Through our modeling effort we have developed a new formulation of fluids density functional theory. We also determined that we needed an improved coarse-grained model for the lipids and have spent this fiscal year to date developing the new model. We are now continuing our calculations of nanoparticle insertion into bilayers using our new, optimized model.

Significance

This project has potential benefit to both applied and basic science sponsors at Sandia. The proposed work will provide the scientific underpinning for developing a wide range of responsive membrane-based nanocomposites for both homeland defense and energy applications. On the applied side, this project positions Sandia to respond to specific research needs that have been called out by DTRA dealing with responsive materials to meet the needs of chemical and biological defense. Specifically, the military, DHS, and DTRA are each interested in the development of responsive films or fabrics to meet two mission needs: 1) responsive materials for protecting personnel from chemical and biological threats, and 2) materials for adaptive camouflage. The proposed research will provide fundamental understandings of nanoparticle interactions within bilayer assemblies mimicking the responsive behaviors that occur in cellular membranes.

On the basic science side, the development of biomimetic nanocomposites is one of the frontier areas in nanoscience that maps onto Sandia's new DOE/Basic Energy Sciences-funded Center for Integrated Nanotechnologies. This work will provide Sandia with opportunities for enhanced programmatic and operating budget from the Office of Basic Energy Sciences.

Characterization and Control of the Thermal Fluctuations of Nanosensors for Next Generation Sensitivity and Robustness

130770
Year 2 of 2
Principal Investigator: R. E. Jones

Project Purpose

Nanoelectromechanical systems (NEMS) are spawning a new generation of novel devices. For example, a NEMS beam-like oscillator's small size promises smaller activation energy and greater sensitivity than traditional sensors. This sensitivity comes at the price of greater susceptibility to thermal "noise." Device design and characterization methodologies are often based on simple linear continuum approaches with little or no modeling of the stochastic nanoscale dynamics. These traditional methods become inadequate at the dimensions of NEMS, which are akin to complex molecules and viruses. Specifically, recent experiments using an atomic force microscope with an attached molecule of DNA to measure binding energies and function as a bio-sensor have demonstrated the device's resolution is currently limited only by the thermal fluctuations. In addition to stochastic behavior introduced directly by the environment, recent fluctuation theorems (FTs) from nonequilibrium statistical mechanics show that nanoscale devices observed for short time periods have a finite probability of acting contrary to the well-known macroscale second law of thermodynamics. Using the structure and insight of FTs, we intend to quantify and control this behavior not predicted by the simplified design techniques and, up to now, inadequately "explained" as uncharacterized system noise.

Summary of Accomplishments

In this project we furthered the fundamental understanding of the thermal fluctuations of nanostructures and how these vibrations affect the application of these structures to mechanical sensors like resonators. The project focused on cantilevered carbon nanotubes (CNTs) with functionalized tips sensing small molecules in a gas-phase environment, but our results apply to a broad range of other configurations and applications. The theoretical and experimental work was documented in one publication, with other papers under review or in preparation.

The most-recent work is notable because it documents the high-yield, reliable method we developed to produce single tube devices with contacts. Given the widespread use of this type of configuration and the lack of a reliable method for their production, we foresee high impact of the newly developed process. Our characterization and filtering work are also notable. The characterization work discovered the fundamental noisy resonance structure of beam-like nanostructures such as the carbon nanotube. We employed this characterization in a novel, high-performance algorithm that we developed to do real-time detection of small molecules on the order of 1/100 the mass of the CNT and on a timescale of nanoseconds. We expect to use this theoretical development as the basis of a proposal for follow-on funding through an external agency.

Significance

Characterization of short-time fluctuations will improve the fundamental understanding of NEMS. This will lead to methods for effectively filtering and possibly controlling thermal noise. These methods will enable the detection of molecules with extremely short binding duration, for example. Ultimately, this project will enable novel, extremely sensitive NEMS sensors to be designed and employed in several of the laboratories' strategic management units and defense missions.

Refereed Communications

E.H. Feng and R.E. Jones, "Equilibrium Thermal Vibrations of Carbon Nanotubes," *Physical Review B*, vol. 81, pp. 125436-125441, March 2010.

Enabling Graphene Nanoelectronics

130771
Year 2 of 3
Principal Investigator: S. W. Howell

Project Purpose

We are combining a complete array of expertise and resources towards investigating three innovative and synergistic synthesis approaches for advancing reproducible fabrication and fundamental scientific understanding of high-quality graphene films on technologically relevant substrates (Si and SiC). Recent work has shown that graphene, a 2D electronic material (with 1D nanoribbon semiconducting properties) amenable to the planar semiconductor fabrication processing, possesses tunable electronic material properties potentially far superior to metals and other standard semiconductors. Despite its phenomenal electronic properties, focused research is still required to develop techniques for depositing/synthesizing graphene over large areas, enabling the reproducible mass-fabrication of graphene-based devices.

For this project, we are focusing synthesis efforts toward four complementary techniques:

1. A novel non-ultrahigh vacuum annealing-based synthesis approach for dramatically improving the quality and lateral size of graphene on SiC (medium risk)
2. Evaporation of carbon atoms onto an interfacial carbon layer (buffer layer) that is formed on SiC
3. Chemical vapor deposition (CVD) carbon deposition on metals substrates such as copper and nickel,
4. Electrostatic transfer/assembly of graphene from SiC onto metal oxide semiconductor (MOS)-relevant substrates

To develop vital fundamental understanding of these fabrication processes, characterization techniques such as low energy electron microscopy (LEEM), Raman spectroscopy, and scanning probe microscopy (especially atomic force microscopy/ scanning capacitance microscopy [AFM/SCM]) will be utilized to provide deeper insight into anneal-driven domain size, thickness, morphology, work function characteristics, and defects. Electronic characterization will also be conducted to gauge the quality of the graphene materials. If successful, our efforts will develop a suite of available synthesis strategies for addressing the unsolved challenging problems prohibiting the realization of next-generation graphene-based devices (i.e., disruptive complementary metal oxide semiconductor [CMOS]-based devices, novel high-frequency devices). Our team possesses complementary expertise and capabilities (synthesis, characterization, integration and modeling) necessary for high-impact mission-related graphene research results in this emerging competitive field.

Summary of Accomplishments

Accomplishments for FY 2010 include the following: 1) development of a graphene synthesis approach that uses Ar at atmospheric pressure and high temperature; 2) achieved a domain size of 100 μm^2 that is very competitive with the graphene research community; 3) observed record electron mobility of 14,000 cm^2/Vs for epitaxial graphene on SiC(0001); 4) achieved excellent uniformity of electrical properties across synthesized areas (6 x 12 mm^2); 4) achieved understanding of growth front mechanism for graphene on SiC by utilizing AFM and LEEM; 5) developed an alternate method for large area graphene growth by depositing carbon on SiC; 6) developed CVD process to synthesize graphene on Cu foils; 7) observed rotational domains in CVD synthesized graphene using LEEM; 8) observed Integer Quantum Hall Effect (IQHE) in multiple devices on the same sample (one of four groups in the world to observe IQHE in epitaxial graphene); 9) developed a scalable process for the electrostatic transfer of graphene from SiC (000-1) and Si (0001) to Pyrex and Zerodur (FY10 ; 10) demonstrated chip level transfer of monolayer graphene (6 x 12 mm^2); 11) fabricated first-generation gate field effect transistor devices and observed field effect modulation of current of several mA with ± 6 V gate voltage modulation; 12) down-selected (dropped) the thermal decomposition of acetylene on Si approach due to the greater promise of the other synthesis methods.

Significance

Despite the abundance of research activity in this area, there is presently insufficient organized research aimed towards realizing next-generation high-speed and high-frequency graphene devices. This project will enable Sandia to establish proven graphene expertise and capability for meeting anticipated National Security and DoD needs. Our fundamental studies of growth mechanism during FY 2010 has established Sandia as a leader in the graphene research community (especially in terms of graphene on SiC materials synthesis results), paving the way for development of high-speed (GHz to THz) devices for a wide variety of Sandia national security needs. Our results have also attracted the attention of leading graphene researchers (Cornell, Massachusetts Institute of Technology, Arizona State University) stimulating new collaborative opportunities that leverage our expertise. Our additional activities in graphene transfer will blaze new opportunities for graphene hybridization with current CMOS and microelectromechanical system processes, potentially creating new categories of devices and sensors that exploit graphene's unique electronic and material properties for improved performance. This expertise/capability is also facilitating efforts towards the successful establishment of a DOE Basic Energy Sciences graphene materials basic research program.

Refereed Communications

T. Ohta, N.C Bartelt, S. Nie, K.Thurmer and G.L. Kellogg, "Role of Carbon Surface Diffusion on the Growth of Epitaxial Graphene on SiC," *Physical Review B Rapid Communications*, vol. 81, p. 121411, March 2010.

E. Starodub, S. Maier, I. Stass, N.C. Bartelt, P.J. Feibelman, M. Salmeron, and K.F. McCarty, "Graphene Growth by Metal Etching on Ru(0001)," *Physics Review B*, vol. 80, p. 235422, December 2009.

E. Loginova, S. Nie, K. Thurmer, N.C. Bartelt, and F. McCarty, "Defects of Graphene on Ir(111): Rotational Domains and Ridges," *Physics Review B*, vol. 80, p. 085430, August 2009.

J.M. Wofford, S. Nie, K.F. McCarty, N.C. Bartelt and O.D. Dubon, "Graphene Islands on Cu Foils: the Interplay Between Shape, Orientation and Defects," to be published in *Nano Letters*.

Y. Murata, E. Starodub, B.B. Kappes, C. V. Ciobanu, N.C. Bartelt, K.F. McCarty and S. Kodambaka, "Orientation-Dependent Work Function of Graphene on Pd(111)," to be published in *Applied Physics Letters*.

E. Starodub, N.C. Bartelt and K.F. McCarty, "Oxidation of Graphene on Metals," *Journal of Physical Chemistry C*, vol. 114, pp. 5134-5140, March 2010.

W. Pan, S.W. Howell, A.J. Ross, T. Ohta, and T. Friedmann, "Observation of the Integer Quantum Hall Effect in High Quality, Uniform Wafer-Scale Epitaxial Graphene Films Grown on the Si-Face of 6H-SiC(0001)," to be published in *Applied Physics Letters*.

Hierarchical Electrode Architectures for Electrical Energy Storage and Conversion

130772
Year 2 of 3
Principal Investigator: K. R. Zavadil

Project Purpose

This project will develop the fundamental knowledge base necessary for the creation of stable hierarchical electrode architectures for electrical energy storage and conversion. Hierarchical electrodes are an enabling technology necessary to produce revolutionary improvements in the performance characteristics of electrochemical devices capable of storing electrical charge (e.g., ultra- or redox- capacitors) or interconverting electrical charge and chemical energy (e.g., batteries and reversible fuel cells). Such revolutionary improvements are necessary to ensure a secure energy future for the nation. An important barrier to achieving stable hierarchical electrodes is Ostwald ripening of these nanoscale structures driven by dissolution and redeposition dynamics. As a consequence, constructing stable hierarchical electrodes requires a fundamental understanding of the impact of overall geometric shape, surface energetics, and environmental factors on the dynamics of ripening.

We propose to address the problem of electrode stability by studying ripening-resistant metal structures recently discovered and developed at Sandia. In situ measurement diagnostics will be used to study the evolution of nanostructure topography as a function of electrode morphology and electrochemical factors. Local metal dissolution and redeposition rates will be measured and used in computational simulations to develop a mechanistic understanding of the origins of stability. Computational methods will be expanded to take into account the electrochemical double layer contribution to nanoscale stability. Synthetic methods will be developed to produce new hierarchical electrode architectures to enhance and explore the limits of stability. The role of alternate metals, chemical passivation schemes, and the inclusion of functional charge storage materials on structure stability will also be explored. In addition, new in situ diagnostics for characterizing charge storage mechanisms at electrode surfaces will be developed. The knowledge gained from a tightly coupled synthesis, characterization and computation approach is anticipated to impact a range of electrochemical charge and energy storage devices.

Summary of Accomplishments

We used computational methods to explore the origin of zero-curvature induced stability observed for dendritic forms of platinum. We developed a new Monte Carlo/Molecular Dynamics method to calculate the free energy of arbitrary off-lattice nonperiodic structures, and we tested this method for planar solid-vapor surfaces and compared it to an alternate pressure tensor route to determine the interfacial free energy with satisfactory results. We applied classical density functional theory (DFT) to study the free energy of holes for on-lattice structures. We performed electronic DFT calculations for holey metal sheets comprised of Pt and Ag to study principal strains and whole stability. We developed a Kinetic Monte Carlo approach for simulations, to provide first-principles time scale.

We developed a generalized covalent linking scheme for dendritic Pt nanostructures based on diazonium chemistry. Scanning probe microscopy was used to image bound nanostructures under conditions of electrochemical control. Synchrotron based x-ray absorption fine structure was used to aid in determining the orientation of the linker molecules and, as a result, demonstrate that covalent binding had indeed taken place. We also developed methods for forming high surface area ruthenium and manganese dioxide particles on carbon electrode surfaces as electroactive charge storage materials. Shape change of dendritic Pt foam nanostructures was explored under electrochemical control using scanning tunneling microscopy.

A new two-step platinum photocatalytic seeding and growth process has been developed and exploited for growing dendritic nanostructure directly onto carbon surfaces. The resulting dendrites grow conformally on the carbon surface. Electron microscopy shows that the dendrite size and size distribution can be controlled by systematic variation in the growth parameters. Synthetic routes were discovered for producing nanowheels, a new form of dendritic structure, using surfactant formed bicelles as templating agents. Variation in the reaction growth conditions were shown to be a method of tuning the shape and size of the resulting nanowheels.

Significance

The significance of our photocatalytic seed and direct growth of dendritic (meaning high surface area) electrocatalytic platinum structures on carbon is that such a process enables ultralow loading of precious metals for fuel cell applications. Tests of similar materials synthesized within this project have shown a degree of resistance toward ripening and retention of electrochemical surface area. The discovery that growth takes place conformally with the carbon substrate suggests that not only is enhancement of catalytic function expected, but also that we anticipate enhanced stability of the structures over the service life of the envisioned fuel cell electrode. We believe (patent application filed) that this approach could be applied to other readily reducible metals, alloys, and co-catalysts through control of the templating reagents used in the process. The development of bicelle templated nanowheels offers an alternate soft chemical approach to synthesizing catalytic structures. These nanowheels exhibit a similar degree of resistance to thermal sintering, as we have previously documented for several nanometer-thick holey sheets. Electrochemical surface area has been measured and compares quite favorably to commercial Pt-based fuel cell catalysts, with the added benefit of electrochemical sintering resistance. Our computational work highlights the reason for this observed sintering resistance, as simulations show that a donut hole is the energetically favored structure to form from cylindrical holes in dendritic ligaments. The source of stabilization can be thought of as a situation of zero net curvature reducing the surface energy of the overall nanostructure. We have made significant progress toward a full computational simulation of the evolution of a dendritic structure driven by electrochemical ripening through the use of our new hybrid Monte Carlo/Molecular Dynamics approach.

Our work on covalent linking schemes of preformed nanostructures on electrode surfaces is significant because this approach allows the assembly of optimized electrode structures based on best catalytic structures combined with best electrode scaffolds without the constraints of bottom up or top down synthesis approaches. Linking strategies are equally applicable to other electroactive materials such as transition metal oxides. New diagnostic tools, such as spectroscopic electrochemical scanning tunneling microscopy (STM) are being developed within our project to explore charge transport at and within electroactive materials to establish structure-activity relationships at the individual particle level. This level of information is not currently available and will greatly aid in understanding the origin of favorable nanoscale perturbation on electrochemical properties. The STM work reported in our accomplishments promises new insights into the length and time scales that govern nanostructure stability under the influence of electrochemical stress. We expect that results will validate simulation results and further refine the computational methods by providing relevant chemical and physical inputs to our models.

Refereed Communications

R.M. Garcia, Y. Song, R.M. Dorin, H. Wang, A.M. Moreno, Y. Jiang, Y. Tian, Y. Qiu, C.J. Medforth, E.N. Coker, F. van Swol, J.E. Miller, and J.A. Shelnutt, "Templated Growth of Platinum Nanowheels Using the Inhomogeneous Reaction Environment of Bicelles," to be published in *Physical Chemistry Chemical Physics*.

Hierarchical Morphology Control for Nanocomposite Solar Cells

130773
Year 2 of 3
Principal Investigator: J. W. Hsu

Project Purpose

The proliferation of new, high-technology devices requires ever more portable and reliable energy sources. To meet these new needs, organic photovoltaic (OPV) technology, with its lightweight, flexibility, and inexpensive manufacturing process, appears to be uniquely suited for these applications. New materials and technologies must be developed to lower the manufacturing and deployment costs while maintaining good performance (> 10% power conversion efficiency). A subset of OPVs, called hybrid photovoltaics, uses inorganic metal oxide semiconductors as the electron acceptor material. The advantages of hybrid photovoltaics over purely organic counterparts include environmental stability, better electron transport, and the ability to optimize interfacial properties. In this project, we focus on nanostructured hybrid solar cells that employ metal oxide nanoparticles to form a network of electron acceptors embedded in a conducting polymer matrix, which acts as the light absorber and hole transporter. Our goals are to optimize the network structure to achieve improved photocurrent and power conversion efficiency while being compatible with inexpensive manufacturability of OPVs. Our approach is to use interfacial chemistry to control and direct hierarchical morphology in the nanocomposites. In addition, the team is collaborating with an organic photovoltaic group at the National Renewable Energy Laboratory (NREL), where they have secured an NREL LDRD project to focus on new polymer development. Energy independence and security have become a key DOE mission and national urgency. The success of this project will position Sandia in a frontier research position in future generations of solar cell technologies.

Summary of Accomplishments

In the first two years of this successful joint Sandia/NREL hybrid photovoltaic project, over a dozen papers have been published in high-profile, peer reviewed journals, detailing multiple advances made on hybrid photovoltaic (PV) devices. These hybrid PV devices, based on ZnO electronic acceptors and poly(3-hexylthiophene) electron donors between current collectors, are promising as a roll to roll compatible processing technology, given improvements in device voltage and efficiency. Among the major advances have been the following:

1. doping of ZnO with MgO to increase band gap and increase open circuit voltage (VOC) to from 0.5 to 0.9V;
2. use of 5-nm TiO_2 coatings and CdS coatings on undoped ZnO to limit electron-hole recombination and increase VOC from 0.3 V to 0.6 V and 0.8 V, respectively;
3. development of long-shelf-life inverted photovoltaic devices; and
4. demonstration of roll-to-roll processable devices with efficiencies of 0.55-1%.

Strong research ties with the photovoltaics program at NREL have been established, enabling rapid advances in the field. Key milestones have largely been met, particularly on engineering hybrid PV voltage and stability, but a critical need for a roll to roll processable, low cost transparent conductive oxide remains; this is the focus of the current continuation project.

Significance

The project supports Sandia's mission by developing new knowledge and technologies for sustainable, future energy generation. The collaboration among researchers with a wide range of expertise enables the team to attack an important energy problem that cannot be accomplished by each research team working alone.

High-Temperature, Large Format FPAs for Emerging Infrared Sensing Applications

130774
Year 2 of 3
Principal Investigator: J. K. Kim

Project Purpose

Our objective is to develop a third-generation focal plane array (FPA) technology to supplant HgCdTe (MCT) and thereby enable emerging infrared imaging and sensing missions called for by multiple agencies. Sandia's unique strengths in semiconductor science are being leveraged and significantly extended to understand and ultimately control the novel materials and device physics that are required to leapfrog the MCT technology, which has already begun to saturate in performance and size scaling. Our progress to date gives us confidence that Sandia will be able to synergize advances in both science and engineering to close the gap between theoretical and actual performance of novel FPAs for the mid-wave infrared (MWIR) and for long-wave infrared (LWIR). Success will expand the fundamental knowledge of this novel material system and establish key modeling and experimental capabilities that Sandia lacks.

Summary of Accomplishments

In FY 2010, we have succeeded in developing a comprehensive 2D device physics model that enabled the optimization of the device structure and demonstrate dark current performance equaling or, at lower temperatures, surpassing MCT. Employing this optimized device, we have internally assembled a 320 x 256 FPA. We have also developed a robust atomistic bandstructure model that calculates the bandgap, band alignments, and dispersions of strained-layer superlattice (SLS) that enables us to optimize the material for LWIR sensing. This model is being deployed in the analysis of SLS material properties and defect characteristics, for which we have established experimental methodologies and capabilities in FY 2010. We have met all proposed milestones.

We made great progress in experimentally demonstrating high-performance devices, empirically understanding the behavior, modeling and explaining the characteristics in detail using first principles, and reiterating the design/experiment cycles to optimize the devices. Currently, Sandia is at the forefront of the engineering capability. The engine powering this rapid progress is our comprehensive predictive numerical model (that includes Shockley-Reed-Hall, Auger, diffusion, trap-assisted tunneling, and band-to-band tunneling mechanisms) developed during this project that allows us to perform many design iterations numerically before committing a design to experimental confirmation. This allows at least an order of magnitude savings in time and cost. We have demonstrated that optimizations of the nBn device eliminate the generation-recombination dark current.

Significance

This project benefits tactical and strategic MWIR/LWIR imaging systems that are important to DOE/NNSA and DoD for nonproliferation assessment, tactical surveillance, missile defense and combat support. High-temperature MWIR/LWIR detectors developed through this project will enhance the performance and functionality of infrared imaging systems that are currently limited by scalability and excessive cooling requirements of the focal plane array.

Narrow-Linewidth VCSELs for Atomic Microsystems

130775
Year 2 of 3
Principal Investigator: D. K. Serkland

Project Purpose

Vertical-cavity surface-emitting lasers (VCSELs) are the laser of choice for photonic microsystems due to their low power consumption, ease of integration, and single frequency operation. For example, the 1 mW power consumption of a VCSEL is more than an order of magnitude lower than the nearest alternative: traditional edge-emitting lasers. However, the typical VCSEL linewidth (100 MHz) is approximately ten times wider than the natural linewidth of atoms used in atomic beam clocks and trapped atom research, which degrades or completely destroys system performance.

We propose to develop a new external-cavity VCSEL (EC-VCSEL) having a linewidth narrower than 1 MHz, specifically for use in emerging atomic microsystems, such as primary frequency standards and atom traps. In order to reduce the VCSEL linewidth, we must simultaneously increase the Q of the laser cavity and decrease the linewidth enhancement factor of the active region. We will increase the stored optical energy and thus cavity Q by extending the cavity length to 30 microns (over 10 times longer than normal), terminating the extended cavity with an external high-reflectivity dielectric mirror. The 10-fold increase in cavity length precludes an all-semiconductor structure, but is still small enough to permit wafer-scale microfabrication of the device. Significant metal organic chemical vapor deposition epitaxial growth development will be undertaken to allow the extended cavity geometry, minimize free-carrier absorption losses, and develop active quantum wells that achieve minimum linewidth enhancement (alpha) factor. VCSELs have long been a differentiating technology for Sandia, due to the complexity of VCSEL design, epitaxial growth, and microfabrication. If we are successful in wafer-scale fabrication of narrow-linewidth VCSELs, these new devices and our advances in scientific understanding could enable significant follow-on work to tailor these devices for use in specific high-performance atomic-physics microsystems.

Summary of Accomplishments

In the second year, the overall goal has been to microfabricate an EC-VCSEL that will ultimately meet the linewidth goal of 1 MHz by increasing the optical cavity length from 2 μm (for a standard VCSEL) to 30 μm. In the first 7 months of year 2, we conceived a new fabrication approach, designed a new 16-level mask set, developed new microfabrication process steps to produce the curved external-cavity mirror, and completed the first device fabrication run. The first devices were finished in April 2010, completing the first major milestone of year 2. In the remainder of FY 2010, we improved the fabrication process to reduce laser linewidth, which we measured in August 2010.

In addition to meeting our second-year milestones, we have significantly improved the monolithic (all-semiconductor) extended-cavity VCSEL that we first demonstrated in year 1 of this project. Although we demonstrated a narrow 23-MHz linewidth in year 1, the high-order mode suppression was not sufficient to achieve even 1 mW of single-mode output power. In the second year we modified the VCSEL structure to achieve higher single-mode output power, obtaining single-mode operation up to 6 mA of input current with over 2 mW of output power, while maintaining a narrow 24-MHz linewidth.

Significance

Sandia's differentiating capabilities in compound semiconductor epitaxial growth, VCSEL microfabrication, and optical microsystem integration will be enhanced by this research project. Success in making a narrow linewidth VCSEL could generate significant follow-on work in a variety of areas: primary frequency standards, neutral atom and ion traps, and quantum information research. Applications range from improved military communication and navigation to quantum encryption.

Phonon Manipulation with Phononic Crystals

130777
Year 2 of 3
Principal Investigator: I. F. El-Kady

Project Purpose

We propose to develop a fundamental understanding of, and a methodology for, deterministic phonon spectrum control at the THz region (100 K-phonons) using a top down phononic crystal (PhonC) approach. Present approaches to phonon control are based on texturing the surface to increase phonon scattering or shrinking the diameter of the material to prevent bulk propagation much like a cutoff waveguide, or phonon scattering off grain boundaries. All such approaches are either highly nondeterministic or are capable of only targeting a narrow spectral range. In contrast, PhonCs utilize physics similar to Bragg-scattering. In a fashion reminiscent of photonic lattices, spectrally wide bandgaps can be deterministically produced in which phonons are inhibited, accompanied by a redistribution of the phononic density of states. This offers a unique vehicle for tailoring the phonon spectrum for a variety of applications and awards a larger degree of control. For example, by selectively enhancing the efficiency of phonon propagation in specific spectral bandwidths, enhanced thermal-to-RF frequency tags and micro-coolers can be realized. Conversely, by selectively suppressing THz phononic spectral bands, exceptionally high ZT materials can be achieved.

Furthermore, other important processes, such as the electron-phonon interaction that cap the performance in high-TC superconductors, and phonon-photon interaction essential for quantum-well or dot based solid state lighting could potentially be impacted by the profound phonon control provided by PhonCs. If successful, this approach will lead to a wide range of new thermal applications such as efficient and directional heat removal from integrated circuits, thermoelectric materials with improved efficiency, and new approaches to thermal harvesting. Finally, by extending the existing phononic-photonic crystal homomorphism this project will lay the foundation for realizing the first phononic metamaterials essential for high-precision focusing and manipulation of vibrational energy for a wide range of ultrasonic imaging devices and deep-sea cloaking.

Summary of Accomplishments

In the theoretical area, we were able to extend our 2D model to 3D and account for the actual thickness of the PhonC. We were further able to incorporate hybridized lattice geometries into the model. This allowed us to evaluate the density of states and from it estimate the reduction in thermal conductivity due to a PhonC. The result was a 98% reduction in silicon thermal conductivity at less than 20% porosity, which we attributed to the anomalous dispersion of the PhonC, especially the existence of flat dispersionless bands and negative or backward scattering bands. This result was validated via thermal reflectance measurements which enable us to measure the phonon lifetimes and deduce the thermal conductivity of the sample. These results indicate that we may be able to realize ZT=5 in silicon at room temperature, the largest thermoelectric figure of merit realized to date (ZT<1). To validate this, we need to perform direct electrical and thermal conductivity measurements. To this end we integrated serpentine heaters with the current PnC samples in the Microsystems and Engineering Sciences Applications facility. Furthermore, our collaborators at the University of New Mexico have also developed focused ion beam (FIB) masking techniques to produce ultrahigh-aspect ratio air-holes in silicon. This enables fabrication of phononic crystals on thick substrates, thereby eliminating the parasitic slab mode as well as lending rigidity to the sample. Current efforts indicate that over 50:1 aspect ratio will be achievable — the largest such demonstration to date. In addition, we have created a four-port test arrangement for the FIB PhonC samples to enable full conductivity characterization under varying temperature. This is necessary to fully discriminate (for the first time) the harmonic versus inharmonic phonon dispersion effects in the PhonC by temperature tuning the spectral peak of the phonon population.

Significance

This research could result in a new class of thermal materials for heat control and thermal energy scavenging and will lay the foundation for realizing the first phononic metamaterials essential for high-precision focusing and manipulation of vibrational energy for a wide range of ultrasonic imaging devices and deep-sea cloaking. Furthermore, it promises to put Sandia at the forefront of a new branch of science of direct interest to DOE and DoD.

Refereed Communications

P.E. Hopkins, P.T. Rakich, R.H. Olsson III, I.F. El-Kady, and L.M. Phinney, "Origin of Reduction in Phonon Thermal Conductivity of Microporous Solids," *Applied Physics Letters*, vol. 95, pp. 161902-161905, October 2009.

P.E. Hopkins, L.M. Phinney, P.T. Rakich, R.H. Olsson III, and I.F. El-Kady, "Phonon Considerations in the Reduction of Thermal Conductivity in Phononic Crystals," to be published in the *Journal of Applied Physics A Meta 10 Special Issue*.

Y.M. Soliman, D.F. Goettler, Z.C. Leseman, I.F. El-Kady, and R.H. Olsson III, "Effects of Release Hole Size on Microscale Phononic Crystals," to be published in *SEM Annual 2009*.

Real-Time Studies of Battery Electrochemical Reactions Inside a Transmission Electron Microscope

130778
Year 2 of 3
Principal Investigator: J. P. Sullivan

Project Purpose

In this project we will develop a capability to investigate lithium-ion (Li-ion) battery electrochemical processes in real time inside a transmission electron microscope (TEM). This unique capability could have impact in a number of research areas, including the science of catalysis, electrodeposition, corrosion, capacitive energy storage, and electrochemical energy storage (i.e., batteries), which is the focus of this study. Currently, there are serious fundamental issues in Li-ion batteries regarding performance degradation during cycling and aging that are unresolved and poorly understood. Furthermore, the fundamental study of these problems has been hampered by the lack of experimental and theoretical techniques that can identify structural changes in battery electrodes with atomic- to nanoscale resolution during actual battery operation.

We will develop both a sealed silicon micromachined fluidic platform as well as a simple open platform using a vacuum-stable ionic liquid (IL) electrolyte to measure structural changes within and at the surfaces of battery cathodes and anodes. We will explore the mechanism of Li intercalation in carbon-based anodes and phase changes that occur as Li inserts and de-inserts in nanoscale cathodes. We will identify and characterize solid-electrolyte-interphase (SEI) compounds that form on the electrode surfaces during polarization and potential cycling. We will use molecular dynamics (MD) and ab initio MD to model the Li intercalation in ideal carbon nanotube electrodes and the formation of SEI compounds on carbon-based anodes. We will also develop versatile silicon-based electrochemical platforms that should have great utility for both in situ as well as ex situ electrochemical investigations. To our knowledge, this would be the first real-time study of battery reactions inside a TEM and, potentially, the first study that demonstrates atomic resolution of electrochemical processes inside a TEM.

Summary of Accomplishments

In the second year of this project, we made major advances in each of the main project areas. Specifically, we have achieved one of our major objectives of performing in situ TEM measurements of real-time battery reactions. We also made important progress in modeling, wherein we used ab initio simulations to reveal important new electrochemical processes that occur at electrode-electrolyte interfaces. We have, 1) performed our first electrochemical experiments inside a TEM using ionic liquid electrolytes and have observed structural changes in electrode materials (tin oxide nanowires) as a result of electrochemical lithiation (submitted for publication to the journal *Science*); 2) discovered an important, but previously unrecognized, reduction mechanism for ethylene carbonate electrolytes in contact with lithiated graphite electrolytes using ab initio molecular dynamics simulation, and we suggest that this work now shows the tremendous potential for computer modeling of important mechanisms of SEI generation involving realistic electrodes and electrolytes; 3) nearly completed full fabrication of a sophisticated microelectromechanical system encapsulated TEM liquid cell, and we have begun to use these test chips for electrode material assembly and to test flip-chip encapsulation; and 4) completed full fabrication of single-sided (non-encapsulated) electrochemical cells, and have successfully used these structures for electrochemical characterization of individual manganese dioxide nanowire cathodes (this involved assembly of the nanowire electrodes onto the platform, electrochemical testing in ethylene carbonate-based electrolytes, electrical characterization, and TEM characterization).

Significance

This project impacts lithium-ion battery and novel electrical energy storage technologies. These are critical for remote and mobile energy systems (remote sensors, vehicle propulsion, electricity storage for the grid). DOE has requested new research that focuses on renewable and alternative energy technologies, and research on electrochemical energy storage is a critical component of that initiative.

Refereed Communications

K. Leung and J. Budzien, "Ethylene Carbonate Decomposition at the Graphite Anode at the Initial Stages of Solid-electrolyte Interphase Formation," to be published in *Physical Chemistry Chemical Physics*.

J. Yu, P.B. Balbuena, J. Budzien, and K. Leung, "Hybrid DFT Functional-based Static and Molecular Dynamics Studies of Excess Electron in Liquid Ethylene Carbonate," to be published in the *Journal of the Electrochemical Society*.

J.Y. Huang, L. Zhong, C.M. Wang, J.P. Sullivan, W. Xu, L.Q. Zhang, S.X. Mao, N.S. Hudak, X.H. Liu, A. Subramanian, H.Y. Fan, L. Qi, A. Kushima, and J. Li, "In Situ Observation of the Electrochemical Lithiation of a Single SnO_2 Nanowire Electrode," to be published in *Science*.

Science-Based Solutions to Achieve High Performance Deep UV Laser Diodes

130779
Year 2 of 3
Principal Investigator: M. H. Crawford

Project Purpose

A number of mission-critical applications would greatly benefit from a compact, deep ultraviolet (< 340 nm) laser diode (LD); however, commercial LDs are currently limited to longer UV wavelengths. AlGaN semiconductor alloys are the most promising materials for deep UV LDs, with potential for emission across the 200-365 nm region; we note the recent demonstration of mW-level 275–300 nm AlGaN light-emitting diodes (LEDs) by our Sandia team. To date, realization of deep UV LDs has been thwarted by the lack of fundamental insight and solutions to key AlGaN materials challenges. These challenges include, 1) nanoscale point defects, 2) p-doping limitations, and 3) high internal optical losses and limitations to optical gain.

We propose a science-based approach that will apply our state-of-the-art AlGaN metal-organic vapor-phase epitaxy capabilities, innovative materials growth and heterostructure design strategies, differentiating materials characterization techniques, and advanced device modeling to gain fundamental insight into these three critical challenges. In this project, we will apply those insights and Microsystems and Engineering Sciences Applications microfabrication processing capabilities to design and fabricate AlGaN LDs in the 300–340 nm region. If successful, our project will yield the shortest wavelength deep UV LDs to date, relevant to a range of applications including fluorescence-based bioagent sensing. Materials insights gained from this project could be applied to a range of III-Nitride materials and devices, enabling advances in deep UV LEDs for water purification, visible LEDs for solid-state lighting, and InGaN solar photovoltaics. This project therefore offers a unique opportunity to leverage Sandia strengths and achieve both science and technology breakthroughs with strong relevance to DOE missions.

Summary of Accomplishments

FY 2010 efforts include studies to quantify the properties and impact of defects in constituent layers of AlGaN laser heterostructures, including quantum well (QW) active layers and doped cladding layers. We combined deep-level optical spectroscopy and photoluminescence to investigate how QW growth temperature mediates the interplay between defect incorporation and luminescence efficiency. Our studies revealed three distinct deep levels in AlGaN quantum wells and a quantitative correlation between increased growth temperatures, reduced density of all observed deep levels, and enhanced luminescence efficiency. We expanded our defect task to include strategies for reducing non-radiative extended defects including threading dislocations. Development of a novel growth approach resulted in > 10× reduction of threading dislocations in select regions and notable enhancement of AlGaN quantum well luminescence. We continued development of p-type short-period superlattices (p-SPSL) as an approach to achieve more effective p-type conduction in cladding layers needed for shorter-wavelength laser demonstrations. Advances include identification of growth conditions that maintain coherency of superlattices over thicknesses sufficient for laser claddings. Our p-SPSL work was published in the *Journal of Crystal Growth*. Finally, we employed a 1-D waveguide model to develop laser cavity designs, including the optimization of quantum well thickness and electron block layer designs.

Significance

This project supports DOE's strategic goal of conducting world-class science to address mission needs. Nitride materials insights from this project could lead to advances in solid-state lighting, a major Sandia investment area aligned with DOE's energy mission. Deep UV laser diodes will enable a new technology applicable to compact systems for fluorescence-based bioagent sensing and trapped-ion-based quantum computing, applications of interest to DHS and agencies including Defense Advanced Research Projects Agency and Intelligence Advanced Research Projects Activity.

Refereed Communications

A.A. Allerman, M.H. Crawford, M.A. Miller, and S.R. Lee, "Growth and Characterization of Mg-Doped AlGaN-AlN Short-Period Superlattices for Deep-UV Optoelectronic Devices," *Journal of Crystal Growth*, vol. 312, pp. 756-761, January 2010.

Mechanisms for Charge Transfer Processes at Electrode-Solid-Electrolyte Interfaces

130780
Year 2 of 3
Principal Investigator: K. F. McCarty

Project Purpose

The purpose of this project is to develop and apply new in-situ spectroscopies to understand and improve electric charge transfer in electrochemical devices such as fuel cells. Electrochemical technology will play an increasingly critical role in meeting the nation's energy challenges in both stationary power applications and transportation. The essential physical phenomenon occurring in all electrochemical devices is the transfer of electrical charge across material interfaces. How this charge transfer occurs and its relationship to the device's performance and reliability is largely unknown. This project develops fundamental understanding of interfacial charge transfer by characterizing it in real time during electrochemical operation.

We are studying the charge-transfer process in solid-oxide fuel cells (SOFCs) for three reasons: (1) SOFC interfaces are more accessible for in-situ characterization than in other electrochemical devices. (2) Within the same technology platform, electricity can be generated from fuels and vice versa when run as fuel cells or as electrolyzers. (3) SOFCs can operate on a variety of fuels, including hydrogen and hydrocarbons. Thus, SOFCs could potentially contribute significantly toward low-carbon energy systems for both fixed and portable (transportation) applications. But like all electrochemical-based technologies, they suffer from performance and cost issues. The advances needed, especially those for lower-temperature vehicular operation, have been hampered by inadequate understanding of elementary processes. In particular, detailed microscopic measurements of interfacial species concentrations, their spatial distributions, and transport rates under operating conditions have not been made. We are determining this information by characterizing the species present on SOFC materials during operation. We are using micro- and nanofabrication to develop a new experimental "platform" with accessible surfaces and enhanced performance. We then characterize operating SOFC surfaces at realistic pressures and temperatures using ambient-pressure x-ray photoelectron spectroscopy.

Summary of Accomplishments

We made substantial progress in our second year.

1. We used ambient-pressure x-ray photoelectron spectroscopy to directly measure the electrical "overpotentials" present in a solid-oxide electrolyte device. The overpotentials critically control the efficiency at which charge is transferred across material interfaces. We use the kinetic energy of the photoelectrons to measure the local electrical potential across a device. Our results are the first direct (i.e., unambiguous) measurements of overpotentials, which we performed in two systems using zirconia electrolytes, one with Ni and Pt electrodes and the other with ceria electrodes. Results from both these systems have been submitted to peer-reviewed journals.
2. We were able to quantify the relationship between ceria oxidation state and electrochemical activity. We found that the electrochemically active region was delineated by the region where the ceria oxidation state changes, which was a stripe about 100 microns wide. This effort is the first time that the size of the active region has been measured in solid-oxide electrolyte systems.
3. We characterized the phases that form when Ni is electrochemically oxidized in the presence of hydrogen, as occurs in a Ni-metal-hydride battery. This result shows that our approach of using in-situ diagnostics can apply to batteries as well as fuel cells/electrolyzers.

4. We drafted a manuscript that describes our design and operation of our custom electrochemical platen. This device provides robust electrical contracts using spring-loaded probes and has the ability to heat the devices, all while providing good optical access for diagnostics.
5. We have designed, fabricated, and tested new hardware that will allow characterization of electrochemistry in situ with separate gas environments at the anode and cathode.

Significance

This work is directly relevant to DOE's mission to provide the science and technology to power the US without contributing to climate change. This project is developing new ways to characterize the electrochemical technologies that will be increasingly relied upon to achieve energy security by efficiently storing and converting energy. This project also supports Sandia's goal of having a substantial program in electrical energy storage and conversion to support our mission space in energy security. The improved basic understanding, including predictive modeling tools developed by intimately coupled external collaborators will ultimately accelerate technology development of energy storage and conversion systems based on fuel cells, electrolyzers, and batteries. In addition to benefiting the scientific and industrial communities, this work will lay a science foundation for broader programs in electrochemistry.

Refereed Communications

F.E. Gabaly, M.E. Grass, A.H. McDaniel, R.L. Farrow, M.A. Linne, Z. Hussain, H. Bluhm, Z. Liu, and K.F. McCarty, "Measuring Individual Overpotentials in an Operating Solid Oxide Electrochemical Cell," *Physical Chemistry Chemical Physics*, vol. 12, pp. 12138-12145, 2010.

J.A. Whaley, A.H. McDaniel, F.E. Gabaly, R.L. Farrow, M.E. Grass, Z. Hussain, Z. Liu, M.A. Linne, H. Bluhm, and K.F. McCarty, "Fixture for Characterizing Electrochemical Devices In-Operando in Traditional Vacuum Systems," *Review of Scientific Instruments*, vol. 81, p. 086104, August 2010.

C. Zhang, M.E. Grass, A.H. McDaniel, S.C. DeCaluwe, F.E. Gabaly, Z. Liu, K.F. McCarty, R.L. Farrow, M.A. Linne, Z. Hussain, G.S. Jackson, H. Bluhm, and B.W. Eichhorn, "Measuring Fundamental Properties in Operating Solid Oxide Electrochemical Cells by Using In Situ X-ray Photoelectron Spectroscopy," *Nature Materials*, vol. 9, pp. 944-949, September 2010.

Calculations of Charge Carrier Mobility and Development of a New Class of Radiation Sensors for Real-Time 3D Source Location

141512
Year 1 of 3
Principal Investigator: M. S. Derzon

Project Purpose

For national security reasons, there is a critical need to rapidly identify and locate ionizing radiation sources with a high degree of accuracy. For this project, we propose the manufacture of detectors of the same scale as traditional detectors but divided into a large number of micro-sized voxels (volume pixels with sizes of 50–700 microns). We estimate that such detectors with associated electronics and analysis software will greatly decrease the time to detect, identify, and locate a radioactive source compared with traditional radiation detectors. This benefit arises because each voxel gathers independent geometrical and timing information as if it were a single detector. Software tools will enable the assembly of the geometric information. The timing information will benefit from the fact that each voxel is very small. Furthermore, this timing will be determined by the most mobile carrier. For example, this would be the electron in Si or GaAs. The slowly extracted current from the slower carrier will contribute less and less as the voxel size is reduced because the likelihood of another radiation event in a particular voxel becomes unlikely. Because both Compton and photoelectric events contribute to the useful signal, the convergence in angle can be very rapid. These devices will not require external apertures (which reduce signal strength) and the whole cross-sectional area contributes to the sensitivity (unlike traditional Compton cameras which have a central spectrometer and external coincidence sensors). These devices are also expected to operate at room temperature and low power. Preliminary calculations indicate that the concept is worth pursuing.

Summary of Accomplishments

The bulk of this year's effort has gone into either modeling or enabling performance of next year's experiments. Regarding the modeling, we developed a framework using the continuous slowing down approximation for the statistical spread of initial angles from photon collisions in Xe. This model is averaged over an artificial resolution or pixel size in order to represent our detector options. This provided a continuous distribution look at how the energy is distributed in angle. Subsequently, we utilized the Integrated TIGER Series Code to obtain distributions of energy along a Cartesian grid of pixels. This demonstrated that only the early part of any track has directional information. The late part of the track may contain features of a Bragg peak and hence allow determination of the start versus end of a track. We are now working to identify the patterns created and the relationship between initial pixel-intensity patterns and incident angle. Subsequent to this, the patterns will be related to the statistical distributions to determine direction. We have also been developing a model for transient current and timing at the electrodes. On the experimental side, we have substantially completed the assembly of the high-pressure sell and gas supply to begin the Xe experiments. They are expected to begin the first week of the fiscal year. The electronics initiated last year is due out of the silicon fabrication facility on September 17th, and testing will begin as soon as it is available.

Significance

We believe that when fully developed, these proposed concepts will dramatically improve the ability of the DOE, NNSA, DHS and DoD to meet the nation's radiological and nuclear detection needs. We believe by bringing together the breadth of Sandia's science, technology, and engineering capabilities to address this critical national security need illustrates Sandia's role as a leader in transformational research for the nation. Our concepts offer numerous benefits over current detection technology for our missions associated with defense, counterproliferation and weapons of mass destruction detection.

Chirality-Controlled Growth of Single-Walled Carbon Nanotubes

141513
Year 1 of 3
Principal Investigator: S. M. Dirk

Project Purpose

Single wall carbon nanotubes (SWNT) may be the most promising material to achieving game-changing impacts for future nanosystems and computing in the next decade. Much of the excitement surrounding SWNTs is their ability to be either semiconducting or ballistic conductors based on their individual crystalline structure, or chirality. SWNTs consist of a single rolled sheet of graphene; rolling along different lattice vector lines produces SWNTs with differing chirality and diameter, each with its own unique electrical properties. All known synthesis methods produce SWNTs in mixtures of semiconducting and conducting types. Typical chemical vapor deposition (CVD) processes, such as the Rice University high pressure carbon monoxide method, simultaneously produce 80 different SWNT chiralities, where two-thirds are semiconducting, each with a different bandgap. Great efforts have been made to produce SWNT batches that are primarily semiconducting with narrow chirality distributions, most using post-growth chemical separation techniques including the use of sequence-dependent DNA assembly or cosurfactant extractions. Note that these methods do not address how SWNTs of a given chirality will be placed onto a microchip, such that even a successful chemical isolation of a given SWNT chirality will be difficult to implement in next-generation nanoelectronics.

This project seeks to develop a method to grow SWNTs with a given chirality (or bandgap) directly onto Si substrates, exactly where they are needed, using a process that is ultimately compatible with microelectronics processing. No further chiral sorting will be required, nor the development of complex nanoscale placement methods for device fabrication.

Summary of Accomplishments

In order to accomplish the controlled chiral growth, work needed to be completed on a number of areas including, template growth, catalyst placement within the templates (or underneath), nanotube growth, and nanotube characterization.

Work on templates focused on the synthesis of several types of zeolites including MFI (Mordenite Framework Inverted, 0.55 nm pores) and AFI (aluminophosphate-five, 0.73 nm pores). Growth chemistry enabled formation of the preferred pore orientation and controlled zeolite thickness. Synthesized thin layers of MFI were subjected to typical catalyst pre-treatment conditions used in SWNT growth including 600 °C in the presence of a reducing atmosphere. In most cases, the MFI/Si wafers were unchanged chemically.

Work on catalyst development and placement focused on the development of two approaches. The first process includes depositing the catalyst layer (using thermally degradable metal oxalate complexes) prior to zeolite formation and then depositing the zeolite atop this catalyst layer. The second process, involved electrochemical reduction of a metal salt within a zeolite template from the catalyst after the template had already been grown atop the noncatalytic substrate. Both of these methods have been used to deposit catalyst prior to or after zeolite deposition.

A milestone for FY 2010 included the demonstration of SWNT growth between 400 ˚C and 600 ˚C. Scanning electron microscopy and high-resolution transmission electron microscopy images showed high densities of SWNTs grown at temperatures as low as 530 ˚C with our current CVD methods. Growth at lower temperatures was sporadic and efforts will continue to optimize growth at lower temperatures via appropriate catalyst selection and catalyst diffusion barriers.

We have developed a standard Raman procedure to assess the growth of SWNTs in the challenging environments needed to control chirality. Using this procedure, we have demonstrated the capability to decipher between the underlying zeolite film, multiwall, and SWNTs.

Significance

Sandia is currently engaged in researching next-generation microelectronics, energy production technologies, defense applications, and intelligence applications. Singled walled carbon nanotubes offer unique properties that if taken advantage will enable more efficient energy collection systems, faster microelectronics, and smaller sensors. This research will provide Sandia with a game-changing core technology that will benefit DOE, NNSA, DoD and other national security agencies.

Several key accomplishments have been realized during FY 2010, including demonstration of carbon nanotube (CNT) growth at temperatures as low as 530 °C. CNTs growth can be incorporated directly into the silicon fabrication facility, if the growth temperature is sufficiently decreased, enabling the fabrication of very small vias and novel CNT transistors. Furthermore, we have demonstrated the ability to characterize the CNTs that are "grown in house" at Sandia. In addition we have acquired the support (and use of equipment) of an expert in SWNT characterization at Los Alamos National Laboratory, which will aid in eventual transition of the growth techniques to a fabrication setting.

Control of zeolite growth and catalyst deposition techniques are also being developed that will enable the fine control of the diameter and thus the chirality and bandgap of the final SWNTs, which will enable the large-scale production of smaller, faster transistors and improved materials for chemo-selective sensors.

Refereed Communications

M.P. Siegal, D.L. Overmyer, P.P. Provencio, and D.R. Tallant, "Linear Behavior of Carbon Nanotube Diameters with Growth Temperature," *Journal of Physical Chemistry C*, vol. 114, pp. 14864-14867, August 2010.

Development of Electron NanoProbe Technique for Structural Analysis of Nanoparticles and Amorphous Thin Films

141514
Year 1 of 3
Principal Investigator: P. Lu

Project Purpose

We propose to develop two electron nanoprobe based techniques in transmission electron microscopy (TEM) to determine pair distribution functions (PDFs) for structural analysis of nanoparticles and amorphous thin films. The PDFs that describe the local, bonding structure such as neighbor distances and coordination number are essential for structural analysis of the nanomaterials. Our first approach uses the electron nano-scattering pattern (NSP) to extract local bonding structures, i.e., PDFs. Our second approach uses the electron scattering equivalent of extended x-ray absorption fine structure, namely electron extended energy loss fine structure (EXELFS). This approach is complementary to the NSP-based PDF in that EXELFS measures interatomic distances for a given scattering atom. The electron based techniques offer the key advantage of higher spatial resolution (<1 nm) and have not been realized for two key reasons: 1) lack of signal to noise and 2) strong dynamic scattering in electron-specimen interaction that complicates analysis far beyond what is required for x-ray and neutron-based scattering.

We propose two main technical approaches to address these issues: 1) collecting spectrum image (SI) datasets for NSP and EXELFS in the scanning tunneling electron microscope (STEM) and using multivariate statistical analysis (MVSA) techniques for pre-processing datasets, and 2) molecular modeling of structural models coupled with iterative refinement of the structural models by comparing the calculated and experimental patterns. Furthermore, we will take the novel approach of automating collection and analysis to spatially map the bonding structure. The newly developed techniques will be applied to study fundamental materials phenomena such as crystal-amorphous transformation in nanoparticle oxides, and phase segregation and interactions in semiconducting polymers. The success of this project will provide use capability to characterize structure of nanoscale and amorphous materials at very high spatial resolution (<1 nm), not available by other techniques. The research is highly risky and of a fundamental nature.

Summary of Accomplishments

Our accomplishments include the following: 1) we have established the necessary theory and written computer programs to perform PDF analysis based on electron scattering patterns; 2) we have performed molecular dynamics structural modeling on Au and ZnO nanoparticles (NPs), and the results of the Au NPs have been used to confirm the PDF analysis and to understand new physical phenomena; 3) we have established the necessary experimental conditions for STEM NSP SI data collection, developed the scheme for MVSA analysis of the SI dataset, and demonstrated structural recognition and mapping capability based on the NSP-SI technique. The success of project has led to two publications (either submitted or in the process of submission). We have firm confidence that we are on track for meeting all milestones for the project.

Significance

The project will develop two electron-based PDF techniques for structural analysis of NPs and amorphous thin films. The success of this project will provide an ability to characterize the structure of nanoscale and amorphous materials and will impact DOE critical missions, contributing to key national efforts such as energy transport, and homeland security and defense. Research projects in NPs and amorphous thin films are closely related to applications in renewable energy sources, energy storage, and alternative fuel technologies. In addition, these techniques could be applied to identification and understanding of thin film corrosion products that are of critical importance to NNSA missions.

Dynamically and Continuously Tunable Infrared Photodetector Using Carbon Nanotubes

141515
Year 1 of 3
Principal Investigator: F. Léonard

Project Purpose

Infrared photodetectors play a key role across Sandia mission areas being used, for example, in space-based surveillance, thermal imaging, aerial surveillance, and nondestructive imaging of components. IR detectors rely on pixel arrays, each pixel having a dimension in the ten to twenty micron range. Pixels are often made of exotic semiconductors like $Hg_{1-x}Cd_xTe$ because the bandgap (and thus the sensitivity to different optical wavelengths) can be controlled by varying the composition x. However, once a composition is chosen, this fixes the sensitivity to a specific range of wavelengths leading to black-and-white detection. As everyday experience with human vision shows, color detection improves discrimination significantly, and the same applies to IR detectors. Thus one important need is dynamic multiwavelength detection in the IR.

Current technology achieves two-color detection at the pixel level using a triple-layer thin film approach, where two films with different compositions contact a common electrode layer. Unfortunately, this does not provide an obvious path for continuous multiwavelength detection. To address this issue, we propose to utilize the unique properties of carbon nanotubes (CNTs) to demonstrate an infrared pixel with continuously and dynamically tunable absorption. The concept relies on the fact that the bandgap of CNTs is sensitive to strain, with a change of 100 meV per percent strain, as demonstrated experimentally and theoretically. By fabricating a CNT nanoelectromechanical (NEM) device, we will control the strain applied to the CNTs and achieve tunability of the optical absorption. Such CNT NEMs have been demonstrated with resonant frequencies of tens of MHz, and can thus be rapidly tuned. Our experimental work will be coupled with theory and modeling of the photophysics of strained CNT devices. Finally, we will test the radiation hardness of these devices.

Summary of Accomplishments

Because the envisioned nanotube NEMs devices rely on using a gate to bend the nanotubes, one question that arises is how the charge induced on the nanotube by the gate will impact its electronic and optical properties. To address this question, we developed a new many-body, ab initio approach to calculate the electronic and optical properties of doped carbon nanotubes. We combined the GW (Green's function–based) approach with the Bethe-Salpeter equation and included dynamical screening effects due to plasmons. The results show that bandgap renormalization due to doping is unusually strong in nanotubes. In addition, the exciton binding energy is also strongly decreased. However, we found that the exciton excitation energy is relatively unchanged upon doping.

We have also used our ab initio many-body approach to calculate the electronic and optical properties of carbon nanotubes under uniaxial strain. We found that the absorption wavelength can be tuned by several hundred meVs due to strain. These calculations support the assertion that applying strain to carbon nanotubes allows control over their electronic and optical properties.

We also began the radiation testing of carbon nanotube devices. We fabricated carbon nanotube field-effect transistors on four different chips that were then subjected to gamma radiation at the Gamma Irradiation Facility. Each of the samples was exposed to different doses of total radiation ranging between 100 krad and 10 Mrad. Most, if not all, of the devices that we measured maintained their transistor functionality.
We modified a variable temperature probe station in our laboratory to allow controlled optical illumination and

electrical testing of nanophotonic devices, which will be used to probe the photodetection properties of the nanotube devices.

Significance

Infrared photodetectors play a key role across DOE mission areas being used, for example, in space-based surveillance for nonproliferation, thermal imaging for energy, and for stockpile stewardship. The proposed work with carbon nanotubes will allow the development of IR detectors with new functionality that will impact all of these areas. Because IR photodetectors are used in many science applications from the nanoscale to the astrophysical scale, this work will also impact DOE's science mission.

Refereed Communications

C. Spataru and F. Léonard, "Tunable Band Gaps and Excitons in Doped Semiconducting Carbon Nanotubes Made Possible by Acoustic Plasmons," *Physical Review Letters*, vol. 104, p. 177402, April 2010.

Efficient, High-Voltage, High-Impedance GaN/AlGaN Power FET and Diode Switches

141517
Year 1 of 3
Principal Investigator: A. G. Baca

Project Purpose

High-voltage solid-state power conversion technology is a key enabler for increasing the penetration of renewable energy electricity sources through the ability to enable a wide variety of power conversion needs: high-voltage DC transmission, DC/AC, AC/DC, or DC/DC conversion for transmission or distribution. Conventional solid-state power conversion either operates at insufficient voltage levels or, as in light-triggered thyristors, is costly; it also lacks sufficient ruggedness and efficiency to be widely deployed. Conventional bulk drift devices (e.g. Si thyristor) are sufficiently mature that theoretical and practical limits to breakdown, based on the minimum controllable doping level, have not significantly changed in 30 years. We propose to study and improve the lateral GaN/AlGaN transistor because its conductive properties arise from charge polarization effects without intentional doping, and therefore, may have a considerably higher breakdown limit. The goal is to achieve breakdown beyond 20 kV. Such a goal does not lend itself to an engineering solution because the wide variety of device structures and material combinations that must be fabricated and tested at high voltages is uneconomical. Rather, a science-based approach is indicated; studying and understanding the effects of device design and material combinations on leakage currents that limit breakdown at <5 kV (wafer probe limit), in order to build a model that scales beyond 20 kV. The main technical challenges include understanding the factors limiting the breakdown field in these lateral devices, understanding the role of material/geometry/voltage on leakage, peak electric fields, the role of surface passivation, etc.

A science-based approach dictates that innovative solutions depend on which factors are found to limit breakdown. We have planned for novel controlled-ambient passivation (metal organic chemical vapor deposition [MOCVD] SiN or AlN, for surface leakage limiting), multiple field-plate electrode design (peak electric field limiting), and structural back confinement approaches (buffer leakage limiting).

Summary of Accomplishments

We have completed the milestone “quantify efficiency benefits.” Calculation and simulation, of the GaN/AlGaN transistor was used to compare to the main alternatives, Si and SiC. Losses can be grouped in three main categories: on-state, off-state, and switching losses. Off-state losses are theoretically zero. On-state losses derive from the relation of on-resistance vs. voltage. The calculation for Si, SiC, and GaN/AlGaN showed that GaN/AlGaN offers the best solution if performance at its material limits can be reached, confirming one premise of this research project.

Towards the second part of that milestone, evaluating switching losses, a boost converter circuit was chosen as a simple but representative circuit. Model parameters for a 20 kV transistor were estimated from scaling a much smaller device. Simulations indicate that 98% efficiency can be achieved at 250 kHz.

We have also completed a second milestone, “1st MOCVD/AlGaN, by 3/31/2010.” We designed and purchased a mask set with more than 40 types of transistor geometries and test structures and initiated a first growth campaign to establish a baseline MOCVD growth with particular emphasis on the choice of substrate and nucleation layer. From a fully fabricated device, equality metrics of on/off current ratio greater than seven orders of magnitude and a breakdown voltage greater than 350 V were achieved for a transistor with 10 micron separation between the source and drain. These results position us well to continue with the rest of the experimental work necessary to succeed in this project.

Significance

Energy independence is a DOE mission and national security issue. As our nation develops alternative energy sources, a smarter and more efficient electric grid is needed to connect to distributed energy sources and to manage and balance the resulting loads efficiently and with robust security built into the system design, and high-voltage solid-state power conversion technology is a key enabler in this regard. Sandia has a mission to assess and provide technology solutions for enabling and securing a future electric grid that meets these needs.

Electrodeposition of Scalable Nanostructured Thermoelectric Devices with High Efficiency

141518
Year 1 of 3
Principal Investigator: P. A. Sharma

Project Purpose

The purpose of this project is to use electrochemical and electroless chemistry routes for the scalable synthesis of nanostructured thermoelectrics (TEs). Nanostructured TEs have much greater efficiency than traditional bulk materials, but their limited dimensions and costly vapor-phase fabrication routes make them useless for most applications. Liquid-phase chemistry is inexpensive and rapid, often achieving deposition rates of microns per minute, while stoichiometry and microstructure can be reliably varied at the atomic scale under different experimental conditions. TE-based power generators or refrigerators would have numerous commercial and military applications if bulk high-efficiency nanostructured thermoelectric materials could be synthesized.

We will use both electroless and electrochemical liquid-phase chemistry to synthesize TE materials based on Bi_2Te_3 with an eye towards scaling materials to bulk dimensions. We focus on two promising nanostructured geometries: 1) superlattices of Bi_2Te_3 and Sb_2Te_3 and 2) Bi_2Te_3 and Sb_2Te_3 nanoparticles. We will demonstrate control over stoichiometry and microstructure using these synthesis methods. We will also explore the structure-property relations in electrodeposits and electroless nanoparticle synthesis. Experiments are coupled with theoretical modeling of materials. At the end of this project, we plan to develop a nanostructured TE device prototype at the millimeter scale.

Summary of Accomplishments

Our primary goal in FY 2010 was to establish electrodeposition and other liquid phase chemistry methods for the synthesis of TE materials based on Bi_2Te_3. For our electrodeposition activity, we have synthesized stoichiometric, homogenous films of Bi_2Te_3, Sb_2Te_3, and $(Bi,Sb)_2Te_3$ alloys and examined their microstructure using transmission electron microscopy. The grain size and stoichiometry of electrodeposits could be tuned using different complexing agents and pulsed plating conditions. This accomplishment has allowed us to identify routes towards the scalable synthesis of superlattices and has yielded materials that will be useful for controlled transport experiments. We have also successfully achieved the high-yield (>100 mg) chemical precipitation of $Bi_2Te_3$and Sb_2Te_3 submicron particles using electroless liquid phase chemistry. Temperature, solvents, and surfactant molecules affected the size, morphology, and stoichiometry of the particles. We have also identified promising ways of consolidating particles into bulk forms for measurements/devices.

Another goal of this project is to understand the mechanisms for TE performance improvements in nanostructured geometries. Therefore, we performed measurements and theoretical calculations for Bi_2Te_3 materials with superlattice structures. Bi_2Te_3 can incorporate large amounts of excess Bi in a bulk alloy by forming Bi_2 bilayers interleaved with Bi_2Te_3structural units. Using density functional theory (DFT) and transport measurements, we have shown that these materials are semimetals with unusual Fermi surfaces. Under hydrostatic pressure, we found that the electronic properties support superconductivity at liquid helium temperatures, possibly due to topological changes in the Fermi surface, as predicted from ab initio DFT calculations.

Significance

TE devices have a wide range of applications in long-lived power sources, harvesting of waste heat, and compact, cryogen/gas-free refrigeration, which also cuts across many of Sandia's mission areas. In these areas, more efficient TE devices have been a long sought-after goal. The poor efficiency of existing TE devices limits their use to niche applications. For example, while TE devices are invaluable as power sources for deep space missions, they are not a viable alternative to conventional gas-phase refrigeration due to poor efficiency, despite being emission-free and extremely compact. Nanostructured TE materials offer great promise in this sense due to enhanced efficiency, but cannot be produced economically at the appropriate device length scales. Our results point to ways of scaling up nanostructured materials for use in bulk devices. Bulk nanostructured TE devices with much higher efficiency could, for example, be competitive with gas-phase refrigeration or enhance the conversion of automobile waste heat into useful electricity.

Greater than 50%-Efficient Photovoltaic Solar Cells

141519
Year 1 of 3
Principal Investigator: G. N. Nielson

Project Purpose

We propose a new approach for photovoltaic (PV) cells that will allow solar power conversion efficiencies in excess of 50%. Commercially available PV cells are from 6%–28% efficient at best. Even "hero" cells tested in carefully controlled environments have only achieved 40.8%, less than half the theoretical maximum. Monolithically grown multijunction PV cells have a number of difficult constraints that limit efficiency, including lattice matched material requirements resulting in non-optimum bandgap choices and inefficiencies in converting time-varying solar spectra from series connected cells. To achieve a multijunction cell with efficiencies greater than 50%, we will stack individually grown and individually connected junctions. This will avoid degradation due to crystal imperfections from lattice mismatch, reduce series resistance losses by contacting the junctions individually, allow targeting ideal bandgaps for maximum efficiency, and eliminate current matching so the cell stack can operate well in any solar spectrum.

The key challenges in this project will be the development of materials for junctions of the proper bandgaps, the development of cells (i.e., p-n junctions, passivation, metallization, release, etc.), the heterogeneous integration of materials that typically have not been combined previously, and developing microconcentrators. The first prototype structure will be a three junction cell of Si, GaAs, and InGaP. Next, we will develop a four-junction cell comprised of InGaAs, Si, GaAs, and InGaP. To the four-junction cell we will later add a fifth junction out of InGaN. In parallel, we will also look at InGaN-GaN nanowire architectures that can absorb the entire solar spectrum. All aspects of this project provide significant advances to PV technology and semiconductor material growth and development.

Summary of Accomplishments

We have made significant progress toward our goals. The materials and cell development efforts are on schedule or ahead of schedule. We have demonstrated key packaging elements required for the stacked PV cell structure. We have designed, fabricated, and tested the first prototype microlens concentrator/tracking system. Finally, we have also modeled key aspects of the interconnection scheme for optimized efficiency from the individual junctions.

The material development is progressing well. We have demonstrated a fully relaxed, 1-micron-thick, 21% indium composition InGaN layer grown on a porous GaN layer. This is the first demonstration of a InGaN layer of this indium composition at this thickness. We have taken advantage of InGaAs thermophotovoltaic cells at Sandia that provide very high performance at 0.6 eV. This allows us to eliminate the development of a Ge cell. The device structure and contacting scheme will need to be modified but this puts the project much further along than it would otherwise be. The Si and GaAs work has also progressed. We have demonstrated backside contacted GaAs cells that are 11% efficient and are only 3.6 microns thick. We will need to improve the efficiency but this is a significant step forward.

We have demonstrated the ability to create plated indium bumps on aluminum for the packaging of the cells. This will allow us to create the complicated multi-level package required for the stacked cell structure. We have designed and fabricated the first microlens system prototype allowing concentration of 49% and in-plane tracking of up to 20 degrees in both axes.

Finally, we have created a system model that has given interesting preliminary designs; allowing optimized performance of the stacked cell structure, such as improve shading performance and fault tolerance.

Significance

This project develops a new PV cell with the potential to exceed 50% efficiency. This would provide a higher amount of output power per area than any previous PV technology. This revolutionary energy source is useful for reducing size and weight of satellites, enabling remote military operations by reducing the need for batteries and/or fuel, and providing a pathway toward cost reductions for solar power for the nation's electric grid; all key missions of DOE.

Refereed Communications

J.J. Wierer, Jr., A.J. Fischer, and D.D. Koleske, "The Impact of Piezoelectric Polarization and Nonradiative Recombination on the Performance of (0001) Face GaN/InGaN Photovoltaic Devices," *Applied Physics Letters*, vol. 96, pp. 051107-1-3, February 2010.

V.P. Gupta, J.L. Cruz-Campa, M. Okandan, and G.N. Nielson, "Microsystems Enabled Photovoltaics: A Path to the Widespread Harnessing of Solar Energy," *Future Photovoltaics*, vol. 1, p. online, May 2010.

Microfabricated Nitrogen-Phosphorus Detector: Chemically Mediated Thermionic Emission

141520
Year 1 of 3
Principal Investigator: R. J. Simonson

Project Purpose

This project seeks to elucidate the mechanism of selective ionization of heteroatomic species at thermionic emitter surfaces, and use that knowledge to develop a novel chemical detector microsystem. In spite of the long history (~ 30 yrs) of Nitrogen-Phosphorous Detectors (NPDs), the details of this chemically mediated emission phenomenon are currently not understood. While the N- and P-sensitivity of such devices for detection can exceed that for other hydrocarbons by 10,000×, the NPD signal current ultimately depends on the transfer of electrons across the surface potential barrier of the thermionic cathode (emitter). As military and homeland security needs drive requirements for smaller and more powerful detection technologies, operational problems including limited source lifetime and high power consumption become increasingly severe. This necessitates the development of a new micro-NPD. Such devices will improve selectivity, speed, sensitivity, and portability of detectors of explosives, toxic industrial chemicals, and chemical warfare agents.

Two reaction mechanisms have been proposed in the literature to account for the chemically selective ionization observed in NPDs: 1) gas-phase ionization models or 2) surface-mediated electron emission. The latter mechanism is considered more likely based on observations from the literature. In order to both investigate the proposed surface-mediated ionization mechanism and to improve performance of microfabricated NPDs, our team is conducting a systematic study of novel candidate thermionic emission materials. Candidate materials include sol-gel deposited alkali-doped high-porosity silicate films, as well as mixed oxide films based on electron device cathode materials. Our approach engages a multidisciplinary team to develop several unique NPD aspects, including direct measurement of surface variations in work function of novel materials by scanning probe methods, systematic correlation of novel cathode material composition and microstructure with both work function and NPD performance, and the design and testing of novel microfabricated cathode structures for micro-NPD applications.

Summary of Accomplishments

In the first year of this project, our team has synthesized and characterized novel barium alkoxide precursors for emitter cathode film formation. Also, we have demonstrated selective ionization using doped silicon micro-reactor devices as thermal substrates for Cs-doped silicate emitter films. We are now modifying our apparatus to allow quantitative measurements of ionization sensitivity and selectivity. These substrates have survived extended operation at 600–950 °C temperatures in air, demonstrating the viability of our microfabrication approach. However, we have also observed unexpected biphasic film segregation of the silicate-based emitter materials across this temperature range. This unexpected phase segregation could lead to significant variation in emission current density across the films. We are investigating these phases by electron microscopy, x-ray diffraction, and x-ray fluorescence analysis while continuing our efforts to modify solid-state emitter film chemistries as well as substrate surface composition. In addition, we have procured a scanning Kelvin probe instrument to directly measure spatial variations of emitter film work function vs. structure and composition, in order to supplement diode emission current measurements of the global work function of our candidate emitter films. Our initial milestone of modifying a scanning probe microscope station for high-temperature local work function measurements has been deferred due to difficulties in temperature control. We will return to this approach once the temperature control issues and global work function measurements have been resolved.

Significance

To date in this project, we have successfully demonstrated selective detection of a phosphorus-containing organic compound (dimethyl methyl phosphonate, a chemical warfare agent simulant) with high signal to noise at parts per million concentrations. This detection was carried out using a doped-silicon microfabricated device that is operable in air at temperatures exceeding 750 °C. This thermal robustness is a key milestone in the development of a successful detector microsystem. Our team has also synthesized and characterized new classes of soluble barium and cesium aryloxide thin film precursors for patterned deposition of thermionic emitter films on the microfabricated device structures. These results provide progress toward our goal of developing a robust, low-power, sensitive, and chemically selective sensor technology. Sandia is a leading developer of microscale chemical detection technologies for defense, homeland security, and intelligence missions. Several agencies (Defense Threat Reduction Agency, intelligence agencies) have expressed interest in fieldable NPD microsystems, but the presently available knowledge of selective emission/ionization materials is insufficient for successful device scaling. Success in this project will enable new devices to meet not only DoD but homeland security chemical monitoring requirements.

Nanoporous Polymer Thin-Films from Tri-Block Copolymers

141521
Year 1 of 3
Principal Investigator: J. G. Cordaro

Project Purpose

Ultrafiltration devices can be fabricated from nanoporous polymer membranes, and the performance of such devices is directly related to the surface chemistry and pore size of the polymer. The goal of this project is to make nanoporous membranes, with discrete pore sizes and selectivity, from triblock-polymers, containing a functionalized middle block. By tuning all these properties, we aim to develop a flexible platform from which to create new membranes.

Our approach has been to use self-consistent field theory (SCFT) calculations to determine the block sizes of copolymers so that phase-separation at the nanoscale occurs in the bulk polymer. Through an optimization calculation, have predicted the optimal length of a poly(styrene-b-ethylene oxide) polymer, or PS-b-PEO, that will phase separate into a bi-continuous gyroidal morphology. Three exemplary polymers were synthesized and thick films (>300 nm) were annealed and then probed by scanning electron microscopy (SEM). The SEM images reveal that phase separation does indeed occur to give a gyroidal morphology as predicted by SCFT calculations. Etching the PEO block using an oxygen plasma gave higher contrast in the SEM images and further supported the formation of a bi-continuous morphology in the bulk. Our experimental results confirming the SCFT calculations are significant because they prove that a predictive approach to controlling polymer morphology at the nanoscale can be accomplished. We will continue to employ SCFT calculations to guide the synthesis of new block polymers, especially tri-block polymers.

Summary of Accomplishments

Using numerical SCFT calculations, one can predict the stable nanoscale morphology into which a diblock copolymer will self-assemble. However, as engineers, we seek the solution to a different (albeit related) problem: for a given morphology, which diblock copolymer should one make? Using SCFT and the optimization package in Sandia's Dakota code, we can accomplish this goal. Dakota searches in parameter space for the optimal parameters in which the free energy of the target morphology is farthest below the free energies of other structures. We first applied our method to a diblock copolymer melt in which the entire phase diagram is known. The Dakota package successfully found the optimal parameters which correspond to an intermediate temperature. Next, we considered a diblock copolymer that more accurately models a PEO-b-PS diblock copolymer, a molecule of interest for our membrane applications. Here, Dakota found the unexpected result that the gyroid-structure is most stable at the lowest temperatures. The prevailing wisdom in polymer physics claimed that other structures such as cylinders and lamellae should be more stable at comparable temperatures since these simple structures allow for the best packing of polymers. However, we find this presumption to be inaccurate, and our result has real implications for preparing a PEO-b-PS diblock to become a membrane.

We have begun characterizing films of PEO-b-PS with segment lengths predicted by our SCFT calculations. Using SEM and in situ plasma etching, we have confirmed that the selected block polymers do indeed phase-separate to the desired gyroidal morphology — as predicted by our calculations. This observation demonstrates the predictive power of our optimization method.

Furthermore, we have made progress towards synthesizing macro-initiators so we can make triblock polymers. Ultimately, we envision using SCFT theory to guide the synthesis of these complicated polymers so we can obtain a double-gyroidal morphology.

Significance

Our accomplishments for FY 2010 are the following.

1. We have integrated SCFT calculations into Dakota.
2. Using the optimization code, we have minimized the free-energy of the system to predict thermodynamically favorable morphologies for bulk polymer melts.
3. Our calculations have predicted an unexpected result — that for a given block polymer, the gyroidal morphology is more favorable than the cylindrical or lamellar morphology.
4. We have confirmed experimentally using SEM that the predicted morphology for a specified block polymer in the bulk is observed.

Our results have the following impact:

1. Proven ability to use SCFT calculations to predict polymer morphology.
2. Reversed conventional wisdom regarding the stability of polymer morphology and temperature.

We envision our work to be integrated into many projects that seek to control materials properties at the nanoscale. Specifically, we envision applying our SCFT calculations to guild polymer synthesis for use in lithography, thin-film preparation, and polymer self-assembly, For the S&T community at large, it is extremely beneficial to have a proven predictive method for designing synthetic polymers.

Surface Engineering of Electrospun Fibers to Optimize Ion and Electron Transport in Li^+ Battery Cathodes

141522
Year 1 of 3
Principal Investigator: N. S. Bell

Project Purpose

The purpose of this research is to understand and find a solution to degradation of a Li ion battery cathode material in order to improve lifetime cycling and reliability of batteries. We will fabricate cathode fiber materials using the electrospinning process as a model system for energy storage cathode materials, and use this system to investigate and mitigate interface processes that result in capacity or rate loss with cycling. The major challenge for Li ion batteries requires a solution to several materials issues governing cost, safety, durability and capacity.

This project will develop the understanding needed to form a stable, integrated surface layer that is optimized for fast Li^+ and electron transport through surface engineering of electrospun cathodes. We are investigating $LiMn_2O_4$ spinel (LMO); a commonly researched cathode material. In practice, this material experiences several degradation mechanisms ranging from capacity fading due to non-stoichiometric oxygen content, the Jahn-Teller distortion phenomenon leading to changes in the oxidation state of the material and dissolution in the electrolyte phase, and the formation of surface films by degradation of the electrolyte, and/or phase transitions at the surface to form Mn_2O_3. This project is developing a core-shell fiber architecture using co-electrospinning, where the shell layer will be optimized to permit rapid Li^+ transport, good electron conductivity, a stable interface and no formation of the solid-electrolyte interphase (SEI) layer by electrolyte degradation. These shell compositions will be focused on organic carbon layers primarily, with an inorganic layer of metal oxide as a secondary research effort. The unique core-shell geometry enabled by co-electrospinning of nanoscale fibers will allow independent control over the core cathode material as well as the outer shell, which in our design, governs electron and ion transport and protects the core from degradation.

Summary of Accomplishments

We tested and developed sol-gel based chemistries for the formation of lithium manganese oxide spinel (LMO) cathode materials using the electrospinning method. Conversion from nitrate, acetate, mixed acetate-chloride, and chelated acetate polyacrylic acid (PAA) systems were studied. Low-temperature conversion and reaction to form the desired inorganic phase and to combust the organic precursors were investigated using x-ray diffraction and thermogravimetric analysis/ differential thermal analysis methods. We learned that high temperature reaction in the mixed Mn-acetate-LiCl system was successful for forming electrospun fibers at elevated temperatures on substrates of Au coated silicon wafers. Electrospinning testing is ongoing with the chelated acetate PAA system. Co-electrospinning with a shell of the desired protecting material is being evaluated for success with the higher loading of acetate-PAA.

To form a conformal shell, a shell material based on graphite oxide have both been successfully electrospun. A carbon based surface coating will meet the requirements for a shell layer that increases electronic conductivity and rapid Li^+ transport, and will be explored first. The process to form carbon fiber by electrospinning often utilizes fiber drawing of polyacrylonitrile. We are investigating an alternative approach using dispersed nanoflakes of graphite oxide, which are water soluble. We have developed compositions of these dispersed nano-flakes with PVA and successfully electrospun fibers. A route using polyvinylalcohol (PVA) was investigated. Laboratory testing was conducted to determine the correct molecular weight for fiber production, and determined that an 8 wt% solution of PVA (molecular weight 64–85 kD) would successfully produce electrospun fiber mats. The graphite shell material survives calcination in air needed for incorporation with the core material. These fibers retain their uniformity on calcination in air, and therefore represent a viable route to the formation of carbon based shell materials.

Significance

Currently, Li ion battery performance is severely limited by several degradation mechanisms, including slow Li^+ transport and loss of active cathode volume upon cycling, the uncontrolled formation of a SEI by electrochemical degradation of the electrolyte, and cathode material degradation by phase conversion or dissolution. This project is developing an understanding of the mechanisms for capacity loss during cycling through fundamental mechanisms of degradation, and implementing a strategy to mitigate or eliminate these capacity loss processes. Our ability to synthetically optimize the surface layer properties, in order to achieve high charge/discharge rates, and persistence over thousands of cycles with limited degradation, would represent a revolutionary breakthrough in battery technology. A significant advance in the area of electrode-electrolyte interface stability would lead to benefits for the DOE science and energy mission areas regarding the understanding of interfacial properties affecting material and device performance for electrical energy storage and release. These advances would further impact development of components and designs applicable to nuclear weapon and military force applications.

Understanding the High Temperature Limit of THz Quantum Cascade Lasers (QCLs) Through Inverse Quantum Engineering (IQE)

141523
Year 1 of 3
Principal Investigator: M. Wanke

Project Purpose

This project hopes to answer the following question: "Is there a fundamental maximum operating temperature for THz quantum cascade lasers?" The answer will have significant impact on determining what applications THz QCLs can address. Although the maximum operation temperature increased rapidly after THz QCLs were first invented in 2001, there has been very little improvement over the past few years and the maximum operation temperature achieved (185 K) still requires cryocooling. The slow progress has led many to speculate that the maximum operation temperature is fundamentally limited by the ratio of the photon energy to the thermal energy in the system (hv/kT >1). While much data seemed to support this theory, recent results have significantly shattered the hypothesis and no good theories have yet replaced it. Many studies have explored how different design parameters affect laser performance, but with the existing techniques there has been limited direct connection between the studied parameters and the laser physics. This use of indirect measurements has resulted in a lack of systematic understanding. We propose to use the unique capabilities of our inverse-quantum-engineering (IQE) algorithm to systematically disentangle temperature-dependent, performance-limiting physics from the many interdependent material parameters of THz QCLs. This project's goals focus on the elucidating device physics rather than on devising a specific application.

Summary of Accomplishments

In order to evaluate the capabilities of the IQE algorithm theoretically, we dramatically improved our predictive simulation capabilities by replacing the standard QCL rate equation model with a fully microscopic quantum kinetic theory. As a result, steady-state populations, stationary current, and gain spectra can be simulated without any phenomenological parameters. We are applying the code to simulate device behavior, which provides trends that we can correlate with experiment and compare between designs.

We have grown and tested many of these designs, and have demonstrated that our algorithm can produce new laser designs at different frequencies starting only from a known laser design. The laser frequencies scale with the design energies. In addition, we have observed that the maximum operation temperature does not follow a 1/kT trend, which is one of the major questions we were hoping to address. So far this year, two papers from work on this project have been accepted for publication.

Significance

Understanding the temperature limitations of THz QCLs will determine which national security applications THz QCLs can address for DOE, NNSA, DHS and DoD, such as screening applications (package inspection, concealed weapon detection), component inspection, and molecular identification applications (explosives detection and space-based remote sensing). It will also provide Sandia with unique design and predictive simulation capabilities for THz QCLs and other complex heterostructure devices.

The ability to compare devices that are nearly identical except for a well-defined specific change should allow the scientific community to explore questions relating to the performance of the lasers in a more systematic manner than previously. Also having such systematic samples should allow more complete comparisons between model results and experimental results, so that predictive codes can be improved further.

Refereed Communications

I. Waldmueller, M.C. Wanke, M. Lerttamrab, D.G. Allen, and W.W. Chow, "Inverse-Quantum-Engineering: A New Methodology for Designing Quantum Cascade Lasers," *IEEE Journal of Quantum Electronics*, vol. 46, pp. 1414-1420, October 2010.

D.G. Allen, T.W. Hargett, J.L.Reno, and M.C. Wanke, "Optical Bistability From Domain Formation in Terahertz Quantum Cascade Lasers," to be published in the *IEEE Journal of Selected Topics in Quantum Electronics*.

Novel Approaches to Artificial Photosynthesis Using Biomorphic Cooperative Binary Ionic Solids

147259
Year 1 of 1
Principal Investigator: J. A. Shelnutt

Project Purpose

Current US energy sources are not sustainable because they primarily exploit limited and insecure natural resources and are causing unacceptable climatic and environmental damage. Solar energy is a clean and renewable replacement source provided that sunlight can be efficiently harvested and converted into electrical or chemical energy. It is widely expected that the advances in nanomaterials for light harvesting and energy transduction can make solar energy a major component of our renewable energy production. In this regard, we have discovered a new type of solid that can potentially provide the enabling solar nanomaterials required. Cooperative Binary Ionic (CBI) solids are self-assembled from large anionic and cationic organic molecules that are organized in new ways that result in emergent properties. These CBI solids in the form of biomorphic nano- and microstructures composed of highly versatile and functional porphyrin molecules can be directly applied to light harvesting and to the conversion of the harvested light energy into electrical and chemical energy. Being related to chlorophyll (biological light harvesting) and heme (biological electron transport, catalysis, sensing), the synthetic porphyrin derivatives used in making these CBI materials perform these types of functions well. In fact, the porphyrins used in the CBI nanomaterials have enhanced functionalities and stabilities not available in biological counterparts. Most importantly, because of the new way the molecules are organized and interact in these binary solids, we are able to demonstrate new functionalities that are tunable in functional type and effectiveness. Emergent collective properties such as enhanced charge separation and exciton, electron, and hole mobilities amplify their attractiveness for solar energy applications, including for organic solar cells and solar fuel-producing technologies. We have synthesized and characterized the CBI nanomaterials to understand their light-harvesting properties, molecular structure (using small-angle and single-crystal x-ray diffraction), photoconductivity, and performance in artificial photosynthesis systems for producing hydrogen.

Summary of Accomplishments

The key research goals were to develop efficient light-harvesting systems, synthesize supramolecular assemblies for efficient light-induced charge separation, and to couple artificial photosynthetic charge separation to multielectron/proton transfer and catalysis to produce fuels. We have successfully completed the investigation of ionically self-assembled nanostructures prepared from synthetic porphyrins and their nanocomposites with metals to produce systems for solar fuels production. We pioneered the synthesis of new CBI nano- and microscale structures, based on the ionic self-assembly of synthetic porphyrins, for use in solar technologies. We designed and synthesized integrated composite nanodevices based on zinc and tin porphyrins, characterized their light-harvesting and photocatalytic properties in metal reduction (self-metallization) reactions, showed that they exhibit photoconductivity, and evaluated their ability to produce solar hydrogen from water. Although these cutting-edge nanomaterials have only been developed by us during the last few years, they already have been shown to simultaneously address multiple problems in the development of artificial photosynthesis systems. For example, our studies of the Zn/Sn system have shown that the CBI nanomaterials can provide efficient and stable artificial photosynthesis systems for hydrogen production. In addition, for the first time, we have demonstrated hydrogen production using porphyrin CBI nanostructures without the aid of soluble components such as an electron relay or light-energy receptor. Moreover, the use of an electron relay enhances hydrogen generation lasting for at least 3 days of continuous operation at 1 sun without significant degradation of the platinized CBI nanostructures as determined by scanning electron microscope images and UV-visible spectra. The results demonstrate that the CBI nanomaterials have considerable potential for producing efficient and durable artificial photosynthesis nanosystems that are capable of integrating processes of light-harvesting, charge-separation, and catalytic activity at the nanoscale. Other combinations of metal porphyrins (e.g., zinc and cobalt) raise the possibility of solar reduction of carbon dioxide.

Significance

The research ties to US and global strategies for developing a renewable energy infrastructure, and renewable transportation fuels in particular. The development of a new type of ionic binary solid with potential uses in light harvesting and utilization of solar energy responds to the national need for new solar energy technologies. The research provides a better basic understanding of the critical photochemical and photophysical processes involved in artificial photosynthesis. The CBI nanomaterials indirectly tie to DHS and national security missions through potential use of these optoelectronic nanomaterials in sensors and small power source technologies. Development of these new materials will also generally enhance nanoscience in the US.

Refereed Communications

K.E. Martin, Z. Wang, T. Busani, R.M. Garcia, Z. Chen, Y. Jiang, Y. Song, J.L. Jacobsen, T.T. Vu, N.E. Schore, B.S. Swartzentruber, C.J. Medforth, and J.A. Shelnutt, "Donor-Acceptor Biomorphs from the Ionic Self-Assembly of Porphyrins," *Journal of the American Chemical Society*, vol. 132, pp. 8194-8201, May 2010.

Characterization of Failure Modes in Deep UV and Deep Green LEDs Utilizing Advanced Semiconductor Localization Techniques

147374
Year 1 of 3
Principal Investigator: M. A. Miller

Project Purpose

The III-nitride material system has shown great success in light emission from deep ultraviolet (UV) to deep green wavelengths. The nitride alloys of AlN, GaN, and InN possess tunable direct band gaps and have the potential to cover the entire visible spectrum and well into the UV. In order to broaden the commercial availability of III-nitride emitters, reliability, lifetimes, and low efficiencies of optoelectronic devices emitting in the deep UV and green must be improved. Applications for UV emission wavelengths include water and air purification, bioagent sensing, and optical communication at wavelengths where there is no solar background. Light emitting diodes (LEDs) with wavelengths of ~240 nm are now available commercially and research groups report wavelengths of 210 nm. Solid state lighting stands to benefit greatly from more-efficient deep green LEDs with emission wavelengths longer than 530 nm.

Critical to the efficiency and performance of these nitride-based LEDs as well as the continued expansion of available device wavelengths is the identification and fundamental insight into the failure modes of these devices. We will use innovative Failure Analysis (FA) techniques, particularly Sandia-developed laser-based integrated circuit techniques, to study degradation mechanisms over the lifetime of the optoelectronic devices emitting in the deep UV (270–280 nm) and the deep green (530 nm or longer). There is a high risk involved with determining the actual failure mechanism in materials with very high threading dislocation densities(10^8–10^{10} cm^{-2}). Identification of degradation mechanisms and subsequent corrective actions to reduce defects responsible for their degradation will lead to improvements in optical efficiency and increased lifetimes in III-nitride LED devices benefiting a host of applications from solid state lighting to bioagent detection.

Summary of Accomplishments

Several UV (~275 nm) and green (~530 nm) LEDs were characterized with thermally induced or light-induced voltage alteration (TIVA or LIVA). Stimulating the UV LEDs with a 532 nm laser revealed electrically active defects represented by dark signals in the –IVA map. In TIVA, a dark spot suggests a decrease in circuit resistance, possibly achieved with a leakage path along a threading dislocation. A dark spot in LIVA indicates an increase in current or a potential two-step electron-hole pair generation event involving a deep-level state. Only 0–4 defects were imaged per device, localized within the active region and along the mesa edge. Defects were bias dependent, appearing at low currents (0.6–1 µA) and were not present with zero applied bias or reverse bias. Each defect in the active region matched a physical defect in that device. Fortunately, the TIVA/LIVA technique could differentiate between electrically active defects and a high density of optically similar structures.

Electrically active defects were also imaged in the green LEDs as bright spots. As the 532-nm laser scanned across these areas, either the resistance increased due to TIVA or the current decreased from electron-hole pair recombination (LIVA), resulting in a positive spike in voltage. Unlike the UV LEDs, no signals were observed at 1064 or 1340 nm, suggesting photocurrent recombination (LIVA). There were a significant number of defects per device (3–10) and the LIVA intensity of the defects varied and was bias dependent. All spots reduced intensity to where they were indistinguishable from background noise near 1–5 mA, well below typical device operation currents. Upon examination at higher magnification, none of the identified LIVA sites matched with obvious surface defects. The behavior of the observed defects in the UV and green LEDs will be monitored as the LEDs are aged at high temperatures and high currents to promote accelerated failure.

Significance

If successful, this work will isolate particular defects that lead to premature degradation and failure mechanisms in green and UV LEDs. Subsequent processing modifications may be suggested to reduce the density of the targeted defects, potentially leading to increased lifetime, increased efficiency, and a broader nitride-based spectrum of available device wavelengths. Therefore, this may impact a wide variety of applications including solid state lighting (DOE), bio-sensing (DHS), water and air purification (DOE and DHS), polymer curing, a large number of medical applications, and various Nuclear Weapons and Defense Systems and Assessments projects. Another potential benefit may be collaboration with in-house optoelectronic device development.

Photoelectronic Characterization of Heterointerfaces

147942
Year 1 of 3
Principal Investigator: M. T. Brumbach

Project Purpose

The purpose of this project is to discover new interfacial phenomena at electronic material interfaces through the development of sophisticated surface characterization and rational design of interfaces. Additionally, model surface structures will be developed to capitalize on the surface sensitivity of X-ray and UV photoelectron spectroscopies (XPS and UPS). Photoelectron spectroscopy will be used to map the alignment of the energy level structure at inorganic/organic material interfaces. Energy band structures have been well characterized for inorganic semiconductors, however, the translation of those techniques towards understanding complex, hybrid interfaces has been severely lacking. These characterization procedures are complicated, difficult, and require instrumentation and capabilities that are generally not accessible to many researchers. Consequently, results from this work will have a high impact on emerging technologies for cheap, flexible electronics, where inorganic materials are being interfaced with organic materials, typically conducting polymers. Despite the tremendous advances that have been made to develop these devices, there remain large discrepancies and assumptions of their electronic structure. This work will require the development of several photoelectron techniques which have not previously been utilized at Sandia, and will develop UV-photoelectron spectroscopy as a new capability for Sandia.

Summary of Accomplishments

A number of different polymers and substrates have been evaluated to define the experimental parameters for obtaining relevant XPS/UPS data. Polymers analyzed include poly(3-hexylthiophene), poly(ethylene dioxythiophene), poly(aniline), and poly(thiophene). Electrode materials evaluated include gold, ZnO, and indium-tin-oxide (ITO). A novel polymer was electrodeposited to give varying thicknesses on ITO, a typical transparent conducting oxide for photovoltaics. The polymer, poly(tris(4-(thiophen-2-yl)phenyl)amine) (N3), is a potential photovoltaic absorber. Through the study on N3 we determined that this polymer could not be purified from trace metals used in the synthesis. These trace impurities were observed in XPS/UPS and significantly impacted the spectral interpretation. Also, we determined that the rate of film growth via electrodeposition was not linearly dependent on the time of deposition. An initial nucleation period is required followed by film growth. These observations have led to the use of physical deposition of polymers via spin coating for sample preparation, since film thicknesses can be tightly controlled by varying solution concentration and spin speed. however, since N3 appears to be a metallo-organic rather than a conducting polymer, we did not pursue it further.

These investigations have allowed us to demonstrate UV UPS characterization of polymer/inorganic interfaces.

Significance

This work ties to DOE missions in science, energy security, and energy infrastructure by providing fundamental insight on materials for hybrid devices with applications including solid-state lighting, photovoltaics, and batteries. This work will provide important interfacial characterization studies and develop a new capability for Sandia while promoting collaborations in the rational design of complex devices for energy conversion and storage.

Ion-Photon Quantum Interface: Entanglement Engineering

148549
Year 1 of 3
Principal Investigator: D. L. Moehring

Project Purpose

Distributed quantum information processing requires a reliable quantum memory and a faithful carrier of quantum information. Trapped ion quantum bits (qubits) are the leading realization for quantum information storage due largely to their very long coherence times and well-developed laser interaction techniques. Photonic qubits, on the other hand, are the natural choice for the transport of quantum information as they can quickly travel long distances with minimal decoherence. The capability to entangle photons with trapped ions in a technologically relevant and scalable fashion would be a singular, game-changing achievement. We propose here to leverage the active and successful development of microfabricated semiconductor ion traps at Sandia's Microsystems and Engineering Sciences Applications facility, and to integrate a micro-optical cavity. Compared to current efforts in academic settings combining macro-sized ion traps and optical components, a microdevice will result in the dramatically increased speed and fidelity of ion-trap based quantum networking protocols. Indeed, integrating smaller components will directly allow for a stronger quantum coherent interface between a single trapped ion and a single photon. If successful, this effort will result in a new quantum information science and technology (QIST) capability for Sandia and will further its strategic objective of providing technologically relevant engineering solutions for QIST implementation.

Summary of Accomplishments

A number of important steps have been taken to achieve timely experimental demonstrations of the milestones of this project. The first of these is the design and layout of the ion-trap chip that will be fabricated for the observation of increased light collection. Final modifications to this design have been completed and fabrication will begin shortly. A second important step was the testing of a chamber within which the traps of interest will be installed. To this end, a complete system was tested for ion trapping functionality using a trap chip similar to the desired final products from this project. Finally, design has begun for the year-two milestone of creating an integrated cavity system. Specific desired cavity parameters have been identified and necessary optics and mounting structures have been designed and ordered.

Significance

This project will complement Intelligence Advanced Research Projects Activity ion trap quantum information efforts by developing a foundation for quantum networking capabilities. This research would also benefit the DOE missions in nuclear security, and science and technology discovery, as well as DHS missions.

Active IR Materials for Beam Steering

148958
Year 1 of 1
Principal Investigator: E. A. Shaner

Project Purpose

The term "plasmonics" encompasses a large range of customizable optical structures based on charge oscillations at a metal/dielectric interface or in a semiconductor. We propose to develop active plasmonic structures where a voltage bias controls resonance frequencies in order to enable new functionality. In particular, we will focus on mid-infrared beam steering devices that operate in the 3–12 micron wavelength range.

Using epilayers of varying doping densities, we have demonstrated that free-carrier dielectric tuning can create resonance shifts of up to 1 micron in devices designed for 10-micron operation. In a steering device, we estimate this would correspond to approximately 15 degrees of beam deflection. While this range is significant, we need to pursue other low-loss tunable materials such as electro-optic ceramics, along with transistor style free-carrier designs.

Summary of Accomplishments

Our primary work under this effort related to the implementation of hafnium oxide as a gate dieletric on doped GaAs. We evaluated films formed by atomic layer deposition (ALD), sputtering, and electron beam deposition. We found the sputtered and electron beam deposited films to be highly defective without the use of a post-growth anneal process. Hafnium oxide films deposited by ALD were not annealed, but were of much higher initial quality than films grown using the other techniques.

We fabricated various mid-IR plasmonic and metamaterial structures on hafnium oxide devices and found that the basic level of performance was not degraded. Attempts at depletion tuning of such devices were not successful due to leakage issues that still remained in our large area structures.

We also investigated a commercial material known as OptiCeramic. While this material is noted to have less tuning than can be achieved through carrier depletion, it is electro-optic in nature and has lower loss. Devices were fabricated on this material and shown to have good performance. Slight shifting of plasmonic resonances were observed, however, the material was destroyed through application of high voltage bias.

Significance

This work can lead to a class of infrared optical components with new or improved functionality over mechanical solutions. Infrared beam steering would greatly benefit countermeasure applications. The mission need for infrared sensing of biological and chemical materials has been elevated in importance. In this context, plasmonic devices may play a role in reaching new levels of sensitivity or improved detection schemes.

Red and Yellow Emitters Using Dilute-nitride (AlGa)(PN) Alloys

149208
Year 1 of 1
Principal Investigator: J. G. Cederberg

Project Purpose

Dilute-nitride compound semiconductors based on (AlGa)P have the potential to be a superior alternative to the (AlGaIn)P alloy system for light emitting diodes (LEDs) in the red and yellow wavelengths relevant to solid-state lighting (SSL). We will investigate the performance of (AlGa)(PN) materials for LEDs at wavelengths from 615 to 575 nm to determine their viability compared to existing (AlGaIn)P-based materials at these wavelengths. The red wavelength (615 nm) represents an optimal constituent for red-green-blue (RGB) multichip color mixing to produce white light emission, but is poorly rendered by (AlGaIn)P-based LEDs. For any RGB color mixing platform, reducing the peak wavelength of the red component will improve luminous efficacy (LES) at a given color rendering index (CRI). Further improvements in LES can be obtained by incorporating yellow wavelengths (575 nm) producing red-yellow-green-blue color mixing. (AlGa)(PN)-based alloys hold potential for improving the efficiency of solid-state lighting, but they have not been investigated for this purpose.

To achieve these targets, we will first grow Ga(PN) films of varying nitrogen content by metal-organic chemical vapor deposition (MOCVD). The addition of nitrogen to GaP converts it to a direct bandgap semiconductor, capable of emitting light efficiently. We will use temperature-dependent photoluminescence to determine the amount of nitrogen incorporated and the radiative efficiency of the material. Incorporating nitrogen into Ga(PN) increases the emission wavelength above that needed to achieve the target wavelengths.

Summary of Accomplishments

We established a process to grow GaP films by MOCVD at relatively low processing temperatures (< 700 °C), compatible with incorporating atomic concentrations of nitrogen from dimethylhydrazine. We prepared a series of GaPN films with varying nitrogen contents. Simulation of x-ray diffraction lineshapes were used to determine the film nitrogen composition. We discovered that most growth conditions produced samples that luminesce at room temperature. The most intense emission was observed for samples with between 0.5 and 1 atomic percent nitrogen. The spectrum of these samples was centered at 600 nm, a critical wavelength for LED color-mixing approaches for SSL. Compositions outside these concentrations resulted in lower brightness and produced broadened spectra. We discovered that the growth conditions have a strong impact on the apparent bandgaps, as well as the internal quantum efficiency. Photoluminescence measurements identified a defect-related radiative band centered at 700 nm that competes with the band-to-band radiative transition at low excitation power densities. At higher excitation, the defect-related photoluminescence saturates, and the band-to-band transition dominates. Early samples exhibited internal quantum efficiencies below 0.1%. Improvements in the growth conditions allowed us to demonstrate 1% internal quantum efficiency for GaPN. We believe that modifications to the structure can increase this above 10%. Comparison of the low-temperature luminescence intensities from both samples supports the argument that nonradiative recombination dominates the net recombination rate at elevated temperatures. Our temperature dependent luminescence data suggests that the peak emission wavelength shift at elevated temperature is less than half the shift associated with AlGaInP up to 125 °C. The internal quantum efficiency declines rapidly at elevated temperatures, and is projected to decline further at 125 °C. The band offset of GaPN to GaP is over 150 meV, favorable for reducing thermal leakage that dominates AlGaInP LEDs at elevated temperatures.

Significance

The energy challenges faced by the world in the coming century are recognized by national leadership as one of the most pressing missions. Once it is widely adopted, solid-state lighting (SSL) will reduce US electricity consumption by 10%, saving ~$25B/year, and reduce the need for generating capacity by 50 GW. Improving the quality of SSL directly improves its acceptance by the public. This impacts the efficient energy consumption that DOE is responsible for advocating and implementing. In addition, the availability of lighting technology to developing countries can provide more productive time in a day, could improve safety, and has the potential to improve the general quality of life. This would reduce the apparent wealth gap between the developed and developing world, and increase geopolitical stability.

Our demonstration of a short-red semiconductor emitter at 600 nm provides an alternative route to color mixing approaches. The alternatives would be to use inferior AlGaInP LEDs or use phosphor approaches with the inherit inefficiencies due to Stokes losses associated with photon pumping. While 1% internal quantum efficiency is low compared with other LED materials, this material is still immature and a path to higher quantum efficiencies can be identified from this work. Improvements in nonradiative recombination should be possible by investigating thermal annealing. Modifications to the structure can further minimize nonradiative losses. Although our work is still at a very early stage, we believe that 20 to 30% quantum efficiency can be obtained from GaPN.

A Simple and Rapid Method for Detecting Contamination by Engineered Nanoparticles

149381
Year 1 of 1
Principal Investigator: G. Bachand

Project Purpose

The increasing volume of literature concerning the detrimental health effects of engineered nanoparticles (e.g., asbestos-like carcinoma) has resulted in a significant push toward understanding the environmental health and safety risks posed by these materials. Current work at Sandia, as well as at numerous other sites, has focused on understanding the acute toxicity posed by engineered nanoparticles. These studies involve exposure to relatively high concentrations of nanoparticles that can produce an acute response. However, there is a greater likelihood that workers will be exposed to low doses of nanoparticles over time (i.e., chronic exposure), similar to the case for beryllium and asbestos. In this respect, the occupational exposure of workers to engineered nanoparticles is very difficult, if not impossible to monitor based on the lack of detection technologies that are quick, easy-to-use, and cheap. The goal of the proposed work is to develop a simple and rapid methodology for detecting nanoparticle contamination in a laboratory environment that will leverage diagnostic approaches such as the home pregnancy test. The basic model system will be analogous to wipe tests for radioactive materials that are routinely used in laboratories, but also will also include selectivity and signal amplification elements common to immunological assays. The purpose of this project was to demonstrate key foundational technologies necessary for this technical approach. Specifically, the objectives were to demonstrate selective binding of synthetic peptides to target nanomaterials, and develop and characterize signal amplification methods to rapidly and sensitively detect peptide binding.

Summary of Accomplishments

The project was divided into two major technical objectives: 1) demonstrate selective binding of synthetic peptides to target nanomaterials and 2) develop and characterize signal amplification methods to rapidly and sensitively detect peptide binding. With respect to the first objective, we demonstrated binding of a number of synthetic peptides to gold (Au), silver (Ag), and silicon dioxide (SiO_2) surfaces. Peptide variants were produced in-house as well as commercially in order to evaluate key parameters such as linker length and composition, as well as linker position. Peptides with AHX (aminohexanoic) and PEG12 (polyethylene glycol) were placed on either the carboxylic acid or amine terminus of the peptides. While binding selectivity was lower than expected, we learned that the selectivity can be influenced by the number of peptide repeats, as well as the location and length of the peptide linker. In addition, surface blocking prior to enzyme detection was identified as a key aspect to the selectivity. High background signals were obtained when the surfaces were not properly passivated to prevent non-selective enzyme binding during the detection stage. With respect to objective 2, we developed a rapid means of assaying the binding of peptide binding to surfaces. Specifically, we functionalized the peptides with a molecular handle consisting of biotin, which is specifically recognized by the protein streptavidin. Enzymatic conjugates consisting of streptavidin and horseradish peroxidase were used as a mean of detecting peptide binding through substrate catalysis and spectroscopic measurement of changes in the substrate's absorbance. Overall, the implementation of the enzyme system enables significant signal amplification, and a simple means of assaying peptide binding.

Significance

The proposed work will provide a novel system for detecting/monitoring acute and chronic occupation exposure for workers to engineered nanoparticles. This area is being increasingly supported through various agencies such as the National Institutes of Health (NIH). This system may also be applied to homeland/military situations for detecting acute exposure. Agencies such as the Defense Threat Reduction Agency are already considering the possibility of nanoparticle weapons, and may also represent a potential future sponsor. The short-term goal of this project was to demonstrate key enabling technologies for the proposed approach, as a basis for developing a strong, more comprehensive follow-on project.

Chemical Strategies for Die/Wafer Submicron Alignment and Bonding

149402
Year 1 of 1
Principal Investigator: L. E. Rohwer

Project Purpose

This project explores chemical strategies that will enable submicron alignment accuracy of dies and wafers by exploiting the interfacial energies of chemical ligands. We have micropatterned commensurate features, such as 2D arrays of micron-sized gold lines on the die to be bonded. Each gold line is functionalized with alkanethiol ligands before the die are brought into contact. The ligand interfacial energy is minimized when the lines on the die are brought into registration, due to favorable interactions between the complementary ligand tails. After registration is achieved, standard bonding techniques are used to create precision permanent bonds. We have computed the alignment forces and torque between two surfaces patterned with arrays of fine lines or square pads to illustrate how best to maximize the tendency to align. We also discuss complex, aperiodic patterns such as rectilinear pad assemblies, concentric circles, and spirals that point the way towards extremely precise alignment.

Summary of Accomplishments

This project demonstrated a new alignment concept that enables submicron alignment of micropatterned features on die and wafers with those on other die and wafers. This is a significant improvement over the alignment accuracy of ~2-5 microns that is currently achievable with the highest precision alignment equipment.

We patterned gold line arrays (25 microns wide, 50 microns pitch) on Pyrex to test our alignment concept. The gold was coated with a self-assembled monolayer (SAM) of dodecanethiol. When two commensurate surfaces were brought into contact, the favorable interactions between complementary ligand tails were shown to have a self-aligning effect, causing the lines to come into registration.

The results we obtained from our experiments with simple, periodic gold line patterns point the way towards more complex patterns. Using mathematical modeling, we found that an array of lines with a sinusoidal modulation in their spacing could greatly reduce the need for precision placement, while still retaining the high registration force given by simple periodic lines. Other promising patterns were identified, such as concentric rings and spirals.

The concept demonstrated in this project points the way toward a practical process that may be applied at Sandia. The patterns might be placed at opposing edges of die to be aligned. Once they are brought into alignment, the features on the die can be permanently bonded using standard methods. We developed a low-temperature gold-gold bonding method. We found that dodecanethiol SAM-coated gold features bond at 150–185 °C and have shear strengths that meet Mil-Std-883F (DoD microelectronics standard) requirements.

Significance

The results of this project revealed new patterns for alignment and a practical process for microsystems integration at Sandia. Submicron alignment enables the integration of devices with ever-smaller feature sizes and increasing interconnect densities. If implemented, the submicron alignment and bonding techniques we demonstrated could enable more complex device functionalities that benefit DOE's national security mission. These advances include 2D tiling to produce larger focal plane arrays for remote sensing, and 3D stacking of devices having a high density of interconnects and a small form factor, for high-speed signal transmission.

Microchannel Sampling for Climate Change Monitoring

149403
Year 1 of 1
Principal Investigator: R. P. Manginell

Project Purpose

Ubiquitous, accurate, and inexpensive measurement of atmospheric constituents for the purposes of monitoring greenhouse gas (GHG) emissions presents a technology challenge where the application of microsystems could be advantageous. In situ atmospheric sampling schemes as a function of altitude rely on large, flask-based systems that must be flown over the target area either in a small plane (for targeted measurements) or a commercial airliner (for normal flight paths). Such deployment methods are not able to deliver the density and widespread coverage that is desired for climate monitoring at an acceptable cost. Weather balloons or small unmanned aerial vehicles (UAVs) offer significantly lower deployment costs, but their cargo weight limitations preclude the use of the bulky flask systems needed for the full suite of high-sensitivity measurements, and thus such deployments typically produce only rudimentary data. Our ultimate goal is to develop micro-analytical instrumentation that could be deployed in this fashion and produce the full suite of high-sensitivity measurements needed. In this project we propose to tackle the underlying materials and surface science challenges that must be solved to develop a low-cost, low dead volume, inert microvalve suitable for GHG measurements. Success in this endeavor would enable the eventual development of a novel, phase-change valve required for a miniaturized GHG sampling system suitable for balloon or small UAV deployment.

Summary of Accomplishments

This project demonstrated the feasibility of creating, 1) low-cost, small-volume sampling chambers and 2) low-cost, low-power hermetic valves to seal the chambers once a sample is collected in them. The sample chamber fabrication was based on inexpensive circuit board, brazing and machining techniques in chemically inert alumina ceramics. Two embodiments of the sampler chamber were investigated. The first explored batch fabrication of a 16-element array of chambers by layering of laser-machined ceramic sheets. These layers were stacked upon one another with intervening laser-machined braze layers and sandwiched between two capping layers. The top capping layer had a laser-machined sample inlet in each element of the array. Electrical valve-actuation heaters were patterned on the top layer. Microcracks in the braze in the first sealing attempt prevented hermeticity, but the technological maturity of the brazing system provides confidence that further optimization will yield hermeticity. The second embodiment consisted of individual sample chambers created from commercially available hollow alumina tubes with one end presealed. This design was attractive as only one braze joint to a capping layer was required. We demonstrated creation of nine samplers simultaneously with assembly fixturing. The capping layer contained the sample inlet hole and resistive valve actuation heaters. Mil-spec hermeticity (helium leak rate below $1x10^{-8}$ atm-cm^3/sec) was demonstrated.

The novel micro-valve design, based on phase-change in a low-melting-point metal alloy, could be actuated as low as 72 °C. For this process, we created an approximately hemispherical alloy dome with a sample entrance hole, aligned to the sample chamber hole. The entrance hole was closed by reflowing the alloy, sealing off the chamber entrance. Manufacturing was based on standard thick and thin-film processes and solder technologies used commonly in industry, offering promise for low-cost, high-volume fabrication. We demonstrated mil spec hermeticity, and achieved a high-degree of repeatability, even after valve aging.

Significance

This work is pertinent to the science and technology of atmospheric sampling, but also to a host of defense, homeland security, industrial, commercial and residential chemical detection scenarios. This project addresses specific goals within the Sandia mission space by laying groundwork for new microsystems technology that could contribute to the basic scientific and technological understanding of climate and climate change. For national security applications, the same technology can also be used to take samples for the detection of chemical and explosive threats at high-value facilities and for border protection. In addition, climate change is increasingly being recognized as a national security issue. A 2 °C change in global average temperature will have a dire impact on US naval bases due to rising sea levels. Much more daunting is the potentially increased demand on the armed forces as the world's population is displaced due to changing environmental conditions, food shortages, and fresh water shortages. Additionally, the economic costs of transitioning to a "green" economy will provide motive for future climate treaties to mandate the measurement of GHG emissions, from their signatories, in order to verify compliance. The required density of atmospheric data acquisition to determine treaty compliance and provide basic scientific understanding of climate change demands the low cost, small size/weight/power and high performance of microsensor systems. This project directly addressed the sampling component of such a microsensor system and should provide a differentiating role for Sandia in climate monitoring. In particular, this project demonstrated a means of creating low-cost, small-volume sampling chambers and attendant low-cost, low-power hermetic valves to collect gas samples. The small size of a sampling system built with this technology could also allow integration of microfluidics and microsampling technologies with UAVs and other miniaturized platforms.

From an engineering and materials standpoint this project provided a more thorough understanding of the sealing and wetting behavior of metal materials within microdevices. This research has laid the groundwork for future studies of such behavior and should continue to reveal mechanisms useful for the engineering of a wide variety of microfluidic and gas handling structures and devices. To date, the use of metal-alloys within microdevices has been very limited. This project has contributed greatly to the use of metal-alloys as functional elements of microsystems.

Ultrathin Coatings of Nanoporous Materials as Property Enhancements for Advanced Functional Materials

149405
Year 1 of 1
Principal Investigator: E. Coker

Project Purpose

Nanoporous materials such as zeolites, templated silicas, and metal-organic framework materials are well known for their gas and liquid sorptive, catalytic, molecular sieving, ion exchange properties, etc. In a few cases, layers of such materials have been applied, for example, as sensor platforms or gas separation membranes; these layers are typically of thickness from several hundred nanometers up to several microns. At such thicknesses, the rate of diffusion of molecular, ionic, and atomic species through the layers is restricted by the path length for diffusion. For many potential applications, vast improvements in the response of a device (e.g., sensor, separation membrane, etc.) could be realized if the thickness of the porous layer were reduced to the range of tens of nanometers. For such applications, adsorption capacity is not important; rather the control of molecular (atomic, ionic) access through the pore opening defines the response or efficiency of the device. However, a basic understanding of how to synthesize or fabricate such ultrathin layers is lacking.

One concern with state-of-the-art, thick, nanoporous layers is their limited resiliency. For example, they have low resistance to mechanical deformation due to their rigidity, and thermally induced degradation due to mismatch of expansion coefficients between layer and substrate. With ultrathin layers, the substrate-layer interface becomes strong relative to the intralayer cohesion forces, allowing the layer to flex and be resilient to deformation and thermal shock. An additional ramification of the availability of such thin layers is the possibility of generating asymmetric, or chiral, coatings through intentional deformation of the substrate during or after layer growth. This will enable a new family of sensor and separations devices.

Summary of Accomplishments

In this project, we demonstrated that the degree of orientation of crystallites within thin layers of zeolite grown on silicon wafers was sensitive to the solution chemistry and temperature used during the growth process. We synthesized a number of highly ordered, thin layers of zeolite MFI (Mordenite Framework Inverted), as shown by x-ray diffraction, however electron microscopy revealed that surface topology was quite rough, and a number of twinned crystals were present in the layers. The growth conditions were modified in order to improve layer fidelity, with limited success. We discovered a novel route to the growth of thin layers, and are preparing an invention disclosure. Depending on the conditions used, layers were comprised of crystallites with either random orientation, or preferred orientation.

Significance

The capabilities developed at the successful conclusion of this work have potential to impact several areas, including homeland security (enhanced, fast responding sensors), DOE Energy Efficiency and Renewable Energy (advanced catalytic and separations devices), and microelectronics/ microelectromechanical system thrust areas (thermal management on-chip).

Diamond Nanowire Modeling and Synthesis

149559
Year 1 of 1
Principal Investigator: A. M. Morales

Project Purpose

The properties of bulk diamond such as its wide bandgap, negative electron affinity, chemical and biological inertness, radiation hardness, and high thermal conductivity make it a promising material for applications in electronics, chemical/biological detection, and radiation monitoring. However, the realization of devices based on bulk diamond has been hampered by the inability to efficiently dope bulk diamond. Based on recent work in similar nanowire systems, it is possible that the mechanical and electronic properties of a one-dimensional diamond nanowire may be quite different than the properties of doped bulk diamond and may allow for more-efficient doping. In this project, we propose to develop modeling tools to predict the effects of doping on the electronic properties of diamond nanowires, and to develop methods to fabricate doped diamond nanowires. By exploiting our ability to selectively dope these diamond nanowires, it may be possible to tune the electronic properties within these single-crystal structures. This project is complemented by theoretical modeling in order to both understand and verify experimental measurements on these unique one-dimensional nanostructures.

Summary of Accomplishments

In this project, we explored modeling methods that may allow us to predict the effects of size on the electronic properties of diamond nanowires, developed a novel method to fabricate diamond nanowire devices with ohmic metal contacts, and measured transport properties of polycrystalline and single crystal diamond nanowire transistors. Modeling shows that a direct bandgap may develop in very small nanowire devices. Transport measurements on the diamond nanowire devices indicate that the devices display semiconductor behavior when current is injected across an ohmic Pt-diamond interface and that a Schottky barrier develops when the current is injected across a tungsten oxide-diamond interface.

Significance

Nuclear weapons, homeland security, and broader DoD and national security missions will benefit from the advanced electronics and sensing devices that can eventually be made based on diamond nanowires. In this project, we have made progress at modeling, fabricating, and characterizing such devices.

Switching Dynamics of a MEMS Controlled Thyristor

149573
Year 1 of 1
Principal Investigator: C. Nordquist

Project Purpose

Future smart grid concepts and integration of renewable power generation require power electronics that are more flexible and more efficient than existing technology. Power metal oxide semiconductor field effect transistors and metal oxide semiconductor (MOS)-controlled thyristors are useful switches within their voltage and current ratings, but MOS control is infeasible for the highest voltages and currents. Alternative thyristor topologies require either AC current to reverse the anode voltage or a large reverse gate current to turn off the device, limiting their usefulness and efficiency.

A microelectromechanical system (MEMS)-controlled thyristor using a MEMS switch for gate control will offer a high impedance drive port for shutting off the thyristor, allowing simpler logic control of power devices. Compared to MOS-controlled thyristors, MEMS-controlled thyristors should have improved current handling, lower on-state losses, higher noise immunity, and higher radiation hardness. This, in turn, will improve the efficiency and opportunities for power electronic devices in future smart grid applications. In addition to allowing higher power, MEMS would remove the MOS susceptibility to radiation and could be integrated with a number of material systems, including Si and wide bandgap materials.

In this project, we investigated the potential and limitations of the MEMS controlled thyristor. It is a new concept, and this project investigated some of the fundamental behaviors of this type of device. The knowledge gained during this project will define the MEMS and thyristor device requirements and help identify the essential experiments for realizing the MEMS controlled thyristor.

Summary of Accomplishments

We have investigated the feasibility of using MEMS switches to control semiconductor thyristors. The MEMS switch controls the thyristor by providing a shunt path to ground for the regenerative gate current, turning off the thyristor. To demonstrate the concept, we simulated the switching dynamics of a MEMS controlled thyristor circuit, verified the role of the shunt resistance by performing measurements of on-wafer GaAs thyristors, assembled a chip-and-wire demonstration circuit, and performed DC and transient characterization of the MEMS/thyristor circuit.

From the simulation and modeling effort, we learned that the placement of the MEMS switch, the value of any pull-up resistor, and the triggering current of the thyristor determine the demands placed upon the MEMS switch and the switching speed of the thyristor. The simulation and modeling effort also verified that the MEMS switching environment is relatively benign, with hot switching of less than 2 V required under normal operation. We experimentally verified that a closed MEMS switch can be used to prevent turn-on of the thyristor by shunting the gate current to the cathode. In the closed state, the switch limits the gate junction voltage to less than 0.3 V, preventing the forward bias and turn-on of the thyristor. In the open state, a pull-up resistor is used to supply gate current and trigger the thyristor, in which case the forward-biased gate-cathode junction limits the voltage across the MEMS switch to 1.4 V, creating a relatively benign hot switching environment.

Significance

This revolution in power electronics for high-voltage, high-current applications has the potential to enable DOE strategic goals in energy security and infrastructure. Additionally, this component technology can also enable electric vehicles, all-electric aircraft, and other platforms. Also, the approach can be applied to materials without a suitable gate oxide, and eliminating the charge sensitive oxide layer may allow for radiation hard devices.

This project has identified the feasibility of this concept, providing opportunity for follow-on work in the context of power electronics for smart grids. Specific focus areas include realizing thyristors with low trigger currents to reduce the demand on the MEMS switch, monolithic integration of the MEMS switch with the thyristor, and assessing the lifetime of the MEMS switch in the MEMS-thyristor application.

Tailored Control of Bismuth Telluride-Based Thermoelectric Nanowires

149579
Year 1 of 1
Principal Investigator: D. L. Medlin

Project Purpose

Thermoelectric devices have important applications in solid-state energy conversion for both cooling and power generation. This technology is presently limited because of the poor energy conversion efficiencies of existing thermoelectric materials. High thermoelectric performance requires achieving a high thermopower, α, and balancing the competing requirements of high electrical conductivity, σ, and low thermal conductivity, κ. A useful parameter that characterizes the energy conversion efficiency of a material is the so-called thermoelectric figure-of-merit, ZT. One approach to improving this efficiency is to draw on nanoscale effects to improve the electronic and thermal transport properties. For instance, theory predicts large enhancements to thermoelectric performance for materials in nanowire geometries. Yet, despite these predictions, the performance of existing nanowire thermoelectric materials is poor, with the best-reported ZTs achieving only a small fraction of the values for conventional, bulk materials. Based on a detailed literature survey, we believe that the underlying problem is poor materials quality in thermoelectric nanowires. In particular, composition, compositional uniformity, and crystalline structure have been too poorly controlled to achieve suitable transport properties. This problem is challenging because of the complex chemistries and crystallography typical of thermoelectric compounds. Our goals for this project are to establish a capability for thermoelectric nanowire growth, to achieve control of material composition and structure, and to test the sensitivity of thermoelectric nanowire performance to material quality. This work will establish a key new capability for state-of-the-art synthesis and analysis of thermoelectric nanowires and lead to fundamental new scientific knowledge. Demonstrating improvements in nanowire performance would, in itself, generate broad scientific interest by showing a pathway to eventually realizing the benefits predicted for nanowire geometries.

Summary of Accomplishments

Under this project, we have focused on establishing a capability for growing Bi_2Te_3-based nanowires of well-controlled composition and crystallinity. In our initial work, we developed appropriate electrodeposition procedures to produce the correct phase and composition. This is a significant challenge, since compositional control is critical to materials properties, and is particularly difficult since the materials we are considering are ternary alloys. Specifically, we concentrated on obtaining material of composition $Bi_2(Te_{0.9},Se_{0.1})_3$ composition since this is the optimal composition for bulk, n-type Bi_2Te_3 materials. We thus put significant effort into first growing blanket films and optimizing the electrodeposition chemistries and growth conditions to allow control of the composition and uniformity. Having obtained the correct compositions, we have now begun growing nanowires using these conditions as a starting point, and tuning the conditions to ensure correct compositions in the more challenging environment of a nanowire pore. Our initial results are showing a uniform growth front, which is a key to eventual realization of the necessary dimensional control to allow for high quality thermoelectric nanowires. In parallel with our synthesis effort, we have further refined our nanowire characterization methods using TEM and atom probe tomography to allow quantitative composition and structural measurements to further optimize the growth processes.

Significance

Advancing thermoelectric materials performance will enable new technologies for cooling and power generation that are relevant to the national security missions of DOE and other agencies, including DoD. Potential applications include new solutions for long-lived power sources for remote, unattended operations as well as advanced cooling technologies for improved detector operations.

First-Principles Predictions of Electronic Properties in Functionalized Graphene Nanoribbons

149657
Year 1 of 1
Principal Investigator: B. M. Wong

Project Purpose

Graphene nanoribbons are promising organic semiconductors for thin-film transistors, displays, and photovoltaics due to their high electron mobilities and ease in chemical modification. Smaller nanoribbons such as pentacene have already found use in organic field-effect transistors, organic light-emitting diodes, and organic photovoltaics. While these materials have been the subject of intense research within the last five years, a fundamental lack in their rational design has prevented scientists from exploiting their full potential in devices. For example, although medium-sized nanoribbons possess extremely high charge-carrier mobilities, these nanostructures are susceptible to photodegradation. Larger nanoribbons are inherently more interesting due to their smaller bandgaps, but they can rapidly oxidize in air, a characteristic which limits their routine use in optoelectronic and other electronic applications. The larger nanoribbons also have open-shell, di-radical ground states and can have an uncontrolled reactivity. In principle, one can chemically functionalize the nanoribbon edges to stabilize the nanostructure; however, an unguided experimental approach to explore this vast parameter space would be extremely costly and inefficient. To address these complex issues, we will use predictive computational methods and chemical intuition to search for functional groups that enhance stability and electron transport. Using novel density functional theory (DFT) methods, we can carry out a substituent-effect study to determine the factors that simultaneously prevent photooxidation while maintaining the low bandgap of the original parent nanoribbon. Predictive computational screening of candidate functionalized nanoribbons will allow a guided, rational approach to harness the unique electronic properties in realizable nanoelectronic devices.

Summary of Accomplishments

The optoelectronic and excitonic properties in a series of linear acenes were investigated using range-separated methods within time-dependent DFT. In these highly-conjugated systems, we found that the range-separated formalism provides a substantially improved description of excitation energies compared to conventional hybrid functionals, which surprisingly fail for the various low-lying valence transitions. Moreover, we found that even if the percentage of Hartree-Fock exchange in conventional hybrids is re-optimized to match wavefunction-based coupled-cluster doubles benchmark calculations, they still yield serious errors in excitation energy trends. Based on an analysis of electron-hole transition density matrices, we also showed that conventional hybrid functionals overdelocalize excitons and underestimate quasiparticle energy gaps in the acene systems. The results of the present study emphasize the importance of a range-separated and asymptotically-correct contribution of exchange in time-dependent DFT for investigating optoelectronic and excitonic properties, even for these simple valence excitations.

Significance

A major upcoming frontier of significant interest to DOE's science strategic goals is the topic of efficient energy conversion. In particular, DOE's nanoscience initiative, as realized by the Center for Integrated Nanotechnologies at Sandia, has a direct interest in novel, nanoscience-based approaches for controlled electronic transport. The work proposed here is also relevant to Sandia's interest in post-Moore's Law capabilities, where carbon nanostructures provide advantages over existing computer circuitries.

Quantifying the Debonding of Inclusions Through Tomography and Computational Homology

149658
Year 1 of 1
Principal Investigator: A. Mota

Project Purpose

Most metals and alloys contain a certain amount of arbitrarily distributed cavities or voids, with their growth and finally coalescence being the basic failure mechanism in ductile fracture. It is widely believed that the creation or nucleation of voids generally occurs at the interfaces between inclusions (residual particles from the manufacturing process) and the alloy as the material is subjected to loads which lead to stress concentrations at these interfaces.

We propose the use of synchrotron-radiation computed tomography (SRCT) data to determine the conditions and mechanisms that lead to void nucleation in rolled alloys. Data obtained from SRCT consist of grayscale 2D images that show attenuation to soft x-rays (5–60 keV, 0.248–0.021 nm). This attenuation can be correlated to the mass density of the material, with bright areas being zones of higher density (inclusions) than dark areas (voids). These images are processed further to obtain full 3D representations that reveal the internal structure of the material.

The Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) has provided SRCT data of two samples of 7075-T7351 aluminum plate (widely used for aerospace applications) stretched to failure, loaded in directions perpendicular and parallel to the rolling direction, respectively. The resolution of SRCT data is 900 nm, which allows elucidation of the mechanisms governing void growth and coalescence.

This resolution is not fine enough, however, for nucleation. In collaboration with the University of California, Berkeley, we have submitted a proposal to the ALS to conduct an extensive set of experiments that will provide sufficient data to determine the kinetics of growth and coalescence. We propose the use of statistics and image processing techniques to obtain sub-resolution scale information from these data, and thus determine where in the sample and when during the loading program nucleation occurs and the mechanisms that lead to it.

Summary of Accomplishments

The Octopus software used for the reconstruction of the tomography data was the only one available to us. It is very fast, being able to perform a reconstruction of a 5 GB to 25 GB data set from 20 minutes to 1 hour. The accuracy of the reconstruction may be good for qualitative analysis, but, as our results show, it proves inadequate for quantitative analysis.

Nevertheless, we believe that the tools developed for quantitative and statistical analysis of tomographic data are robust and sound, and we plan to use them in the context of more-accurate reconstructions.

Alternate, more-accurate reconstruction methods exist, although they are more computationally expensive. Unfortunately, there was no time available for research and implementation of alternate reconstructions schemes. We hope to pursue the use of other, more powerful reconstruction methods as a follow-on effort to this project.

Significance

The fundamental nature of the investigating debonding in structural aluminum alloys benefits Nanoscience to Microsystems, Defense Systems and Assessments, Energy, Resources and Nonproliferation,and Nuclear Weapons mission technologies. The computational tools developed in this project will also foster collaboration with the DoD. The ALS is one of the premier microtomography facilities in the US. The increased interaction with ALS and LBNL that has resulted from this project (and will continue) strengthens our laboratory and DOE research efforts.

A Novel Method of CO_2 Capture and Conversion

149938
Year 1 of 1
Principal Investigator: R. Kemp

Project Purpose

The conversion of CO_2 into useful chemicals and fuels is a topic of worldwide interest as the need to mitigate global warming becomes more urgent. In a current project, Sandia has a major research thrust in reducing CO_2 levels by using high-temperature, solar furnace methods. Reduction of CO_2 at lower temperatures, ideally ambient temperature, would be a major scientific breakthrough and assembling a catalytic process for this transformation would be a technological game-changer for CO_2 fixation. Therefore, emphasis on a single, high-temperature approach from Sandia is not adequate to ensure success in this arena of CO_2 activation. Additionally, Sandia projects are examining the capture and chemical sequestration of CO_2 via a number of routes, primarily using heterogeneous or polymeric supports.

In this project we wish to combine aspects of these Sandia interests by developing a novel approach to capturing CO_2. The overall concept is based on a generalized type of metal- CO_2 "adduct" that we have discovered and characterized very recently at Sandia and the University of New Mexico. It is known from the literature that direct electrochemical reduction of CO_2 is disfavored largely due to the energy required to "bend" the linear CO_2 molecule after addition of electrons. Our proposed approach should overcome the primary barrier of efficiently reducing CO_2 electrochemically — that of the energy requirement to "bend" CO_2 after addition of these electrons — by forming coordination adducts of CO_2 that "pre-bend" CO_2 using electroactive metal catalysts. Moreover, the metals used in our suggested experiments are inexpensive and readily available, and the CO_2-adduct formation reaction takes place at room temperature. This project, if successful, will position Sandia as a leader in nonsolar reduction chemistry of CO_2.

Summary of Accomplishments

Our results have yielded many intriguing findings to those working in energy-related research. While our results are preliminary, they show promise for future development. As importantly, these results also demonstrate some technical issues that must be overcome in order to develop this subject more fully. We have prepared two examples of CO_2-adducts of main group metals. One of these complexes has CO_2 bound to Zn while the other complex shows similar binding of CO_2 to Sn. In both these cases, the CO_2 moiety is bent to about 130° from linearity. We have shown the use of novel ligands based on the –N(PR2)(R') fragment. We have also demonstrated that the CO_2 complexed to these main group metals can be desorbed by either slight heating, or by allowing the adduct complex to remain at room temperature for several hours. We have subjected the Sn complex of adducted CO_2 to cyclic voltammetry in non-aqueous solvent to examine whether our initial hypothesis of easier reduction of CO_2 using bent adducts was correct. Unfortunately, the electrochemical results were ambiguous due to the fragility of the ligand group. These complexes, in part due to the delicate N(PR2)(R') ligands attached, are not stable to water or protic solvents, which can be detrimental to the electrochemical experiments. In order to combat this issue, we designed and prepared a number of other related ligands that are expected to be more stable to other reagents. We have prepared new ligands based on bis(dialkyl)- or bis(diarylphosphino)propan-2-ol, bis(quinolin-8-olato), (2,6-bis(dimethylamino), and bis(benzotriazole-methoxide), and have prepared main group metal complexes from them. However, CO_2 reactions of these complexes have as yet produced only insertion products rather than the desired CO_2-adducts. Ligand modifications are ongoing.

Significance

There are many important technical points already developed during this brief project that can be utilized by the general scientific community, as well as potentially by industry. As well, there is interest within the Sandia community on CO_2 capture and conversion. First, the overall concept that we are addressing is of fundamental importance: can CO_2 be coordinated to a metal (either highly electrochemically active or not) in an unusual bent fashion, and if so, will the subsequent chemical or electrochemical conversion of this adduct be facilitated by the bent nature of the CO_2? While we have demonstrated the initial part of this concept — the preparation of bent CO_2-adducts — the important answer to the second part is not yet resolved. The initial examples we have prepared of these metal CO_2-adducts have shown electrochemical activity; however, the complexes appear to undergo other reactions believed to be due to the instability of the ligand framework. Thus, the definitive answer to this question must await modification of the ligand structure to yield more stable ligands. However, the synthesis and characterization of these complexes and the introduction of this new class of CO_2-complexes is scientifically intriguing in itself. As well, the design and preparation of new ligands useful for metal complexes is of interest to a broad range of chemists funded by a wide variety of agencies, such as Department of Energy, National Scientific Foundation, and National Institutes of Health. New ligands are basic components of the synthetic inorganic/organometallic chemist's toolbox. The publication and dissemination of these synthetic results will be of broad interest. The use of inexpensive metals such as Zn and Sn will be intriguing to industrial companies, such as power-generating companies, that must deal with CO_2 capture and sequestration. The initial results in this project has led to follow-on funding from DOE in order to widely expand the approaches that we are trying to demonstrate. Additionally, the fundamental reaction of CO_2 with various metals is a topic studied by a large number of researchers funded by DOE.

Refereed Communications

C.A. Stewart, D.A. Dickie, M.V. Parkes, J.A. Saria, and R.A. Kemp, "Reactivity of bis(2,2,5,5-tetramethyl-2,5-disila-1-aza-cyclopent-1-yl)tin with CO_2, OCS and CS_2 and Comparison to that of bis[bis(trimethylsilyl)amido] tin," to be published in *Inorganic Chemistry*.

Spectral Imaging Sensor with Pixelated Custom Filter Array for Environmental Measurements

149944
Year 1 of 1
Principal Investigator: S. A. Kemme

Project Purpose

This work will test our proposed strategy of fabricating a hyperspectral sensing/imaging array with a proof-of-principal midwave infrared (IR) subarray of pixelated filters, an important component of a sensor capable of collecting and interpreting environmental emissions and climate change effects locally so that they can be attributed and exploited for national security. Successful demonstration of this array would allow us to demonstrate the utility of this approach; both to potential end-use government agencies as well as interested Focal Plane Array (FPA) fabrication partners such as Raytheon and Santa Barbara Focal Plane, with whom we have already established a relationship.

Ultimately, this sensor is a pixelated, multispectral arrayed optical component integrated with a midwave infrared FPA. The key optical component is a pixelated hyperspectral filter array fabricated within the Microsystems and Engineering Sciences Applications facility. With this arrayed approach, data may be accumulated with a non-scanning, “snapshot” imaging system. The filtering action is based upon a transmissive array of pixels with narrow (10–100 nm) spectral resolution and independent choice of center wavelength. These pixelated filter wavebands need not be contiguous, as each filter’s center wavelength array is determined by lateral patterning; placement within the array is arbitrary. We target the midwave (3–5 microns) and atmospheric water bands (5–8 microns), so that we can sensitively monitor water vapor, clouds, and the short CO_2 emission band at 4.3 microns. These fourth-generation hyperspectral targets are identified as significant in the National Oceanic and Atmospheric Administration /National Environmental Satellite, Data, and Information Service (NOAA/NESDIS) “Impact of High-Temporal and High-Spectral Resolution IR Observations.”

Summary of Accomplishments

We determined that a 10-nm filter would be too wide to discern 1-nm waterbands in the mid-IR (3–6 microns). Classical thin film filters (e.g., Fabry-Perot) require thick film cavities of several microns that cannot be fabricated (e.g., germanium), or a large number of layers (>150).

We designed resonant subwavelength gratings (RSGs) to perform the filter function. RSGs can provide a ~1 nm narrowband filter comprised of a shallow grating etched on 0.5 microns of germanium film and 0.5 microns of zinc sulfide on top. These devices do not use more than two layers in reflection mode or nine layers in transmission mode. We selected the reflective devices given the simplicity of fabrication.

Two groups of devices were fabricated; three substrates were used in each group, each with three tests and thirty demonstration devices. The first group was centered at 4.25 microns (CO_2 absorption band) and the second group was centered at 5.214 microns (H_2O absorption band).

Test filters were measured and determined to be wavelength centered within the test setup. The demonstration devices were imaged using an InSb camera at the resonance wavelength of the demonstration filters. The test and the demonstration setup showed that the resonance wavelength of the filters could be changed by shifting a lithographically controlled parameter, the grating period. Previous work with filters at Sandia required the modification of their cavity thickness to change their resonance wavelength, a more difficult process than changing the periods on an RSG.

Significance

We target the mid-wavelength infrared, encompassing atmospheric water bands so that we can sensitively (over 1–10 m distances) monitor water vapor, clouds, CO_2 emission band at 4.3 microns, and SO_2 at 7.2 microns as a function of altitude. Our national database includes data from satellites in the longwave IR (8–12 microns). However, these absorption spectra are spatially low resolution and integrated through the entire atmosphere. With this proposed sensor, we can address local effects associated with a population or region of a country. This regionally attributed information is necessary to accurately pinpoint climate change cause and effect. Secretary Chu specified this problem as worthy of DOE "big science." Moreover, fourth-generation hyperspectral targets such as water vapor and greenhouse gasses are identified as significant in the National Oceanic and Atmospheric Administration /National Environmental Satellite, Data, and Information Service white paper "Impact of High-Temporal and High-Spectral Resolution IR Observations" and directly address Sandia's S&T climate change technology roadmap. This goal is synergistic with Sandia's traditional efforts in remote sensors and global monitoring.

Furthermore, Sandia has experience with small hosted payloads, (e.g., United States Nuclear Detonation Detection System payloads on GPS satellites). Currently Sandia is conceptualizing work on a small payload that can piggy-back on a medium-Earth orbit satellite (e.g. iridium, GPS) for environmental monitoring. Available space for a hosted payload, does not allow for a large spectrometer system such as the "orbiting carbon observatory" satellite or the atmospheric infrared sounder which is a primary payload on the AQUA satellite. An array of narrowband filters attached to a FPA could provide the means to conduct spectral reconstruction and therefore environmental monitoring. This package should be small enough to fit as a hosted satellite payload. RSGs are ideal devices that can provide the narrowband response for this application.

Thermal Desorption Coupled Gas Chromatography-Mass Spectrometry

150124
Year 1 of 1
Principal Investigator: M. Van Benthem

Project Purpose

Thermal Desorption Coupled Gas Chromatography-Mass Spectrometry (TD/GC-MS) is a powerful analytical technique for analyzing chemical mixtures. It has great potential in numerous analytic areas such as chemical warfare agents, sports medicine in the detection of designer drugs, and biological research for metabolomics. Data analysis is complicated, far from automated and can result in high false positive or false negative rates. We have demonstrated a step-wise TD/GC-MS technique that removes more volatile compounds from a sample before extracting the less volatile compounds. This creates an additional dimension of separation before the GC column, while simultaneously generating three-way data. Sandia's proven multivariate analysis methods, when applied to this data, have several advantages over current commercial options, and show good success in finding and enabling identification of trace compounds. Several challenges remain, however, including understanding the sources of noise in the data, outlier detection, improving the data pretreatment and analysis methods, developing a software tool for ease of use by the chemist, and demonstrating our belief that this multivariate analysis will enable superior differentiation capabilities. In addition, noise and system artifacts challenge the analysis of GC-MS data collected on lower cost equipment, ubiquitous in commercial laboratories.

Summary of Accomplishments

We examined the thermal decomposition of poly dimethyl siloxane compounds, Sylgard® 184 and 186, using thermal desorption coupled gas chromatography-mass spectrometry (TD/GC-MS) and multivariate analysis. We explored a method of producing multi-way data using a stepped thermal desorption. The technique involves sequentially heating a sample of the material of interest with subsequent analysis in a commercial GC/MS system. We analyzed the decomposition chromatograms using multivariate analysis tools including principal component analysis, factor rotation employing the varimax criterion, and multivariate curve resolution. The results of the analysis show seven components related to offgassing of various fractions of siloxanes that vary as a function of temperature.

Significance

This project addresses the nuclear weapons mission technology investment area to reduce cost, enhance the ability to assess life-cycle surveillance, and reduce the use of hazardous materials. The resulting methods will enable more-detailed surveillance and provide new capabilities for the measurement of materials aging and characterization of material failures.

Dual-Etalon, Frequency-Comb Spectroscopy

150255
Year 1 of 1
Principal Investigator: D. W. Chandler

Project Purpose

Optically monitoring atomic and molecular species requires spectroscopic tools. This project proposes a new spectroscopic tool for the recording of high-resolution spectra with broad-band light. Consider a short (tens of femtoseconds long) pulse of light. It will have a frequency bandwidth of tens of thousands of GHz. If that light passes through an etalon or a stabilized Cavity-Ring-Down (CRD) cell (an etalon that can be filled with gas) a train of pulses will come out the end of the etalon. This chain of equally spaced pulses is a frequency comb and its Fourier transform is a series of sharp frequencies at the mode spacing of the cavity across the entire bandwidth of the mirrors on the etalon cavity. If an absorber is placed within the etalon (cavity ring down geometry) or after the etalon then some of the frequencies will be absorbed by the absorber. The challenge is to ascertain which of the frequencies, spaced a few hundred MHz apart, within the bandwith of the light source have been absorbed. This is accomplished with the use of a second etalon having a slightly different mode spacing (length). If the frequency comb associated with this reference cell is combined with frequency comb of the first cell, then by analyzing the cross beats between the two signals, one can determine which cavity modes have been absorbed. If resolution higher than a few hundred MHz is required, then scanning the length of the CRD cell containing the gas over only one free spectral range (a few hundred MHz) records the entire spectrum with the resolution of the etalon. This process converts an optical spectrum into the frequency range of conventional electronics for recording. Possible applications are all-solid-state miniature sensors that can record multiple species at once and single-shot temperature measurements.

Summary of Accomplishments

We demonstrated that dual etalon frequency comb spectroscopy is viable and will work. We built a dual etalon spectrometer and took spectra with it. We were able to take spectra of iodine lines with ten times better resolution than that inherent to the light source. These proof-of-principle experiments will set the stage for future proposals to pursue experiments in the infrared and THz spectral regions as well as an effort to identify high-value targets for spectroscopic monitoring, such as chemical agents and reactive intermediates.

Significance

The mission of the DOE is to perform state of the art experiments in areas of energy and national security. This project is central to both as it will provide a new technique from which chemical and biological sensors can be made and fundamental chemistry can be monitored. An example is the search for the spectroscopy of combustion intermediates important to DOE and the monitoring of combustion products of biofuels.

Polyoxometalate “Solutions” for Energy Storage

150774
Year 1 of 3
Principal Investigator: T. M. Anderson

Project Purpose

The projected two-fold increase in global energy consumption by mid-century will partially be met through the use of renewable energy sources. However, the intermittent nature of these resources requires the development of new and large-scale energy storage sources. Concentrating on promising flow battery technologies, we are working to prepare new cathode and anode solutions to increase energy density. The primary challenge of this work is to produce new dissolved charge storage species that will yield a higher energy density than current technologies.

Building on the extensive materials synthesis and characterization expertise and capabilities at Sandia, we are utilizing metal-oxide clusters (so called polyoxometalates or POMs) as new, dissolved-charge storage materials. We are applying a suite of analytical and electrochemical techniques to evaluate the stability and other fundamental properties of POMs in various battery electrolytes in order to gain an understanding of the structural and electrical properties of these transformational complexes. Although mononuclear and infinite-array metal oxides are common battery materials, the use of nanometer size metal-oxide clusters in any energy storage technology is unprecedented. This is due, in part, to a paucity of data on how these systems react with protons. In addition, most of the fundamental electrochemical properties have never been thoroughly examined under the conditions often necessary to achieve high battery efficiency. There is also a lack of correlation between structural and electrochemical properties. The ultimate goal of the project is to select one POM as the cathode, and a different POM as the anode in a flow configuration, and rely on the energy difference of the two different POMS to establish cell voltage and store charge.

Summary of Accomplishments

We completed a set of solubility/stability studies on a family of prototypical heteropolymolybdates and heteropolytungstates and established that this chemistry is sensitive to both the solvent-inaccessible “heteroatom” and the solvent-accessible metal-oxo sites. The former is a charge density effect (lower charge density enhances acid stability) and the latter is a geometrical effect where the higher distortion of molybdenum relative to tungsten enhances solubility. We successfully stabilized three highly electroactive compounds in battery acid. More importantly, we learned that all of the heteropolyacids are highly soluble and more stable in acetonitrile. This is surprising given the fact that the compounds have a high surface charge and therefore are less compatible with the lower dielectric constants of polar organic solvents. We devised a more direct synthesis of the Wells-Dawson diphosphotungstate salt by direct crystallization from its synthetic components. That allowed for high yields and complete elimination of carbonate impurities from the ambient environment. We created a new route to the diphosphotungstic acid via the formation of an etherate complex. We established compound stability monitoring capabilities by phosphorus and silicon nuclear magnetic resonance (NMR). We performed cyclic voltammetry measurements on a representative cluster, shown to be stable in battery acid by phosphorus NMR, on a series of solutions with varying concentrations of acid, but with constant ionic strength. The positions of the waves associated with molybdenum reduction shifted in the positive direction as the concentration of acid was increased, indicating that reversible reduction becomes more efficient in the battery acid. However, the highly acidic medium significantly suppresses the current. This led us to determine that the future direction of the project needs to focus on organic solvent systems with low ionic strength. In addition, preliminary electrochemical results on a cluster containing both iron and tungsten centers may simultaneously serve as both an anode and a cathode.

Significance

The primary accomplishment of this work to date has been the discovery of new techniques for preparing energy storage materials by the systematic variation of charge density, molecular symmetry, and metal populations. The elucidation of more of the fundamental properties of metal-oxide clusters will inevitably lead to the successful preparation of advanced materials with potential applications ranging from catalysis and molecular magnetism to medicine, as well as energy storage technology. This new base of scientific expertise and technical capabilities in the directed synthesis and characterization of energy storage materials will be disseminated through journal publications and international conferences. We also anticipate our results will be leveraged in the acquisition of funding for future flow battery projects, primarily through the Office of Electricity. This project focuses on the DOE's goal to create a more flexible, more reliable, and higher capacity US energy infrastructure by applying advanced science and technology to develop new materials for energy storage applications. It will further support DOE's missions to promote carbon neutral technologies, reduce petroleum imports, and to incorporate intermittent renewable energy sources into our electrical grid. We anticipate our results will enable widespread incorporation of low-carbon sources into stationary power generation for future US energy security. In short, we will provide a new path to boosting the energy efficiency of flow batteries.

Elucidating the Role of Interfacial Materials Properties in Microfluidic Packages

150968
Year 1 of 3
Principal Investigator: T. L. Edwards

Project Purpose

Microsensors for chemical and biological detection have seen relatively little field application because the small size and low cost of the microsensor are offset by the large size, high cost, and complexity of the balance of the sensing system — principally, the required external pumps and valves. Attempts to integrate these components into the sensor's microfluidic package have been limited by the lack of software design tools to simulate microfluidic device performance. Software simulation, in turn, is limited by our understanding of the materials properties at the interfaces of plastic laminate layers comprising the package. This project will address these shortcomings through the following initiatives: 1) designing experiments to extract the relevant mechanical, thermal, electrical, and chemical properties of plastic laminate interfaces; 2) developing a multiphysics model incorporating these parameters for plastic laminate microfluidic devices; and 3) demonstrating the model's capabilities by designing, fabricating, and testing a microfluidic pump.

A number of technologies have been employed to create microfluidic packages for microsensors. Of these, plastic laminate packaging provides an attractive combination of low capital and material cost, rapid prototyping, and complex mechanical and fluidic structures. This technology employs a variety of thin polymer and metal films bonded by adhesives, solvents, thermal fusion, and ultrasonic welding. The properties of these interfaces — thermal and electrical conductivity, mechanical deformation, adhesion strength, and chemical resistance — vary from the bulk properties of the laminate films and depend on the laminate composition and joining method employed. These interface properties will be the focus of this project. We will develop the experimental techniques required to measure them, use this information to populate a multiphysics model describing plastic laminate behavior, and, as a proof of concept demonstration, apply this model to design an integrated micropump, a critical component for high-performance microfluidic systems.

Summary of Accomplishments

We are collaborating with Rinco Ultrasonics USA, Inc. on the development of ultrasonic welding of laminates using high-frequency sources. If successful, this will lead to the acquisition of an ultrasonic welder to be used for further experiments. We developed a process for thermally bonding plastic laminates (thin and thick) using 3M™ Bonding Film 588. This process will be used for the development of other thermal joining processes for other plastics. We are also beginning the development of a laminate joining process using a single-molecule bridge.

Significance

This project will develop the capability for integrated microfluidic packaging design that will enable a greater range of fieldable chemical and biological microsensor systems for a variety of national security applications.

Fundamental Study of Metal/Oxide/Metal Memristor Physics and Device Optimization

151174
Year 1 of 3
Principal Investigator: M. Marinella

Project Purpose

In 2008, Hewlett Packard (HP) discovered that a titanium dioxide (TiO_2) capacitor was behaving in a similar manner to the “missing circuit element” theoretically predicted 40 years earlier. Since then, this resistor with a memory of the amount of electric charge passing through it, or memristor, has gained attention for its potential ground-breaking advancement of applications such as neural networks. For example, by functioning as a synapse, the memristor could enable complex learning and brain-like functionality in computers. However, before these applications can be realized, we must develop an understanding of memristor device physics and derive a detailed, predictive model of metal/insulator/metal (MIM) memristors. While HP has gained a solid understanding of the physics of the TiO_2 memristor, they have neglected other material systems that may offer significant advantages over TiO_2. A major scientific challenge will be to develop an understanding of memristor physics in novel materials, which offer significant advantages over TiO_2. For example, using TiO_2, HP has only been able to achieve a relatively low endurance of 10,000 cycles.

Understanding the physics of various material systems and will give us insight into which one is most appropriate when integrating it into a specific new application. Therefore, for this project, we propose to perform a fundamental study of the physics of resistive switching in MIM structures. This study will consist of three parts:

1. Theoretical analysis of physical theories describing memristive behavior in various materials;
2. the fabrication of MIM memristors from novel materials and characterization of these devices; and
3. the development of analytical models that reflects understanding of the physical properties of the memristor gained from 2, and can be used to predict and simulate memristor behavior.

Summary of Accomplishments

We have configured a computer with customized Labview programming dedicated to making measurements on memristors and storing memristor measurement data. Special routines have been added that allow measurement of the “pinched hysteresis loop” that is a fundamental attribute of the memristor. Additional programs are being developed that will sense the switching of the memristor and avoid overstressing it (which results in premature end of life). We also gained significant understanding of the TiO_2 memristor after studying and discussing HP’s work on the device at length with experts at Sandia and the originators at HP. From these discussions, we have concluded that HP researchers have a very accurate physical model of the phenomena occurring in this material system. There are a number of materials that may have significant advantages over TiO_2 in stability, endurance, and other novel properties. The memristor functionality in materials other than TiO_2 likely have differing physical origins. We have a much greater chance of contributing to the field by studying these more-novel materials. Along these lines, we have already fabricated working sol-gel ZnO memristors on glass substrates. We are in the process of experimentally optimizing these devices, after which we plan to make flexible ZnO memristors on Kapton (plastic) substrates. We have also demonstrated a working AlN memristor that was fabricated in the Microelectronics Development Laboratory. There has never been a memristor or even resistance switching effect demonstrated with this material, and thus, we have an excellent opportunity to explore the physics of a new memristor material system.

Significance

Eventually, we hope to use results from this project to spark interest in integrating memristor technology with Sandia's complementary metal oxide semiconductor (CMOS)7 technology. An integrated memristor/CMOS technology is expected to have a broad scope of potential impact with implications beyond present capabilities of CMOS-based technologies. Two areas where memristors should have a major potential for impact are as a memory, as well as in neural network applications. Neural networks have been touted as a useful algorithm to process information and efficiently solve certain problems. However, a hardware implementation of neural networks is inefficient because standard devices, such as the MOSFET, do not function in a manner that allows holding a synaptic weight as do biological synapses. However, the memristor is well suited for this operation. Acting as an electronic version of a human neuron, the memristor may allow the development of revolutionary computers capable of complex learning and "thinking." These systems have numerous possible national security applications.

The most immediate impact is for use as a non-volatile memory (NMV). The MOM memristor offers advantages over the traditional CMOS NVM cells such as flash and SONOS (Silicon-Oxide-Nitride-Oxide-Silicon). The major technological advantages of these memories are that they require low voltages (often less than 2V), fast program and erase speeds, and, depending on the material system, are capable of excellent endurance and retention. Furthermore, with nano-imprint technology, it is possible to create memristors with feature sizes smaller than 10 nm. This should enable memory densities greater than those possible with even the most aggressively scaled flash memory. From the perspective of Sandia's National Security Mission, evidence suggests that memristor based memory may be advantageous in both secure and radiation hardened applications. Along these same lines, it is possible to use the memristor in non-volatile logic circuits. This type of technology may form the basis of a low-power, high speed, non-volatile field programmable gate array.

Finally, the general S&T community will benefit from our work with novel material systems. There are a large number of possible material systems that are known to exhibit memristive behavior. However, due to the limited resources of the community working in this field as a whole, attention can only be given to a select handful of materials thought to show the most promise. Our work with sol-gel ZnO memristors involves a material that has not been well studied, but may provide a useful, inexpensive method of creating a flexible memristor. Furthermore, we have demonstrated the first AlN memristor.

NEW DIRECTIONS INVESTMENT AREA

This investment area focuses on research areas in which Sandia is newly embarking or has recently embarked, and hence, tends to encompass national security initiatives that seek to draw existing Laboratory expertise into new applications for national security. Best exemplifying such initiatives are projects in biological sciences — with emphasis on alternative energy and biothreat reduction — projects at the nanotechnology-bioscience interface, and those in the cognitive sciences — particularly as applied to support for decision-makers.

Atomic Magnetometer for Human Magnetoencephalography

Project 117842

Current magnetoencephalographic (MEG) imaging of a functioning human brain is difficult because its use of superconducting quantum interference devices (SQUIDS), requires large cryogenically cooled expensive hardware. Recently, atomic magnetometers based on measuring the spin precession of alkali atoms in a magnetic field have demonstrated equivalent sensitivity to SQUID-based MEGs. These atomic magnetometers do not require cryogenic cooling, thereby resulting in a much smaller package. This project, a collaboration with the University of New Mexico and its Mind Research Network has developed a prototype atomic magnetometer for human MEG measurements. The atomic magnetometer reads out the atomic response to a magnetic field via optical interrogation by a laser beam. The engineered device is a single optical-axis instrument that utilized a two-color pump/ probe scheme with four-channel output. Its long slender design with a 5 cm x 5 cm footprint on the human head allows high-density arraying around a subject's head. The project culminated in the successful measurement of MEG signals with two four-channel sensors on either side of the subject's head. In addition to its primary application in studying human cognition, a portable MEG has potential applications to several other DOE missions.

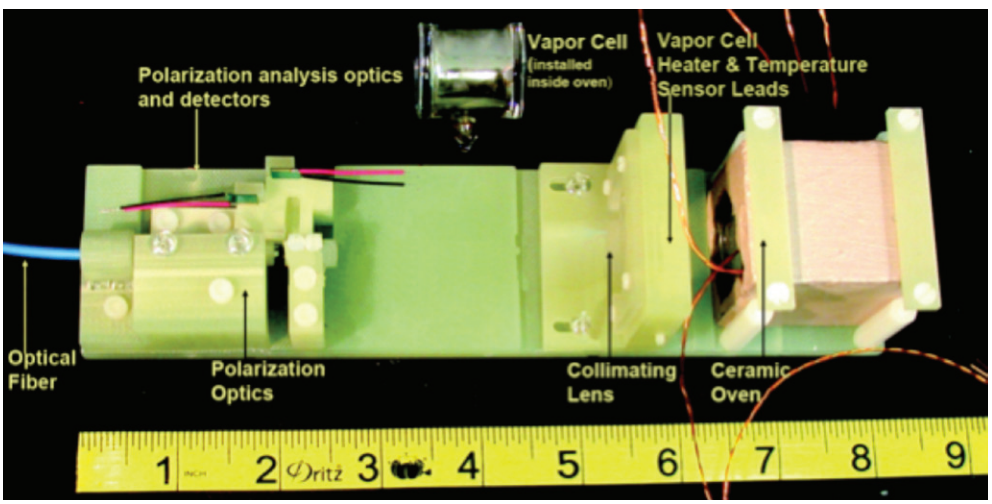
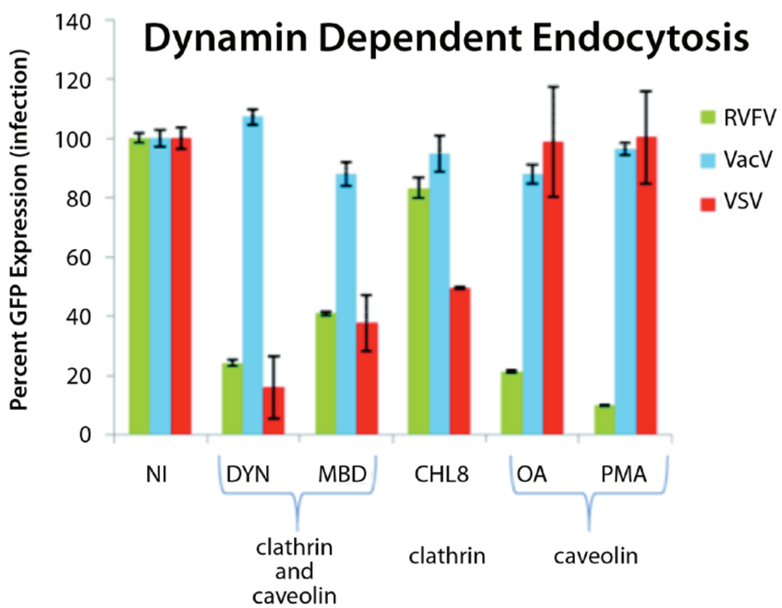


Photo of the instrument developed in this project.

Genome-Wide RNA Interference Analysis of Viral Encephalitis Pathogenesis

Project 141530

Over the past 10 years, the biological phenomenon of small interfering RNA (siRNA) silencing of gene expression (postranscriptionally) has been characterized and adapted to the experimental silencing of genes for various R&D purposes. Most notable is the ability to use this phenomenon to determine the involvement of specific genes in specific functions, by selectively silencing them (preventing the appearance in a cell of the proteins encoded by a gene). This project is developing a gene-silencing technology, based on siRNA, in order to investigate the human proteins involved in lethal encephalitis induced by two biothreats — Rift Valley Fever Virus (RVFV) and Nipah Virus (NiV).



Data indicating the probable route of internalization into cells (dynamin-dependent, caveolin-mediated endocytosis) during infection by Rift Valley Fever Virus (RVFV).

By systematically silencing more than 20,000 individual host genes and analyzing their involvement in viral infection, a comprehensive portrait of virus-host interactions should be revealed, that would then allow strategies for intervention. The project is developing microfluidic platforms that combine cell and siRNA arrays for high-level biocontainment compatible RNA-interference screening adaptable to an analysis of other biothreats at the molecular level.

NEW DIRECTIONS INVESTMENT AREA

Biomolecular Transport and Separation in Nanotubular Networks

117838
Year 3 of 3
Principal Investigator: D. Y. Sasaki

Project Purpose

A new pathway in cellular communication that uses lipid nanotubes to transfer biomolecules and organelles between cells has been discovered in macrophages, lymphocytes, and neural cells. These recent findings could completely alter our concept of cell communication and immune response. We propose to develop platforms, models, and methodology that will enable us to study nanotubule networks with live cells and cell model systems using micro- and nanoscale characterization tools. We shall develop lipid nanotube constructs that would couple into optical and electronic probes to investigate: 1) the formation of lipid nanotubes, 2) chemical/physical/biological phenomena that dictate selectivity of transported biomaterial, 3) the origin of forces used to shuttle biomaterials across the nanotube, and 4) the biological significance of the nanotubule connections.

Our approach brings together several strengths developed at Sandia to provide a thorough understanding of the role of lipid nanotubes in cellular networks and how they might be exploited for mediating immune response and cell communication. A proposed cell immobilization array platform coupled to a confocal microscopic imaging system and micromanipulator system could precisely interrogate the cellular processes leading to nanotube formation and cell activation by controlling cell spacing and biomaterial transport while monitoring cellular response. Sandia is particularly suited to address this important biological problem through its expertise in lipid membrane assemblies, theory of membrane structure and dynamics, unique 3D imaging methods, and transport via microelectrophoresis and motor proteins. The proposed work will advance the biochemical analyses, measurement technologies, and modeling of cell responses to pathogens. Understanding cell-pathogen interactions and the resultant cellular processes are critical to DOE's mission of national security. This research is exploratory in nature, and as an LDRD project, we can immediately address a new area of research that could lead to very high scientific impact in the biosciences.

Summary of Accomplishments

Over the course of the project we have developed new cell membrane model systems that enabled direct examination of protein-membrane interactions, such as mechanical stretching, steric crowding, and pulling forces of motile cytoskeletal filaments, that lead to lipid nanotube formation. We have successfully demonstrated the basic biophysics of steric interactions between bound proteins in domain structures that lead to membrane deformation into buds and tubules. We also explored the forces available from cytoskeletal network motility and their ability to generate extensive lipid nanotube networks. The relationship between membrane bending rigidity and the forces presented in a particular system was found to be key to the formation of nanotubular structures. Toward this understanding, we designed and prepared new lipids that partition toward specific structural phases in bilayers, such as liquid ordered phases that mimic the behavior of lipid rafts in cells. Results from our project provide valuable insights into the processes that are mediated by lipid rafts, such as signaling, pathogen invasion, and endocytosis. We demonstrated, for the first time, a totally synthetic system that generates membrane buds via protein affinity and provides physical insight as to how budding events may occur in cells.

We have also designed and developed a microfluidic device that allows the capture and manipulation of giant lipid vesicles to direct the formation of lipid nanotubes and the creation of network structures. In the device, both domains and lipid nanotubes on giant vesicles were readily oriented in a matter of seconds using a mild electric field. Lipid-tethered surfaces were developed to selectively capture the giant vesicles.

With cell studies, we established facilities and protocols for time-lapse imaging of cells growing in culture to study nanotube formation. We found that nanotubes formed with macrophages in the presence of toll-like receptor 3 (TLR3) and toll-like receptor 2 (TLR2) stimulants.

Significance

We have discovered a number of unique insights and processes from studies with model cell systems that will provide a foundation for scientific understanding of the physics, chemistry, and mechanics of membrane curvature. Most importantly, we showed that the structural transformation of microdomains in cell membranes, such as budding for endocytosis or tubule formation upon virus entry, which were thought to be brought about by specific membrane insertion processes, can be induced through the basic mechanics of steric repulsion of particles bound to a surface. The results of our work introduced new paradigms for the understanding of membrane structural transformation and the interplay between membrane bending rigidity, line tension of lipid domains, and protein affinity to direct specific membrane curvatures and architectures. These results call into question the long-held theory of protein wedging into membranes as the main route for curvature induction in biological systems.

With the development of vesicle capture surfaces and microfluidic devices to manipulate and orient structured vesicles we have prepared the foundation for a new concept in fluidic architecture. Using giant vesicles as reaction vessels and lipid nanotubes as pipelines we can construct nanofluidic systems that could synthesize molecules and materials at picoliter volumes with biocompatible materials and systems for in vivo applications. We have prepared novel tethered surfaces that selectively capture giant vesicles from solution with minimal perturbation to the vesicle structure. The vesicle is then oriented using a mild electric field (< few volts) and nanotube formation stimulated using one of our nanotube growth processes. We will continue the development of these platforms and techniques with a goal towards reconfigurable nanofluidic devices.

We have built up significant capabilities during the course of this project regarding imaging platforms and microscopes. One of the platforms allows long-term imaging of cells under culture conditions. This has enabled us to follow the interaction of cells and the growth of cellular nanotubes over a period of greater than 16 hours. What we have learned is that these nanotubes form as cells roam over a surface, form intimate contacts, and then separate from one another. These processes occur over a period of many hours and are only made evident through time-lapse imaging. Such capabilities provide a unique window on cellular activities regarding motility, aggregation, and morphology. Another platform capability is the microfluidic jetting system for the preparation of giant unilamellar vesicles. This platform allows the formation of vesicles with precise internal contents and membrane composition. Such capability is part of the enabling technology for the nanofluidic systems described above. Regarding imaging, we have assembled new microscopes with cooled cameras for low-light detection allowing single molecule tracking and high resolution (~220 nm).

Refereed Communications

J.C. Stachowiak, C.C. Hayden, and D.Y. Sasaki, “Steric Confinement of Proteins on Lipid Membranes can Drive Curvature and Tubulation,” *Proceedings of the National Academy of Sciences*, vol. 107, pp. 7781-7786, April 2010.

Initiation of the TLR4 Signal Transduction Network — Deeper Understanding for Better Therapeutics

117839
Year 3 of 3
Principal Investigator: M. S. Kent

Project Purpose

The innate immune system represents our first line of defense against microbial pathogens. Toll-like receptor 4 (TLR4) is the cell-surface receptor primarily responsible for initiating the innate immune response to lipopolysaccharide (LPS), a major component of the bacterial cell envelope. TLRs represent a possible point of intervention by which we can effectively control inflammatory responses. However, much remains to be discovered about the molecular mechanisms underlying TLR4 activation. Design of small molecule therapeutics to modulate immune activation stand to benefit greatly from a better understanding of TLR4 activation and membrane proximal events. Prior studies have shown a strong ligand specificity for human TLR4/MD2 (an extracellular molecule associated with the extracellular domain of TLR4), and also strong variations in signaling response to a specific ligand among TLR4/MD2 receptors from different mammalian species. Recently, the crystal structure of dimeric TLR4/MD2 with bound ligand was published. This showed that TLR4/MD2 dimers are stabilized by rather subtle interactions upon ligand binding; a hydrophobic interaction between an exposed tail of MD2-bound LPS and conserved phenylalanines of TLR4, and ionic interactions between the phosphate groups of LPS and positively charged residues of TLR4 and MD2. These results suggest that variations in the number of acyl chains of LPS or in specific residues of TLR4 and MD2 near the dimer interface will alter the stability of the heterotetrameric complex. Thus, the data to date suggest that small changes in the dimer-monomer equilibrium or in the average lifetime of a dimer may explain the wide range of signaling responses observed. Therefore, we are developing a model system and biophysical probes to examine the equilibrium and dynamics of ligand-induced dimerization of TLR4/MD2 with the goal of correlating these data with variations in signaling levels in live cells.

Summary of Accomplishments

- Determined conditions for LPS-induced complexation of soluble TLR4/MD2
- Discovered strong variation in LPS-induced complexation of TLR4/MD2 when CD (cellular differentiation antigen)14 and lipopolysaccharide binding protein (LBP) are present
- Developed new total internal reflection fluorescence TIRF-based method to quantify distribution of oligomers in soluble protein complexes that complements the qualitative information from gels (manuscript in preparation)
- Observed first evidence of LPS-induced complexation of soluble TLR4/MD2 by fluorescence resonance energy transfer, but the signal was weak
- Obtained cryo-electron microscopy images of TLR4/MD2-bound to liposomes for several surface coverages, analysis in progress (collaboration with University of Texas Medical Branch)
- Developed TIRF-based method to study LPS-induced complexation of membrane-bound TLR4/MD2, but results were inconclusive. Further developmental work is needed
- Obtained first evidence for LPS-induced oligomerization of membrane-bound TLR4/MD2 by fluorescence correlation spectroscopy

Significance

To date, the relationship between LPS-induced TLR4 receptor oligomerization and intracellular signaling, which controls the innate immune response, is not clearly understood. This is important for improved design of adjuvants of vaccines and small-molecule therapeutics to modulate the immune response. These capabilities are relevant to NIH, and DHS and DoD biodefense missions.

Diversity in innate immune response and infectious disease outcome is known to arise from genetic variability in TLR4 and its coreceptor MD2 among hosts and from diversity among LPS chemotypes. In the present work, we developed in vitro methods to study LPS-induced oligomerization of TLR4/MD2 as a function of LPS and TLR4/MD2 concentration. This methodology can be used to determine association constants for TLR4/MD2 oligomerization induced by LPS from various organisms and to understand how those association constants are altered by the presence of therapeutic molecules (both agonists or antagonists). The in vitro studies of TLR4/MD2 oligomerization could be correlated with expression levels of signaling in mouse macrophage cells using a fluorescent reporter. This would establish if a direct correlation exists between the association constant for receptor oligomerization and intracellular signaling through the TLR4 receptor. If such a correlation exists, our method will provide a rapid and inexpensive screen for innate immune system modulators targeting TLR4 that can be used prior to animal testing. Furthermore, knowledge of the association constants for receptor oligomerization would allow development of therapeutic agonist or antagonists that are only as potent as needed.

The fact that LBP alone, but not CD14 alone, resulted in a decrease in the TLR4-MD2 concentration for the onset of LPS-induced oligomerization is very important. The role of LBP may be due to extraction of LPS from micelles with its shuttling to TLR4/MD2. However, since CD14 alone has no apparent affect on the association of the receptor, it is not clear what role CD14 plays. Yet CD14 has been shown to have a critical effect on TLR4 signaling. More work is needed to understand this.

Refereed Communications

M.S. Kent, J. Murton, D.Y. Sasaki, S. Satija, B. Akgun, H. Nanda, J.E. Curtis, J. Majewski, C. Morgan, and J.R. Engen, "Neutron Reflectometry Study of the Conformation of Nef from HIV Bound to Lipid Membranes," *Biophysical Journal*, vol. 99, pp. 1940-1948, September 2010.

"Trojan Horse" Strategy for Deconstruction of Biomass for Biofuels Production

117840
Year 3 of 3
Principal Investigator: M. Hadi

Project Purpose

Our proposed disruptive technologies are focused on developing a unique biomass deconstruction technology through transgenic plants (using model systems, *Arabidopsis thaliana* and *Brachypodium distachyon*) that will enable later implementation in the bioenergy feedstocks of switchgrass and poplar. A portfolio of the enzymes involved in cellulosic deconstruction will be expressed individually and in potentially synergistic combinations within plants. The unique aspects of this approach combine the substrate (cellulosic biomass) with the biocatalyst (cellulose enzymes; rationally engineered highly productive extremophilic enzymes), and use the native plants' protein expression machinery to combine all of these elements into a single system, targeted to specific cellular locations. The actuator will remain inactive during normal plant proliferation but is triggered to become a "Trojan horse" during pretreatment conditions (high temperatures, >90 °C and extreme pH, <3 and >9). This approach is a significant departure from established biomass conversion platforms that typically separate the pretreatment step and enzymatic depolymerization into two distinct unit operations. These two unit operations represent approximately 40–50% of the costs within second-generation biorefineries. These costs would be greatly reduced by combining these two process steps, in addition to the decreasing costs associated with eliminating the need to produce these enzymes off site, in lieu of expressing the enzymes within the biomass itself.

Summary of Accomplishments

- This project validated Sandia's investment/capability in enzyme engineering by demonstrating an industrial lignocellulose bioprocess and autohydrolysis of cellulosic material through a partnership with the US Department of Agriculture.
- Cell-wall-degrading enzymes, when expressed in plant tissue and activated, resulted in similar sugar yields when compared to exogenous addition of Novazyme enzyme cocktail.
- We achieved noteworthy savings in enzyme and heating input costs normally associated with acid hydrolysis.

Significance

The current research would benefit a broad spectrum of ongoing DOE and Sandia activities, especially those associated with low-carbon transportation fuels. In particular, the production of integrated systems that can reduce costs of biomass conversion into fermentable sugars is of significant interest to DOE.

Enhanced Performance of Engineered Neural Networks using Nanostructured Probes and Predictive Computational Modeling

117841
Year 3 of 3
Principal Investigator: C. D. James

Project Purpose

Functional enhancement and repair of neural tissue circuitry requires the ability to engineer neural-tissue networks that can be designed, measured, and modified to test hypotheses regarding the relationship between network architecture and function. We are currently developing methods to repair/enhance higher cognitive functions in the central nervous system with applications in deciphering the mechanisms involved in human decision-making. These methods rely on microfabricated chemical and topographical cues for guiding dissociated neurons into functional networks. We are utilizing patch-clamp electrophysiology techniques to detect synaptic memory in the form of long-term potentiation (LTP) and long-term depression (LTD) in engineered networks. This will be the first characterization of LTD/LTP in engineered networks, with a first demonstration in homogeneous hippocampal neuron cultures. With our collaborator at the University of Texas at Arlington, we will combine these techniques with microfluidic compartmentalization to control the development of functional connections between different cell types, such as motor neurons and muscle cells. This work will then enable the development of heterogeneous cultures of cortical and striatal neurons in order to engineer replicates of corticostriatal networks, a region of the brain with a strong role in integrating reward, sensory, and motor information for making complex decisions. In addition, we are currently collaborating with LDRD project 105936, to utilize optical electrophysiology probes to measure neural activity in large populations of neurons, a feat not possible with patch clamp technology. Finally, experimental data from engineered networks will then be used to train a computational model to predict network architectures with enhanced performance, and the model will be validated with experimental measurements on the constructed neural-tissue network. We will fabricate and characterize cell network guidance substrates in the Microsystems and Engineering Sciences Applications (MESA) facility. Cell culturing and electrophysiology will occur at the Center for Integrated Nanotechnology (CINT).

Summary of Accomplishments

First, we developed a new dual guidance cue method for generating topographical and chemical patterns to influence neuron cell attachment and outgrowth. Utilizing this technology, we were able to correctly polarize neurons in terms of their directional growth of axons and dendrites, and we provided insight into the strategic geometric design of those cues for controlling polarization. Specifically, we found that a gap distance of 6 microns was optimal for polarizing neurons. Second, we developed a novel method for guiding neurons on artificial substrates using buried microfluidic channels.

After these demonstrations, we utilized polydimethylsiloxane micromolding technology to create compartments for cortical and striatal neurons, with interconnecting channels to permit controlled interactions of neurites between cell populations. We used immunostaining to identify cell compartments (axons, dendrites, cell bodies) as well as GABA-ergic synaptic connections. Electrophysiological recordings showed that the cells were functioning, given that spontaneous and elicited action potentials were measured in both cortical and striatal neurons. Perforated patch recordings also detected synaptic activity in an engineered network in the form of inhibitory post-synaptic potentials. We also conducted preliminary experiments with fluorescent quantum dots

(QDs) showing that QDs successfully interacted with neuron cell membranes and were not taken up into the cytoplasm by healthy neurons. However, additional testing is required to determine if such probes can be used to detect action potentials and/or subthreshold events.

With respect to computational modeling, we imported many of the biophysical mechanisms of neurons into Xyce, and then we adapted and combined several models from the computational neuroscience literature to explore the expected response of medium spiny neurons (found in the striatum) to the input stimuli used in our experiments. Using the open-source code NEURON, we have reached the level of examining the calcium dynamics involved in signaling within the medium spiny neurons that dominate the striatum.

Significance

We successfully leveraged the technology developed in this project to an external university collaborator, who is successfully utilizing the microfluidic compartmentalization technology to study the development of the cells involved in the neuromuscular junction (NMJ). Our results show that segregation of muscle cell and sensory neuron cell bodies may be crucial for proper development of the NMJ, and we are the first to report that spontaneous activity in skeletal muscle cells can be suppressed upon compartmentalized co-culture with spinal cord neurons. This provides just one example of how co-culturing multiple cell types can be used to study the formation and development of complex tissues. We believe this technology has far-reaching potential for use as a research tool in laboratories for in vitro studies of living cells at barriers, including lung tissue, stomach lining, etc. These areas of research would be of significant interest to the defense community in that this technology would provide a test-bed for understanding routes of infection and mitigation strategies for infectious disease and biologically engineered threats.

The next step with respect to computational modeling—pursued in a separate project—is to finalize several of the neural plasticity components such as the neurotransmitter glutamate receptors, AMPA (α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid) and NMDA (N-methyl D-aspartate), and the CB1 (cannabinoid type 1) receptor. This advancement would open up the doors to allow Xyce to be utilized for a large range of biochemical processes that rely on complex signaling networks, including immune response to infectious or environmental agents (vaccine development) and molecular mechanisms involved in cognitive processes.

Atomic Magnetometer for Human Magnetoencephalography

117842
Year 3 of 3
Principal Investigator: P. Schwindt

Project Purpose

Magnetoencephalography (MEG) is one of only a handful of noninvasive techniques for measuring electrical activity in the brain. MEG requires a magnetic field sensor with a sensitivity of a few femtoTesla/Hz$^{1/2}$ and thus has historically been performed with cryogenic superconducting quantum interference devices. Recently, atomic magnetometers, based on measuring the spin precession of alkali atoms in a magnetic field, have demonstrated equivalent sensitivity but do not require cryogenic cooling, resulting in a much smaller package. With an atomic magnetometer, one can envision a much more cost-effective, smaller device. We propose to develop an atomic magnetometer for human MEG measurements.

To develop the atomic magnetometer, we need to design for high sensitivity while keeping in mind the requirements of the human subject. A major component of the effort will be to collaborate with MEG experts at the Mind Research Network (MRN) and the University of New Mexico to provide us guidance in the design and use of the device for human subjects. The high spatial resolution of MEG comes from using multiple sensors around the head. Because the atomic magnetometer reads out the atomic response to a magnetic field via optical interrogation, we can readily achieve multichannel operation by simply detecting separate regions of the probe laser beam. We will first focus on achieving high sensitivity and proper magnetic shielding. Then we will develop highly sensitive, semi-transportable devices that can be largely operated by the neuroscientist, culminating in a high quality MEG measurement of a human subject at MRN.

Summary of Accomplishments

The key accomplishments of this project have been to develop a compact single-optical-axis atomic magnetometer and using it to measure MEG signals in a human subject. For MEG, the active area of the sensor (the atomic vapor cell) needs to be as close a possible to the subject's head. In addition, the sensor needs to be compact to allow the sensors to be densely arrayed around the head. In a conventional atomic magnetometer, the atomic state is prepared and interrogated with a pump and a probe beam propagating perpendicular to each other. We constructed a sensor where the pump and probe beams are combined on a single optical axis. The beams are retro-reflected after passing through the vapor cell to create a long slender sensor with the cell at one end. This geometry places the cell within 1 cm of the head and allows dense packing of sensors. To maximize sensitivity in the single axis design, we have developed a novel two-color pump and probe scheme where the pump at 795 nm is easily separated from the probe at 780 nm for high-fidelity detection. We have demonstrated a sensitivity of 4.5 fT/Hz$^{1/2}$ with a bandwidth of 12 Hz.

Using a pair of atomic magnetometers placed on either side of the head just above the ears, we have recorded the evoked response near the auditory cortex due to auditory stimulation at 1000 Hz and 2000 Hz and the evoked response near the somatosensory cortex due to median nerve stimulation. These measurements were taken in the magnetically shielded room at MRN. Unfortunately, the noise is this room is on the order of 1000 fT while brain signals are ~100 fT. By averaging signals ~300 stimuli, we observed the expected response in both the auditory and somatosenory cortex.

Significance

. Because an MEG system using atomic magnetometers could become portable and miniaturized, numerous national security applications are enabled by this work. One promising area of application is to deploy an atomic-magnetometer-based MEG system near the battlefield to help detect and diagnose traumatic brain injury (TBI) and post traumatic stress disorder (PTSD), the "signature injuries of the wars in Iraq and Afganistan." Because atomic magnetometers do not require cryogenics, it is realistic to conceive of such a portable system. Recent research with conventional MEG systems is showing that MEG is a good tool for diagnosing TBI and PTSD. In addition, precision magnetometry can be applied to applications critical to DOE, such as, underground detection, remote sensing, and materials reliability.

High-Throughput Discovery and Validation of Biomarkers for Biodefense

117992
Year 3 of 3
Principal Investigator: G. Chirica

Project Purpose

The goal of our project was to discover a candidate biomarkers profile that was potentially Anthrax (*Bacillus anthracis*) specific, and that could reduce the impact of outbreaks/bio-terrorist attacks. The mouse model is ideal for this type of study, but the small amount of serum available significantly limits the breadth of infectious studies, including biomarker discovery studies. Towards that end, we developed a high-throughput platform for automated multidimensional processing, mass spectrometric analysis of µL volumes of serum, to enable multiple time point analysis and infection studies. This Modular Automated Processing System (MAPS) is unique in the field because it allows rapid prototyping and methodology development in processing trains designed for meso and microfluidic applications. In particular, the platform is designed to enable construction of multiple serial and parallel workflow combinations that can focus on various protein classes and minimize the huge background typical of bodily fluids such as serum, plasma, urine, cerebrospinal fluid, etc. We developed a module that executes most of the current benchtop protocols in an integrated automated fashion.

A major limitation is the lack of technology that enables verification of such biomarkers panels, particularly in clinical settings, i.e., point-of-care analysis. During this project, we also developed and tested a multiplexed portable device for rapid, cost-effective and sensitive assays for biomarker panel verification. This fiscal year, to our 8-channel chip and rotary scanner detector, we added the capability of multistage isoelectric focusing (IEF) fractionation in the chip, which combined with immunoassays, would also enable detection of biomarkers and distinguish their posttranslational modifications.

Summary of Accomplishments

Our unique Modular Automated Processing System (MAPS) matured to include real-time monitoring of the various processing steps, automated injection, collection, etc., offering essentially 24/7 operation. It includes modules for depletion of high-abundance proteins, size fractionation based on size — high- and medium-molecular-weight class, and the peptidome (proteins of < 30 kDa often cited as potential time-sensitive descriptors of the physiological conditions). We built modules for selective protein enrichment based on posttranslational modifications: phospho-enrichment using IMAC (immobilized metal affinity chromatography) or TiO_2 matrices, and glyco-enrichment using lectin columns. We built and tested systems of 3, 4 and 5 dimensions, including size fractionation, followed by immunodepletion, cation-exchange, buffer-exchange and digestion. The result of automated processing is rapid processing (20 times faster than gel methods, in some cases, or 10 fold faster than other benchtop workflows) while enabling simultaneous analysis of post-translational modifications.

To further test and understand the advantage of our platform compared to state-of-the-art technologies, we analyzed pooled mouse serum using three distinct workflows and compared the duration, fractionation effectiveness, and the protein coverage. We have shown, for the first time, that although these three trains target the same group of proteins (the peptidome), there are only 10% of proteins common to all three workflows. This is significant because a wider protein pool increases the chance to discover the most robust, stable, high-concentration and specific biomarkers. We tested this platform on serum from mice prior to and following intranasal exposure to Anthrax. We identified over 30 proteins that show much higher concentration in the infected versus naïve sample. Some of these proteins are acute inflammatory markers. This fiscal year, we added multistage IEF fractionation to our 8-channel chip and rotary scanner detector, combined with immunoassays to enable detection of biomarkers and distinguish their post-translational modifications.

Significance

The Modular Automated Processing System (MAPS) was initially designed to address a much broader application spectrum. It can analyze and process not only proteins, but also nucleic acids, metabolites in samples such as cell cultures, homogenized tissues, any bodily sample. Its versatility and ability to rapidly prototype a sample customized system will enable us to tackle a wide variety of biodefense, biofuels and health related applications. Its small footprint makes it readily adaptable for use in Biosafety level 3 and 4 laboratories where the safety of the operators analyzing highly toxic substances is a major issue.

We expect to be able to expand our preliminary data on potential Anthrax biomarkers and run more complex infectious studies experiments in which larger cohorts, mice and non-human-primates, infected at various doses and monitored at frequent time points, can give a clearer picture on what the most robust biomarkers are, how specific they are for various infectious diseases (including differentiation among various biological warfare agents), and most importantly, what the markers that indicate exposure prior to symptomatic onset are.

Refereed Communications

G.J. Sommer, A.K. Singh, and A.V. Hatch, "Enrichment and Fractionation of Proteins via Microscale Pore Limit Electrophoresis," *Lab on a Chip*, vol. 9, pp. 2729-2737, September 2009.

A Systems Biology Approach to Understanding Viral Hemorrhagic Fever Pathogenesis

130781
Year 2 of 3
Principal Investigator: B. Carson

Project Purpose

Arenaviruses such as *Lassa* cause lethal hemorrhagic fever in humans and are pathogens of bioterror concern. They may be transmitted by airborne routes and have incubation times under two weeks with mortality up to 30%. A fundamental problem in understanding their pathogenicity is that infected and uninfected cells can exchange information, reciprocally influencing their behavior. Thus, cell population level experiments will never tell us why some people survive while others die from Lassa fever because many ill effects of viral infection are mediated by the immune system rather than by the virus itself. Excessive type I interferons (IFNalpha/beta) drive hemorrhagic symptoms, but arenaviruses paradoxically appear to block production of these cytokines. We hypothesize that this apparent contradiction is due to differential effects of the virus on the infected cell versus uninfected neighboring cells. This hypothesis is impossible to test by conventional means that asynchronously infect thousands of cells simultaneously, thereby masking the difference between first- and second-order effects. We will deconvolute this system by isolating and infecting individual cells then performing unprecedented measurements of IFNalpha/beta and other response-critical cytokines such as tumor necrosis factor alpha (TNFalpha) with novel fluorescent transcriptional reporters. Using a microfluidic cell isolation platform, we will compare isolated cell to population level infection to discover how these viruses provoke lethal cytokine production. The devices we will use were originally developed to study toll-like receptor signaling in response to bacteria. However, with some modifications and new experimental protocols, we will use these flexible devices to address otherwise impossible fundamental biological questions. This project is high risk because we will attempt difficult high-sensitivity cytokine and transcription factor measurements on isolated cells, which has never been done. Although this may not be possible, there is currently no other way to obtain this critical information.

Summary of Accomplishments

We successfully acquired viruses and developed infection and propagation protocols. We established a collaborative contract with the University of Texas Medical Branch. We generated and tested fluorescent cytokine reporter constructs and stable cell lines expressing them. We validated the reporters using microscopy and flow cytometry both on and off-chip. We demonstrated responsiveness of the reporters to Sendai virus infection as well as to purified viral and bacterial components. We found that the reporters respond rapidly (2 hours) to stimulation and are also responsive to stimulus withdrawal over a period of days. We designed and made plasmids encoding nuclear factor kappa B (NF-κB) p50 fused to cyan and cherry fluorescent proteins. We built pressure control and valving equipment required for our experiments and completed fabrication of our single-cell array microfluidic chips. We redesigned the user interface to be less error-prone and to automatically record system status. We captured and isolated individual reporter cells in a microfluidic device and measured their cytokine production in response to viral components. Measurements of this kind have never been done before. We generated a preliminary NF-κB network model and began predictions for the kinetic behavior of individual transcription factor subunits. We built a training set for host-virus protein-protein interactions and generated a list of predictions to test empirically.

Significance

This project benefits the DOE scientific and defense and DHS awareness and response strategic goals by addressing a key deficiency in our understanding of emerging infectious hemorrhagic fever virus pathogenesis. We will employ Sandia's advanced microfluidic technologies to develop biomarker assays of unprecedented sensitivity to study the response of individual cells to a National Institute of Allergy and Infectious Diseases category-A virus, ultimately supporting therapeutic and vaccine strategies to combat these viruses.

Biomolecular Interactions and Responses of Human Epithelial and Macrophage Cells to Engineered Nanomaterials

130782
Year 2 of 3
Principal Investigator: S. M. Brozik

Project Purpose

Nanotechnology holds a vast promise of enabling a wide range of transformational technologies, but also has inherent risks with respect to human health and environmental effects. In fact, engineered nanoparticles are already being used in a variety of commercial products including “wrinkle-free” clothing (silver nanoparticles) and sunscreen (metal oxide nanoparticles) despite the overall lack of knowledge concerning the associated health impacts. Examples such as the ability of carbon nanotubes to cross the blood-brain barrier, however, suggest that nanomaterials may represent a significant and serious risk to human health. Thus, the National Nanotechnology Initiative (NNI) has recognized that there is an immediate and critical need to establish a basic understanding of the health-related issues regarding engineered nanomaterials. A critical challenge embodied within this problem arises from the ability to synthesize nanoparticles with a wide array of physical properties (e.g., size, shape, composition, surface chemistry, etc.), which, in turn, creates an immense, multidimensional problem in assessing toxicological effects. We propose to address this challenge by establishing fundamental relationships between the physical and chemical properties of engineered nanoparticles and the associated biomolecular interactions and response of cells. Based on the most likely routes of exposure (i.e., inhalation, ingestion, and dermal) and highest associated risk, we investigate the cell-surface interaction and response pathways of epithelial and immune cell lines that are involved in the toxicological response to xenobiotics (e.g., nanoparticles) using advanced imaging techniques, biochemical analyses, and chip-based sensor arrays.

Summary of Accomplishments

We have made significant progress in developing correlations between toxicity/response of immune cells and the size, surface functionality, and shape of quantum dots (QDs). QDs of seven different sizes and two different functionalities (amine-, carboxylic-terminated) were characterized using brightfield and fluorescence microscopy. QDs exhibit different photoluminescent properties based on size and differential quenching in media, as demonstrated in prior work in this project. Therefore, we quantified the emission properties of each QD in the cell media and developed normalization factors to compensate for these differences and normalize the uptake measurements. Three-way analysis of variance was used to discern significant differences based on main effects as well as interactions. Results suggest significant interaction between QD size, surface chemistry, and concentration, illustrating that the relationship between uptake and QD properties is not one dimensional, but is affected differentially by a variety of factors. For example, uptake generally increases as a function of increasing QD size, reaching a peak with QDs emitting at 605 nm and 620 nm in our studies. Interestingly, uptake decreased significantly between QD 620 and 655 particles. We hypothesize that this observation results from differences in shape and not size. We are currently performing transmission electron microscopy (TEM) analysis of all QDs to discern size and shape. Our initial data from TEM images reveal that while overall particle size increases with emission wavelength, QDs emitting at 605 have markedly larger aspect ratio than the other samples, thus appearing more rod-like. We have also employed total internal reflectance fluorescence microscopy to selectively study particle behavior very near the cell membrane, tracking single QDs on the cell surface. Hyperspectral imaging was utilized to study the distribution of QDs after internalization. These two imaging techniques further demonstrated that the rod-shaped quantum dots resided in the cell membrane longer than more spherical ones, and were thus taken up more slowly.

Significance

This project will discover fundamental science important to the human health impact of nanoengineered materials. The entry and interaction of nanoparticles into the human body has generated critical scientific questions and an increasingly fearful perception within federal funding agencies and the general public. For example, the Department of Energy has undertaken a strong, proactive commitment to the safe handling and disposal of nanoparticles at the five DOE Nanoscale Science Research Centers. The primary caveat is that the environmental safety and health recommendations are largely based on properties of the bulk materials (e.g., cadmium for QDs) or inferred similarities (e.g., asbestos and carbon nanotubes), and may not correlate directly with the intrinsically different properties of nanoparticles. Thus, this project will provide a scientific understanding of how nanoparticles interact with cells and how their physical properties may have deleterious effects on cell health and physiology.

In this project, Sandia has anopportunity to establish a leadership position with respect to evaluating the health-related implications of nanoparticle exposure. Issues of nanotoxicology and nanomaterials safety will directly impact Sandia's mission in nanoscience (e.g., the Center for Integrated Nanotechnologies) and National Security (e.g., nefarious use of toxic nanoparticles), as well as provide fundamental science beneficial to the larger nanoscience, biological, and toxicological communities.

From Algae to Oilgae: In Situ Studies of the Factors Controlling Growth and Oil Production in Microalgae

130783
Year 2 of 3
Principal Investigator: S. Singh

Project Purpose

Transforming algal oil into biodiesel requires solving the problems of growing large robust algae populations that produce high fractions of easily harvested specific fatty acids. Current efforts somewhat ignore the fundamental biological processes in play. As a consequence, important issues regarding cell growth, utility of the fatty acids produced, and efficient oil recovery have been difficult to resolve. We will use our unique in-situ imaging capabilities (fluorescence and Raman) to develop fundamental, science-based detailed insights into triacylglyceride (TAG) production. Fatty acid composition and production vary between algae and in response to altered environmental conditions. In FY 2010 we will focus on the quantification and compositional analysis of TAGs produced by algal cells in real time with newly developed label-free hyperspectral imaging methods to determine the molecular factors controlling fat composition and production. Problems associated with efficient lipid extraction and lack of reliable lipid characterization techniques have so far made it difficult to generate multifactorial response curves of the important factors and to explore lipid triggers. The electrochemical and in-situ imaging studies will yield information needed for discovering and manipulating lipid triggers in algae to achieve enhanced TAG production. This project will undertake the first comprehensive study of important biotic and abiotic factors for fast growth and enhanced lipid production and may enable discovery of ion channels responsible for ion efflux. We will track channel activity in live algae stressed by various environmental factors to discover the significance of ion efflux to algal growth and to identify channels to manipulate for optimized growth, adaptation to fluctuating environmental conditions, and response to impaired water. Knowledge of the biological mechanisms and algal cell functions will provide the missing foundation for efficient transformation of algal oil into biodiesel thus directly furthering Sandia's commitment to energy, water, carbon sequestration, and national security.

Summary of Accomplishments

During FY 2010, we accomplished several outcomes important to meeting our milestones, and we are positioned to complete our goals by the end of this year. The research has brought basic bio-mechanistic understanding to problems confronting a cost-effective algal biofuel strategy. Furthermore, we have made significant progress in extending our analyses to include the impact of osmotic shock and photosynthetically active radiation modulation, in addition to the nutrient flux lipid triggers studied previously. Finally, we have developed and applied novel optical and electrochemical interrogation techniques to complement and clarify methods commonly used in the broader algal bioenergy community.

The first significant achievement for this fiscal year was to extend our hyperspectral imaging efforts to additional algal biofuel genera (*Dunaliella*, *Nannochloropsis*, *Chlamydomonous*, *Botryococcus*, *Neochloris*) and expand the growth conditions to include varying light exposure levels and salinity. Next, we performed experiments to establish the prospects for a divergent strategy based on algal biomass accumulation in autotrophic conditions followed by a hetero-autotrophic phase for accumulation of TAG. In order to address questions concerning photosynthetic efficiency, a novel single-cell pulse amplitude modulation (PAM) fluorometer was developed to overcome repeatability problems associated with PAM fluorometry of algal suspensions. Our current effort combines this and our previously developed methods to probe the interdependence of environmental factors of algal adaptation in a multi-parametric assay.

Significance

Development of a robust supply of renewable biofuels is a priority, and algae is a potential source of biofuel production. This research can help establish procedures for optimizing biofuel algal biomass for enhanced lipid production. This work complements current biofuel, energy-water nexus, and water desalination projects. Our project expands the knowledge base to support the biofuels mission, and advances capabilities that will benefit DOE Offices of Science and Energy Efficiency and Renewable Energy, and industry.

K-Channels: On/Off Switches of Innate Immune Responses

130785
Year 2 of 3
Principal Investigator: S. Rempe

Project Purpose

Infectious diseases from pathogenic microbes annually account for one-quarter of all deaths worldwide and, in a pandemic year, one single pathogenic strain can kill more than 2% of the world's population. Current efforts to stave off the "inevitable" next infectious disease pandemic focus on the traditional prescription of developing new vaccines and drugs that kill microbes, so far with disappointing results. In order to progress, a new paradigm in medical treatment is needed for fighting infectious disease. Inspired by recent work, we will look to the immune cells, not the microbes, for potential drug targets. New evidence strongly suggests that a molecular switch exists in the cell membrane that can actively modulate immune responses to pathogenic attacks. Unexpectedly, the switch exists in the form of a potassium-selective channel protein. We propose to discover the role of K-channels in innate immune responses to pathogens of importance to biodefense using a fundamental bioscience research and development strategy that capitalizes on our recent advances in molecular modeling, high-resolution optical and electronic cell interrogation techniques, and microfluidics platform development. With these unique methods, we will interrogate the relationship between K-channels and immune responses with unprecedented accuracy and scope, ranging from the atomic resolution of single protein channels, to signaling processes of individual immune cells and cell populations. The scientific insight gained should enable rational manipulation of channel activity in order to boost or suppress innate immune responses, depending on the pathogen threat at hand. Our proposed work supports Sandia's considerable commitment to biodefense and emerging infectious disease, homeland security and defense, and public health.

Summary of Accomplishments

We have identified channel types in mouse immune (macrophage) cells by biological assays and whole cell electrophysiology. We have tracked the immune response after stimulation by molecules that block channel proteins and molecules that initiate immune responses (using the pathogenic factor from *E. coli*) using fluorescent probes, and confirmed that blocking the channel also inhibits the immune response. Our studies have provided mechanistic insight about this inhibition that correlates the type of channel protein in macrophage cells with a quantitative analysis of its inhibitory effect on two hallmark events in a toll-like signaling pathway: nuclear factor translocation between cytoplasm and nucleus, and induction of cytokine promoter. Furthermore we have developed new analytical techniques to resolve protein-protein aggregation at the immunological synapse between toll-like receptor and channel proteins in minimal chimeric cells and applied them to track the spatial distribution and concentration of receptor and channel proteins during the early stages of the immune response. Finally, we have developed combined electrical and optical platforms and extended a new theoretical statistical framework for testing and resolving hypotheses about the correlation between structure and activity in isolated channel proteins. We have published five papers describing our work in peer-reviewed, internationally recognized journals, and presented our work 11 times at national society meetings, scientific workshops, and university seminars.

Significance

If an infectious disease virus wiped out 2% of the world's population, with more than half the dead constituting young adults between 18-40 years old, then social stability, national and global economies, and military capabilities would be weakened. Thus advances made toward understanding innate immune responses to pathogenic infections, so that these could be manipulated for favorable therapeutic outcomes, strongly supports DOE/DHS national security missions.

Refereed Communications

S.B. Rempe and K. Leung, Response to "Comment on '*Ab Initio* Molecular Dynamics Calculation of Ion Hydration Free Energies'," *The Journal of Chemical Physics*, vol. 133, p. 047104, 2010.

R.W. Davis, J.S. Aaron, S.L. Rempe, and J A. Timlin, "Fluorescence Fluctuation Analysis of Mixed Chromophores From a Line-Scanning Hyperspectral Imaging System," *Proceedings of the SPIE*, vol. 757002, pp. 1-11, 2010.

D. Asthagiri, P.D. Dixit, S. Merchant, M.E. Paulaitis, L.R. Pratt, S.B. Rempe, and S. Varma, "Ion Selectivity From Local Configurations of Ligands in Solutions and Ion Channels," *Chemical Physics Letters (Frontiers Article)*, vol. 485, pp. 1-7, 2010.

N.L. Andrews, J.R. Pfeiffer, A.M. Martinez, D.M. Haaland, R.W. Davis, T. Kawakami, J.M. Oliver, B.S. Wilson, and D.S. Lidke, "Small, Mobile Fc Epsilon R1 Receptor Aggregates are Signaling Competent," *Immunity*, vol. 31, pp. 469-479, September 2009.

C.D. James, M.W. Moorman, B.D. Carson, C.S. Branda, J.W. Lantz, R.P. Manginell, A. Martino, and A.K. Singh, "Nuclear Translocation Kinetics of NF-Kappa B in Macrophages Challenged With Pathogens in a Microfluidic Platform," *Biomedical Microdevices*, vol. 11, pp. 693-700, 2009.

S. Varma and S.B. Rempe, "Multi-Body Effects in Ion Binding and Selectivity," to be published in the *Biophysical Journal*.

Modeling Cortical Circuits

130786
Year 2 of 2
Principal Investigator: F. Rothganger

Project Purpose

The neocortex is regarded as being the highest region of the brain, where auditory and visual perception takes place along with many important cognitive functions. One path to understanding perception and cognition is to work out the behavior of the circuits in this system. The neocortex seems to contain a template circuit that is repeated over its surface, and specializations seem to be driven by connectivity to other systems. Therefore it makes sense to reverse-engineer the template.

The goal of this project is to produce a model that takes into account as much of the current knowledge about cortical function as possible. Our approach is to explore the space of candidate algorithms, subject to the constraints provided by current neurophysiological knowledge. We compare a range of cortical models, seeking the best features from each of them. We examine current neurophysiological literature for clues about the connectivity, electrical, and chemical behavior of cortical neurons. It is possible to make progress, despite the limitations of this knowledge: The space of feasible algorithms is constrained not only by physiology, but also by the nature of computation and physics, for which we already have theory to guide us.

Summary of Accomplishments

We developed a framework for structuring neural models based on observations about layering and columns within the neocortex. The key observations are the following: 1) depth within the cortical sheet is related both to cell type specialization and to the channel of information being processed; and 2) cells contribute proportionally to processing within their neighborhood. The framework consists of multiple regularly spaced grids of cells overlaid upon each other (layers), with each cell reading from a neighborhood centered at its position (fuzzy columns).

We analyzed seven computational models and three physiological models of cortical function, compared them to one another, and described their common themes and differences. We developed a minimalist notation that eliminates carefully selected mathematical details in order to focus on the key underlying structure, primarily the relationships among the variables. We represent each set of general functions by a related set of linear functions, use updated equation form to minimize notation related to time, and standardize the names of certain commonly used variables (ascending / descending / lateral inputs and outputs).

We discovered that difference equations could form a useful bridge between the domain of physiology and the domain of algorithms that might describe the function of a brain system. We developed a software framework based on the modeling approach (layering and fuzzy columns) described above. One implementation is multithreaded and takes full advantage of multicore desktop computer hardware. The other operates on large cluster computers and uses basic linear algebra communication subprograms to communicate updates between layers residing on different compute nodes. Within this framework, we implemented the Rao and Ballard model and characterized the effect of fuzzy column organization on the behavior of the network.

Significance

Modeling brain circuits is a key supporting task in modeling human behavior. Human modeling enables us to characterize adversarial behavior and predict/enhance human performance as part of critical systems issues important to DOE/NNSA, DHS, and DoD. Beyond human modeling, a deep understanding of the principles of cognition will enable powerful technical solutions to a range of national security issues, such as monitoring large amounts of sensor data for potential threats, or flexible autonomous military robots.

The modeling of interconnections between neurons, and the larger structures they form in the brain, are a key research area in neuroscience. There is a sense of urgency to develop complete maps of these interconnections, and a belief that this is necessary for us to fully understand the human brain. This project offers a possible approach to interpreting such data, once that data has been fully collected. The real challenge at that point would be to form a reasonably compact description of the function implemented by all the complex neural machinery. While the methods explored in this work need a significant amount of maturation, we believe that they will lead to tools that will help the scientific community find insights into brain function.

Finally, the development of neuromorphic computers requires both specialized hardware and a deep understanding of how neural structures actually serve the computational goals of real brains. It is important to give adequate attention to the algorithms implemented as well as the hardware. This project contributes to neuromorphic computing by pursuing a better understanding of the processing that occurs in the brain.

Refereed Communications

F.H. Rothganger and T.J. Anastasio, “Using Input Minimization to Train a Cerebellar Model to Simulate Regulation of Smooth Pursuit,” *Biological Cybernetics*, vol. 101, pp. 339-359, October 2009.

Robust Automated Knowledge Capture

130787
Year 2 of 3
Principal Investigator: R. G. Abbott

Project Purpose

Various agencies in the national security domain need tools that enable human knowledge and behavior to be modeled at a level of individual specificity that has been largely ignored within the cognitive neurosciences. A prevailing assumption in cognitive theory has been that cognitive processes are largely invariant across individuals and across different conditions for an individual. Attention has focused on identifying a universally correct set of components and their interactions, and individual variability is generally regarded as measurement error. We propose that cognitive adaptability is a trait necessary to explain the inherently dynamic nature of cognitive processes as individuals adapt to ongoing circumstances. Cognitive adaptability does not imply a "blank slate"; instead, we assert that there exists inherent flexibility that may be quantified and used to predict variations in cognitive performance. Previous investments in automated knowledge capture (AKC) provide Sandia unique capabilities in using machine learning techniques to construct individualized cognitive models. Consequently, Sandia is uniquely positioned to conduct this research.

This project has three primary objectives:

Objective 1: Test key hypotheses of cognitive adaptability.
Hypothesis 1: For a given task, individuals will exhibit different strategies with the specific strategy employed being a product of their intrinsic skills.
Hypothesis 2: Individuals will exhibit varying levels of adaptability with an individual's adaptability determining their propensity to switch strategies in response to changing circumstances.

Objective 2: Develop automated knowledge capture techniques to characterize cognitive adaptability. We will develop techniques to: 1) model patterns of selective information retrieval; 2) detect strategic biases revealing beliefs and intrinsic skills; 3) detect shifts in strategy over time; and 4) develop mathematical techniques to bound the uncertainty in the individual cognitive models derived through AKC.

Objective 3: Establish neural correlates for cognitive adaptability. Conduct experimental studies to establish neural correlates of behavioral metrics for cognitive adaptability.

Summary of Accomplishments

We created a drawing task requiring subjects to draw figures under a wide range of task conditions and feedback conditions. We also developed a test suite integrating numerous psychological individual difference measures to administer with the drawing test.

We performed three experiments on approximately 300 subjects creating over 57,000 drawings. Each experiment consisted of 12 to 17 distinct test conditions to elicit individual differences.

<u>Experiment 1</u>: we discovered correlations between propensity to shift strategies and psychometrics for creativity and verbal ability. This experiment offered a wide range of drawing conditions allowing us to search for causes of strategy selection and shift, e.g., speed vs. accuracy.

Experiment 2: By altering the drawing stimulus, we discovered that subjects are more likely to shift strategies after negative feedback, and higher-performing individuals switch in response to smaller negative rewards.

Experiment 3: By manipulating a reward score, we discovered surprising individual differences in response to time pressure. Subjects repeatedly drew a figure, while the allotted time was reduced until completing the task required a severe compromise in accuracy. Some subjects increased drawing speed sufficiently, while others increased speed somewhat, but not enough to complete the task. These groups are surprisingly distinct, revealing that individuals do not fall along a continuum but into one of the two groups.

Experiment 4: We repeated the experimental methodology on a more complex task — the NASA Multi-attribute Task Battery — to determine whether the findings still apply. This task offers varied challenges: verbal, spatial, executive control, and motor skills. We are now analyzing data collected from 24 subjects to find patterns of strategy selection and attention allocation.

We developed a model called "Rum Runner" that predicts individual instances of strategy shift with surprising accuracy (approaching 90%) based on factors including time on task, stimulus change, and time on task.

Significance

Sandia's current AKC capabilities have already demonstrated value in several DOE and DoD applications including physical security, tactics training, and intelligence applications. However, the limiting factor for AKC in these applications is predictive accuracy of individual models in varied contexts and the inability to characterize the accuracy of these predictions. Cognitive adaptability is a confound for current models that disregard it; this research will fill that gap.

Construction of an Abiotic Reverse-Electron Transfer System for Energy Production and Many Biocatalytic Pathways

141524
Year 1 of 3
Principal Investigator: E. Ackerman

Project Purpose

The guiding principles of all renewable energy production from biomass are as follows: 1) the energy is present in the high-density electron carriers, either organic (e.g., EtOH, butanol) or inorganic (e.g., H_2 or electricity); and (2) sunlight is the ultimate source of energy, powering photosynthesis to synthesize organic molecules. Converting biomass energy to fuels (concentrated electron carriers) is biochemically feasible and performed by many microbial and eukaryotic communities. Yet the thermodynamic constraints of keeping cells alive mandate that energy yields from many pathways are, and will remain, suboptimal. Excess reducing equivalents are generated during metabolic reactions; e.g., bacteria channel 2/3 of their electron flow during glycolysis to make acetic acid rather than H_2. Overcoming the problem of excess reducing equivalents in living cells is a major bottleneck that must be overcome to increase yields. This project seeks to harness components of known metabolons derived from multiple species to ultimately create an abiotic reverse electron transfer (RET) system. Although many of the RET components will consist of proteins and cell-like and/or synthetic membranes, the core reaction centers will be enzyme based, albeit optimized for our abiotic system, rather than living organism(s). The work is challenging because not all components have been defined, even from living symbiotic systems surviving at the edge of what is thought to be thermodynamically possible and considerable recombinant cloning and expression of "difficult" proteins will be required. (Difficult proteins are those requiring considerable effort to express in active form in milligram quantities.) Since this system will be uncoupled from sustaining life, we will have considerably more reaction design freedom, including unnatural amino acids, (electrically active) nanoporous materials, and artificial membranes. If successful, the approaches described below could revolutionize basic approaches to economically feasible bio-inspired reactions.

Summary of Accomplishments

We rendered operational the key robotics equipment necessary for high-throughput protein expression and began preliminary biochemical activity assays.

We are utilizing metabolic pathways to select genes from *Syntrophus aciditrophicus* for disposing reducing equivalents and more common species such as *E. coli* for glycolytic metabolic pathways. Producing/stabilizing/optimizing proteins will be performed by a combination of cell-free synthesis and immobilization in functionalized nanoporous materials.

- We identified numerous candidate cytoplasmic and membrane proteins, and designed polymerase chain reaction (PCR) primers to clone them, including: F1-ATP synthase, oxidative and non-oxidative glycolytic proteins (glucose 6-phosphate dehydrogenase, phosphogluconolactonase, 6-phosphogluconate dehydrogenase, ribulose 5-phosphate, hydrogenase, nitrogenase, and accessory proteins).
- We demonstrated synthesis of both control and candidate proteins with simple functional assays using multiple instruments that were calibrated for the assays; e.g., green fluoresent proteins, an oxidase, and hydrolases. We cloned the genes for these proteins using methods based on PCR driven by specific priming from genomic DNA. This project alone represents orders-of-magnitude greater numbers of recombinant protein than have been produced in the history of biological work at Sandia.

- A key issue in making proteins is that they must be shown to be active using rigorously defined assays that are initially labor intensive and require calibrated instruments. This project requires multiple recombinant proteins and assays and a subset of the spectrophotometrically based assays were made to function for hydrolases, oxidase, and dehydrogenases.
- We overcame largely instrument-based problems that yielded inconsistent data for some enzyme activity measurements.
- We prepared assay conditions for proteins that will only work under anaerobic conditions. This is necessary because a key part of our approach uses enzymes from synergistic species surviving under different growth conditions, necessitating optimization of different enzyme assay conditions in different compartments.

Significance

Biologically based approaches to energy production, remediation, security-based sensors, and chemical syntheses all face the same thermodynamic limitations related to disposing of excess reducing equivalents. This R&D is relevant to all these missions because it could provide a general solution to utilizing valuable biologically based reactions. If successful, this project could revolutionize energy production because it would use relatively inexpensive biologically based reagents behaving catalytically to produce energy from cheap feedstocks, e.g., sugars. Once the proof of principle is demonstrated, the enzymes and reaction pathways could be enhanced for even greater activity and stability.

Overcoming one of the main thermodynamic problems of metabolic energy production could revolutionize energy production. The reactions should be scalable because they would rely on relatively inexpensive components such as proteins and artificial membranes. Biochemical production of either organic or inorganic energy carriers all generate excess reducing equivalents that limit overall yields. Even photosynthesis reduces NAD to NADH as do natural methanogenic reactions converting CO_2 to CH_4. Thus, a reverse electron transfer system could enable an enormous variety of important reactions to provide power on scales from sophisticated sensors to industrial plants and the desired end-products need not be consumed by a syntrophic partner.

From Benchtop to Raceway: Spectroscopic Signatures of Dynamic Biological Processes in Algal Communities

141528
Year 1 of 3
Principal Investigator: J. A. Timlin

Project Purpose

Microalgae are emerging as serious contenders for alternative energy biomass. Like lignocellulosic materials, there are major scientific challenges to an industrial-scale algal biofuels program. Recently four broad areas of R&D needs have been identified for economically viable, industrial-scale cultivation of algae: culture sustainability system productivity; nutrient source scaling and sustainability; and water conservation, management, and recycling. Progress in each of these areas is limited by significant knowledge gaps in algal biology. In this project, we focus on the important biological problems impacting algal cultivation. We will investigate the effects that culture compositional dynamics (species, predators, light levels) have on key algal biology and health parameters (growth, lipid production, photosynthesis) at the lab, greenhouse, and raceway scales. This fundamental knowledge of the underlying biological processes will simultaneously enable the discovery of robust spectroscopic signatures correlated to algal pond composition, algal health, photosynthetic efficiency, and oil production at scale. Quoting the Algal Biofuels Draft Roadmap: "Methods for automated biological and chemical monitoring in production settings will be essential for assessing the health and compositional dynamics of algal ponds." Currently, monitoring is done with off-line measurements (e.g., gravimetric assays for lipid content) that are too slow and too sparse to provide the real-time process control required for efficient algal production in a large-scale algal raceway. This project takes the first step towards addressing this shortcoming by applying bioanalytical spectroscopy, chemical imaging, remote sensing, genomics, and computational modeling to investigate the effects that pathogens, predators, and competitors and fluctuations in light intensity have on photosynthesis, algae growth, and lipid production. The knowledge gained should enable significant gains in productivity and sustainability that are critical for optimizing industrial-scale algal facilities for cost-efficient algal biofuels production.

Summary of Accomplishments

The overall goal of our project is to develop a fundamental understanding of the effects that dynamic abiotic and biotic stressors have on algal culture health and lipid production at multiple culture scales, then use this information to identify spectral signatures for algal pond health, as well as to develop predictive models of algal growth and productivity. Select highlights of our technical accomplishments in FY 2010 are the following:

- Designed and began experiments to determine the relationship of the CO_2 concentrating mechanism to lipid production and spectral composition in three diverse species
- Design of transcriptomics experiments in model organism *Chlamydomonas reinhardtii* to evaluate CO_2 and programmed cell death
- Initiated collaboration to understand natural diversity and dynamics of algae in Southwest ecosystem
- Imaged four algal species with nanoscale resolution to understand pigment differences and predictive capabilities
- Explored differences in carotenoid composition using Raman spectroscopy and hyperspectral fluorescence imaging
- Conducted proof-of-principle reflectivity measurements at greenhouse scale

- Added capability of limited algae growth if CO_2 is scarce to our computational fluid dynamics (CFD) model of open channel algal cultivation
- Completed a parameter sensitivity study to identify necessary data for improving CFD model accuracy
- Completed experiment to generate species-specific constituent data to improve model

Significance

This project will provide fundamental scientific discoveries in algal biology that address difficulties faced in cultivating algae at scale. Advances in algal bioscience enabling cost-efficient industrial-scale algae facilities are critical to achieving DOE's mission to promote energy security through reliable, clean, affordable energy. This project has already positioned Sandia strategically to respond to future funding opportunities in algal bioscience and bioenergy. Two additional algal biofuels projects have been funded as a result of our efforts.

Refereed Communications

S.C. James and V. Boriah, "Modeling Algae Growth in an Open-Channel Raceway," *Journal of Computational Biology*, vol. 17, pp. 895-906, July 2010.

From Sensing to Enhancing Brain Processes

141529
Year 1 of 3
Principal Investigator: L. E. Matzen

Project Purpose

We aim to further a dynamical systems theoretical framework for engineering systems in which measures of brain activity provide a basis for interventions that enhance human cognitive performance. We will characterize patterns of brain activity associated with good and poor memory in decision-making tasks. Then, we will test three intervention techniques hypothesized to improve memory by influencing brain activity: cognitive training, neurofeedback, and transcranial direct current stimulation. Our project uses these techniques in novel ways with the objective of advancing cognitive science research and applications. In addition, we will apply Sandia's strengths in computation to model good and poor memory performance for individuals and to assess the success of each intervention technique in terms of its ability to optimize brain activity for specific individuals and tasks.

The proposed research will contribute to a deeper understanding of the memory processes involved in decision-making. It will strengthen ties with the Beckman Institute (University of Illinois at Urbana-Champaign [UIUC]) and the MIND Research Network through collaborations and consultation with EEG (electroencephalography) and tDCS (transcranial direct cortical stimulation) researchers at those institutions. Most importantly, this project will lay the foundation for technology that could dramatically enhance human performance in high-consequence settings. It will provide the science basis for engineering closed-loop systems in which neurophysiological sensors provide the input used to model an individual and implement interventions to optimize that individual's cognitive performance. Such a capability closes a critical gap in the practical application of neurotechnologies, given the state of the art wherein there are broad-based advances in sensor technology, but little progress with respect to the application of brain sensors in systems engineered to improve human performance.

Summary of Accomplishments

In FY 2010, we have established an EEG laboratory at Sandia and completed the first full-scale EEG study to be run at Sandia. In addition, we completed two EEG studies in collaboration with researchers at UIUC, and began to develop computational modeling techniques that will be applied to the EEG data.

The EEG lab at Sandia includes a 128-channel EEG recording system from Advanced Neuro Technologies, four electrode caps with active shielding, a testing environment for participants, and a full suite of EEG recording and analysis software.

Through our collaboration with UIUC, we designed two EEG studies in support of our research goals of characterizing good and poor memory performance using the Dm Effect. Data collection for both experiment has been completed. The first experiment revealed new information about the nature of the Dm Effect (an index of brain activity at encoding that distinguishes subsequently remembered from subsequently forgotten items). The preliminary results from this study were presented at the *2010 InterBrain Symposium* and at the Society for Psychophysiological Research. The second and third experiments revealed the role of the Dm Effect in memory errors and hemispheric differences in memory.

We are using the data from the EEG studies to develop a computational model of the brain activity associated with good and poor memory performance. We have tested numerous modeling techniques to determine how well they are able to characterize brain activity associated with good and poor memory. These are novel applications of computational techniques to EEG data, and if they are successful they will advance the cutting edge of EEG analysis techniques. This advance will support our goal of building a scientific framework for using real-time EEG data to improve human performance.

Significance

This project will provide a scientific framework for engineering innovative neurotechnologies, establishing Sandia as a leader in this area. This project creates a unique capability for conducting classified or sensitive electrophysiology research. These developments position Sandia to provide science-based technology solutions to national security agencies with interests in enhancing human performance, training, and assured readiness.

The research will contribute to a deeper understanding of the memory processes involved in decision-making. It will strengthen ties with the Beckman Institute and the MIND Research Network through collaborations and consultation with EEG and tDCS researchers at those institutions. This research engages the sensing and imaging, scientific computing, and surety engineering interests of the Cognitive Science and Technology investment area. If successful, this project will lay the foundation for technology that could dramatically enhance human performance in high-consequence settings. It will provide the science basis for engineering closed-loop systems in which neurophysiological sensors provide the input used to model an individual and implement interventions to optimize that individual's cognitive performance. Such a capability closes a critical gap in the practical application of neurotechnologies, given the state of the art wherein there are broad-based advances in sensor technology, but little progress with respect to the application of brain sensors in systems engineered to improve human performance.

The results of each study will be submitted for publication in leading peer-reviewed cognitive neuroscience journals. The results will also be presented to the scientific community at conferences such as the annual meetings of the Society for Neuroscience, the Cognitive Neuroscience Society and the Society for Psychophysiological Research.

Genome-Wide RNA Interference Analysis of Viral Encephalitis Pathogenesis

141530
Year 1 of 3
Principal Investigator: O. Negrete

Project Purpose

The highly pathogenic viruses that cause encephalitis (acute inflammation of the brain) include a significant number of emerging or re-emerging viruses that are also considered potential bioweapons. Rift Valley Fever virus (RVFV) is a prime example of such a virus that causes serious morbidity and mortality in both humans and livestock. The lack of efficient countermeasure strategies, the potential for dispersion into new regions, and the pathogenesis in humans and livestock make RVFV a serious public health concern. RVFV infects a broad host range indicating that the host requirements for virus entry and replication are widely distributed. To date, a systematic analysis of the host factors involved in RVFV infection and pathogenesis has not been described. To identify host proteins that are required for RVFV infection we have chosen to use RNA interference (RNAi) technology, a powerful genomic approach used to investigate host factors involved in virus replication on a genome-wide level. Furthermore, to improve the efficiency and speed of genomic screening in high-level biocontainment, we will develop a high-throughput microfluidic platform to perform genome-wide RNAi. The microfluidic-based device will combine cellular microarray, cell transfection, and microfluidic channels to efficiently introduce RNAi libraries into primary cells within a portable and cost-effective platform. Computational network analysis will compare genome-wide molecular pathways of the attenuated RVFV-MP12 strain (Biosafety Level [BSL]-2) and the pathogenic RVFV-ZH501 strain (BSL-3) to identify key host proteins involved in viral encephalitis pathogenesis. Extension of these studies to other viral encephalitides such as Nipah virus, West Nile virus, and Venezuelan Equine Encephalitis virus, may lead to the development of novel broad spectrum therapeutics that target common host proteins involved in viral encephalitis pathogenesis to treat these diseases for which no effective therapeutics currently exist.

Summary of Accomplishments

In preparation for a genome-wide RNAi screen to identify the host factors involved in Rift valley fever virus (RVFV) infection, we completed assay development, optimization and pilot screening using the attenuated RVFV-MP12 strain (BSL-2) and traditional small interfering (siRNA) delivery methods in microtiter plates. During assay development, we identified RNAi host protein targets used for controls in the screen by testing endocytosis small molecule inhibitors that dissected the pathways involved in RVFV entry. We discovered that RVFV enters cells through dynamin-dependent, caveolin-mediated endocytosis. We then demonstrated that siRNA against dynamin was a potent positive control for RNAi screening of RVFV. During RNAi screening optimization, we tested several transfection reagents, concentrations of transfection reagents, cell plating densities, multiplicity of virus infection, duration of siRNA inhibition and duration of infection to design the final RNAi screening protocol. Lastly, during pilot screening, we tested the optimized RNAi screening protocol with siRNA controls with a limited number of the siRNA library targets at the University of California-Berkeley screening center to measure the variability between plates using high-throughput robotic screening equipment.

Concurrently, we designed a prototype microfluidic device that combines microarrays of nucleic acids and microfluidic channels for cell transfection and RNAi screening. This microfluidic platform was designed for portability and transfer into high-level biocontainment facilities with minimal capital equipment, reagent, and cell expense associated with traditional screening. Microchambers within the microfluidic platform were designed based on experiments performed with endothelial cell loading in previously fabricated microfluidic chips. The endothelial cell line used during these experiments was obtained from Bay State Health and these cells recapitulate inherent features of primary endothelial cells. Collagen-coated microfluidic channels were shown to support endothelial cell viability for greater than 3 days, therefore providing the experimental window needed for RNAi screening of viral pathogens.

Significance

This project benefits the DOE scientific and defense and DHS awareness and response strategic goals by providing an understanding of the mechanisms by which biodefense viral pathogens cause lethal encephalitis. By providing an automated microfluidic platform capable of high-throughput genome-wide RNAi screening to elucidate virus-host interactions, we are specifically targeting the Sandia's biological science and technology area objectives. In doing so, we will improve the speed at which host genes and pathways involved in viral infection are identified to support our laboratory missions in homeland defense and national security. Follow-on projects could use our platform to study other viral pathogens and, through comparative analysis, identify common host proteins involved in a variety of biodefense pathogen infections. The identification of common host proteins involved in multiple viral infections would be applicable to the development of broad-spectrum therapeutics.

Neurological Simulations for Emerging Brain Maps

141531
Year 1 of 3
Principal Investigator: R. Schiek

Project Purpose

Advances in imaging and reconstruction technologies are driving many research projects to map all of the neurons in some small animal brains. While these projects will produce detailed topology of their targeted subjects, the ability to then simulate the neural physiology in detail is limited to high-fidelity simulations of a few neurons, or lower-fidelity simulations of thousands of neurons. Sandia's parallel circuit simulator, Xyce, can address large-scale neuron simulations in a new way by greatly extending the range within which one can perform high-fidelity, multi-compartment neuron simulations. This enables new science in understanding how collections of neurons produce macroscopic behavior. Additionally, the network simulation framework provided by Xyce can be used to migrate high-level, cognitive models to a high-performance computing platform and couple such models to lower-level neuron based systems. To be successful, this work must engage the neuroscience community and researchers developing the brain maps by providing access to Xyce and demonstrating that Xyce can tackle complex problems. Since the topology of a neural system is more highly linked than a circuit, improved preconditioning and new solver technologies may also be needed, as well as new computational tools (i.e., reduced order modeling). Programmatically, this project will connect the cognitive science work at Sandia to the high-performance computing community and provide context for further engagement between Sandia and the neuroscience simulation community.

Summary of Accomplishments

The constitutive models for a neuron fiber as described by a cable-equation have been implemented in Xyce. Fundamental model types are in place (e.g., the Hodgkin-Huxley and Connor-Stevens equations). Synapse models are still under development. Thus, from a software development perspective, the key goal of implementing specific devices (i.e., specific model equations) has been achieved. An important challenge in this work is making this computational tool accessible to the neuroscience community. Our initial approach was to use the emerging standard description language of NeuronML to allow new users to run or import problems into Xyce. However, upon further investigation, it is not clear that the neuroscience community has fully embraced this description language. Thus, our current approach is to implement a translation layer that can convert problems described in the input language of the currently most popular simulators (Neuron and Genesis) to the format used by Xyce. An important advantage is that we fully use the existing parallel parsing technology in Xyce to efficiently process large problem description files. Finally, in addressing the multilevel nature of neuron-to-cognitive modeling, we have used our collaborators to define two target applications. First is one in neuron population modeling and the second is in pattern recognition/pattern completion. These problems will focus the scientific work and produce results of interest to the broader community

Significance

A key component of this work is expanding the feasible domain for high-fidelity, multi-compartment neuron models. Currently, when one is modeling a neural system, a researcher can choose between a high-fidelity, biophysically realistic model or a lower-fidelity, simplified model. The simplified models are often chosen because they allow researchers to perform simultaneous simulations of more neurons. Our goal is to use the best in currently parallel computing, problem partitioning, and solution techniques to expand the size of problems addressable with multi-compartment neuron models. Additionally, we will make efficient use of the full problem solution (i.e., response function calculation and derivative calculations) to better optimize simulations to experiments.

Additionally, we will couple simulation work at the sub-neuron level to research at higher levels. This can be envisioned via population models of neurons and how a given population's behavior results from individual neuron behavior. There is risk in this approach in that it is not well understood how behavior of individual neurons results in population level behavior. However, this work is well positioned to answer these questions with the simulation tools we are creating.

Refereed Communications

R. Schiek and C. Warrender, "Using Uncertainty Quantification to Constrain Dynamic Neuron Modeling Parameters," Design Automation Conference, Anaheim, CA, 2010.

Real-Time Neuronal Current Imaging of the Human Brain to Improve Understanding of Decision-Making Processes

141532
Year 1 of 3
Principal Investigator: H. D. Jones

Project Purpose

Understanding the cognitive processes that underlie decision-making will enable Sandia to determine variables that positively and negatively impact the ability to make optimal decisions under stress and uncertainty situations regularly encountered in national security domains. A major limitation in understanding the neuronal basis of decision-making is the lack of imaging technologies capable of directly measuring the neuronal response to cognitive challenges with high temporal and spatial resolution. Magnetoencephalography (MEG) and electroencephalography (EEG) have impressive temporal resolution (millisecond), but are limited in their ability to localize the neuronal signal, especially for deep sources. In contrast, functional magnetic resonance imaging (fMRI) has high spatial resolution (millimeter), but poor temporal resolution due to its dependence on the temporally sluggish vascular response. The proposed project will develop complementary technologies (fMRI and proton magnetic resonance spectroscopy [^{1}HMRS]) to directly detect neuronal responses during perceptual decision-making by investigating the effects of synchronously firing cortical neurons (and their associated magnetic fields) on the water proton signal. These event-related magnetic fields (ERFs) are putatively the same fields that would be detected by MEG. However, by detecting them with a magnetic resonance–based method, the sources of the fields can be precisely located and a true neuronal current imaging method can be devised. The ERF's effect on the ^{1}HMRS signal is expected to be weak and hampered by scanner and physiologic noise. Therefore, Sandia's demonstrated area of expertise in signal processing and multivariate data analysis of spectral image data will be applied to the ^{1}HMRS data to improve the sensitivity to small neuronal responses during decision-making events. This novel approach is intended to provide brain researchers with a new and powerful functional brain imaging capability that will have unprecedented spatial and temporal resolution and can ultimately be used to improve our understanding of decision-making.

Summary of Accomplishments

We have met all scheduled project milestones and have completed additional experiments to understand the significance of our FY 2010 neuronal current (NC) studies. We completed contracts with our Mind Research Network and University of New Mexico collaborators, and all required approvals for human studies have been granted. We have completed noise characterization studies of the ^{1}HMRS instrument using both water (agar) phantom and human phantom data with the use of statistically designed experiments. The noise structure of the data and the influence of instrument parameters and physiological perturbations on the spectral signal of water have been thoroughly characterized as a function of operating condition. Methods and software were developed to add realistic NC to both agar and human phantom ^{1}HMRS data. We also completed the integration of the simulation software with very flexible free induction decay (FID) preprocessing software and software to orthogonally remove spurious instrument and physiological variations from the data. With the use of realistic NC simulations applied to human phantom data, we were able to optimally design experiments to investigate the feasibility of detecting NC using ^{1}HMRS single-voxel techniques. We conducted three sets of experiments to determine feasibility: 1) Pilot studies to confirm and adjust the design of the feasibility experiment, 2) the NC feasibility study conducted using a visual stimulus while minimizing the BOLD (blood oxygen-dependent) response, and 3) confirmation studies to definitively demonstrate that we are observing NC. These confirmation studies consisted of changing the location of the NC within the FID and changing the location of the single voxel to interrogate the prefrontal grey matter (where no NC should exist as a result of visual stimulus). Early analysis results are encouraging for the detection of NC and we are in the process of analyzing these confirmation study results.

Significance

Understanding the factors in the brain that affect the performance of human decision-making under stress and uncertainty is important to the national security mission of Sandia, DOE, and other federal agencies such as DoD and DHS. The development of NC imaging techniques and equipment capable of directly measuring the NC in the human brain with both high spatial and temporal resolution would help provide researchers with a new tool to facilitate this research.

A Bio-Synthetic Interface for Discovery of Viral Entry Mechanisms

148895
Year 1 of 1
Principal Investigator: J. C. Stachowiak

Project Purpose

Understanding and defending against pathogenic viruses is an important public health and biodefense challenge. The focus of our project is to uncover the mechanisms that viruses use to identify and invade host cells. We propose to accomplish this by constructing a unique interface between a virus and a synthetic lipid bilayer. This approach will provide a minimal setting for investigating the initial events of host-virus interaction, namely, recognition of and entry into a host cell. This understanding will enable rational design of therapeutics that block viral entry as well as future construction of synthetic, nonproliferating sensors that detect infectious virus in the environment.

In the study of host-pathogen interactions, traditional top-down assays of host cells have been very useful but are limited by the stochastic, redundant nature of cellular processes and the need to maintain viability. An emerging complementary approach, enabled by increasing knowledge from top-down studies and critical technical advances, is to build cell-like systems, component-by-component, from the bottom up. By reconstituting specific biochemical and synthetic components in a cell-like environment, this strategy will capture the essential functionality of cellular processes in a simplified and controllable setting. Using the proposed biosynthetic interface, we will determine the minimal biochemical requirements of viral entry into host cells.

Summary of Accomplishments

We have built a variety of model systems for virus particles and lipid membranes to reconstitute the interaction between enveloped viruses and host cell membranes. We have demonstrated fusion between Vesicular Stomatitis Virus (VSV) particles and synthetic vesicles, making VSV a good model system to study. We have discovered that the preferred vesicle composition for VSV fusion contains liquid-liquid phase separations when reconstituted in giant vesicles. Future studies could investigate whether VSV fuses preferentially to one liquid phase over the other. We have reconstituted Nipah virus–like particles as well as Ephrin-B2 functionalized membranes. Expression and purification of our own recombinant Ephrin B2 is likely needed to observe fusion in this system. We have developed total internal reflection microscopy and cushioned lipid bilayers to address challenges we encountered with quantitative imaging and substrate fluidity, respectively.

Significance

This project is relevant to several DOE missions. (1) Basic understanding of host-pathogen interactions is critical to national security. (2) Cell-like synthetic interfaces developed for basic science objectives of this project can also serve as novel platforms for diagnostics to combat bioterrorism. (3) Biomimetic interfaces provide an environment for integration of nanoscale materials with biological components to create functional nano-bio systems for DOE missions in nanoscience.

Diffusion Among Cognitively Complex Agents in Limited Resource Settings

148898
Year 1 of 3
Principal Investigator: K. Lakkaraju

Project Purpose

The objective of this project is to study information diffusion in complex settings i.e., those that exhibit the following characteristics: 1) socially complex agents (agents with differing numbers of neighbors, captured through a social network); 2) cognitively complex agents (agents that exhibit continuous, interdependent belief structures that change over time, rather than the often-used binary, independent belief structure, captured through a cognitive network); and 3) limited resources (bounded rationality, modeled by limiting the resources each agent has available for communicating and integrating information from others). Current diffusion models focus on complexities of social structure, with simple structures for the cognitive agents. We propose to develop a novel model of diffusion that exhibits these three characteristics. This is a high-risk project because, to our knowledge, no one else has developed a model with complex cognitive agents. The project exhibits high potential because understanding the factors that influence the speed of diffusion is important in numerous areas: DOE (diffusion of climate change information), DoD (understanding the spread of tactics, techniques, and procedures), and DHS (developing communication strategies to quickly spread safety-critical information to enhance community resiliency).

The hypothesis of this project is that diffusion will become more rapid as a function of an increase in the connectivity of the social network and a decrease in the connectivity of the cognitive network. We propose to test this hypothesis by developing a model of diffusion, implementing the model in a simulation framework, and measuring the speed of diffusion (number of interactions) as we vary the connectivity of the cognitive and social networks. The intention of this project is to develop a model that will allow researchers to ask basic questions about the interaction between cognitive networks and social network structure.

Summary of Accomplishments

We have focused on collecting real-world case studies that will help validate our model and identifying key variables/processes that should be included in our model. Initially we focused on identifying key variable/processes from the extensive attitude-change literature. A major insight was that individuals sometimes distort information to maintain consistency among attitudes; incorporation of information distortion will now be an important part of our model. In addition, we are considering the impact of persuasion route (systematic vs. peripheral), attitude type (implicit vs. explicit) and social context (social network heterogeneity) on attitude change. A preliminary document describing these important processes for attitude change has been submitted to the 2010 Institute of Electrical and Electronics Engineers Homeland Security and Technologies Conference.

In parallel, we have undertaken an evaluation of current computationally based attitude-change models. The majority of these utilize a framework called parallel constraint satisfaction (PCS). To explore this model for population-wide attitude change, we developed a proof of concept simulation in which agents were represented with PCS networks. Preliminary results have been submitted to the 2010 Association for the Advancement of Artificial Intelligence Fall Symposium on Complex Adaptive Systems.

We are collecting real-world case studies, by organizing a network/cognitive sciences reading group, in which we intend to assemble stakeholders within Sandia who have worked on, or are interested in, information diffusion and by attending the Phoenix seminar. We have also begun to collaborate with the Network Dynamics

Simulation Center at Virginia Tech. This group has data on real social networks that can be used as a basis for our simulations.

Significance

The computational socio-cognitive model developed in this project can be used to explore “what-if” scenarios to help analysts make decisions. In addition, the model will provide insight into the diffusion of information, of interest to numerous entities, including DOE, DoD, and DHS.

Sensitivity Analysis Techniques for Models of Human Behavior

149047
Year 1 of 1
Principal Investigator: A. Bier

Project Purpose

Models of human behavior have inputs that are difficult to quantify and are highly variable among people or groups. This necessitates sensitivity analysis techniques that can deal with large variations in many model variables simultaneously, a challenge that has not yet been sufficiently explored. Sensitivity analysis is used to determine which model components have the largest impact on model response, to identify where valuable data collection resources should be directed, and to identify leverage points where intervention can have a substantial and robust effect on results. Sensitivity analysis is a required component of rigorous data-based model validation.

The variability inherent in models of human behavior indicates that sensitivity analysis techniques designed to deal with the highly nonlinear nature of these models will be more effective than traditional techniques. This project will explore the advancement of cutting-edge global sensitivity analysis methods, which, unlike traditional local methods, consider how model inputs work together to influence results. Human and social modeling has emerged as an important research area at Sandia due to its potential to improve national defense-related decision-making in the presence of uncertainty, and improved sensitivity analysis techniques will directly enhance this capability.

Summary of Accomplishments

To learn about the sensitivity analysis techniques that are most suitable for models of human behavior, different promising methods were applied to an exemplary model, tested, and compared. The exemplary model simulates cognitive, behavioral, and social processes and interactions, and involves substantial nonlinearity, uncertainty, and variability. Results showed that some sensitivity analysis methods create similar results, and can thus be considered redundant. However, other methods, such as global methods that consider interactions between inputs, can generate insights not available from traditional methods.

Significance

Sensitivity analysis is used to strengthen models and understand their implications, and therefore can be used to identify where valuable data collection resources should be directed to most effectively improve a model. For example, it can be used to find leverage points where intervention into a system can have a substantial effect on results, and also to understand model robustness, thereby assessing where a model can be simplified with minimal effect on outcomes. Given the numerous models used by Sandia to support its national security mission in such areas as weapons performance, materials science and engineering, energy research and others, an improved understanding of the applicability of sensitivity analysis is poised to improve understanding and thereby strengthen the Laboratories' modeling initiatives across its DOE/NNSA mission space.

A Method to Mathematically Compare Neurocognitive Models to Humans

149639
Year 1 of 1
Principal Investigator: M. L. Bernard

Project Purpose

Due to the vast complexities of the brain, it is a computationally intractable problem to create a software model that exactly duplicates its neuroanatomy. Rather than being able to produce an exact replica, model developers instead focus upon differing theories of neural function and connectivity. Furthermore, implementations vary widely based upon the preferences of particular developers. For example, some developers focus upon artificial neural networks that seek to mimic physiology, whereas others are more interested in the functionality of modules without concerns about the realism of the implementation. Differing opinions, both with regard to the ideal implementation method and neural functionality lead to the creation of multiple models of similar or even of the same neural regions. The existence of multiple models necessitates evaluating them in some manner that is both consistent and comparable to neuroanatomy.

It is common practice to either make a qualitative comparison or to base evaluations upon human behavior and/or performance. Such techniques provide an excellent basis for guiding model design and are directly related to the experimental data that often drives neurocogntive theories. However, such comparisons are subjective. Making a comparison with behavioral data typically requires generalizations because neurocognitive models are usually focused upon a particular neural region and lack all of the necessary neuroanatomy to perform the task with which the model is compared. Alternatively, to simply access a model based upon its functional performance from a qualitative standpoint captures the necessary performance but lacks scientific rigor. In contrast, this project will serve as a proof of concept regarding the feasibility of utilizing the mathematics of information theory as a means of quantitatively assessing neurocognitive models.

Summary of Accomplishments

Information theoretic techniques showed significant promise as a rigorous mathematical means of comparing neurocognitive models. We have leveraged the Sandia developed Memory and Reasoning (M&R) Cortical-Hippocampal model as a specific architecture to test our approach. For this proof-of-concept assessment, we were able to compare various versions of the M&R model. Specifically, we were able to compare instances of the model at different time steps with differing neural activation patterns and were also able to compare the model against a modified version of itself in which parameters were altered. These preliminary studies serve as a first step in characterizing a model-to-model comparison procedure. Future research is needed to improve upon the techniques as well as to extend them to compare two differing models.

Significance

The research in this project directly benefits Sandia's Cognitive Science and Technology thrust by serving as a first step in characterizing a quantitative model-to-model comparison procedure. Future research is needed to improve upon the techniques as well as to extend them to compare two differing models. In addition to further investigating information theoretic comparison techniques, this research has set the groundwork for other types of model comparisons. For example, the mathematics of game theory provides alternative techniques with intriguing potential.

Furthermore, by comparing a model against an altered version of itself, information theoretic comparison techniques may be used for uncertainty quantification (UQ). Depending upon the particular implementation, a neurocognitive model may often have modifiable parameters such as learning rates, representational capacity, or generalizability. Depending upon the particular values of parameters such as these, model performance may vary significantly, and, in effect, alter how closely the model represents the neuroanatomy it is supposed to be depicting. Consequently, the ability to compare a model against an altered version of itself provides a quantifiable means of examining the effects of model implementation parameters so that models may more accurately represent the desired neural theory. Such quantitative modeling assessment can enable better characterization and prediction/enhancement of human performance as part of critical systems issues important to DOE/NNSA, DHS, and DoD.

Toward Exascale Computing through Neuromorphic Approaches

149704
Year 1 of 1
Principal Investigator: C. D. James

Project Purpose

While individual neurons function at relatively low firing rates, naturally occurring nervous systems not only surpass manmade systems in computing power, but accomplish this feat using relatively little energy. Many neuroscientists assert that the next major breakthrough in computing power will be achieved through application of neuromorphic approaches that mimic the mechanisms by which neural systems integrate and store massive quantities of data for real-time decision-making. The purpose of this project is to create a conceptual foundation through which Sandia can make unique advances toward exascale computing. First, we coordinated a team consisting of experts from the high-performance computing, Microsystems and Engineering Sciences Applications, cognitive and biological sciences, and nanotechnology domains to conduct an exercise with the outcome being a concept for applying neuromorphic computing to achieve exascale computing. This concept will involve innovative extension and integration of Sandia capabilities in MicroFab, material sciences, high-performance computing, and modeling and simulation of neural processes/systems.

Summary of Accomplishments

We have identified key attributes for next-generation computing architectures to afford the low-power and high-flexibility characteristics of biological neural networks: 1. connectivity, parallel, distributed; 2. tunability, adaptability, plasticity; 3. self-preservation, healing, robust, recoverable; 4. compact, high-density, 3D geometries; 5. standardizable, predictable, specifiable; 6. flexibly sustained. We focused the efforts of this project on attributes 1 and 4. Recently developed memristor technology meets many metrics of both of these attributes. Through a literature search, we discovered that this technology has the potential to scale to biological synaptic densities (10^{10} connections per cm^2). In this project, we designed a memristor structure and developed a nanofabrication process for building an array of these structures. We also further developed a framework for simulating memristor structures in Xyce utilizing established work in the literature and employing SPICE to simulate memristors.

Significance

This accomplishments of this project will further DOE's mission of advancing the field of scientific computing, including the development of new nanotechnology-enabled high-performance computing strategies. We now have a clear path forward for designing, fabricating, and simulating memristor structures in order to develop new computational architectures for next-generation exascale computing. Sandia's strengths in micro- and nanofabrication, as well as high-performance computing and computational modeling will be leveraged in future work.

Ultrasensitive, Amplification-Free Assays for Detecting Pathogens

149705
Year 1 of 3
Principal Investigator: R. Meagher

Project Purpose

Quantitative analysis of nucleic acids (DNA or RNA) is a powerful approach for detecting and identifying pathogens, including potential bioweapons and pandemic threats. All current approaches for nucleic acid detection short of direct sequencing (e.g., microarrays, PCR [polymerase chain reaction], blots) rely upon hybridization of nucleic acid primers or probes to a specific target sequence. Most assay formats require an enzymatic amplification like PCR to generate a high enough concentration of nucleic acid for detection. PCR-based methodologies are sensitive and powerful, but require a well-equipped lab, with cold storage and clean samples. Enzymatic approaches are sensitive to contaminants and inhibitors in environmental samples.

Rather than using PCR to generate 10^8 or more copies of a template in a ~100 microliter reaction volume, we propose to confine the total nucleic acid content of a sample into a volume of ~100 pL adjacent to a nanoporous polymer membrane (roughly 10^6-fold increase in concentration). The total contents of the concentrated sample volume can be directly analyzed by microchannel electrophoresis, with minimal dilution of the sample plug. A simple detector with ~100 pM sensitivity could thus detect hybridization of ~6,000 target molecules, roughly corresponding to the number of ribosomal RNA molecules in a single bacterial cell.

We propose a proof-of-concept study, including experimental demonstrations of the assay with model bacterial and viral targets, coupled with analytical and computational modeling of the underlying transport and kinetic processes. Transport modeling will provide an estimate of the maximum rate of nucleic acid concentration, and concentration profiles of multiple ionic species involved in hybridization, which will be used to develop a kinetic model for hybridization. The resulting theoretical estimates of assay performance will be used to benchmark our experimental investigations, enabling us to optimize parameters such as membrane chemistry, buffer systems, electric field, and temperature cycling.

Summary of Accomplishments

Accomplishments in Q3 and Q4 of FY 2010 help to lay the groundwork for individual steps for performing amplification-free DNA hybridization assays.

We have performed experiments characterizing the rate of concentration for DNA at photo-patterned membranes. We performed the following experiments:

- on short single-stranded DNA (similar to the probes for hybridization assays),
- on longer double-stranded DNA (similar to the targets for the hybridization assays),
- concentration experiments for high-concentration polyacrylamide membranes, either uncharged or with a small amount of fixed negative charge.

The negatively charged membranes outperformed the neutral membranes, in several ways. The charged membranes were nearly impermeable to all sizes of DNA tested, including the short probes, while the uncharged membranes allowed some DNA (particularly probe) to transit. DNA concentration proceeded linearly with respect to time for the charged membrane, but plateaued within several minutes for uncharged membranes, indicating a slow leakage of DNA through the membrane. Both the rate of DNA concentration and the measured current scaled proportionally with applied voltage for both types of membranes, suggesting relatively minor impact from ion concentration polarization effects. In addition, a more realistic target (1420-base single-stranded DNA) has been constructed using a viral sequence (bacteriophage M13) that will be used going forward as a model for single-stranded bacterial or viral RNA targets.

Simultaneous with the start of this project, a paper was published by an outside group that summarizes recent theoretical analyses of electrokinetic transport at microchannel-nanochannel interfaces, which are directly analagous to our microchannel-nanoporous membrane interface. We have begun testing these theoretical models against our experimental observations. Using best estimates for our experimental parameters, the model predicts concentration polarization propagating away from the charged membrane, which is not what we have observed in most cases. Further investigation into this apparent discrepancy is underway.

Significance

Biological warfare agents and infectious diseases present a real threat to homeland security and public health. Existing assays for these agents range from highly rapid but nonspecific, to very specific but slow and complex. The proposed research will introduce molecular specificity into the space of rapid assays for biological threats. The assay could also serve as a useful research tool in its own right, for detecting and quantifying nucleic acids in a wide variety of research contexts. This ties to both DHS and DOE science missions.

Working Memory Metrics for User Interface Evaluation

149945
Year 1 of 1
Principal Investigator: L. A. McNamara

Project Purpose

This is a pilot proof-of-concept usability metrics project that will break ground in the field of software usability evaluation. State-of-the art usability assessment relies on observations of users engaging in predefined tasks, generating data (e.g., time on task, completion rate) specific to the application at hand. However, a validated metric that assesses cognitive load could provide a platform-independent way of evaluating whether user interface designs increase (or mitigate) cognitive burden, particularly when people are learning a new tool. We believe that working memory tasks are one way of leveraging the concept of cognitive load to provide metrics for assessing if particular design options require more cognitive resources than others for a given task. To test our metrics idea, we will collaborate with the Capable Manpower (CMP) team to design and conduct a user-interface (UI) evaluation study of its Debrief Player. Developed for the Navy, the Debrief Player is an after-action review tool that allows an instructor to review a video playback of student performance, make annotations on a timeline of the training session, and observe other annotations made by Sandia-developed machine learning technology. It was chosen for this study because, at its current stage of development, it offers a simplified interface and limited features.

If our proof-of-concept project is successful, we will be poised to introduce a novel objective metric for the evaluation of interfaces. Metrics based on cognitive science could provide designers with objective information on the effectiveness of prototypes, improving the quality of deployed applications, and reducing waste due to excessive iterations. No such objective measure exists today. We expect this work to break ground in applying experimental psychological methods to the practical challenge of designing and evaluating user interface designs, as well as more complicated applications.

Summary of Accomplishments

We implemented a 10-participant pilot study to investigate the application of working memory (WM)-based evaluation methods for assessing user interface designs. Human-computer interaction (HCI) literature describes a range of UI evaluation approaches, from heuristic evaluation, to subjective usability evaluations, to more controlled user studies organized around specific tasks. However, objective metrics that allow designers to assess cognitive workload for a particular interface, and to compare workload across different interfaces and users, are not currently a normal part of UI evaluation practice. Instead, workload assessments tend to be derived from subjective reporting; e.g., using the NASA Task Load Index.

Our study examined if a Sternberg task would provide relevant data on cognitive load in user interface evaluation. Rather than focus on complicated information visualization software, we decided to deploy our technique in assessing the cognitive workload associated with two different user interfaces for a simple video viewer and annotation package. We found that participants took nearly twice as long, on average, to complete the task set using the second video viewer than they did with the first video viewer.

We are cleaning data from the Sternberg task and analyzing it across the two sets of primary tasks. Because we designed parallel task sets, we will be able to compare the participants' Sternberg task accuracy and response time across CMP Viewer versions for each task. We expect to find that response times on the Sternberg task are significantly longer for each task performed using the difficult video viewer compared to the parallel task in the easier viewer. We expect to present the findings from the present study and the graph study at the Beyond Time and Error: Novel Methods for Information Visualization Evaluation workshop at the Association for Computing Machinery, Special Interest Group on Computer-Human Interaction meetings in April 2011.

Significance

Both DOE and DHS develop and acquire novel software applications. Our metrics study will provide software developers, users, and decision-makers with a means of assessing if critical applications are placing undue cognitive burden on users, and identifying design parameters that can improve how users interact with applications. We believe that incorporating measures of cognitive workload into UI evaluations may provide quantitative comparisons that can help researchers to more precisely assess features of user interfaces that facilitate a user's operation of the interface. In much the same way as in other technology design and evaluation projects, it is reasonable to expect that users will expend greater mental resources compensating for a bad UI design, and that tax on their resources will show up as a drop in performance on a concurrent secondary task. If this is true, it has important implications for the design of software for more complex analytical and problem-solving activities: as a user devotes more cognitive resources to navigating a difficult interface or interpreting a confusing UI, s/he will have fewer resources available for actually applying the tool to real-world data for real-world problems. Well-designed user interfaces should minimize cognitive load extraneous to the problem at hand.

We believe that memory-based metrics may provide an objective way to assess cognitive load in user interface design, and that this is a basic but critical "first step" to a more comprehensive methodology for assessing how information visualization and visual analytics tools influence the users' problem-solving processes. Although we are still in the process of cleaning and analyzing our data from this study, we expect the findings to provide useful information about the utility of Sternberg tasks in assessing cognitive workload associated with user interface designs, both generally and in relation to information visualization toolsets.

Group Automated Knowledge Capture

150118
Year 1 of 1
Principal Investigator: A. J. Scholand

Project Purpose

Sandia's programmatic road map calls for extending psychological modeling and automated knowledge capture across the component, the component interaction, and the systems level. The central technical challenge is that, within group and organizational settings, individual psychological states and their influence on cognition are not directly observable—only the resultant behavior and language are. This project responds to this road map call with research in a quantitative knowledge capture technique that is a novel combination of social network analysis with top-down psychological linguistic classification. This approach leverages both subtle psychological clues in natural language and the purposeful and non-random structure of human social networks. The results of this research condense raw linguistic field data into quantitative formulas that can be used either to make falsifiable predictions or retrospectively describe group or organizational interactions with a sound psychological basis. Given their mathematical formulation, these system-level results may then be especially useful in the development of new generative representations (models) for computational experiments.

Summary of Accomplishments

We discovered a novel application of information retrieval topic modeling that is able to differentiate and measure the value of individual contribution to group distributions, assess the relative distribution of per-topic expertise across this group, and identify the locus of attention of various subgroups. Computed metrics correlated moderately well (Spearman correlation of 0.56 and $p = 0.024$, 14 degrees of freedom) with survey-elicited self-reports of proficiency with instant messaging technology. Distribution of scores matched patterns predicted by "legitimate peripheral participation" theories of community engagement, and aggregated scores by gender are consistent with the social psychology finding that social relations are of greater importance for women than for men.

At a practical level, we were surprised to find that a popular topic modeling technique, Latent Dirichlet Allocation (LDA), was of limited utility for analyzing smaller chat corpora (our corpus consisted of approximately 1000 documents). We were not able find a previously published lower bound on the size of the corpora suitable for analysis by LDA. For smaller corpora, principle component analysis appears to perform better in identifying and extracting major themes.

Significance

Anticipated benefits from the proposed research relate to DOE Strategic Goal 5.2 (Human Capital) due to the applicability of likely findings to work settings (group and organizational functioning). We also anticipate that the research will contribute to DOE's Strategic Goal 3.1 of achieving scientific breakthroughs in the computational sciences, because the proposed method, if successful, could radically transform our ability to study and understand computer-mediated activity.

An Adaptive Approach to Modeling Human Reasoning

150966
Year 1 of 3
Principal Investigator: D. J. Stracuzzi

Project Purpose

The human mind is designed to support practical action in the face of a complex and uncertain world. The purpose of this project is to create a psychologically plausible reasoning system that reflects the strengths of human reasoning. As a part of this objective, the project also aims to develop an understanding of the fundamental mechanisms that guide human reasoning. The approach will be to combine multiple reasoning methods and modalities in an effort to emulate the powerful and pragmatic nature of human reasoning, and a key goal will be to identify a mechanism for determining which reasoning steps to pursue next. As a result, the project will address a variety of questions about how to represent knowledge, combine reasoning techniques, and incorporate the effects of learning, experience, and bias on reasoning. The approach of combining multiple reasoning techniques and using learning as a guide also distinguishes the proposed work from past efforts at computational reasoning that tend to focus on a single technique and ignore the question of how to decide the appropriate method to use in a given situation. The work is both high-risk, due to the novelty of the effort, and high-impact, due to the potentially broad applicability of the results. If successful, this work will provide a solid foundation for future research on human decision-making, automatic knowledge base acquisition, fusion of low-level state descriptions into high-level, actionable knowledge, and neurally plausible models of high-level reasoning mechanisms, all of which are likely to play critical roles in future sponsored projects.

Summary of Accomplishments

Accomplishments on the project to date include the following: 1) identification of relevant psychological theories of reasoning; 2) identification of relevant reasoning frameworks from artificial intelligence and mathematics; 3) identification of relevant psychological literature on cognitive biases; 4) an initial design for the reasoning architecture that integrates reasoning and learning and includes several cognitive biases; and 5) a partial software implementation of the reasoning architecture (approximately 75% complete).

Significance

The ability to understand and emulate human reasoning plays a key role in developing technologies that both aid humans in their work and monitor for errors and malicious acts. From the perspective of DOE, which must provide physical and virtual security to its complexes, models of human reasoning can help anticipate and determine possible points-of-attack, strategy, and tactics of malicious individuals or groups. Similarly, an understanding of human reasoning can help predict possible sources of error in human operators and users. For example, this work could contribute to research in alarm communication and display by providing decision support to operators and by simulating human operators in the context of system tests. From the perspective of DoD, a robust and scalable reasoning system can contribute to automated battlefield assessments, and serve as decision aids to local commanders. Moreover, a reasoning system that emulates human capability will be primed to anticipate the needs of its users, an increasingly important field of study.

SCIENCE OF EXTREME ENVIRONMENTS INVESTMENT AREA

The Science of Extreme Environments (SEE) investment area seeks to create new knowledge that enables revolutionary advances in the areas of high energy density physics, radiation sciences, pulsed power, and fusion energy for national security needs. A synergistic combination of experiments and theory provides insights into the nature of electronics under exposure to x-rays, gamma rays, neutrons, and other charged particles, and enables the production of high power density x-rays from impressive pulsed power systems. Theoretical computational studies reveal the nature of the complex plasmas formed and aid in such pursuits as the production of high power microwaves for missile defense. This investment area clarifies scientific understanding about environmental conditions rarely encountered in everyday experience (save for example, rare situations such as lightning), but which are nevertheless commonplace in several Sandia national security mission areas.

Fundamental Hydrogen Interactions with Beryllium Surfaces: A Magnetic Fusion Perspective

Project 148957

Magnetically driven fusion, exemplified by the massive ITER project is an important path to alternative, carbon-neutral energy production, based on magnetically driven fusion of hydrogen (in the form of a plasma of its deuterium and tritium isotopes) within a chamber known as a tokamak. With the conversion of a small amount of mass to energy during fusion, the potential exists for the infusion of electromagnetic energy to be more than counterbalanced by significant energy liberation. The inner lining of the tokamak is formed of beryllium, and thus is the surface that the hydrogen plasma directly faces and can interact with. Hence, an important fundamental question involves the details of this hydrogen-beryllium interaction at the atomic scale. Such is the research challenge undertaken by this early career LDRD project.

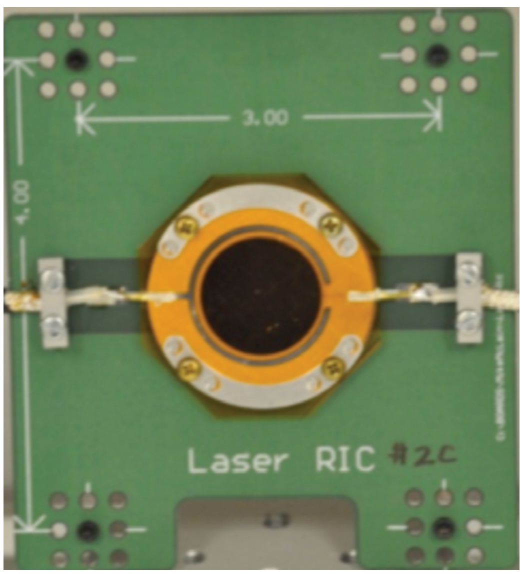
With the unique capabilities of Sandia's ARIES (angle resolved ion energy spectrometer), the project is able to study hydrogen-beryllium interactions in the detail necessary to begin to understand the fundamental physics of the interaction, which will likely be a key to the ITER project's success. Adding Auger electron spectroscopy to the analytical capabilities has assisted the experimental effort, which is complemented by simulation of the ion scattering using the binary collision code, MARLOWE, as well as pair potential calculations with the molecular dynamics code, Kalypso.

Experimental setup utilized in this project

Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates

Project 148196

Radiation-induced conductivity (RIC) is an important phenomenon for electronics components exposed to high-radiation environments, for example weapons components in certain situations or satellite components and those of other space vehicles. The challenge of shedding light on this incompletely understood phenomenon presented an inviting opportunity for an early career LDRD proposal in pursuit of enhanced phenomenological understanding. Focusing on the dielectric, Kapton®, as a representative material, part of this project's motivation derives from the linearity of the RIC response to radiation at dose rates below 10^{10} rad(Si)/s, with, however, only an assumption, based on modeling studies, that the same effect linearity holds at higher dose rates. (Kapton is used in, among other things, flexible printed circuits and the outside layer of space suits, and is the material of choice for the sunshield of the James Webb Space Telescope.) This project's hypothesis is that it should be possible to experimentally test the dose-rate phenomenon by substituting high-intensity, short-duration laser pulses for the linear accelerators (LINACs) and flash x-rays normally used to deliver the ionizing radiation for inducing RIC. This would render the experimental procedures both more tractable and less expensive, and ultimately, allow experiments to provide validation — or, if relevant, disconfirmation — of dose-rate–RIC linearity at higher doses, for both Kapton and other dielectrics. Given the importance of this radiation effect to a diverse group of Sandia missions for DOE and NNSA — and indirectly for other agencies such as NASA— this accomplishment would represent an important step for better understanding and testing this phenomenon for both currently available and future materials.



Indium tin oxide electrode for laser-RIC experiments

SCIENCE OF EXTREME ENVIRONMENTS INVESTMENT AREA

Measuring High-Pressure Strength on Pulsed Power Machines

117856
Year 3 of 3
Principal Investigator: C. S. Alexander

Project Purpose

The strength of materials at high pressures and strain rates is a critical aspect of modeling material behavior for DOE weapons applications as well as design of inertial confinement fusion (ICF) capsules for ignition on the National Ignition Facility. Strength is defined as the ability of a material to sustain deviatoric (shear) stresses. It has proven extremely difficult to measure material strength under high-pressure dynamic loading because the governing equations for wave propagation provide no information about stresses in directions normal to the direction of wave propagation. Traditional wave profile techniques to measure strength are limited to ~2 Mbar pressures. The goal of the proposed project is to develop new techniques that will extend this limit significantly. Laser techniques have demonstrated that Rayleigh-Taylor (RT) instability growth is governed by strength properties and offer the only existing capability to measure strength above 3 Mbar. However, sample size is limited to a few microns, prohibiting observation of some effects, such as grain size and internal defects. Further, the interpretation of RT instability data requires the use of computer simulations limiting the accuracy of the results to that of the models used. This project has identified a novel method of inducing and measuring shear motion (normal to the direction of wave propagation) behind an applied pressure wave, by application of an external magnetic field, which will allow a direct measure of material strength without relying on computational models. This approach represents a quantum leap forward in our ability to measure strength at high pressure. The technique has been demonstrated at modest pressure to measure shear strength of aluminum on the Veloce accelerator with the intention of transitioning the technology to Z in the near future. Based on our new technique on Z, we will be able to measure shear strength up to approximately 6 Mbar, twice the present limit.

Summary of Accomplishments

We have demonstrated the new Magnetically Applied Pressure-Shear (MAPS) technique to measure the strength of aluminum at 10 GPa. The results agree with existing data collected by other approaches. The MAPS technique has also been used to measure material properties in order to validate existing computational models. The new technique can be used to measure both longitudinal and shear stresses which was previously not possible without the use of embedded gauges. In addition, we have fielded a transverse-capable velocity interferometer system to allow for the measurement of both longitudinal and transverse motion. Based on earlier Sandia designs, the new system uses fiber optics to effect a safer and more-compact device.

Significance

The project has addressed the need to measure high-pressure strength of plutonium and other relevant materials in support of Campaign 2, where strength measurement is currently the number two priority. In addition, this project will provide data for the development of predictive models in the Advanced Simulation and Computing program and ICF capsule design work. This will be accomplished while maintaining realistic sample sizes relevant to real-world applications.

Refereed Communications

C.S. Alexander, J.R. Asay, and T.A. Haill, "Magnetically Applied Pressure-Shear: A New Method for Direct Measurement of Strength at High Pressure," to be published in the *Journal of Applied Physics*.

Demonstration of Fast Pulsed Neutron Capability for Device and Board Testing

117860
Year 3 of 3
Principal Investigator: V. Harper-Slaboszewicz

Project Purpose

The early time response and recovery of weapon system electronics to intense neutron pulses is a crucial issue for weapons effects. Fast burst reactors have been the facilities of choice to evaluate this response, but the Sandia Pulsed Reactor III is no longer available, and the future availability of the White Sands Fast Burst Reactor is questionable. Currently, the best facility for evaluation of these effects at very early times is LANSCE (Los Alamos Neutron Science Center). It provides 1–2 $\times 10^{12}$ n/cm^2, 1 MeV (Si) equivalent in a 150-ns pulse over ~8 cm^2 at the experiment position. Other neutron test facilities provide long continuous exposures or much lower fluences that do not access the response regime of interest.

Accelerator-based neutron sources consisting of proton and deuteron beams impacting tritium, lithium, or beryllium targets have been used in a variety of applications. However, they have not been coupled with high-power pulsed power drivers to produce large, fast neutron bursts. This project proposes to couple these sources to the Hermes III accelerator to provide a small area (~10 cm^2), high-fluence (~2 $\times 10^{14}$ neutrons), fast neutron burst for electronic device and board testing, which would represent an improvement in capability compared to LANSCE for this application.

The performance of the ion source is key to the success of this project. The required ion efficiency has been observed in earlier experiments, but modern modeling tools have not been applied to this source. Coupled models of the accelerator and the diode have been developed. Initial experiments suggest reasonable agreement between the modeled and observed behavior.

This project will demonstrate the ability to produce useful levels of pulsed neutron fluence to evaluate weapon component reliability in nuclear environments in a nonreactor facility with easy access for diagnostics.

Summary of Accomplishments

We found that the previous pinch reflex diode design did not perform well, so we developed a new type of reflexing ion diode in which the radial gap determined the operating impedance but the axial gap provided the ion beam. By separating the impedance-determining and ion-production region, this design can be better tailored to couple efficiently to the pulsed power driver and produce and a proton beam in the desired geometry. This new diode design substantially increased the proton beam current produced using Hermes III.

This project was plagued by ion and beam diagnostic inconsistency, so we developed a new diagnostic, the compact ion pinhole camera, the images of which can be unfolded to provide unequivocal information on the ion energy and current. The results from this new diagnostic have been folded with the other diagnostics (neutron activation, faraday cups, Rogowski coils) to provide a consistent understanding of ion diode operation.

A third focus area was the ion source itself. Most of the experiments used a plastic anode, which produces copious amounts of hydrogen, but does so nonuniformly and with a significant delay time. We developed an new ion source based on previous experimentation, which promises to provide a more uniform initial hydrogen distribution, and can be used to create a pure deuterium for use in a pulsed-power-driven ion source.

Significance

This work provides the physics basis for a decision whether to proceed with an intense pulsed fast neutron source for characterization of the response of components and boards to fast neutron pulses. The results can be used to determine the pulsed power driver requirements for a beam neutron source using this physics to support neutron effects characterization.

A major component of that decision is the perceived need for an experimental capability to provide this characterization, based on anticipated future needs. That component is beyond the scope of this project.

The work in this project can be extended in a number of directions. For example, it could be used to determine the driver requirements for an ion-beam driven subcritical assembly to provide a fast pulsed neutron environment. It could be used to support the design of a pulsed power neutron source for isotope production. Using a deuterium source, it could be used to design a compact neutron source for special nuclear materials detection.

Scaling of X-Pinch X-Ray Sources from 1 MA to 6 MA

117863
Year 3 of 3
Principal Investigator: D. Sinars

Project Purpose

Experiments studying x-pinch plasmas driven by 0.2 MA have demonstrated that it is possible to create micropinches that are 0.8–1.5 microns in diameter, have temperatures of about 1 keV, densities >10% of solid density, and last for 10–100 ps, making them warm-dense objects of considerable interest. Prior research by other groups has noted that Mo x-pinch plasmas driven by 1 MA might radiate 80 GW from a 1-micron, 10-times-solid-density source, and at 10 MA would radiate 3.4 TW from a 1-micron, 250× solid density source. Such plasmas would be extremely interesting physical objects, and the radiation power is comparable to that produced by high-power lasers, so that it might be possible to use these sources in several applications. This project proposes to extend x-pinch research beyond the 1 MA level available at most university facilities today by conducting experiments on the 6 MA Saturn accelerator. We will determine if indeed such extreme plasma conditions can be achieved at higher currents, or whether additional physical principles limit the micropinch plasma size. Many z-pinch devices, including plasma focus, vacuum spark, and wire-array z-pinches appear to show the presence of small, bright x-ray spots that may be related to those present in x-pinch plasmas. At present, Sandia is the only place in the world where this scaling can be done. There is a high risk entailed in this project, not only in attempting to create such extreme plasmas, but also in accurately diagnosing the conditions achieved.

Summary of Accomplishments

1. We developed a criterion that could be used to estimate the mass/length and diameter scaling of an x pinch to currents >1 MA.
2. We found an optimum load geometry (the "solid" x pinch) that gave good data for high-current x-pinch experiments in the 3–6 MA range, which can also be readily scaled to higher currents as needed.
3. We partially optimized the specific x-pinch parameters of a solid x-pinch target made of tungsten, and succeeded in generating micropinch plasmas.
4. We initially diagnosed x-pinch and micropinch parameters on our 3–6 MA experiments, as follows:
   a. Sources of >6 keV continuum x rays that were 5–10 microns in diameter and <500 ps in duration;
   b. Time-integrated plasma temperatures of 2–3 keV capable of making Cu K-shell radiation from relatively compact (few hundred microns) x-ray sources; and
   c. Bright and compact (~3 mm) sources of soft (0.1–1 keV) x rays, ~4 TW/mm and >60 kJ/mm.
5. This research and related work at the 1 MA COBRA facility at Cornell University has led to four scientific publications in refereed journals, with at least one more forthcoming.
6. Newly hired experimenters in the inertial confinement fusion research group were able to obtain hands-on experience with x-ray instrumentation and large-scale pulsed power prior to their first experiments on Z.

Significance

This project addressed the fundamental physics of magnetically driven implosions using x-pinch targets. What are the ultimate limits for the magnetic compression of plasma using the J×B force? What are the most extreme plasma conditions we can create in the laboratory using magnetic compression? This physics is of interest to Sandia, since most research using pulsed power drivers relies on the J×B force to move, shock, and/or compress material to the extreme conditions required for stockpile stewardship research. This project represents a first step down a path toward understanding the limits of magnetic compression at currents >1 MA. It was primarily a survey of high-current (3–6 MA) x-pinches to understand whether extreme plasma conditions might be occurring in the laboratory. The project succeeded in creating x-ray sources that appear to be interesting.

Though it was not the primary goal of the project, we note that several x-pinch loads produced ~10 TW and ~190 kJ of soft (0.1–1 keV) x-rays from a diameter of ~3 mm. This corresponds to about 4 TW/mm and about 60 kJ/mm from a ~6 MA current generator. In comparing these results to power and yield from tungsten wire arrays on Saturn, we find that the radiation power and energy created at stagnation in the x-pinch loads is comparable to those created in wire-array z-pinches. The two approaches are different, however, in that the wire arrays relied on a high-velocity implosion to reach extreme conditions, whereas in the x-pinch, all of the mass started on the axis from the beginning. That is, the x-pinch does not rely on the conversion of magnetic energy into kinetic energy, and thereafter, to radiation energy, at least not in the traditional way. Rather, it relies on the steady application of the J·B force to plasma on the axis in a way that continuously does work and ultimately compresses at least a small fraction of the plasma to extremely small diameters. In terms of how tight a radius the current achieves, we speculate that the potential that extreme conditions were achieved on Saturn is very high. In at least one experiment, we created a bright >6 keV x-ray source from a tungsten plasma that was 5–7 microns in diameter, or ~3 microns in radius. If one assumes that ~3 MA was flowing at that radius, it would correspond to a magnetic pressure of $140\times(3/30)^2/(3^{-3}\text{ mm})^2$ Mbar, or over 150 Gbar. Even if only 0.3 MA of current flowed to that radius, the pressure would still have been 1.5 Gbar. For reasonable plasma temperatures of 0.6–3 keV, these pressures correspond to ion densities in excess of solid density.

Refereed Communications

T.A. Shelkovenko, S.A. Pikuz, R.D. McBride, P.F. Knapp, G. Wilhelm, D.B. Sinars, D.A. Hammer, and N.Y. Orlov, "Symmetric Multilayer MegaAmpere X-pinch," *Plasma Physics Reports*, vol. 36, pp. 50-66, 2010.

T.A. Shelkovenko, S.A. Pikuz, R.D. McBride, P.F. Knapp, H. Wilhelm, D.A. Hammer, and D.B. Sinars, "Nested Multilayered X Pinches for Generators with Mega-Ampere Current Level," *Physics of Plasmas*, vol. 16, p. 050702, 2009.

Physics of Intense, High-Energy Radiation Effects

117866
Year 3 of 3
Principal Investigator: H. P. Hjalmarson

Project Purpose

Intense, high-energy irradiation of materials is an important activity at Sandia but the information obtained has usually been empirical. In this project, we propose to use physics-based simulations linked to experiments using Sandia and other facilities to explore the phenomena. We will focus on the effects of short pulses of high-dose-rate ionizing radiation on materials such as insulators and semiconductors. The radiation creates high-energy electrons and holes; subsequently, these hot electrons and holes tend to recombine or produce fast transient electrical current. The recombination can create excitons, and these excitons can cause material damage. Furthermore, the localized heating caused by the cooling of the hot carriers will also cause material damage. The expected phenomena will be similar to those encountered in electrical breakdown and laser ablation. The physics will be approached using a blend of continuum and atomistic methods. Continuum methods for such problems will be applied to understand the electrical effects and lattice damage effects at long times after the pulse. These continuum calculations will use information obtained from molecular dynamics (MD) and time-dependent density-functional theory (DFT) calculations focused on transient materials changes during the cooling process. These calculations will be applied to high-dose-rate simulations of radiation-induced conductivity (RIC) in silicon dioxide and other materials. In the project's last year, these calculations will be applied to radiation-induced discharge of capacitors and RIC in foam insulators.

Summary of Accomplishments

This project continued a focus on the effects of transient, high-dose-rate ionizing radiation on the dielectric function of a material. This approach and the information obtained was used as a basis for the development of time-dependent DFT capability in this project. The continuum calculations have focused on a prototypical structure, a simple metal-insulator-metal structure.

In general, the transient radiation applied to the prototypical structure produces a transient current that generates an electromagnetic pulse (EMP). The combined effect caused by the initial current and the response current is called system generated EMP (SGEMP). The continuum calculations have been used to compute the SGEMP response from the prototypical structure. These calculations reveal that electrons, holes and sample defects are all necessary to understand the physics of SGEMP.

The continuum calculations reveal that the present Advanced Simulation and Computing Program method for computing these effects should be improved. This method relies on empirical steady-state RIC data. However, in insulating materials, the RIC varies greatly during a radiation pulse. Thus the use of steady-state data is not valid. These temporal effects were illustrated in a series of calculations for the simple structures.

We have proposed a new method as a consequence of this project. In this method, we use a physics-based model to interpret the RIC data in terms of materials information such as defect densities and defect properties. We then use this materials information in a model to obtain the calculated RIC as a function of time, radiation pulse, and radiation history. Ultimately, we use this calculated RIC for the SGEMP calculations.

A series of MD calculations has focused on transient radiation effects using a two temperature modeling (TTM) capability that has been added to the MD code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). We used this TTM capability in a new set of calculations focused on quartz.

Significance
Sandia has large experimental facilities that expose materials to high-energy radiation for nuclear weapons programs. However, there is little predictive simulation capability focused on understanding the known effects or discovering new effects.

Refereed Communications
C.L. Phillips, R.J. Magyar, and P.S. Crozier, "A Two-Temperature Model of Radiation Damage in Quartz," to be published in the *Journal of Chemical Physics*.

A. Prez, M.E. Tuckerman, H.P. Hjalmarson, and A. von Lilienfeld, "Enol Tautomers of Watson-Crick Base Pair Models are Metastable Because of Nuclear Quantum Effects," to be published in the *Journal of Chemical Physics*.

Advanced Tactical HPM System via NLTL and LWA

130802
Year 2 of 3
Principal Investigator: J. J. Borchardt

Project Purpose

DoD requires tactical high-power microwave (HPM) systems that disrupt or damage electronics in operational environments. Current HPM systems suffer from bulk and weight of radio-frequency (RF) source ancillary systems. The purpose of the project is to develop the nonlinear transmission line (NLTL), a novel HPM RF source component. The NLTL potentially offers game-changing capabilities for tactical HPM systems via frequency tune and high repetition rates — without water, vacuum, cathodes, or undesired x-ray generation typical of traditional, relativistic electron beam HPM source technologies. The primary S&T objectives are understanding, modeling, and controlling nonlinear RF generation and scaling NLTL devices and materials to very high powers. The programmatic objective of this project is to provide DoD with alternatives to traditional HPM technologies that significantly increase tactical utility of HPM systems.

NLTL research includes modeling of the nonlinear dynamics of NLTL creation of a low-power NLTL for rapid experimental iteration; assessment/development of nonlinear electromagnetic materials for high-power scaling; and design, construction, and demonstration of a prototype high-power NLTL. The anticipated benefit of this research is increased tactical utility of future HPM weapon systems through significant increase in power on target per unit system size/weight and significant reduction in HPM system platform integration constraints. The elevated risk in this work derives from the fact that significant basic research on scaling NLTL powers together to the gigawatt regime remains undone (e.g., modeling and materials research). While the potential rewards of this research are great, the technological barriers are commensurate.

Summary of Accomplishments

We demonstrated excellent progress regarding NLTL development in FY 2010. Beginning in FY 2009, we developed a series of low-power magnetic NLTL prototypes using printed circuit board construction. We achieved reasonable agreement between experiment and a simple NLTL nonlinear circuit model and demonstrated several interesting operational regimes, including the "backward wave" regime. Another demonstrated operating regime is a novel result of this project. Both regimes are very important from an HPM system perspective; for example, backward wave operation leads to significantly longer RF pulse output. This potentially increases HPM target effectiveness by delivering more RF energy to the target per pulse. Additionally, we completed an electromagnetic design of a prototype high-power (e.g., 1 MW at 1 GHz) magnetic NLTL during FY 2010. We used a commercial finite element solver to predict and refine the RF performance of the design geometry. This data was compared with a solution of the equivalent circuit that incorporated measured parameters of candidate nonlinear magnetic materials. Once the design was finalized, parts were fabricated during FY 2010; assembly and testing of this prototype will commence in FY 2011. This design process has clarified some finer points of NLTL device physics that can support further device refinement and development. Finally, we designed, assembled, and tested much of the pulsed power driver required to excite the NLTL in FY 2010.

Significance

The core R&D accomplishments of this project are significant to the general S&T community as well as relevant to Sandia's National Security Mission areas. With respect to the latter, the need for nonlethal, counter-materiel weapons to enhance US capability in conventional and irregular warfare is well established. For example, the Department of Defense 2006 Quadrennial Defense Review identifies nonlethal technologies as a needed capability to combat both terrorism and weapons of mass destruction threats. HPM technology is identified as a key capability in the Major Combat Operations Joint Operating Concept document and other DoD planning documents. As such, novel HPM source technology development that enables fundamentally new capabilities (such as frequency tuning and high repetition rates) while reducing size, weight, power, and ancillary system requirements in fielded, tactical systems directly supports DoD technology strategy. Thus, this project falls well within Sandia's national security mission space.

Several other important potential applications for the research undertaken in this project are of interest to the general S&T community. Nonlinear dielectric, nonlinear magnetic, and electromagnetic shock wave phenomena are of general interest to many science and engineering disciplines. For example, nonlinear pulse sharpening devices can provide unique capabilities in pulsed power research systems, as demonstrated in the Sandia Repetitive High-Energy Pulsed Power system. Reduced pulse rise times and refined pulse shaping capabilities in high-energy-density physics and inertial confinement fusion facilities such as the Z-Machine are also possible with the use of nonlinear and electromagnetic shock phenomena. In addition, NLTL technologies developed within this project in particular could potentially serve as compact, high-power RF sources in some radar applications (e.g., air traffic control) and charged particle accelerator applications (e.g., linear accelerators). In particular, compact, high-reliability, and low-cost particle accelerators are desired for medical radiation therapy facilities.

Confinement of High-Temperature Laser-Produced Deuterium Plasmas Using Pulsed Magnetic Fields

130804
Year 2 of 3
Principal Investigator: K. W. Struve

Project Purpose

In this project, we will use the Sandia Z-Petawatt laser to produce a high-density ($10^{19}/cm^3$) deuterium plasma that generates a large fusion neutron flux (10^9/pulse) and to enhance that flux by 10^3 with a strong (100–200 T) externally applied magnetic field. The neutrons have application for materials studies and for dense plasma diagnostics. Measurement of plasma diffusion across the magnetic field also provides critical information on high-density fusion-plasma transport properties. Recent experiments have shown that interactions of intense ultrafast lasers with targets of small atomic clusters with hundreds to thousands of atoms can produce very high ion temperature plasmas. This phenomenon is exploited to produce DD fusion neutrons in the exploding deuterium clusters. Because ion temperatures can exceed 10 keV, it is possible to produce fusion neutrons with a laser energy of a few joules to a few hundred joules.

The fusion yield in these experiments is limited by the fast disassembly time (<100 ps) of the deuterium-cluster plasmas. Enhanced neutron yield is possible if plasma confinement can be improved with an external magnetic field. At the densities of these plasmas ($10^{19}/cm^3$), magnetic fields approaching 100 T are needed for magnetic confinement. The magnetic field will be produced in a magnetic mirror configuration with small coils (5- to 15-mm diameter) driven by a 120-kJ capacitor-bank pulser with currents up to 2 MA. This work is a joint Sandia/University of Texas (UT) project. Sandia will develop the driver and coil to produce magnetic fields up to 200 T in vacuum. This device is being built in two stages, with the first stage, a 50 T prototype, completed and delivered to UT. The UT scientists, who have experience with cluster plasma formation and experiments, will perform cluster-fusion theory and computations, set up the cluster generator, and perform initial laser experiments.

Summary of Accomplishments

For FY 2010, work continued in two parallel efforts. The first was final design, construction, and testing of the magnetic field coil driver and vacuum system at Sandia. The second was to mate the cluster nozzle and diagnostics to the coil driver and vacuum system, and perform initial experiments at UT, Austin. Milestones related to finishing design, constructing, and testing of a prototype device are being addressed, but not yet complete. But we are now in a position to demonstrate capability to produce 50 T or greater magnetic fields by the end of FY 2010.

We have completed building a 50 T prototype, have tested at the 20 T level, and shipped to UT. The team at UT has done initial testing with a coil and nozzle with a smaller version and find that special care must be taken to avoid shorting of the coil by cluster and gas. The 200 T system construction has been delayed until testing with the 50 T system is first done at UT. With the 50-T driver and vacuum-chamber assembly at UT, it is possible to first do laser tests with the deuterium gas nozzle and coil assembly to determine the effect of the magnetic field on the cluster-fusion plasma expansion. These are now being done.

We have fabricated both copper and steel coils, and UT has performed initial testing to investigate potential shorting by deuterium gas jets from the cluster nozzle assembly. Mechanical mounting issues with the nozzle/puff valve assembly have been resolved. UT has designed an optical setup with interferometer and Schlieren imaging to study the cluster jet interaction with the coil, and has written codes to interpret the resulting images.

Significance

As part of this research project, new experimental techniques will be developed to measure the properties of fusion-relevant plasmas in the presence of strong magnetic fields. It is likely that new experimental techniques will be created that will lead to a detailed understanding of how strong magnetic fields effect the fundamental transport properties of high-energy-density plasmas. This is directly relevant to advancing pulsed-power magnetized-target-fusion concepts that are being evaluated. We are also developing a capability to do high-field experiments on the Z Petawatt laser for a variety of other applications.

High-Efficiency High-Energy K-Alpha Source for the Critically Required Maximum Illumination of X-Ray Imaging Optics on Z Using Z-Petawatt-Driven Laser-Breakout-Afterburner-Accelerated Ultrarelativistic Electrons

130805
Year 2 of 2
Principal Investigator: G. R. Bennett

Project Purpose

Upon its completion, Sandia's Z-PetaWatt laser (ZPW) will provide a high-energy, ultrashort-duration x-ray source in order to illuminate an x-ray optic that is imaging a Z-accelerator-driven experiment. Crucial towards outstanding x-ray imaging performance is the attainment of significantly higher conversion efficiencies, ε, of laser light into K-alpha-1($K\alpha_1$)x-rays (for example, 25.2713 keV for Sn) than is presently possible with conventional direct-flat-foil irradiation (DFI). To this end, we have recently conceived of a short-pulse laser-driven two-stage Kα target concept utilizing an approximately 30-nm-thin (for example, carbon) foil, irradiated by ZPW at ~10^{21} W/cm^2 with ultrahigh contrast, followed by a micron-sized converter foil (for example, tin). In this scheme, the thin foil is rapidly and fully ionized, laser energy is efficiently absorbed by the electrons and burns through the foil, and the ions are thus accelerated in bulk via the relativistic Buneman instability to high energies (>1 GeV).

This mechanism, discovered computationally at Los Alamos National Laboratory is termed the laser Break-Out-Afterburner (BOA) effect. The accompanying high-efficiency ultrarelativistic (γ-e >>1) electron cloud then impacts a tin converter foil, creating 25.2713-keV $K\alpha_1$ x-rays. A higher ε is expected largely due to the sheer number of bulk-heated BOA electrons, which achieve highly populated relativistic energies, thereby producing many K-shell vacancies and thus $K\alpha_1$, $K\alpha_2$, etc. x-rays. State-of-the-art numerical simulations with analytical calculations indicate a possibly greater than ten-fold ε enhancement over the present ε~1e^{-4} of the conventional DFI method. If realized, this would be an outstanding benefit to Z, and possibly the advanced radiographic capability on the National Ignition Facility (NIF). Although this project has concluded, additional work will continue for the purpose of numerically investigating/optimizing the target concept. If the simulations continue to be favorable then journal publications may ensue. Thereafter, the same computational/theoretical tools will be used to design, guide, and analyze high-ε experiments.

Summary of Accomplishments

A state-of-the-art predictive/computational capability has been established allowing $K\alpha_1$ and $K\alpha_2$ x-ray production to be modeled for a target of any material irradiated by a petawatt short-pulse laser. The capability is continuingly being advanced, but at present, the tool has already closely predicted the measured x-ray yields from simple Sn targets irradiated by the so-called 100-TW system. This device will eventually become the ZPW. (Ongoing numeric advances include investigating the effect of a preplasma created by the finite prepulse of a petawatt-class laser.)

The computational tool's success in predicting experiments provides confidence that more-complicated, novel target concepts can be numerically investigated with accuracy, in particular, the two-stage BOA idea. The BOA-produced beams from the "first stage" are used to effectively heat a larger source(s) second stage. (Sn has been the main interest so far). Notably, Los Alamos National Laboratory–published BOA simulations were reproduced during the early course of this work. Moreover, the preplasma level as a function of prepulse can now be predicted; however, incorporation of a particular preplasma into a BOA simulation has not yet been performed. Should the two-stage concept be successful for Sn- Kα_1 (25.2713-keV, and success is defined as a greater than ten-fold ε enhancement), the technique should also work for higher atomic number (Z) elements. However, it is believed that the electron impact K-shell ionization cross section sigma for such elements decreases. The overall outcome would likely be an ε lower than that of Sn (Z=50), despite the fact that the nonradiative Auger "loss" would be close to zero. For elements Z <50, it is believed that sigma rapidly increases. This could dramatically increase ε for x-ray energies around 6 keV, a photon energy that is routinely used on many Z accelerator experiments. This would require the use of a low-Z element, with the drawback that the nonradiative Auger loss is high. It is therefore unclear if a low-Z two-stage target would be advantageous compared with a long-laser-pulse, thermally generated 6.151-keV radiation from Mn. If the low-Z two-stage technique does indeed show a greater advantage, then consideration should be given to converting the long-pulse Z Beamlet Laser (ZBL) into a ZPW device, with the option of reverting to long-pulse mode, if desired. The two-stage, nonthermally produced 6-15 keV (elements Co through Zr) x-rays would — unlike ZBL — create blur-free images.

Two other fundamental outcomes are yet needed for the very highest quality inertial confinement fusion (ICF)/ high-energy-density physics–relevant x-ray imaging.

1. An exquisitely sensitive Multiframe Ultrafast Digital x-ray camera, and
2. A high-collection-efficiency, high-spatial-resolution 25-keV x-ray imager.

Significance

This project is relevant to two areas of the DOE Strategic Plan:
First, is an enhancement in NIF experiments supporting the nuclear weapons stockpile, via improved high-energy x-ray imaging from our novel source (and also the same beneficial return from the Z accelerator for x-ray-imaged defense-related experiments). Second, is an enhancement in fusion related research (ICF on Z or NIF with our source).

A state-of-the-art predictive/computational capability has been established allowing Kα_1 and Kα_2 x-ray production to be modeled for a target of any material irradiated by a petawatt short-pulse laser.

Modeling Ramp Compression Experiments using Large-Scale Molecular Dynamics Simulation

130807
Year 2 of 3
Principal Investigator: A. P. Thompson

Project Purpose

Sandia is a leader in characterizing materials in off-Hugoniot regions of phase space using experimental ramp-wave loading. However, leadership in dynamic material response also requires state-of-the-art theory and modeling. Molecular dynamics simulation (MD) is an invaluable tool for studying problems sensitive to atom-scale physics such as structural transitions, nonequilibrium dynamics, and elastic-plastic deformation. There are, however, significant difficulties in utilizing MD for extreme environments. First, current atomic potentials are based on ambient material properties and are inadequate for multimegabar and high-temperature regimes. Second, ramp loading on Z, shock-induced transitions, and melting occur over timescales too long to be simulated with today's methods, which are systematically limited to timescales of 0.1–1 nanosecond.

By generalizing recent innovative methods developed for shock loading, we propose to extend MD timescales by three orders of magnitude, enabling us to model ramp compression and other longer timescale phenomena. We will develop new interatomic potentials specifically for extreme environments. We will develop and implement expressions for calculating plastic strain and dissipative work. Our primary application will be to recent flyer-plate experiments on Z that have shown a gradual drop in wave speed near melt in beryllium. This response is not captured by continuum models. A second application will be modeling shock-induced phase transformations in silicon in collaboration with experiments being conducted at the University of Texas. The techniques we develop will allow us to contribute significantly to the understanding of shock and quasi-isentropic physics relevant to weapons and inertial confinement fusion (ICF) applications, as well as to substantially expand understanding of several current critical areas of material behavior.

Summary of Accomplishments

1. Beryllium potential: Our new potential (Ba09i) was compared with one developed by other researchers (Dr09). Both Ba09i and Dr09 closely matched diamond anvil compression results up to 200 GPa. Hugoniot states generated using Hugoniostat MD simulations indicated that Dr09 melts at a low pressure, while Ba09i remained solid up to 200 GPa, in agreement with quantum calculations by our team and also with a published equation of state model. However, in Ba09i the HCP/FCC structure stacking fault energy is too low, resulting in many stacking faults at temperatures close to melting. We will try to raise the stacking fault energy without negatively impacting other key properties. We are also pursuing automated fitting methods (genetic programming, Gaussian processes) using large amounts of quantum data.

2. MD methods for lamp-loading: We have performed two MD studies of shock compression: phase-transition in shocked germanium, and Hugoniot of polymers. We have developed a method for extracting characteristics curves from MD simulations of materials under ramp and shock loading. We have found that many features of long ramp simulations can be captured by scaling results from much shorter simulations.

3. Continuum Mechanics Quantities: We have performed MD simulations of elastic shock compression in aluminum, comparing a newly published (WKG) potential and three existing potentials. The calculated longitudinal and deviatoric stresses were found to depend significantly on the choice of potential. We have also implemented and performed initial tests of the Cauchy-Born stress, which will be used to calculate elastic and plastic strain.

4. Shock-melting experiments: Subnanosecond measurements of optical signals from shocked silicon targets were performed at the University of Texas. The maximum pressure achieved was not high enough to observe shock melting.

Significance

The techniques we develop will allow us to contribute significantly to the understanding of very high pressure material response to shock waves, rarefaction waves, and quasi-isentropic loading behavior relevant to weapons and ICF applications. Using these techniques to model dynamic response of beryllium is particularly relevant to the Campaign 2 strategic goals.

Refereed Communications

T.R. Mattsson, J.M.D. Lane, K.R. Cochrane, M.P. Desjarlais, A.P. Thompson, and G.S. Grest, "First-Principles and Classical Molecular Dynamics Simulation of Shocked Polymers: Polyethylene and Poly(4-Methyl-1-Pentene)," *Physical Review E*, vol. 81, p. 054103, 2010.

New Density Functional Theory Approaches for Enabling Prediction of Chemical and Physical Properties of Heavy Elements

130808
Year 2 of 3
Principal Investigator: A. Mattsson

Project Purpose

Improving plutonium equation of state (EOS) and strength models through focused tri-lab projects such as the dynamic plutonium experiments and the national boost initiative is of highest NNSA priorities. Generating high-quality EOS and strength data, primarily through Z experiments, is a key aspect of Sandia's dynamic materials program. In this project, we will broaden the scope of Sandia contributions by improving our ability to theoretically predict heavy element properties.

Understanding the microscopic behavior of materials is important for the fundamental understanding of macroscopic properties. Improving our ability to computationally investigate chemical and physical properties of actinide/lanthanide (f-electron) materials serves the dual purpose of advancing our knowledge and providing insights useful for other, present and future, mission areas, for example providing an enhanced science base for technologies needed for nuclear fuels/wasteforms and fusion reactors.

Density functional theory (DFT) is the preferred computational method for exploring materials properties, and Sandia scientists are at the forefront of DFT-based EOS construction. However, present DFT techniques are not adequate for f-electron materials. We propose to remedy the two major deficiencies preventing DFT calculations from providing accurate properties of actinides/lanthanides, namely inaccurate functionals, and inappropriate spin and relativistic treatment. Sandia has a unique opportunity to develop differentiating computational tools for f-electron materials. The RSPt (Relativistic Spin Polarised [test]) code from Los Alamos National Laboratory, already used at Sandia, is specifically designed to handle f-electron materials. However, relativistic effects need to be taken into account nonperturbatively in f-electron systems. We will add this important physics to RSPt. Available functionals are not accurate enough to capture the complex interactions in f-electron systems. We will develop a new functional appropriate for f-electron systems using Mattsson's promising subsystem functional scheme. Solving those fundamental problems will enable quantitative prediction of the behavior of heavy element materials under normal and extreme conditions, for the benefit of the entire nuclear weapons complex.

Summary of Accomplishments

A Rice University postdoctoral research associate pursued functional work, while a graduate student from the Colorado School of Mines was engaged to pursue implementation work in the RSPtDirac code.

We published a study of the harmonic oscillator gas, a candidate system for basing a subsystem functional for actinides on, "Subsystem Functionals and the Missing Ingredient of Confinement Physics in Density Functionals" and presented this study at the 2010 American Physical Society meeting.

The Quantum Monte Carlo results for jellium spheres will be used for a confinement physics correction scheme, and in the construction of a correlation functional. The approximations made to the relativistic Dirac scheme in available DFT codes were surveyed in a review article in *Energy and Environmental Science*, assembled from contributions by participants in the Materials Models and Simulations of Nuclear Fuels workshop, held October 2009 in Albuquerque.

The presentation, "The Subsystem Functional Scheme: The Armiento-Mattsson 2005 (AM05) Functional and Beyond" was chosen together with 13 others from a pool of 310 contributions for oral presentation together with 18 invited talks at the DFT09 conference in Lyon, France in late summer 2009.

We also presented and discussed subsystem functional and Dirac work during three weeks in late 2009 as an invited participant in the Kavli Institute of Theoretical Physics in Santa Barbara workshop "Excitations in Condensed Matter: From Basic Concepts to Real Materials."

The RSPtDirac code is now ready for the inclusion of the Dirac equations.

Significance

Developing improved models of plutonium EOS and strength through focused trilab projects such as the dynamic plutonium experiments and the national boost initiative is one of the highest DOE/NNSA priorities. Generating high quality EOS and strength data, primarily through the design and execution of Z experiments, is a key aspect of Sandia's dynamic materials program. Improving DFT's ability to theoretically predict plutonium properties will broaden the scope of Sandia contributions. Improved ability to computationally investigate chemical and physical properties of heavy elements will also provide an enhanced science base for technologies needed, for example, for nuclear fuels/wasteforms and fusion reactors.

Refereed Communications

F. Hao, R. Armiento, and A.E. Mattsson, "Subsystem Functionals and the Missing Ingredient of Confinement Physics in Density Functionals," *Physical Review B*, vol. 82, p. 115103, September 2010.

A.E. Mattsson and R. Armiento, "The Subsystem Functional Scheme: The Armiento-Mattsson 2005 (AM05) Functional and Beyond," *International Journal of Quantum Chemistry*, vol. 110, p. 2274, May 2010.

R. Devanathan, L. Van Brutzel, A. Chartier, C. Guéneau, A.E. Mattsson, V. Tikare, T. Bartel, T. Besmann, M. Stan, and P. Van Uffelen, "Modeling and Simulation of Nuclear Fuel Materials," to be published in *Energy and Environmental Science*.

Study of Radiative Blast Waves Generated on the Z-Beamlet Laser

130809
Year 2 of 3
Principal Investigator: A. Edens

Project Purpose

This work is motivated by a desire to probe various hydrodynamic theories and simulations forwarded in the astrophysical literature that predict the growth of instabilities on shock fronts in strongly radiating blast waves. These instabilities are thought to give rise to much of the spectacular structure observed around supernovae remnants and may play an important role in star formation. We will undertake a collaborative project with the University of Texas to study these instabilities, particularly the Vishniac instability. In particular, there are three aspects of these blast wave instabilities that we may be able to measure for the first time. The first observation we hope to make is an unambiguous measurement of the growth rate of the Vishniac instability. We have seen evidence of growth in previous experiments, but the data has been clouded by small sample sizes and difficulties in diagnosing the blast wave conditions. Use of a high-speed charge coupled device (CCD) camera and streaked spectroscopic diagnostic will allow us to overcome these difficulties. In addition, the spectroscopic diagnostic will give us a direct indication of the blast wave's properties at the shock front, a resource that has not previously been available. Finally, the astrophysical theories predict that the instability should cause an oscillating perturbation on the blast wave surface, but this oscillation has never been observed experimentally. Previous data taken on the Z-Beamlet laser (ZBL) suggests that we can reach conditions necessary to observe a perturbation oscillation using the new high-speed CCD camera. All of this work leverages the high-energy capability of the ZBL laser pulses. The >1 kJ laser pulse energy achievable with this system can only be reached by a few laser systems and is necessary to ensure the long-lifetime blast waves necessary for this work.

Summary of Accomplishments

The primary technical challenge of this project has turned out to be modification of the probe laser beam to operate in a multi-shot mode, which would allow for multiple measurements of a single laser shot. We have engaged several vendors trying to procure the critical component for this capability upgrade over the past 15 months, and are only now close to acquiring the needed part. This change to the probe laser is a central facet of the work and the delay in procurement of the part has significantly slowed experimental work. In addition, the ZBL laser system has been down for upgrade during most of the fiscal year. Because of these obstacles, we have not completed many of the experimental milestones we had originally hoped to meet during the second year.

We should, by the end of the year, have finished upgrading the laser, and finished with the building of at least the time-integrated spectroscopic diagnostic. The milestones now in danger of not being achieved by the end of the third project year are most likely the spectroscopic ones, as this diagnostic was planned to be fairly complicated and involve significant technical risk and is now delayed essentially a year from when we had hoped to begin. However, the statistically verified growth rates and oscillation observation primary goals do not rely on this diagnostic and should still be quite viable to achieve.

Significance

The experiments proposed in this project create well-diagnosed radiative hydrodynamic systems that can be used to benchmark the radiation hydrodynamics capabilities of various codes used in our NNSA stockpile stewardship work. The systematic variation of both the physical and radiative aspects of the experiments provide a particularly robust and varied set of problems that should prove useful for verification and validation efforts. In addition, the modifications to the Z Backlighter facility and the diagnostic development there can be useful to other experiments and add to the overall facility capabilities at Sandia. The results themselves are useful as a example of the testing of an astrophysical theory in the laboratory, a still emerging field of great interest.

Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z

141533
Year 1 of 3
Principal Investigator: B. M. Jones

Project Purpose

This project seeks to demonstrate and develop a novel load concept for generating K-shell x-rays in support of radiation effects research on the Z machine.

Summary of Accomplishments

The advanced concept was evaluated using numerical modeling, and based on these design calculations, four shots were executed on the Z machine in FY 2010. These successfully produced power, yield, and spectral data from this novel x-ray source configuration. These data will be further analyzed and compared to models throughout FY 2011, and have put an initial set of points on the map for the first application of this load concept to K-shell cold x-ray sources. Physical insights already gained have suggested improvements to the loads for experiments planned for FY 2011.

Significance

Successful development of this novel source for cold x-ray generation will expand the portfolio of sources available on the Z machine for nuclear survivability studies. They have the potential to enable new capabilities in radiation effects research. This first year has set the stage for load improvements and continued concept development in the second year.

High Peak Power / Pulse Energy Laser Sources

141534
Year 1 of 3
Principal Investigator: R. Bambha

Project Purpose

High-performance lasers can perform critical tasks in areas such as high-current switching and probing using ultrashort pulses, but suitable lasers have typically been very unwieldy. Compact lasers capable of producing diffraction-limited pulses with energies of 1–10 mJ and subnanosecond duration are desirable but not currently available. Current laser systems, such as mode-locked Ti-sapphire and microchip master-oscillator/power-amplifier architectures employing low-gain bulk amplifiers, are inherently large and may require multiple stages of amplification, increasing cost, size, and complexity. In this project, we will attempt to build lasers that can achieve all the desired optical properties simultaneously in a compact size by leveraging recently developed phosphate glass fibers with very high rare-earth (RE) doping concentration. Phosphate glass can accommodate RE doping levels approximately 20 times higher than conventional fused silica. This feature enables high gain, single-stage, mJ-level amplifiers with lengths of only a few centimeters, nearly eliminating the nonlinear effects that limit energies in conventional silica fibers. We anticipate that the proposed approach will reduce cost, size, and weight of the system while preserving diffraction-limited beam quality. Furthermore, phosphate glass has a large amplification bandwidth, offering wideband pulse amplification at wavelengths previously unavailable using crystalline hosts.

Summary of Accomplishments

We had major success in developing methods to process phosphate glass (PG) fibers into amplifiers, managing the heat generated, and measuring the optical behavior, and we expect that we will be able to meet our energy milestone, 2 mJ at 10 Hz. We are able to fusion-splice, and fixture PG fibers to make amplifiers that are unusually short compared to standard fused silica fibers (centimeters compared to meters). The amplifiers that we constructed using Yb-doped glass are easily reaching the energy and spectral performance level of conventional fused silica amplifiers, and with the addition of protective end-caps, these PG amplifiers are expected to produce substantially higher pulse energy. We have designed and received undoped, core-less PG fiber to use as fiber end caps to avoid optical damage. Our gain and emission spectrum measurements have revealed a very significant property of Yb-doped glass — an unexpectedly small separation between absorption and emission peaks, and this property could enable higher amplifier efficiency than was originally expected.

We demonstrated the ability to launch and maintain single-mode signals through the inherently multimode fiber. We fabricated our tapered fibers by heating and stretching large-core/low-numerical-aperture fiber for which the lowest order mode is matched in size to our PG fiber. We have attempted propagation of lowest-order modes in 30-micron core fibers for lengths up to 20 cm, and we have seen no substantial degradation in the mode structure. We modified our fiber design from the initial 20% doping to 5% and obtained new fibers. The new fibers showed high gain (~300 μJ in 20 cm) and rapidly increasing energy with pump power. Surface damage due to inadequate end preparations limited the output. Our fiber processing equipment was refurbished and recently brought back online, which will allow us to make endcaps and tapers and proceed toward performance milestones.

Significance

Our highly doped fiber amplifiers will find applications in Intelligence Surveillance and Reconnaissance using ns-duration pulses, and potentially ultrashort pulse applications will also benefit from chirped-pulse fiber amplification. The techniques we are developing for pulse amplification using highly doped fibers will enable a range of new devices and wavelengths. For instance, many reconnaissance, countermeasures, and other defense applications would benefit from amplifier development in the 2-µm wavelength region. Our architecture can be used with highly doped fibers with Tm and Ho doping to fill 2-µm needs, and Nd or Yb doping will address 1-µm applications.

Fiber lasers offer many practical advantages for high-voltage switch triggering over line-of-sight optical (z-pinch) or high-voltage cable triggers (Saturn). Fiber laser timing can be controlled with a single seed laser pulse that can be sent to many switches over single mode fibers. Small amplifiers located in close proximity to the switches amplifying a common seed pulse would effectively eliminate timing jitter. Furthermore, if the amplifier pump light is delivered using fibers, the connections will be "all-optical" and not influenced by the electromagnetic transients around the switch. Multiple fiber lasers could be used to create multiple channels in gas gaps for lower inductance or to create multiple filaments in photoconductive semiconductor switches (PCSS) for higher total currents. Connecting high-voltage switches with insulating fibers is less invasive to the high-voltage environment than cables and much simpler and more stable than line-of-sight optics. A significant technical advantage of this laser technology over conventional Q-switch solid state or semiconductor lasers for switch triggering is the potential for glass fiber to produce a subnanosecond pulse width using chirped pulse amplification followed by pulse compression. Conventional PCSS and optically triggered gas gaps (e.g., in Z) use 5–15-ns-wide laser pulses. For both types of switches, shorter pulses produce more accurate trigger timing and initiate switching with less optical energy. For high gain PCSS, photo-carriers are "integrated" until a critical triggering carrier density is reached. With longer optical pulses, many photo-carriers are lost during this "integration" due to carrier recombination (2–10 ns exponential loss) before switching is initiated. Furthermore, photons arriving after switching is initiated are wasted. For gas gap triggering, optical intensity is also the key issue, so triggering with shorter pulses requires less energy. For example, on Z, switches presently using 30 mJ delivered in 5 ns can be triggered with energies approaching 3 mJ in 0.5 ns.

Pulsed lasers in the nanosecond and millijoule regime are frequently utilized as seeds or probes in the context of high-energy-density physics (HEDP). Multikilojoule laser systems (such as Z-Beamlet) currently contain complex combinations of fiber-seed, pulse-shaper and consecutive regenerative amplifiers, which bring the originally weak seed (nJ-µJ) up to the millijoule level. The replacement of these first stages with a single fiber based system would not only reduce cost and space requirements, but also streamline operations, reduce maintenance and increase the reliability of a critical element in Sandia's HEDP mission.

Mixed Hostile-Relevant Radiation Capability for Assessing Semiconductor Device Performance

141535
Year 1 of 3
Principal Investigator: E. S. Bielejec

Project Purpose

The combined and likely synergistic effects of high-dose-rate ionizing radiation and displacement damage is critically important to understanding the response of semiconductor devices to hostile radiation environments. Existing radiation test facilities cannot controllably simulate both effects independently with variable exposure timing in the absence of extraneous background radiation. The purpose of this project is to provide a research tool for achieving detailed understanding of the mechanisms that affect semiconductor device response; we propose combining controlled, variable ionizing irradiations (produced by modulated, pulsed electron and laser beams) with controlled, variable introduction of displacement damage (produced by pulsed high-energy silicon ions) to create a high-fidelity simulator of the threat environment. The ability to independently control both the magnitude and timing of the introduction of ionization and displacement damage will permit creation of unique mixed neutron-gamma simulated radiation exposure conditions, discovery of new synergistic effects, and confirmation of device physics models that cannot be performed at existing radiation test facilities. Controlled modulation of the time-dependent ionization will also permit the examination of device response to a range of stockpile-to-target-sequence scenarios. By using both electron and laser beam systems to introduce ionization to a device, differences in oxide and bulk Si ionization effects will be independently characterized. This factorization of these two effects will permit a more-detailed validation of device models. The basic science aspect of this project is research into unexplored synergistic effects of displacement damage and ionizing radiation. Our goal is to develop a mixed radiation exposure capability that can be used to confirm our understanding of the underlying physics of these unique radiation environments and to evaluate the effects that may arise in new device designs considered for insertion into the stockpile.

Summary of Accomplishments

The initial steps this year involved setting up and adapting the electron beam gun to the existing qualification alternatives to the Sandia pulsed reactor (QASPR)-III chamber, which will be used for all exposures, with the configuration of the laser source proceeding in parallel. The electron gun was modified for higher-current operation by the manufacturer and then installed on the chamber. Our first results for various combinations of ion and electron exposures have been completed. The ion exposures were performed using a 4.5-MeV Si beam (targeting the base-emitter junction of the tested Si Bipolar Junction Transistor [BJT]) with a 100-µs pulse length and a fluence of 10^9 ions/cm^2 (corresponding to a ~2×10^{14} MeV equivalent neutron fluence). The electron beam energy was 70 keV (high enough energy to ensure electron-hole pair creation in the base-collector junction) with a 100-µs pulse length, and a dose rate of ~10^{10} rad(Si)/s. These results already demonstrate that there are dramatic differences between the effects of the ion, electron, and combined exposures, as expected. The observed decrease in the early-time annealing factor as the electron dose rate is increased is suggestive of enhanced annealing due to increased photocurrent and local electron concentration during the electron irradiations. We have also demonstrated the ability to control the timing between the ion and electron exposures. This will be essential to the final capability, where the ion, electron and laser exposures are carefully timed in order to closely simulate various threat scenarios. These results show that we have met the milestone of demonstrating the capability of controlled electron beam exposures, together with an initial demonstration of dual electron-ion exposures. We have also developed the capability for laser exposures and tested a series of Si BJTs to combined electron and laser exposures. Initial cross-calibration is ongoing for the combined laser-electron exposures and modeling efforts.

Significance

The successful completion of this proposed project will improve our basic understanding of the combined ionization and displacement damage environments, and benefit the nuclear weapons complex by providing a means to quantify synergistic radiation effects on electronics in nuclear weapons to the threat environment (considered beyond the scope of the existing QASPR program). In addition, the ability to field a programmable, pulsed, gamma-plus-neutron flux simulation tool for simulating the radiation threat environment would be an unprecedented NNSA capability. The improved basic understanding would further Sandia's knowledge of radiation effects and support Sandia's ongoing efforts in radiation hardness assurance testing. This mixed radiation exposure system would provide a simulation fidelity (at the 1 mm^2 scale of device testing) that would exceed that attainable at any alternate facilities. This capability would greatly benefit future life extension programs and new weapon systems.

Shock Compression of Liquid Helium and Helium-Hydrogen Mixtures

141536
Year 1 of 1
Principal Investigator: D. L. Hanson

Project Purpose

The purpose of the project is to develop a cryogenic system to generate liquid He samples for high-precision equation of state (EOS) measurements using the Z accelerator current drive. The properties of dense He and He-H mixtures in the Mbar pressure regime are critical to understanding the internal structure, origin, and evolution of the Jovian and extrasolar giant planets. Liquid He (LHe) data have been obtained at lower pressures using conventional gas gun techniques, but recent first-principles calculations suggest a significant increase in compressibility (max 5.5-fold compression) just beyond the available data. More recent results using the Omega laser suggest even higher compressibility (max 7-fold at ~100 GPa). This pressure regime is well within the range of dynamic experiments at the Sandia Z facility. Given the longstanding controversy surrounding the compressibility of liquid D_2, it would be highly beneficial to obtain similar experimental results on LHe with the mature Z platform. Limited high pressure He EOS data exist because of the difficulty of condensing LHe samples at very low temperatures on gas guns, magnetic and explosive compression devices, and lasers. The present approach to condensing LD_2 samples at 20 K on Z cannot access the required temperature range of < 2 K because the large standoff of the cooling source from the sample holder (to allow cryostat survival) is not feasible for an extreme low-temperature system. The existing sample holder assembly also lacks adequate radiation shielding to minimize heat loading. The primary goals of this project are to identify a suitable cooling method for condensing LHe samples in an appropriate geometry for high-precision EOS experiments on Z; and to develop a detailed design and prototype test hardware to demonstrate the feasibility of generating LHe samples for Z experiments.

Summary of Accomplishments

As a result of work performed under this LDRD, we have accomplished the following:

1. developed a conceptual design for an expendable cryogenic system of reasonable cost and complexity to condense large area superfluid LHe samples at 1.5–1.8 K for dynamic high-pressure He experiments on Z;
2. developed a detailed final design and drawing package for a basic test cell cryogenic system prototype configured for flow impedance development and cooling optimization;
3. developed a detailed final design and drawing package for a liquid sample holder cryogenic system prototype configured for demonstration and optimization of LHe sample condensation and containment;
4. developed and fabricated flow impedance components with both packed powder and coiled capillary structures, designed to operate over a wide range of flow impedance values and cooling power; and
5. fabricated, assembled, and instrumented a prototype system for the basic test cell configuration, and fabricated components for liquid sample holder prototype assemblies. Lab testing for demonstration and optimization of basic test cell cooling is currently in progress.

Significance

The result of a successful conclusion to this project will be a new cryogenic capability for condensing LHe samples for dynamic material properties studies, an operating cryogenic system with an extreme low-temperature cryo-cell that, with some additional effort, can be adapted directly to measurements on the Z current drive. The successful development of this cryogenic capability for Z will produce a legacy of S&T

advances in the form of fundamental dynamic studies of He properties at high pressure. Implementation of this capability on Z will impact DOE strategic needs in nuclear weapons stewardship by enabling very accurate EOS measurements of material relevant to the nuclear weapons program and will enhance the capacity of the Z facility for basic research of extreme interest to both theoretical physicists and astrophysicists. The dynamic compression capability developed on Z over the last decade has become a mature platform, enabling material dynamic experiments in the Mbar pressure regime with unprecedented accuracy. The development of a cryogenic capability for the measurement of LHe properties at high pressure on Z has been a goal of Sandia's Dynamic Material Properties group for several years. Use of this new cryogenic capability for the study of He properties at high pressure will provide additional widespread visibility for the Z dynamic materials capability in areas of both programmatic and basic science interest. Features of the improved cryogenic technology in this system targeted on He will also enable or enhance the ability to perform fundamental science studies on other materials of interest.

Stability of Fusion Target Concepts on Z

141537
Year 1 of 3
Principal Investigator: D. Sinars

Project Purpose

Achieving inertial confinement fusion ignition in the laboratory requires matter to be compressed and heated to pressures in the range of 100 to 1000 Gigabars. Pulsed power drivers offer efficient, inexpensive ways to heat and compress matter, but it is not yet known if they can reach the tremendous pressures needed for fusion ignition. A new concept, Magnetized Liner Inertial Fusion (MagLIF), reduces the required pressure to about 10 Gigabars by magnetizing and preheating the fusion fuel. Modeling suggests that this concept could lead to scientific break-even on Z (fusion energy comparable to energy delivered to the fuel). The key scientific issue for the MagLIF concept is the stability of the annular cylindrical liner used to compress the fuel. In particular, the outer surface of the liner is susceptible to the Magneto-Rayleigh Taylor (MRT) instability, which may be enhanced by an electrothermal instability. At present, there are no stability studies of liner implosions with drive pressures greatly exceeding the strength of materials, as would be the case for MagLIF. With the recent development of 6 keV backlighting and the ability to fabricate beryllium liners, the Z facility provides a unique venue to simultaneously study the inner and outer surfaces of the imploding liner. This will be critical to determining the liner integrity during the implosion. The goal of this project would be to understand the stability of cylindrical implosion systems relevant to the MagLIF concept. The project will study a new high-risk fusion concept that does not produce high yields, but that could be useful for fusion-fission hybrid concepts.

Summary of Accomplishments

We have met or are on track to meet all of our project milestones in FY 2010. We have done both LASNEX and HYDRA simulations to benchmark the codes against the experimental data collected to date. We have had success in obtaining agreement between LASNEX code simulations and the experimental data. Our HYDRA code simulations have been less successful in matching the data, though we have made progress in identifying problems with the code as a result of these attempts. There are two sets of Z experiments in FY 2010 in support of this project (February and June 2010). Our target supplier, General Atomics, had problems procuring targets for the February shot series because the targets kept breaking during machining. We did succeed in procuring and fielding two Be targets in February, but due to problems with the backlighter, we only obtained images on one of them. The images we obtained clearly show both the inside and outside liner surfaces using the 6.151 keV backlighter, and we are in the process of analyzing the data and comparing it with simulations. The June 2010 series continued this work and we shot several more Be targets during various stages of the implosion. The surface roughness of the Be targets to date has been worse than scoping tests with flat test pieces suggested, and this continues to be an active area of research. The MagLIF concept that is central to this project was presented as an invited talk at the 2010 American Physical Society Division of Plasma Physics meeting and has also been published. Our Z experiments to date have been presented in an invited talk (with a second scheduled) and a manuscript was submitted to *Physical Review Letters*.

Significance

This work is relevant to DOE strategic needs in nuclear weapons stewardship and energy security (could decrease the cost of future z-pinch driven inertial fusion energy sources), and it improves the capacity of existing facilities for high-quality science in the area of magnetically driven implosions, which could lead to additional capabilities for the high-energy-density physics community.

The Magneto-Rayleigh-Taylor instability is fundamental to all magnetically driven implosions, and the research in this project will likely impact most of the work being done on Sandia's Z facility either directly or indirectly through validation of the relevant stockpile stewardship computer codes.

Refereed Communications

S.A. Slutz, M.C. Herrmann, R.A. Vesey, A.B. Sefkow, D.B. Sinars, D.C. Rovang, K.J. Peterson, and M.E. Cuneo, "Pulsed-Power-Driven Cylindrical Liner Implosions of Laser Preheated Fuel Magnetized with an Axial Field," *Physics of Plasmas*, vol. 17, p. 056303, 2010.

Ultrashort-Pulse Laser-Triggering of Long Gap High-Voltage Switches

141538
Year 1 of 3
Principal Investigator: P. K. Rambo

Project Purpose

Long-gap, laser-triggered high-voltage discharges have numerous applications from super-radiant laser sources and laser wakefield acceleration (both based on extended controlled-density plasmas), to laser-triggered spark gaps used for megavolt switching in pulsed power devices, and to triggered and guided lightning. The problem facing all such efforts is the ability to create long ionized channels with adjustable plasma density and extended plasma lifetimes in order to improve discharge reliability, reduce temporal jitter, and allow for longer gaps and higher hold-off voltages. To overcome these problems, we will attempt to use ultrashort subpicosecond laser pulses to examine switching aspects in long-gap, high-voltage discharges, with special emphasis on extension of plasma lifetime. Application of ultrashort laser pulses (instead of the nanosecond pulses more commonly used in pulsed power switching) can reduce jitter and create the desired extended length plasma channels via nonlinear filamentation processes. However, the ionization and recombination dynamics are complex and are not sufficiently well understood for optimization efforts. To this end, we first propose a systematic study of the relevant gas ionization and recombination rates and pathways. Subsequently, we seek to improve ionization via techniques such as resonantly enhanced ionization and to increase the plasma lifetime via methods like multiple ultrashort pulses (USPs) and additional long pulse heating beams. With sufficiently improved plasma densities and lifetimes over long channels, we can leverage unique expertise in pulsed power, lasers, and complex modeling to maximize long-gap switching by these ultrashort pulses. The realization of these improvements will yield pulsed power switches with higher-voltage operating points and lower jitters.

Summary of Accomplishments

To improve plasma quality, we have initiated gas ionization studies. A gas ionization cell has been constructed, allowing the relevant laser beams to be focused and the resultant plasma probed. The cell can run from vacuum up to 2 atmospheres with gas backfills of common high-voltage switching gases. To benchmark against lasers common in laser-triggered high-voltage switching, we have two types of co-propagating lasers which can generate the ionization: a USP laser (with 350 fs pulses) and a Q-Switched laser (with 8 ns pulses). Laser harmonics and variable delays between pulses allow the same cell to explore both basic ionization and improved plasmas.

Optical probing occurs via an adjustable delay pick-off beam from the ionizing USP beam. The probe beam traverses the ionized plasma and is magnified before encountering an air wedge interferometer. The interpretation of the fringe deviation in the resultant interferograms required a newly written program to determine the phase via the spatial carrier method. Since such phase determination methods wrap the phase with ambiguity, we wrote a phase unwrap routine to reproduce the correct continuous phase. After the final phase determination, we determined the electron density via a modified asymmetric Abel inversion technique. In summary, the gas ionization cell has reached a level of development that will soon allow systematic scans for quantifying laser ionization and plasma improvement.

We have initiated modeling on two fronts, in order to fold back modeling results into experiments. We are attempting to decouple the two key problems in the switch: initial laser-generation of a plasma and subsequent plasma evolution into a streamer to close the switch. We will leverage both efforts against existing codes, with the switch model better developed at this juncture. In this case, preliminary work shows streamer development with a low-density button seed plasma.

Significance

The possibility of longer plasma channels, larger discharge gaps, and higher switching voltages allows for improved conditions in future pulsed power devices, which will continue to be important to the nuclear weapons and inertial confinement fusion communities. Reduced temporal jitter in pulsed power switching improves system reliability and facilitates a more in-depth understanding of the physics.

X-Ray Thomson Scattering Measurements of Warm Dense Matter

141540
Year 1 of 3
Principal Investigator: J. E. Bailey

Project Purpose

Warm dense matter exists at the boundary between condensed matter and plasma physics and challenges theoretical understanding. It is also critical for applications, including z-pinch and inertial fusion laboratory experiments and in astrophysical objects such as white dwarfs and giant planets. Modern high-energy-density facilities have made it possible to create warm dense conditions in the laboratory. Creating warm dense matter is challenging, but thorough understanding also requires accurate detailed diagnostics. This project will advance warm dense matter physics by combining x-ray Thomson scattering, a powerful diagnostic for warm dense matter, with extreme environments created at the Sandia Z facility. X-ray Thomson scattering uses an intense laser (in this case either Z Beamlet or Petawatt) to produce quasimonochromatic x-rays that probe matter at high density. Measurements of the spectrally resolved scattered x-rays determine both temperature and density. We propose to develop a flexible capability suitable for diagnosing either shock or radiation heated samples. The capability will be exploited to advance cutting-edge physics topics selected from candidates such as warm dense matter equation of state, influence of correlations on atoms in dense matter, and spectral line formation in white dwarf atmospheres. The main risk is that x-ray Thomson scattering is complex and it has never been employed on any pulsed power facility. The risk is mitigated by the previous demonstration of x-ray Thompson scattering at laser facilities and by the pre-eminence of Z for creating shock- and radiation-heated samples. Indeed, the proposed research is exciting precisely because it combines two extraordinary capabilities for the first time to advance physics of a rich new field. It will help establish Sandia as a leader in the exciting warm dense matter field and it will help maintain Sandia leadership in dynamic materials and radiation science research.

Summary of Accomplishments

The goal for the proposed work in FY 2010 was to prepare for x-ray Thomson scattering measurements (XRTS) at Z that will be conducted during FY 2011–2012. We have made substantial progress toward all four milestones encompassed in that preparation.

- Experiment selection and design. Following a literature review, prior research in this arena was critiqued in group meetings and discussed with the responsible scientists. XRTS measurements of Be equations of state using the Z magnetic flyer technique emerged as a prime experimental candidate. We performed simulations to evaluate the conditions achievable on Z and the XRTS diagnostic signatures that should be observed.
- Spectrometer design and fabrication. After literature review, we selected a spherical crystal spectrometer for Z XRTS experiments. This instrument should provide adequate sensitivity, high spectral resolution, and the possibility to space-resolve the scattering signal. An integrated product team (IPT) was formed to design and build the spectrometer and work is in progress to build and implement the prototype x-ray scattering spherical spectrometer (XRS3).
- X-ray source selection. The advantages and disadvantages were discussed in group meetings and with Z backlighter experts. Based on these discussions, the Z Beamlet was selected for FY 2011 experiments, while retaining the possibility to exploit PetaWatt capabilities in FY 2012.

- Room-temperature sample scattering calibrations. These experiments are intended to integrate the high-sensitivity spectrometer and x-ray source in proof-of-principle scattering experiments, without the complexity of Z. We are implementing a new calibration capability using steady state Manson sources and to simultaneously design Beamlet calibration experiments using an existing spectrometer. This would provide early identification of any serious impediments that would undermine the overall experiment plan. Z Beamlet calibration time has been tentatively scheduled for July 2010.

Significance

This work will advance Sandia's national security mission by expanding the capability to perform highest-quality dynamic materials and radiation science. Temperature and density measurements of warm dense matter with unprecedented quality would stimulate new innovations in theoretical physics. In addition, the proposed experiments will lay a foundation for future applications to other challenging program-critical environments in the weapons and energy arenas. Finally, the community of scientists exposed to high-quality Sandia research will grow, helping ensure continued ability to attract the best scientists.

Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates

148196
Year 1 of 3
Principal Investigator: M. L. McLain

Project Purpose

The presence of radiation-induced conductivity (RIC) in Kapton® polyimide and other dielectric films can have important consequences for electrical components exposed to radiation environments. Previous studies using high-energy electron beam exposures at dose rates up to 10^{10} rad(Si)/s have indicated a RIC response that is approximately linear with dose rate. For dose rates above 10^{10} rad(Si)/s, it is assumed that the RIC response is also a linear function of dose rate. However, the linearity of the response for higher dose-rate exposures cannot be verified with current test facilities. Determining the RIC response characteristics of Kapton and other dielectric materials for higher dose-rate exposures will therefore require the development of innovative testing techniques in order to validate model predictions based on lower dose-rate data. In this project, we propose to use high-intensity, short-duration laser pulses to determine the RIC response of Kapton as a function of dose rate. First-order calculations indicate that a wide range of dose rates can be attained using existing laser exposure facilities at Sandia. The obtained experimental data will ultimately be applied to advanced models for RIC that currently lack high-dose-rate experimental validation data. This approach has cutting-edge character and novelty in that such a method has not been considered for the acquisition of RIC data. Moreover, it appears that a focused study of the photoconductive properties of Kapton as a function of dose rate has not been described in any scientific publication. A key S&T challenge addressed in this project will be the acquisition of radiation effects data without the use of previous testing capabilities. Another key S&T challenge will be to understand how the physical properties of Kapton (e.g., defect levels) impact the radiation response. This will allow higher fidelity RIC models to be created.

Summary of Accomplishments

To date, the main accomplishments toward the originally proposed R&D goals are related to sample preparation and the experimental setup. Specifically, Kapton films have been fabricated with an indium tin oxide (ITO) front electrode and an aluminum back electrode. A second design with a cross-hatch aluminum front electrode (i.e., electrode has areas without aluminum to allow laser penetration) has also been fabricated. From an experimental standpoint, a 532-nm laser exposure system (primary laser) and the necessary optics have been set up and analyzed, test boards have been manufactured, and the mounting box has been built. In an effort to limit the differences between the previous experiments conducted at the linear accelerator (LINAC) test facility and the proposed laser experiments, similar test boards were manufactured. Labview software code is currently being written to automate the control of the various instruments used in the experiment.

In addition to these experiments, transmission measurements using the 532-nm laser system have been performed on the Kapton samples. We found that ~31.5% of the laser light is transmitted through the Kapton, 8.5% is reflected, and 60.5% is absorbed. These results verify previous transmission measurements made at Sandia. In the future, a similar measurement will be completed for samples with an ITO front electrode. Using these absorption percentages and neglecting second-order effects, the 532-nm laser should, in theory, produce measurable photoconductivity increases as a function of dose rate. Measurements that determine the laser-induced damage threshold of Kapton have also been completed. The results indicate that a single laser pulse from our current laser setup will not damage the Kapton samples. Damage threshold measurements for multiple laser pulses are currently being completed. These results/measurements, to our knowledge, have not been previously published.

Significance

Sandia has many test facilities that expose materials to high-energy ionizing radiation primarily to fulfill Sandia's national security mission. In spite of this, there are few reliable and cost-effective alternatives for measuring RIC in Kapton or other dielectrics at dose rates exceeding 10^{10} rad(Si)/s. Success in this LDRD project will provide reliable experimental results and impact the fidelity of RIC and other models. Preliminary experiments suggest that laser-based RIC measurements are a viable alternative to experiments conducted at LINAC or flash x-ray test facilities. Additionally, this project could lead to a better understanding of the photoconductive properties of Kapton and defect levels within the dielectric. These results/measurements, to our knowledge, have not been previously published or are not agreed upon in the general scientific community. Given certain defect levels and properties, it may be feasible to develop a novel, yet unrealized, dielectric with improved RIC properties.

Fundamental Hydrogen Interactions with Beryllium Surfaces: A Magnetic Fusion Perspective

148957
Year 1 of 3
Principal Investigator: R. Kolasinski

Project Purpose

Once completed, the magnetic fusion reactor ITER (International Thermonuclear Experimental Reactor) will demonstrate the first controlled ignition and extended burn of deuterium-tritium plasmas. Because beryllium will be the principal plasma-facing material in the reactor, understanding how it interacts with hydrogen is particularly important. There has been a strong desire to understand hydrogen recycling, implantation, diffusion, and recombination from beryllium surfaces from a fundamental, atomic-scale perspective using first-principles modeling techniques. Examining how hydrogen binds and interacts with basic single crystal systems is an ideal way to validate model predictions. The Be(0001)+H system is particularly interesting because it is an example of a low-index, low-Z system which has been sparsely studied. While reconstructions of Be(0001) induced by H adsorption have been examined using electron diffraction and spectroscopy techniques, such methods do not provide direct sensitivity to the adsorbate configuration. We propose using low-energy ion scattering (LEIS) and direct recoil spectroscopy to directly detect the configuration of surface-adsorbed hydrogen. These techniques offer much more precise information on hydrogen behavior, and neither has been previously applied to Be(0001)+H. In addition, our LEIS instrument at Sandia/California has been uniquely optimized for hydrogen detection, and we have developed a number of innovative techniques to study H adsorption on single crystals. Such methods will also enable us to characterize the exchange between different gas species on surfaces, achieved by heating the sample and monitoring the scattering/recoil intensity from H and D. For more detailed information on the bonding between the H and Be atoms, we propose to use time of flight techniques. The measurements will strengthen Sandia's expertise in the Be+H system within the fusion community.

Summary of Accomplishments

Our work to date includes a combination of LEIS experiments and modeling that focuses on characterizing the composition and structure of beryllium surfaces. All experiments were performed using our angle resolved ion energy spectrometer (ARIES). By mapping ion signals over a wide range of scattering geometries, LEIS analysis of a polycrystalline Be sample revealed the optimal conditions for detecting adsorbed hydrogen. We found that a monoenergetic beam of 3-keV He^+ ions produced a strong hydrogen recoil signal well separated from other contributions to the ion energy spectra, especially at small scattering angles. Furthermore, 1-keV He^+ ions provided high sensitivity to adsorbed oxygen impurities. We have designed and are in the process of setting up a time of flight scattering system for detailed surface structure characterization. In addition, we have added an electron gun to our system, and have performed Auger electron spectroscopy analysis of surface-adsorbed impurities.

We recently completed ion scattering simulations that will provide a pathway for further measurements. Using a modified version of the binary collision code MARLOWE, we find the shadowing geometry for 1-keV He^+ ions scattering from the Be(0001) is favorable for revealing the local atomic structure of the surface. We completed a simulation of a real-space ion scattering map, thereby revealing focusing effects that also contribute to detected scattering intensities. More-sophisticated simulations using a molecular dynamics code are presently underway to better calculate ion trajectories at grazing incidence. This work indicates favorable progress toward accomplishing milestones planned for this year. The experimental findings in particular verify that the ambitious goals for next year are achievable. The new experimental capabilities will enable more sophisticated analyses of the beryllium surface, and will be the basis of much of the work proposed for the upcoming year.

Significance

Our research progress to date aims to enhance the present understanding of hydrogen interactions with beryllium, a key priority for the DOE fusion energy science program. Given the importance of fusion as a future energy source, such work is relevant in the context of establishing energy security and independence from fossil fuels. Furthermore, this project also helps to establish US scientific leadership for large-scale international fusion projects, such as ITER. Our initial measurements of oxygen adsorption on beryllium surfaces provide insight into how the surface of the ITER first wall will react to the adsorption of impurities during plasma exposure. Chemical sputtering of Be+H species is also a key problem that is addressed by this project. Aside from magnetic fusion, beryllium is viewed as an important technological material for numerous applications in the aerospace and defense industries.

Examining hydrogen interactions with Be(0001) is also of interest from a fundamental surface science perspective, thereby fostering DOE's mission of basic scientific discovery and innovation. Beryllium has been sparsely studied, and many aspects of its behavior when exposed to hydrogen are unknown. From our work to date, we are developing an enhanced understanding of hydrogen binding to Be surfaces. The information gained from our measurements is intended to validate and refine first-principles calculations aimed at modeling hydrogen recycling and recombination from surfaces. Our identification of favorable scattering conditions from Be surfaces will provide guidance for future ion scattering studies. Because of its fundamental importance, we anticipate that this work will lead to publications in top-tier surface science and condensed matter journals as our measurements progress. Because the ARIES instrument is unique in its sensitivity to hydrogen, improvements in scattering techniques are another likely benefit of this work. Such results could possibly open other avenues of research, particularly since LEIS is frequently used in conjunction with these techniques to characterize thin films and the behavior of catalysts on surfaces. Furthermore, our novel simulation approach will further advance the field, by enabling detailed analyses of surface scattering processes.

Algorithm and Exploratory Study of the Hall Term in 3D Raleigh-Taylor Instabilities

149522
Year 1 of 1
Principal Investigator: T. A. Gardiner

Project Purpose

Of the many terms in the generalized Ohm's law, the Hall term is particularly interesting in that it leads to both quantitative and qualitative changes in the magnetohydrodynamic (MHD) equations. The Hall term alters the magnetic field evolution by introducing two new wave modes known as the whistler and Hall drift modes. Whistler modes are dispersive with a phase velocity that increases at smaller scales and have been identified as being key to understanding fast, collisionless magnetic reconnection. The Hall drift mode has a compressible character and a phase velocity that scales with the ion inertial length over the characteristic density gradient length scale. As a result, on ion inertial length scales, the nearly incompressible Rayleigh-Taylor (RT) instability in MHD becomes a compressible instability in Hall MHD. The RT instability is a key instability in z-pinch physics and various publications have indicated that the Hall term can have a significant influence on low-density z-pinch implosions.

The goals of this project are to quickly identify or develop a solution method for Hall-MHD and use the method for exploring the influence of the Hall term on the evolution of the 3D Raleigh-Taylor instability. By extrapolating from these results, we will attempt to assess the importance of the Hall term on z-pinch dynamics.

Summary of Accomplishments

This project began with a survey of published numerical algorithms for evolving the magnetic field due to the Hall electric field with a stationary plasma. This is a useful limit because the integration algorithm can be applied directly in an operator split method of integrating the Hall MHD equations, and because in this limit, the properties of the whistler and Hall drift modes can be understood on analytic grounds. We discovered that many of the published explicit algorithms for Hall MHD either have problems with stability for whistler modes or are oscillatory for weak solutions to Hall drift modes. Since these are of paramount importance to the goals of this project, a new numerical algorithm was developed. The method is explicit, consistent with a constrained transport method for evolving the magnetic field, propagates whistler modes without dissipation, and captures weak solutions for Hall drift modes without oscillations. Using operator splitting, this integration algorithm for the Hall term was combined with a Godunov MHD code and applied to simulate the Hall MHD RT instability in two dimensions. The simulations repeat a series of calculations previously published in the literature and include a set of ideal MHD simulations with identical initial conditions. In the first case, the ion inertial length is small compared to the simulation domain size and at late time, the evolution of the mixing was observed to reach a nearly self-similar state. Comparing the simulations, we observed a decrease in the mixing rate and increase in the bubble growth rate by about a factor of 1.7 in the Hall MHD simulations relative to ideal MHD. The second case has a larger ion inertial length and clearly demonstrates the compressible character of the Hall MHD RT instability, and a drastic reduction in the mixing rate.

Significance

The lessons learned in developing the spatial discretization of the Hall term for this work are directly relevant for both structured and unstructured MHD codes. This will be leveraged in the future to guide the implementation of Hall MHD in an Advanced Simulation and Computing high-energy-density physics code over a 3–5 year timescale. The incorporation of additional physics will lead to more-accurate simulations of pulsed power loads and will benefit Science Campaign and inertial confinement fusion programs. In the interim, we will continue to study the relevance of the Hall term to various pulsed power loads by performing local Hall MHD RT simulations with initial conditions taken from production runs. The numerical algorithm and simulation results obtained here are of wide interest to the space physics, astrophysics and pulsed power communities and are expected to result in two refereed journal publications.

All-Fiber Saturable Absorber

149940
Year 1 of 1
Principal Investigator: B. S. Soh

Project Purpose

Femtosecond pulses have numerous applications, including precision metrology, remote sensing, and security/ military measures. Ti:sapphire is the most common femtosecond laser platform; it was developed long ago, but no particular applications have been realized outside the laboratory environment due to its lack of stability. We propose to develop a breakthrough device that enables a compact and robust ultrashort-pulsed architecture, freed of the free-space optics and multiple pulse amplifying and shaping components that plague existing design. The goal of the project is to experimentally demonstrate the concept of an all-fiber saturable absorber, in an ultrashort-pulsed context. The device is a monolithic assembly of four pieces of polarization-maintaining optical fibers that are spliced with a specific angle. It works as a fast optical switch that transmits only high-power optical signal. The device can be used to consolidate a compact all-fiber passively mode-locked fiber laser that can generate pulses at <100 fs.

Summary of Accomplishments

We demonstrated experimentally the performance of the all-fiber saturable absorber device. We have successfully manufactured the first prototype, meeting the stringent requirement of manufacturing, using a fiber ribbonization technique. We subsequently characterized the device in comprehensive detail. First, we have measured the performance of the saturable absorber using a 410-ps pulsed laser. The measured time trace of the input and output of the device clearly showed pulse compression and after-pulse suppression, which are clear signs of a good saturable absorber. We constructed a transmission curve as a function of input peak power, by taking the input and the output pulse time traces at different peak powers. The constructed curve followed very closely the theoretical curve of $\sin^4$. After configuring the device to work as an optical limiter, we measured the transmission curve as well. The transmission curve clearly showed that the device operates as an optical limiter, which transmits the low-power portion while completely blocking the high-power portion. The constructed curve followed the theoretical $(1 - \sin^4)$ curve almost exactly. From these observations, we conclude that the device performed as we intended. We also measured the extinction ratio of the saturable absorber as a measure of polarization-preserving capability. The measured value was 25 dB, which is considered to be very good. Hence, we have successfully demonstrated device performance through manufacturing and subsequent characterization.

Significance

The device is extremely versatile in that it can operate as a saturable absorber, an optical limiter, an all-optical switch, and an optical isolator. This device will enable a truly all-fiber-laser structure, where the environmentally unstable free-space elements are completely removed. Through rugged packaging and simple and robust operation, an ultrashort pulsed fiber laser based on this device will hopefully revolutionize laser usage and adoption. Sandia may benefit from this device in areas such as directed energy, homeland security, and biochemical applications. A compact ultrashort pulsed fiber laser can play a vital role in directed energy application due to its enormous peak power. It also can generate terahertz sources, which can screen behind-the-scene terrorist activities. The broadband nature of the ultrashort-pulsed laser enables truly high-fidelity spectroscopy for biological applications. Additionally, the extremely large peak power from ultrashort-pulsed lasers can be very useful for infrared countermeasures and various military applications.

Electronic Battle Damage Assessment

149942
Year 1 of 1
Principal Investigator: J. T. Williams

Project Purpose

Tactically, one of the greatest impediments to the application of high power microwave (HPM) and other nonkinetic weapons is the current inability to assess their effect on the intended target. This bomb damage assessment (BDA) problem is further complicated because the effects achieved by such weapons can be temporary or permanent, can only partially affect the operation of the target system or completely disable it, and are sometimes not the same for targets that have the same functionality (e.g., effects observed on computers manufactured by A can be different from those observed on computers manufactured by B). Hence, the BDA tools for nonkinetic weapons must be based upon on-site intelligence that is directed at assessing the effects based upon enemy activity, as well as electronic sensing that is directed at assessing the effects based upon electromagnetic surveillance.

An effective electronic sensing BDA (EBDA) tool should be able to detect system changes based upon electromagnetic observables, assess the operational state of the target system given the detected system changes, and classify the success of the attack. Critical to developing such EBDA tools is the identification of tactically feasible electromagnetic observables for as wide a range of targets as possible, which can be exploited by either active or passive electronic sensing systems. The intent of this project is to identify such observables for a meaningful number of target systems. The outcome of this preliminary effort should be a foundation upon which an effective EBDA tool can be based.

Summary of Accomplishments

This project was a first attempt to develop a foundation of knowledge and experience upon which effective EBDA tools can be designed. The target systems studied are representative examples of communications systems (e.g., radios), computer/networking devices, and timers. The electromagnetic observables associated with the targets were sensed at frequencies relevant to the device, nominally over a relatively wide frequency range (~10–2600 MHz). The results clearly demonstrate that unintended emissions from a variety of target devices can be identified, even in the presence of noise, and related to their operational states.

Significance

The US has invested heavily in the development of HPM weapons and systems. The determination of tactically relevant electromagnetic observables that can be used for BDA will ultimately protect warfighters on the ground, and thereby increase the confidence in the deployment of HPM weapons.

Concept Design for a Neutron Source for Short-Pulse Active-SNM Detection

150116
Year 1 of 1
Principal Investigator: T. J. Renk

Project Purpose

The project goal is a design study for a pulsed-ion-beam-generated neutron source of compact size, and making use of time-tied detection methods being developed at Sandia and elsewhere. The advantage of such time-tying is that interrogation of, for example, Special Nuclear Materials (SNM), could be accomplished in a much shorter time than the current ~ 120 sec with conventional neutron generators, and/or with lower false positives. By "compact," we mean vehicle-transportable and operating on AC power, with low stored-energy (as low as 100–200 J). One approach makes use of low output voltage (~100–200 kV) and the D-T nuclear reaction. For applications where a larger system footprint can be tolerated, we will investigate higher-voltage operation using the D-D nuclear reaction. Expected output/pulse is at least ~ mid-1×10^{9} to mid-1×10^{10} neutrons into 4π, based upon previous neutron output measured with the Repetitive High Energy Pulsed Power (RHEPP-1) ion beam facility at Sandia. The RHEPP-1 experimental database is examined for systematic characterization of neutron output as a function of ion beam energy on the neutron-generating target. RHEPP-1 makes use of a magnetically insulated (MI) ion diode and magnetically injected plasma (MAP) ion source. Although an MI diode is theoretically capable of 65 % ion efficiency (i.e., ion current as fraction of total current), the RHEPP-1 design realizes a much lower ion efficiency (< 40%). Experiments were conducted to change the diode focusing optics to increase this number, in order to increase neutron output/pulse.

Summary of Accomplishments

In the case of the 100-kV design based upon D-T, we undertook computer simulation of a self-field ion diode based upon a rod-pinch geometry, using the Large Scale Plasma modeling code. (A self-field diode is more suited to a very compact design than the Mi/MAP diode system.) A deuterium plasma-fill was included in the simulation. Results indicate that with < 150-kV diode operation and 50-ns pulse width, 15% ion efficiencies are possible (400–600 A out of 6–8 kA total). Scaling from the D-D experiments on RHEPP-1, we estimate that ~ 30–50 J energy deposition will result in $1–3\times10^{9}$ neutrons/pulse into 4π. At the size per unit contemplated, more output could be realized by operating multiple such units. Given that D-T neutron output is isotropic, the individual units could be mounted within a larger size such as a cube by using common power feeds and perhaps a single plasma fill system.

A second design is based upon the successful MAP/MI ion diode operated on RHEPP-1, and using the D-D reaction. Gains in neutron output from RHEPP-1 levels could be realized by improving the pulsed power, altering ion orbits so as to decrease the number of ions lost to the cathode structure, and simply raising the output voltage. An optimistic estimate of possible neutron output from a successful MAP/MI diode mounted and operating on the 2.5 MV linear transformer driver (LTD) facility at Sandia, operating at 70 kA, is 2.1×10^{13} neutrons into 4π. A more conservative estimate is in the neighborhood of $5\times10^{12}–1\times10^{13}$ neutrons. Preliminary experiments were undertaken to increase the MAP ion efficiency by altering ion orbits within the diode with added Cu strips. Results indicate more work is needed to understand and increase MI/MAP ion efficiency.

Significance

We have defined two paths for a vehicle-transportable AC-operated compact pulsed neutron source for active interrogation for SNM detection. The neutrons are generated by impacting pulsed intense ion beams on neutron-generating target material. One design based upon 100-kV D-T operation is estimated to produce 1–3×10^9 neutrons in 4π. A grouping of 10 such units is still transportable, and would then be capable of mid-10^{10} neutrons/pulse, or 1–2 orders of magnitude greater than a conventional neutron generator emits per second. A second design is based upon the 3×10^{10} neutrons/pulse generated from 100–150 J on target on RHEPP-1. These numbers benchmark intense beam directed energy performance scaling for future neutron-generating diode experiments. Scaling estimates indicate that a successful MI/MAP design mounted on the 2.5-MV LTD at Sandia could deliver 5×10^{12}–1×10^{13} neutrons/pulse. In either design case, given the appropriate capital investment, we estimate that an operational neutron driver could be built within three years. Combined with anticipated advances in time-tied detection, short-pulse neutron interrogation could significantly affect the ability of active interrogation, i.e., longer interrogation distances and/or greater accuracy and lowered false positives. Use of deuterium beams allows for other applications beyond SNM detection, e.g., use of the 9Be(d,n)10B reaction, which is widely investigated for explosives detection.

Both SNM and explosives detection have strong desirability among sponsors, such as DHS, DoD, and DOE. The pulsed-power based approach investigated here is an emerging capability that should be fully socialized with the sponsor community that is unaccustomed to this technical approach. Necessary follow-on work includes a complete systems-oriented trade study of diode performance, and systems tie-in with time-tied detector investigations ongoing both within and outside Sandia.

DEFENSE SYSTEMS AND ASSESSMENTS INVESTMENT AREA

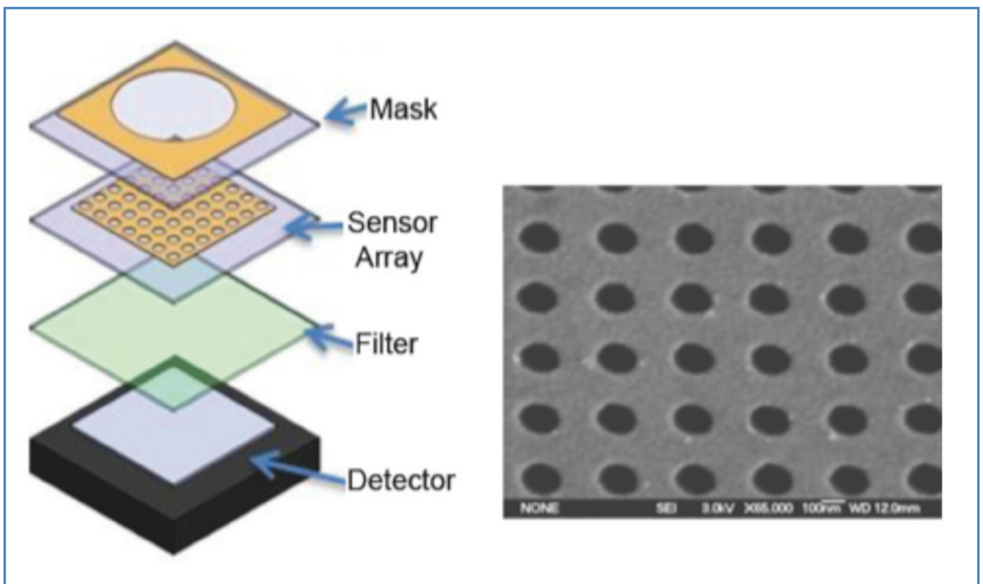
This investment area funds both fundamental and applied research into science and technology that is or can be rendered applicable to national defense — from software to assist the human intelligence analyst by filtering and more-coherently organizing intelligence streams, to virtual training scenarios for analysts and warfighters to a variety of improved detection-science and -technology solutions for chemical and biological threats to populations, and even to improved robotic agents to mitigate risks to soldiers and civilians in dangerous scenarios. Through these and other initiatives, projects in this investment area contribute to national defense and homeland security — and therefore, help diminish the global threat of terrorism.

Extremely Thin Chemical Sensor Arrays Using Nanohole Arrays

Project 117759

The challenge of designing and fabricating concealable sensors for chemical and biological national security threats is underscored by the fact that most existing approaches are difficult to miniaturize, requiring either large areas or significant thicknesses. By contrast, this project is developing extremely thin sensor arrays that can be concealed for national security applications such as space control, surveillance, intelligence, nonproliferation, and armed forces security.

The phenomenon of "extraordinary optical transmission" allows nanohole arrays in thin metallic surfaces to couple incident light to surface plasmons such that a disproportionate amount of light is transmitted through subwavelength-sized nanohole arrays. Such transmission is very sensitive to surface chemistry in the vicinity of the holes, meaning that changes in that chemistry can be detected by spectral shifts in transmission. For example, by functionalizing the metal surface with molecules designed to specifically bind chemical explosives, binding of such explosives to the functionalized surface can be readily detected through such spectral shifts, with sensors small and thin enough to be easily concealed.



Drawing of the elements of a nanohole-array sensor (left) and electron micrograph of the array (right).

Advanced Optics for Military Systems

Project 130699

This research is motivated by a clearly perceived, mission-related need, that of the military's (and DARPA's) search for improved variable field-of-view optics for both weaponry and night-vision goggles. The solution is non-mechanical, in the sense of eschewing traditional lens elements that would move with respect to one another. The research thereby treads into risky unknown territory.

Traditional optical solutions are exemplified by the optical zoom of certain cameras. The "in-out" movement of the lens of a small digital camera is one example of optical zoom. Problematically, for the type of optical magnification and clarity required by the military, these traditional optical solutions tend to be overly large and heavy, requiring significant power to move the lenses.

This project turned, instead, to liquid crystal adaptive lenses, in which liquid crystal molecules within a transparent chamber are reoriented by applying a voltage across the lens, thus changing the index of refraction and focal length of the lens, ultimately producing a fully functional lighter-weight system requiring less power. It has successfully designed and demonstrated a push-button zoom riflescope, building adaptive lenses that vary over their full dynamic range in less than 0.5 seconds and that are currently being integrated into a prototype riflescope for the US Army. The project is also investigating thin-shelled composite mirrors for larger aperture, variable field-of-view systems, and has demonstrated a 10× zoom from a variable radius adaptive zoom design.

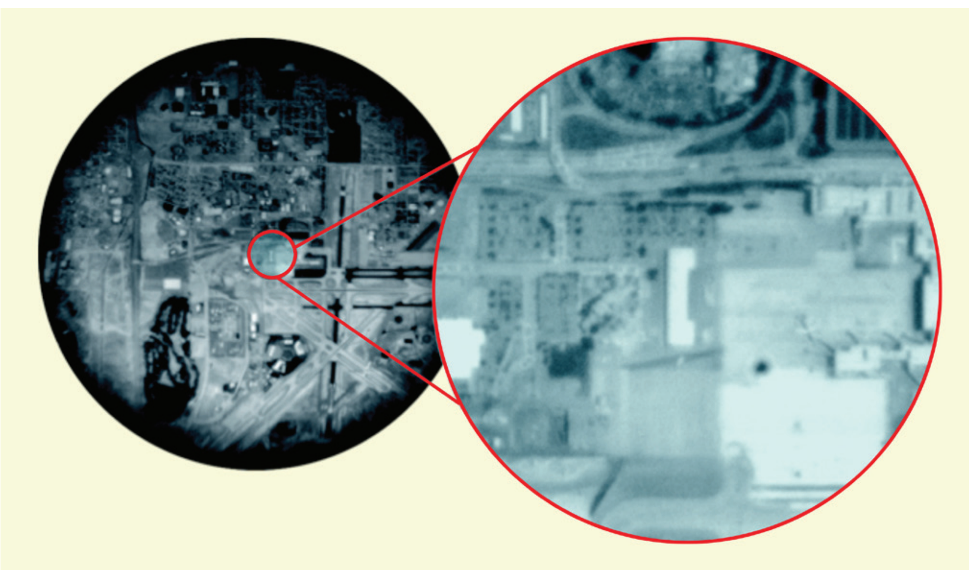


Image illustrating the adaptive lens zoom feature, the right-hand image, a magnification of the circled area of the wider-field left-hand image.

DEFENSE SYSTEMS AND ASSESSMENTS INVESTMENT AREA

Precision Nano-Bumping Technology for Large Format Focal Plane Arrays

117742
Year 3 of 3
Principal Investigator: S. S. Mani

Project Purpose

Large Format Focal Plane Arrays (FPAs) are a key component in numerous remote sensing systems. Mission requirements drive the need for increasing the number of pixels that are multicolor in addition to forcing pixel dimension minimization. This project investigates innovative solutions to this problem by leveraging current capabilities as well as exploring new technologies to produce uniform indium nanobumps for use in readout integrated circuitry (ROIC) and photodetector hybridization. Used for conductivity at cryogenic temperatures, indium nanobumps will be grown with controlled pitch, exact geometry, and uniform thicknesses. Combining advanced lithographic techniques and optimized electrodeposition techniques, controlled pitch, exact geometry, and uniform thicknesses will prevent pixels from shorting between neighbors and effectively limit the pixel pitch. This new nanobump fabrication technology allows for hexagonal or rectangular or any other regular pixel assemblies across large format FPAs with areas greater than 3 cm^3. Techniques for indium interconnect separation of the detector array and ROIC chip will also be investigated. Re-workable interconnect technology will allow for recovery and re-work of a defective part after testing at cryogenic temperatures on proven ROICs before permanent attachment. This innovation in photodetector screening will dramatically increase hybrid FPA yields.

Summary of Accomplishments

We fabricated large area arrays of electroplated indium bumps on silicon based ROICs and detectors for the purpose of progressing towards producing large format FPAs. The newly developed indium electroforming process relies on a highly adaptable and scalable tank for the electroplating process, a novel approach to making distributed electrical connection to the substrate and a tailored electrochemical pulse regime design to flatten and shape the deposit uniformly over large areas. We also developed indium interconnect removal strategies for post-hybridization separation using a selective wet chemistry to dissolve the electroplated indium while preserving the underlying material. A new relationship with an external vendor was established to align and bond our plated substrates. Conclusively, this project demonstrated the viability of electroplating indium bumps for fabrication of highly dense and uniform arrays of interconnects for the FPA community.

Significance

This project proposed to create a new method for hybridizing large format FPAs using precision nanobumping technology, by establishing and optimizing an electroplating process of indium. This work directly supported remote sensing missions that use FPAs as well as future mission space that requires hybridized detectors with small pixel pitches. Sensor systems requiring small and dense hybridization will benefit from this effort. Through the work of this project, we developed a technology that improves FPA yields and enhances FPA resolution (via smaller pixel pitch), all while being easily adaptable into current process flows at various FPA vendors. Improving yield alone could save millions of dollars for Sandia and other parties interested in FPA technologies. Enhancing the resolution of the FPAs increases the system level performance of those programs using FPAs and creates opportunities to design more-advanced systems for new applications.

During the course of this project, we established a relationship with an FPA vendor that could lead to licensing our process and to near term work-for-others agreements. The plating process is sufficiently developed to deposit small features with dense pitch. The limiting factor is the placement accuracy in the hybridization process, a process requiring precision tooling. The vendor is very interested in incorporating aspects of this process into some of its product outcomes. As a result of this effort, a roadmap for this activity was developed and presented to managers. The roadmap is composed of three broad sections: plating setup, overall plating process including details in electrochemistry, and hybridization. Future steps have been specified for each of those areas assuming funding were to become available. Marketing sheets were created in collaboration with the licensing department to summarize our capabilities to the external community.

Advanced Data Processing Module for Future Satellite Projects

117743
Year 3 of 3
Principal Investigator: R. R. Mills

Project Purpose

Sandia has been very successful in implementing static random access memory–based, field programmable gate array (FPGA)-based processing techniques for use in satellite applications. However, the types of parts available for these uses are susceptible to single-event upsets (SEUs) due to the harsh radiation effects of the space environment. In the past, the primary method used to mitigate these SEUs has been to triplicate the logic placed in the FPGAs in order to provide (from a logic standpoint) resistance to such an upset. This cuts the effective usable resources available to an FPGA designer by at least three, which limits the sophistication of image processing algorithms available for use on-orbit. The desire to increase the available processing power in a flight FPGA requires the use of newer, higher density FPGAs. The use of these FPGAs brings with it significant risk, particularly in the areas of printed circuit board (PCB) layout, PCB manufacturability, embedded processor selection, and memory selection. The purpose of this project was to develop a low-power, high-efficiency data processing module based on the Xilinx Virtex-5 FPGA that would be capable of hosting an embedded processor capable of executing real-time image processing algorithms. The module would take advantage of the FPGA's built-in high-speed serial input/output capabilities and would feature a dedicated connector based on an industry-standard form factor that would allow multiple processing modules to be networked together into a node-based system for further study.

Summary of Accomplishments

The project was designed to investigate the suitability of state-of-the-art commercial technology for utilization in future satellite projects. Its goal was to use the technologies to build and demonstrate a network of FPGA-based processing nodes performing an algorithm previously implemented at the ground station due to lack of processing power on-orbit. The end result would be a platform on which to base future flight projects, as well as increased technological competency in both the space processor technology field and the satellite computer-aided design department.

Hardware difficulties prevented the project from achieving all of its initial goals, but valuable knowledge and lessons learned resulted from the project that should prove beneficial for many future satellite projects and proposals.

Significance

While some of the initial goals of the project were not achieved, many valuable lessons learned can be taken from the project that can greatly reduce cost, schedule, and risk in future projects, particularly when using the types of parts and technologies (Xilinx Virtex-5, RapidIO, DDR2 memories) we examined. When applied properly, the techniques and lessons learned from this project should provide a tangible asset to future cutting-edge satellite development at Sandia. The project also benefitted Sandia's competency in the area of complex printed circuit board design and layout, and this knowledge will benefit all future satellite designs.

Adaptive, Lightweight, Coated Fabrics for Protection from Low Velocity Fragments and Projectiles

117748
Year 3 of 3
Principal Investigator: J. W. Foulk III

Project Purpose

Fragmentation weapons such as improvised explosive devices (IEDs) are responsible for 60%–70% of troop casualties and the majority of injuries in modern warfare. The threat of fragmentation weapons has grown dramatically with the urbanization of combat, and this has caused the rate of amputation in the Iraq war to double from previous conflicts. Soft fabric armor offers optimal personnel protection from fragments and other low velocity projectiles (< 800 m/s). However, current designs for bullet-resistant vests are too heavy and bulky to extend protection to the extremities. We propose to develop lightweight, flexible, coated armor with improved interactions among the fibers, yarns, and layers. In addition to extending personnel protection to the extremities, customization of the proposed coated fabrics will offer significant enhancements to current vehicle armor systems and provide innovative solutions to broader surety applications such as drape-cabable fabrics for blast mitigation and asset protection during transport or storage.

The shear thickening behavior of silica colloids has been exploited to enhance the energy dissipation of Kevlar fabric, but little evidence exists that the technology will be applicable for representative IED fragment masses and velocities. Because the benefits reported at lower masses and velocities can be attributed to fiber-fiber and yarn-yarn friction, this project seeks to tailor friction through improvements in synthesis, computational mechanics, and characterization. An increased understanding of the multiple, interacting mechanisms operative during impact will enable Sandia to not only design new materials but also to treat soft armor as a system. A system-level approach also permits the inclusion of additional requirements such as fire retardation. This effort will contribute to the areas of military technology for highly mobile forces in battlefield and urban operations and broader surety technology for the protection of national security and valuable assets.

Summary of Accomplishments

In this project we have:

1. Established the goal of tailoring friction without harming the fiber.
2. Developed multifunctional chemistry to protect against additional threats.
3. Developed a laboratory experimental program for examining frictional effects. Two methodologies, yarn-yarn, and fabric-fabric testing, were explored for numerous polymers.
4. Developed a fundamental testing program to examine wave propagation at the yarn level using a Kolsky bar.
5. Developed and implemented methodologies for modeling woven fabric through yarn-level continuum models in Sierra Mechanics. The geometric models for the plain-weave fabric are parameterized through Matlab and generated through Cubit.
6. Improved our ballistic testing methodologies to simulate an array of fragment sizes and captured yarn level motions via high-speed photography.
7. Collaborated with an external company to employ a methodology to coat fibers within the yarns. The processing methodology is scalable and does not compromise flexibility or breathability.
8. Selected the appropriate monomer and coating thickness based on suitable material properties measured from tensile testing and yarn pull-out testing.

9. Demonstrated an ~10% increase in V50 performance (velocity at which a bullet will have a 50% chance of penetrating a given piece of armor) for coated fabrics

Significance

The V50 directly impacts the battlefield with little increase in weight, or change in breathability and flexibility. Consequently, we are aligned with the US Army Natick Soldier Research, Development, and Engineering Command, the organization responsible for soldier body armor. Our focus on IEDs also enables us to contribute to the Joint Improvised Explosive Device Defeat Organization and an Integrated Warfighter Outcome, Counter-IED and -Mine. Finally, the fundamental knowledge gained from the current effort can be applied to surety issues involving blast mitigation and asset protection.

Real-Time Individualized Training Vectors for Experiential Learning

117752
Year 3 of 3
Principal Investigator: E. M. Raybourn

Project Purpose

Military training utilizing serious games or virtual worlds potentially generates data that can be mined to better understand how trainees learn in experiential exercises. Few data mining approaches for deployed military training games exist. Opportunities exist to collect and analyze these data, as well as to construct a full-history learner model. Outcomes of the present project include results from a quasi-experimental research study on military game-based experiential learning, the deployment of an online game for training evidence collection, and results from a proof-of-concept pilot study on the development of individualized training vectors. This project leveraged products within projects, such as Titan Informatics Toolkit (Network Grand Challenge), Real-Time Feedback and Evaluation System (America's Army Adaptive Thinking and Leadership, DARWARS Ambush NK), and Dynamic Bayesian Networks (STANLEY [Sandia Text ANaLysis Extensible library]) to investigate whether machine learning capabilities could perform real-time, in-game similarity vectors of learner performance, adapt content delivery, and quantitatively measure experiential learning.

The three-year goal of this project was to determine whether machine learning technologies used at Sandia can be used to perform robust, real-time, in-game diagnostics of learner performance and quantitatively provide an individual vector of one's experiential training so that training content can be adapted in real-time to address a learner's strengths and weaknesses.

Summary of Accomplishments

Key accomplishments include:

- The execution of two human subject studies to investigate Experiential Learning Theory (Kolb), Social Learning Theory (Bandura), and metacognition for the assessment of experiential learning in game-based virtual environments. Conducting human subject studies in year 1 allowed us to collect data necessary to scope the use of machine learning technologies in years 2 and 3 of the project. Data collected includes visual learning strategies, meanings attributed to patterns of cues, observer/evaluator performance assessment during game play, actions taken during game-based learning sessions, and psychometric measures.
- The project sponsored Dan Kaufman (Defense Advanced Research Projects Agency [DARPA] project manager) and Total Immersion Software to provide training to Sandia in DARPA's virtual training environment, RealWorld. This activity was part of our milestone to evaluate candidate game platforms. We also evaluated the Ground Truth game environment used by another LDRD project, and the Delta3D game engine used in the Complex Systems LDRD project.
- The project analyzed quantitative and qualitative data collected during year 1 multiplayer and single-player studies. The team collected self-report quantitative data, psychometric data, qualitative training performance data, observer/evaluator trainee performance measurement data, recall data, after-action-review debriefings, and 86 hours of video of training environment, and 86 hours of video of facial expressions and upper body movements associated with the training study.
- Training objectives and metrics for tactical site exploitation scenarios were identified. A training game was developed in the Unity Game Engine to support data collection for the generation of dynamic Bayesian Network models.

- The Sandia Titan Informatics Toolkit was used for analysis and clustering of salient phenomena such as novice vs. expert behaviors.
- Project results were presented at the Army Science Conference December 4-7, 2008. Preliminary results were presented at the Program Executive Office for Simulation, Training, and Instrumentation (PEO-STRI) Defense GameTech Conference 2009, and the Interservice/Industry Training, Simulation and Education Conference 2009, 2010.

Significance

The Defense Systems and Assessments Intelligent Transformation program of which this project research is a part can make a significant contribution by 1) creating new scientific understanding about the challenges involved in using machine learning techniques to adapt training content; 2) developing real-time individualized training vectors for assessing and adapting experiential learning; and 3) accelerating novices' self-directed learning toward expertness. Project results would enable transitioning these methods for adaptive training systems capability to DOE, and NNSA. This will enable DOE to enhance human modeling in areas such as action/counter-action predictive simulations, co-evolutionary training, and precision decision-making. Training of physical personnel for DOE facilities could become a major factor in lowering costs and increasing performance for DOE response to the new design basis threat.

Automated Entity Relationship Extraction

117758
Year 3 of 3
Principal Investigator: T. L. Bauer

Project Purpose

Intelligence analysts have identified the need for automated methods of processing large volumes of textual data with the goal of extracting the most important information and determining how such information is related. This is a task that analysts cannot do with existing tools. Potentially relevant information for aiding analysts in target identification and predictive analysis is generated at a far greater rate than can be manually reviewed. Thus, the need for automated tools for information extraction and organization is crucial to accurate, efficient, effective analysis of emerging threats to national security. In order to provide such tools, this project will develop advanced techniques for automatically identifying relationships between named entities in unstructured text.

This research will develop novel techniques for analyzing unstructured text and apply those methods to the generation of entity relationship graphs (ERG) from unstructured text. ERGs are graphs consisting of nodes that are entities (people, places, organizations, etc.) and links between nodes that represent their relationships (works-for, member-of, lives-at, etc.). ERGs have been used effectively to organize and analyze information associated with individuals and groups, how they are related, and how they interact. However, these ERGs are most often constructed manually by expert analysts intimately familiar with the associated subject matter. The creation and maintenance of such graphs is time consuming and does not scale to the massive amount of data available.

If successful, this project will result in tools that will expand existing Sandia text-analytic and visualization capabilities by enabling automatic ERG generation. These tools will provide a unique graph-generation capability for intelligence analysts, reducing the amount of time spent on manual document processing, thus providing more time for analysis. This will enable analysts to provide more-efficient assessments on national security with a higher degree of confidence in their assessments.

Summary of Accomplishments

There were three main technical accomplishments over the life of this project.

- We developed several pieces of software that will continue to have impacts at Sandia. These interrelated pieces of software (Citrus, CitrusLib, and Citrus-R) are a new desktop-class text analysis library and applications. These applications utilize state of the art third party libraries, integrating them into a flexible platform for text analysis research and end user text processing.
- We started developing an extension of information theory that better takes semantics into account.
- Finally, we developed a new method for identifying relationship-bearing terms in natural language text. This method was derived from the information theory extension and shows good performance on an independently developed test set.

Significance

The software developed in this project is already being tested for use in several different mission areas at Sandia. The library is being integrated with other software at Sandia.

A key problem that plagues developers of analytical tools is making those algorithms and tools usable and relevant to desktop analysts. Countless millions of dollars across the industry has been spent developing tools that use almost every imaginable visualization and form of analysis known. And yet the simple problem of making an advanced analysis tool relevant to an analyst persists. One insight from this project is that the problem might lie in the underlying information theory that is being assumed, unexamined, by algorithm and tool developers. It is possible that by modifying the underlying information theory we will develop new and better algorithms. We believe that the work in this project has laid out a trajectory that is likely to overcome this problem.

Extremely Thin Chemical Sensor Arrays Using Nanohole Arrays

117759
Year 3 of 3
Principal Investigator: I. Brener

Project Purpose

The choices for making sensitive chemical sensors are very limited: for example, most optical-based sensors require enough interaction length (centimeters or even meters). Other approaches require less depth but larger areas. Lately, nanohole-arrays have emerged as a plausible platform for chem-bio sensors. These samples are made by fabricating subwavelength holes (~50-200 nm for visible light) with spacings of 200-1300 nm onto very thin metallic layers. Although subwavelength, a disproportionate amount of light is transmitted through these holes through coupling to surface plasmons, in what has been termed "extraordinary optical transmission." This transmission is exquisitely sensitive to the microscopic surface chemistry in the vicinity of the nanoholes. By using these nanohole-arrays in transmission mode, with small areas functionalized with specifically designed molecules to ligate desired analytes such as explosives and chemical weapons agents placed directly on top of thin photodiode arrays (<50 µm), we can have a complete solution to chemical sensor arrays. This combination of voltage-directed diazonium chemistry on metallic nanohole arrays had not been previously attempted.

Summary of Accomplishments

1. We developed a robust process to fabricate single-layer nanohole array samples with different hole geometries, and we theoretically explored double-layer samples, which show sharper resonances.
2. We designed and synthesized two diazonium compounds designed to sense dimethyl methylphosphonate (DMMP) after a deprotection step and applied them to nanohole array samples.
3. We developed the necessary hardware for controlled exposure (gas) and calibration.
4. We demonstrated a simple proof of concept for a dual sensor based on a nanohole array, a diode pair, and an optical filter.
5. We proved that this approach works for gas sensing, and we were able to show a spectral shift of the transmission upon exposure to the gas, DMMP.

Significance

These sensors can have multiple applications in national security such as space control, surveillance, nonproliferation and the security of our armed forces. We believe that this is a promising technology for thin chem-bio optical sensors.

These sensors can be combined with other thin optoelectronics and provide a complete platform for chem/bio sensors. Additionally this approach can be used for sensing other gas species provided that there is a suitable surface chemistry that provides adsorption and/or binding.

Integrated Point-of-Use Two-Dimensional Fuel Cell

117762
Year 3 of 3
Principal Investigator: K. R. Zavadil

Project Purpose

The Proliferation Assessment (program area Things Thin) within the Defense Systems and Assessments Investment Area desires high-energy-density and long-lived power sources with moderate currents (mA) that can be used as building blocks in platforms for the continuous monitoring of chemical, biological, and radiological agents. Fuel cells are an optimum choice for a power source because high energy densities are possible with liquid fuels and power generation and fuel storage can be decoupled for independent control of energy and power density for customized, application-driven power solutions. Fabrication of two-dimensional, mechanically compliant fuel cells is a technical challenge.

We propose to capitalize on new developments in nanotechnology, advanced fabrication techniques, and materials science to create a planar direct methanol fuel cell that could be collocated with electronics in a chip format. We will use directed assembly of a variety of nanomaterials to fabricate multifunctional electrode arrays encapsulated in an ion conducting membrane. Materials will be largely polymer-based, including a methanol reservoir, to provide a mechanically compliant and possibly optically transparent device. Total dimensions of this device will be less than 100 µm in thickness with an area that could reach 600 cm^2. The fabrication approach is sufficiently flexible to incorporate a wide variety of material types, further expanding the utility and applications of the developed technology pathway. The benefit produced by this proposed research effort will be the creation of a building block power source that is durable, rechargeable and geometrically functional (i.e., conformal and low dimensional). The envisioned technology path is expected to serve as a model for other applications that require the integration of multifunctional nanomaterials, specifically where catalysis, electronic and ionic conductivity are key issues.

Summary of Accomplishments

We created a number of ultrathin (micron-scale) conductive planar electrode arrays based on several different forms of carbon. Photolithography and subsequent pyrolysis of several photoresist materials was used to generate microporous or patterned arrays of conductive carbon films. We demonstrated an ability to release these films and pattern structures from silicon substrates to form free-standing, mechanically compliant electrodes that can be further manipulated into vertically stacked assemblies. Layer-by-layer polyelectroyte self-assembly methods were also used to create patterned conductive arrays based on functionalized multiwall carbon nanotubes (CNT). Electrocatalytic nanoparticles of Pt, PtRu, Pd and Au were incorporated onto the surfaces of these carbon electrodes through addition by layer-by-layer assembly methods or through controlled nucleation and growth at the functionalized carbon surface. We developed the ability to molecularly wire catalytic metal nanoparticles ranging in size from 1.7 to 15 nm to carbon using conductive polymers like polyaniline. The resulting electrodes show high catalytic mass activity for both the methanol oxidation and oxygen reduction reactions required for direct methanol fuel cell (DMFC) technology. We discovered that shape-directed electrochemical growth of Pd can be used to grow nanostructures on carbon surfaces that show highly efficient oxygen reduction kinetics in an aqueous acidic electrolyte while exhibiting no measureable oxidative activity for methanol. Methanol and oxygen active electrode materials were combined in two different form factors to demonstrate the ability of this material set to produce measureable power. Supported planar arrays of CNT electrodes bearing Pt (anode) and Au (cathode) nanoparticles were combined as a strip cell and power production was demonstrated with methanol oxidation (Pt) and oxygen reduction (Au) under alkaline conditions. Alternately, carbon structures films containing PtRu (anode) and Pd (cathode) nanoparticles were vertically assembled with a Nafion ionomer separation layer to demonstrate power production under acidic conditions.

Significance

The creation of functional carbon electrode arrays is an essential step toward the development of planar fuel cell power sources that can be integrated with electronics and signal transmission capability onto mechanically compliant substrate materials, such as ultrathin silicon, plastics or paper materials. Fuel cell functionality was pursued in this research activity as a higher energy density option relative to battery concepts, such as the Li ion technology. The creation of layer-by-layer assembled electrodes based on CNTs is a significant accomplishment because of their electrical high conductivity (130 S/cm at thicknesses of only 0.1 micron), evidence of ample interplanar electron transport, and the resulting possibility of a maintaining this high conductivity on flexible substrates. This project has produced a number of discrete chemistries and processes for conducting layer-by-layer assembly to control electrode composition, properties, and spatial location (i.e., patterning). The same general concepts could be used to produce conformal structures on nonplaner surfaces. We demonstrated efficient electrocatalysis by molecularly wiring nanoparticles to conductive scaffolds.

The significance of this accomplishment is that simple assembly techniques can be used to combine readily available support materials with preformed active structures; specialized structures do not need to be grown in place. The permutations possible with this generalized assembly approach include choosing polyelectrolyte constituents that yield tunable fuel or oxidant permeability, graded hydrophilicity for efficient water management (a byproduct of methanol oxidation and a performance limiting reagent), and stabilization of the catalyst particles toward degradative processes. The discovery of minimal methanol oxidation interference with the oxygen activity of shape-directed Pd nanostructures is significant because electrochemical selectivity is required for ultrathin power sources where fuel and oxidant crossover between anode and cathode becomes a power limiting process. Our work in assembling these material components as either strip or stack style cells is significant as it shows that electrochemical power producing devices can be built using simple assembly methods. Where the catalysts used within this study were not particularly economically viable for large-scale power source production, the assembly methods are sufficiently generalized to be extended to less-expensive, nonstrategic materials. Catalytic energy conversion need not be restricted to simple methanol requiring the incorporation of a wider range of catalytic materials that could be achieved using this generalized assembly approach. The overall layer-by-layer assembly approach is equally applicable to producing a wide range of electrically addressable structures, such as sensors based on the unique properties of carbon nanotubes and other functional nanostructures, in low-dimensional form factors.

Refereed Communications

M.L. Gross, K.R. Zavadil, and M.A. Hickner, “Electrically Conductive Layer-by-Layer Assembled Carbon Nanotube/Polymer Patterned Arrays,” to be published in *Langmuir*.

Understanding and Developing Countermeasures for Botnets

117764
Year 3 of 3
Principal Investigator: J. Van Randwyk

Project Purpose

Computer malware is becoming more virulent every day. Malware, in the form of bots, is now one of the most widespread and dangerous forms of malware. Bots can communicate with each other, passing information between nodes or working together for some nefarious purpose (denial of service, spamming, etc.). This project is focused on studying and characterizing bots and botnets in order to improve our knowledge of this form of malware. We are building tools to assist cyber security practitioners in rapidly analyzing malware. Additionally, we are building an environment in which to study bots "in the wild" without the negative consequences usually associated with having a bot on one's computer.

Summary of Accomplishments

We designed a malware triage system, FARM (forensic analysis repository for malware), which has been further developed and put into operation by Sandia cyber security and multiple external sponsors. This system has enabled malware analysts to more quickly address potential threats on their networks.

We built an in-house capability for analyzing and evaluating malware and botnets. The expertise developed in technical staff has been leveraged by other projects, given validity to proposing further work, and resulted in new sponsored work.

The research team learned that the botnet "problem" is more complex than initially thought and has an entire black market economy built around it. Studying bots and botnets is extremely important as the amount of money being invested into their development has made them very complex.

Significance

DHS and DOE each have an objective in their strategic plans to improve cyber security in critical infrastructure. This work addresses mitigating the problems of malicious software in the form of bots and botnets.

Our research results can help in securing information systems from Sandia through the rest of the federal government. Additionally, bots/botnets pose a threat to almost any computer, meaning that typical home Internet users are susceptible to having this malicious software on their computers. The economic consequences to our country of such a large base of installed malware could be extremely large. Our work contributes to better understanding and mitigation of this malicious software.

High-Speed Spectral Sensor

117775
Year 3 of 3
Principal Investigator: S. A. Kemme

Project Purpose

Spectrally tunable filters that can operate at high speeds can be leveraged for various imaging and spectroscopy applications. For instance, photodetectors paired with narrow band filters that can scan at high frequency through a waveband of interest may be useful in the rapid identification of specific chemical compounds or biological elements.

This purpose has direct relevance to various Sandia missions that seek to reduce the threat of long-range projectiles. Capability to conduct high-speed spectroscopy with a low mass, robust device is important to achieving more detailed kill assessment analyses. Success towards this goal will provide Sandia with a high-speed, small and robust sensor system.

Summary of Accomplishments

This project has been the catalyst for several notable technical achievements in a fairly diverse set of science and technology areas.

- First, high-quality electrooptic thin film deposition has been demonstrated on sapphire substrates. Using the chemical spin deposition technique, several $BaTiO_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$ films have been realized. These thin films exhibit high quality x-ray diffraction patterns and polycrystalline morphology according to atomic force microscope scans.
- Second, we used a variety of theoretical simulations to help guide our device design and determine feasibility. For instance, RCWA (rigorous couple wave analysis) codes were used extensively to help determine the geometry of the fabricated active resonant subwavelength grating (RSG) devices. Each variable such as electrooptic thin film thickness, metal electrode pitch and refractive index was taken into account to achieve some intuition about the overall device. Additionally, dynamic blackbody simulations were carried out to determine the feasibility of these devices within the context of conducting spectroscopy during and following a hypersonic collision event.
- Perhaps most notably, we have successfully demonstrated an active resonant subwavelength grating device for the first time. Although static RSG devices are leveraged in a variety of applications, to our knowledge, this is the first example of an active device using an electrooptic thin film and subwavelength grating to modulate the resonant frequency.
- Finally, we have done a significant amount of work to shrink the form factor of this device down to a demonstration-level box. In particular, we have designed, fabricated and assembled a set of optics and fixturing hardware in order to show prospective interested agencies the operation of the high speed spectral sensor and also to demonstrate the compact, lightweight nature of the technology.
- Three conference talks were presented on this work and three conference manuscripts were submitted and accepted.

Significance

One way to contextualize this work is to describe it in terms of the Department of Defense Technical Readiness Levels (TRL). At the beginning of the project, we were at TRL 2 (technology concept and/or application formulated). In the project, we had conceived of using an electrooptic material to change the refractive index of the material in order to tune the resonance of the subwavelength grating device. Along the way, we demonstrated the working principle of the device (TRL 3, analytical and experimental function proof of concept), and moved towards full component validation in a laboratory environment (TRL 4). Additionally, we pursued a path for TRL 5 (component validation in a relevant environment) by investigating testing possibilities at the Shock Thermodynamic Applied Research Facility and simulating hypersonic collision events.

A high-speed active RSG system could have several potential internal and external applications. Internal applications could include the modulator for a subclass of scannerless range imager (SRI) systems that could trade the amplification of the current intensifier tube for the reduced power consumption and improved resolution offered by an RSG-based system. The SRI team should be engaged when measured performance parameters of high-speed devices are available.

External applications may include a high-speed filter for inclusion with high-speed imagers. Massachusetts Institute of Technology's Lincoln Laboratory has developed a high speed complementary metal oxide semiconductor imager for DOE application that may benefit from front-end optical filtering that could alternate the wavelength sensitivity for interleaved frames.

Lastly, such a device could form the basis for a standoff weapon typing sensor with application to high speed exo-atmospheric missile intercepts. A sensor could be crafted to discriminate between and match the optical signatures of several different materials of interest that are used in weapons systems. This data would provide the administration valuable information for post-incident discussions.

LEEM Examinations

117778
Year 3 of 3
Principal Investigator: M. L. Anderson

Project Purpose

In this project, we developed a high-resolution microscope for advanced imaging. Over the span of this project, we attempted to demonstrated the tool's applicability to several analysis problems, yet in many cases, did not succeed due to the severe technical challenges.

Summary of Accomplishments

Over the past three years, we have successfully proven that the LEEM can be used to image simple test structure devices. We have designed methods for deprocessing and mounting samples in this ultrahigh vacuum system. We continued work towards improving sample preparation, defining the source of image contrast, and determining methods of improving signal-to-noise ratio. We designed methods for imaging these samples in ultrahigh vacuum system. Unfortunately, we were not successful when attempting to apply this to parts other than targeted test structures.

Significance

The application of this tool could give Sandia an important, new, and differentiating technology for imaging. This could be of significant value for Sandia's internal use. However, a significant amount of development would still be necessary to port this technology to applications.

A Toolkit for Detecting Technical Surprise

130697
Year 2 of 2
Principal Investigator: M. W. Trahan

Project Purpose

The detection of a scientific or technological surprise within a secretive country or institute is very difficult. The ability to detect such surprises would allow analysts to identify the capabilities that could be a military or economic threat to our national security. Sandia's current approach utilizing ThreatView has been successful in revealing potential technological surprises. However, ThreatView has limitations.

ThreatView presents data visually, which allows analysts to identify trends, patterns, and relationships that are otherwise very difficult to detect. However, this detection is dependent upon the analyst: some analysts see the patterns; some analysts miss the patterns (false negatives); and still other analysts see patterns that are not real (false positives). In addition, ThreatView uses a single algorithm (LSA) to cluster the data set. There is no way to compare its results to an alternative clustering or to measure the quality of the clustering. We have addressed these limitations by developing a data mining toolkit, which can be used independently or as an extension to ThreatView.

As data sets become larger, it becomes important to use algorithms as filters along with the visualization environments. Our toolkit provides a suite of algorithms to filter the data so that analysts are presented with less, but more -relevant, data increasing the chance of detecting a scientific or technological surprise.

Summary of Accomplishments

- We built a toolkit to perform technology assessments in support of Sandia's Science and Technology Intelligence (S&TI) program. Our goals were to extend our capabilities beyond ThreatView by: 1) being able to analyze and visualize both structured and unstructured data sets; 2) being able to analyze and visualize larger data sets; and 3) being able to use alternative algorithms (non-LSA) and visualizations (non-landscape). We successfully met all these goals. We incorporated tools developed internally at Sandia and Oak Ridge National Laboratory, commercial-off-the-shelf tools, and open source tools into our toolkit.
- We identified several sources of open-source S&T data.
- We developed several collaborations (within Sandia, with other national laboratories, and with commercial vendors) applicable to technology assessments.

Significance

The development and validation of a suite of detection algorithms will greatly enhance Sandia's capabilities to detect and possibly counter scientific and technological threats to national security. Fusing multiple algorithms will allow us to establish confidence limits while reducing the number of false positives/negatives.

Our toolkit has been successfully used for several externally funded technology assessments. It is a core enabling element of Sandia's S&TI program and is important to the successful completion of other research initiatives.

A Zero Power, Motion Sensitive MEMS Wake-Up Circuit

130698
Year 2 of 2
Principal Investigator: R. H. Olsson

Project Purpose

Eliminating standby power is key to extending the lifetime of sensor systems. Ideally, a sensor device would remain in standby, consuming zero power until an event triggers power-up of the entire device for data logging, processing, or transmission. In reality, processing the wake-up event often requires significant power consumption, particularly for complex event signatures, which limits device lifetime and size. We have developed a zero power MEMS circuit capable of waking-up a device upon the detection of simple motion or complex vibration signatures. The wake-up circuit operates based on piezoelectric transduction of mechanical vibration, producing an output current proportional to mechanical displacement. When no acceleration/vibration is present there is zero displacement, zero output current and thus zero power consumption. Under acceleration, a strain induced in a thin film piezoelectric layer produces a current that is passed through a resistor or capacitor to create a voltage that is large enough to turn on a transistor. Since the accelerometer displacement/piezoelectric output current is engineered to respond only to certain vibration frequencies, complex vibration profiles can be programmed into the wake-up circuit and processed in the mechanical domain without consuming power. Major challenges that we had to overcome during the development of the wake-up device were covering the frequency range of interest in a single microfabrication process and realizing a large enough voltage signal swing to trigger tag wake-up in an event, while consuming zero power in standby.

Summary of Accomplishments

We modeled, designed, fabricated, and characterized a zero power wake-up microsystem consisting of three vibration sensors and zero standby power readout electronics. The three vibration sensors were located at different frequencies targeted to a specific vibration profile. When the profile is present, three lights are illuminated. The major research challenges were in the modeling and fabrication of sensors with a large response (Volts/G) and over the desired frequency range. Additional challenges were encountered in the design of the zero power electronics.

Significance

The development of the zero power MEMS wake-up circuit for sensor systems impacts Sandia missions in nonproliferation of weapons of mass destruction and homeland security. The successful development of the wake-up circuit can significantly reduce the power consumption of this important class of devices.

Advanced Optics for Military Systems

130699
Year 2 of 3
Principal Investigator: D. V. Wick

Project Purpose

The military has identified two capability gaps that we are addressing with this project. The first is for a variable magnification rifle scope. In Operation Enduring Freedom/Operation Iraqi Freedom, US forces consistently operate in a mixed-range, rapid transition environment, one in which they are required to enter and clear a building (CQB), dictating short ranges (< 10 m), and then move to an alley, rooftop, or open area where shots might exceed 300-500 m. The first scenario dictates a 1× reflex sight, the second a higher magnification (typically > 3×). Industry has failed to fully address this need, providing only partial solutions using conventional techniques (e.g., Leupold close quarter tactical and Elcan Specter dual role rifle).

For the second capability gap, the military has identified a high-priority technology shortfall for force protection: "The future force must provide a real-time mobile and fixed 360-degree hemispherical area protection. This capability shall include detecting, monitoring, tracking and engaging adversary threats directed against military and civilian personnel." While this capability can be realized with multiple sensors or a gimbal-mounted, pan-tilt-zoom imaging system, these are generally heavy and bulky, and, relatively slow. Although these capability gaps may appear unrelated, our approach to both is to leverage our work in adaptive optics to provide the variable magnification and optical steering necessary to address both capability gaps. We have started developing two related systems that will utilize our expertise in foveated imaging and non-mechanical zoom: 1) an adaptive polymer lens-based rifle scope and 2) a variable field-of-view (i.e., zoom) imaging system that utilizes adaptive optics (Patent # 6,977,777) instead of longitudinal mechanical motion. Both are capable of providing a wide field-of-view for situational awareness and quickly toggling to high magnification with very little motion or power requirements. Industry has only achieved marginal success in trying to address these needs using conventional methods.

Summary of Accomplishments

We have successfully designed and demonstrated a push-button zoom riflescope. Using Finite Element Modeling (FEM) together with experiments on adaptive polymer lenses, the team developed an ANSYS, Inc. model that allowed us to evaluate the material/actuation trade space and build adaptive lenses that varied over their full dynamic range in less than 0.5 seconds. This is currently being integrated into a prototype riflescope for the US Army. Next, we began to investigate thin-shelled composite mirrors for larger aperture, variable field-of-view systems. Composite mirrors are lightweight, replicated mirrors (thus lower cost) that can be actuated to change shape for aberration compensation. We have demonstrated that variable radius-of-curvature is also possible with these mirrors, and we have demonstrated the principles of adaptive optical zoom with a reflective telescope.

Telescope systems rarely have zoom capability. Unlike similar lenses, which refract light, on-axis telescopes have obscurations and/or holes that block on-axis bundles and transmit light through the center of mirrors. This makes it very difficult to design a zoom system where mirrors move longitudinally, as in a conventional zoom lens. Off-axis configurations are also very difficult due to the extremely tight tolerances. The only zoom telescopes that we are aware of were academic demonstrations and were limited to ~4×. In this project, we have demonstrated 10× zoom from a variable radius adaptive zoom design. We have begun making preliminary measurements on the materials. The biggest technical hurdle is overcoming residual aberrations in the mirror as we change its radius-of-curvature. The FEM that we are initializing will go a long way towards understanding the physical limitations of the composite mirrors. If we are successful, this development will allow high-resolution telescopes to vary their magnification by 10× or more in real-time. This work will continue in FY 2011.

Significance

This project serves our national security mission by "providing world-class scientific research capacity and advancing scientific knowledge." Both the adaptive polymer lens and the composite mirror work will serve both DOE and DoD personnel and infrastructure security missions. We are currently in the process of transitioning the riflescope technology to the US Army.

The large-aperture, variable-radius composite mirrors will provide a valuable tool that can be used for multiple intelligence, surveillance, and reconnaissance applications. Sandia has already patented and demonstrated the concept of adaptive optical zoom, and, as part of this project, demonstrated the concept in a direct view riflescope. The Army is funding a transition development, and we believe this could prove extremely advantageous to the warfighter. We fully anticipate that the US Army will be demonstrating a prototype system in the near future based on this work.

The development of these variable radius mirrors will provide a significant advantage for intelligence, surveillance, and reconnaissance (ISR) applications that are restricted in size, weight, and power (SWaP). There is a great deal of interest in persistent surveillance for both air and space platforms, and a system that can vary its field-of-view in a SWaP consistent package will provide a revolutionary benefit to our national security mission.

We are hopeful that we can develop a large-aperture, reflective system using thin-shelled composite mirrors for high-altitude and space ISR missions.

Highly Producible Focal Plane Array

130700
Year 2 of 3
Principal Investigator: S. S. Mani

Project Purpose

Sandia Space Programs presently relies on industry to design and fabricate high-performance focal plane arrays (FPAs). Present and future program performance requirements stress state-of-the-art FPA design and production capability to the point where development risk and cost cannot be adequately managed under traditional contractor relationships. R&D investment in next-generation FPA development is an essential springboard to establish technology and capability that is within reach of a full system development program.

This project addresses the gap between identification of performance and manufacturability improvements for existing products through design and assembly of an engineering prototype. Specifically, this effort for the second year of this project proposes an approach to achieve a producible assembly process for large format FPAs (2K and larger).

This effort proposes to address the manufacturability aspects for a large, two-color FPA by tiling four 1K x 1K pixel, non-stitched, pieces. The first year focused on completing the design of the 1K x 1K readout integrated circuit pieces. In the second year, the verified/validated design will be fabricated in the Jazz Semiconductor, Inc. foundry and the fabricated wafers will be tested at Sandia. Processes addressing the assembly and packaging process will be developed and optimized to produce a two-sided abuttable tiled two-color readout integrated circuit (ROIC) assembly. Processes involving tile planarity, subpixel gap, precision placement, precision singulation, and precision thinning will be among the numerous processes that will be applied to the assembly. The overall process will be worked in collaboration with Teledyne Imaging Sensors (TIS), ensuring the assembled unit will be compatible with their hybridization process. If funds permit, we will start preliminary detector design work working with TIS.

Summary of Accomplishments

In the second year, we placed a contract with TIS for 2-color detector design. We received the final detector design from TIS. The ROIC design elements from TIS have been completed and are being integrated with Sandia designed timing, control, and digital input/output blocks. Initial validation of the entire ROIC design has been completed at the register transfer (RTL)/Netlist level. Auto-place and route (APR) and layout are currently underway. Use of the MMSIM (Multi-Mode Simulation Suite) tool (from Cadence/Michigan Engineering, Inc.) has been important to quickly simulating and evaluating the design. Without this tool, simulations would still be ongoing at the initial simulation stage of RTL and Netlist and the design would probably not be at the APR/layout stage.

We performed preliminary thermal modeling examining strain energy (and subsequent stress field) in the cryogenically cooled packaged environment. The model included static stress analysis of a quartered representation of a ceramic (alumina) package, silicon substrate, and silicon die. In this model, the boundary conditions included a fixed vertex on the bottom face of the ceramic package in the center of the model with a fixed, uniformly distributed temperature across all exposed surfaces of 77 K. Material properties were input relative to the 77 K temperature.

We made additional measurements on the performance of a low-power data multiplexer, serializer, and vertical cavity surface-emitting laser driver integrated circuit developed under LDRD project 95211. The goal of the measurement was to determine the operating speed of the part while it is at cryogenic temperature. We observed data operation at 3.2 GB/s while the component base plate was at 150 K. The component power dissipation was 8.6 mW.

Significance

The user community is looking to Sandia's Space Mission Engineering Program Office to provide concepts for next-generation systems for a variety of government agencies. Advances in FPA architectures, optimized for this mission area, could bring a significant increase in performance, specifically in minimum detectable signal.

Assessing Vulnerabilities of Wireless USB

130701
Year 2 of 2
Principal Investigator: J. S. Duncan

Project Purpose

Wireless USB (WUSB) is a new technology that promises to ease and improve connectivity between peripherals and computers. WUSB will one day replace cabled USB as the primary peripheral connection technology. West Technology Research Solutions projects that 84 million Wireless USB devices will ship in 2010. As WUSB replaces cabled USB, these devices will make their way en masse into national laboratories, research institutions, and military facilities.

This research is aimed at conducting a vulnerability assessment of this new, potentially disruptive (from a cyber security standpoint) technology. It will analyze the protocols, security implementation, and source code to evaluate the strengths and weaknesses present in WUSB implementation. Recommendations for how to use and limit use of WUSB in secure environments will be presented.

There are only a handful of WUSB chipset and driver providers, meaning a vulnerability discovered in one implementation could lead to the exploitation of millions of devices. Another concern is the detection of an attacker trying to exploit WUSB devices. These concerns highlight the need for proper analysis in the use of these devices in secure facilities and laboratories.

Summary of Accomplishments

The team has accomplished the following tasks:

- Established a test lab in a wireless screen room for WUSB vulnerability testing
- Conducted protocol analysis using standard and actual device transmission
- Characterized the security association between two WUSB devices
- Identified vulnerabilities in WUSB protocol and security association process
- Developed Proof of concept demonstration
- Completed four project reports
- Certified wireless (CW-USB) media access control layer
- Security mechanisms of CW-USB

Significance

Protecting classified and sensitive unclassified information is critical to the national security mission of DOE. This research is pertinent to that mission in that it evaluates the security and implementation of a new, potentially disruptive technology that will make its way into most computers and peripheral devices.

Automated AOI Management for Future Sensor Systems

130704
Year 2 of 2
Principal Investigator: K. W. Larson

Project Purpose

A persistent system engineering challenge exists in 24/7 operational satellite systems whose data require sophisticated algorithmic processing for exploitation: the data-rich environment of the sensor is spatially separated from the human perception-, computer-, and power-rich environment of the ground station. One can idealize several naive solutions to the problem that are generally infeasible. For example, transmitting all data to the ground involves downlink resources that are very expensive to obtain and maintain, while implementing all data exploitation algorithms on the sensor involves unacceptable trades between probability of detection, false alarm rate, system maintenance, and mission flexibility. Furthermore, mission flexibility is becoming ever more important, and the sets of targets that need to be detected and characterized are becoming more diverse.

We think the solution to this problem involves a smarter distribution of data exploitation among satellite resources, ground computation, and human operators. We call this strategy Area of Interest (AOI) management. The key concept in AOI management is that the downlink carries data whose spatiotemporal resolution is variable across the sensor's field of view, so that resolution of important features is high, and background noise is sparse. This project will investigate how AOI management can be implemented within a unified flight and ground architecture. We will evaluate and compare architectures by modeling and simulating net system performance under ranges of objectives, constraints, and configurations. We have chosen the problem of tracking moving targets with time-varying intensity as an exemplar of a mission for which AOIs might be particularly important, and will use this mission space to motivate the discovery and refinement of AOI techniques.

Summary of Accomplishments

- We have invented the Scene Kinetics Mitigation algorithm for jitter suppression.
- We have implemented, in cooperation with another LDRD project, a dim moving target detection algorithm in prototype next-generation payload hardware.
- We have implemented and compared velocity-matched filters and Bayesian track-before-detect algorithms for dim moving target detection.

Significance

The results are of interest to a variety of ongoing or potential projects and federal sponsors including DOE and the National Aeronautics and Space Administration.

Boundary-Layer Transition on Maneuvering Hypersonic Flight Vehicles

130705
Year 2 of 3
Principal Investigator: D. W. Kuntz

Project Purpose

Boundary-Layer Transition (BLT) is the phenomenon that occurs within the boundary layer of flight vehicles when the flow changes from laminar to turbulent. As this process occurs, flow properties change significantly and aerodynamic heating rises drastically. Transition on ballistic flight vehicles has traditionally been predicted by correlations based on ballistic reentry vehicle flight-test experience. The new class of maneuvering vehicles intended to fulfill a Prompt Global Strike (PGS) role will fly long duration trajectories, and accurately predicting boundary-layer transition would mean less conservatism in heat shield thickness. Current approaches are insufficient to address this important need. Numerical techniques for predicting boundary-layer transition based on stability theory are becoming the state-of-the-art for hypersonic flight. One such tool, the STABL computer program, funded by Sandia and the Air Force Office of Scientific Research, was developed to provide this predictive capability. The work outlined within this report combines STABL calculations with Sandia maneuvering flight vehicle experience with the intention of developing a prediction capability for transition of maneuvering hypersonic flight vehicles.

The objective of this effort is to develop a state-of-the-art transition prediction capability for maneuvering hypersonic flight vehicles, a capability that is essential for the successful design of the new generation of PGS weapon systems. The Thermal Protection System (TPS) of a PGS vehicle makes up a significant fraction of the mass. The uncertainty inherent in current BLT prediction techniques requires that these vehicles carry a significant margin in TPS thickness. Reducing this uncertainty through the development, application, and verification of state-of-the-art BLT prediction techniques could significantly reduce the required excess TPS material, enabling the design of a system otherwise not possible. An improved transition prediction capability will benefit all subsequent Sandia flight test programs as well as systems currently under development by other organizations.

Summary of Accomplishments

The flight vehicles to be studied have been determined and prioritized. Stability calculations have been completed for fourteen ballistic flight vehicles with thermal protection systems made of four different materials. The N factor, the natural log of the integrated amplification factor of the most unstable disturbance frequency, has been computed for each vehicle at the initial indication of transition. Preliminary stability calculations have been completed for a single maneuvering flight vehicle based on three-dimensional flow field solutions. In addition to these stability calculations, additional studies have been performed, including investigations of: 1) the effects of blowing on stability results, 2) the effect on computed N factors as transition moves forward on a ballistic vehicle, 3) N factor histories during reentry, and 4) surface chemistry of specific thermal protection systems during reentry.

In the original proposal, we had hoped that an appropriate N factor for transition prediction on all ballistic flight vehicles would be determined by these analyses. We have determined that, with the level of physics included to date, a single value of N is not appropriate for all types of vehicles. A technical interchange meeting was held on March 19, 2010, at which the results of the investigations described above were presented to ten transition experts from academia, private industry, and government laboratories. The results obtained to date surprised individuals and have resulted in redirected research at multiple facilities. Because of these results, stability investigations of ballistic vehicles continue, in addition to the planned investigations of stability on maneuvering vehicles.

Significance

The accurate prediction of boundary layer transition is important to the design of PGS vehicles. The proposed effort, if successful, would significantly improve our ability to predict transition on these vehicles, and thus improve our ability to optimize the design of the thermal protection systems.

Directed Robots for Increased Military Manpower Effectiveness

130707
Year 2 of 3
Principal Investigator: B. R. Rohrer

Project Purpose

There continues to be a trend in all branches of the military toward doing more with fewer people. The proliferation of unmanned aerial, ground, and underwater vehicles attests to this, as do stated goals for increased manpower effectiveness in major programs such as Future Combat Systems (FCS). Fully automated unmanned vehicles (UVs) are appealing, since they require no attention during operation. However, full automation has not yet become practical for most systems, particularly for ground vehicles operating in unmodeled environments. Instead, current designs require almost constant supervision from at least one operator.

In order to increase the effectiveness of UV operators, we propose to develop robots that can be “directed” rather than remote-controlled. They would be instructed and trained by human operators, rather than driven. Over time, as they learn appropriate behaviors and world models, directed robots will increase in autonomy and require less supervision. This approach is analogous to how a human apprentice is trained —not through controlling his actions, but through repeated instruction, demonstration, and feedback.

The technical approach will be modeled closely on psychological and neuroscientific models of human learning. Two Sandia-developed models will be utilized in this effort: the Sandia Cognitive Framework (SCF), a cognitive psychology-based model of human processes, and BECCA (brain-emulating cognition and control architecture), a psychophysical-based model of learning, motor control, and conceptualization. Together, these models will span the functional space from perceptuo-motor abilities, to high-level motivational and attentional processes. BECCA will be used to translate raw sensory information into symbolic semantic tags, which will be passed to SCREAM (Sandia cognitive runtime engine with active memory), an implementation of the SCF. SCREAM will process the tags, decide what general action to take and pass the symbolic command back to BECCA, which will then translate that into low-level commands for the robot, appropriate to its current state and environment.

Summary of Accomplishments

We demonstrated the basic principles of structured speech-directed behavior, We directed the robots using scripted speech commands. The robot was directed with specific commands “hide” and “seek.” It was used to alternately search for high- and low-contrast visual scenes in a cave-like structure, relaying images wirelessly to the operator outside. Although similar behaviors can be attained without the cognitive infrastructure used here, the autonomous learning demonstrated in this stage is a steppingstone to the more sophisticated behaviors.

<u>New learning algorithm development:</u>

In order to scale-up the technical approach to more-challenging environments and more-sophisticated hardware, new learning algorithms for state-space reduction have been developed. Although there are many existing state-space partitioning approaches, these were found to assume the number of output categories or make assumptions on their inputs, such as scaling, that were not appropriate for our team’s approach. The first of these algorithms, the S-tree, is a reinforcement learning divisive partitioning algorithm. The second algorithm, the kx-tree, is an unsupervised cluster creation algorithm that also works by divisive partitioning of the state space.

Communication of Results:
The progress achieved in the first 18 months of this project has been reported in a number of forums. A video for general audiences has been produced of the first year milestone demonstration. Eleven conference papers and talks have been submitted and/or presented to a wide variety of technical audiences. A journal article has been published in the *Journal of Artificial General Intelligence* and two others have been submitted to the *IEEE Transactions on Robotics* and the *International Journal of Advanced Robotic Systems*. The focused feedback from technical experts during these exchanges has accelerated development efforts significantly.

Significance

The results of this project will enable the military to increase manpower effectiveness and use robotics as a force multiplier. Today, many men control a single system. This technology, when further developed, will enable the military to have many systems controlled by a single person. This will have a tremendous impact on military effectiveness and enable the warfighter to attain stated goals for increased manpower effectiveness. This capability will also lead to both reduced costs and increased worker safety in other mission areas including energy and environment.

Refereed Communications

B. Rohrer, "Accelerating Progress in Artificial General Intelligence: Choosing a Benchmark for Natural World Interaction," *Journal of Artificial General Intelligence*, vol. 2, pp. 1-28, 2010.

Malware Attribution through Binary Analysis

130715
Year 2 of 3
Principal Investigator: S. A. Mulder

Project Purpose

One of the difficult problems in computer security is attribution of malicious activity. Even correlating the activities of a single group using multiple tools can be challenging. Sandia is in a unique position, through our Footsteps Lab and other related efforts, to develop advanced capability to respond to national level threats to our information systems. We propose to build the foundation for a long-term program in the area of collecting evidence for attribution. Sandia has been one of the leaders in solving these problems manually through our access to interesting data and ties to various government organizations. The focus of this research effort will be to dramatically improve the speed and accuracy of our current attribution efforts through automation and to make new discovery possible through a normalization process.

Our current model of automated malware fingerprinting is to extract a variety of features from a binary and compare them to a corpus of "normal" programs. Our current work in malware fingerprinting is leading edge. Our approach is built on original research published from IBM's Watson Research Laboratory and has been in continual development for almost five years. In addition to our own experience with binary analysis, we have collaborated with and borrowed ideas from the University of Wisconsin program in binary analysis, the most advanced program of its kind in academia. Our tool includes most of the current techniques from published literature and a few that are unique to our effort. This existing capability provides the theoretical underpinnings of the proposed research effort.

Summary of Accomplishments

The project has been very successful in accomplishing our goals, thus far. We have developed a modular framework for performing this type of research that has allowed us to begin performing experiments of a scale that has not been possible previously and has allowed the rapid integration of new research ideas. We have integrated with an existing network analysis framework that is allowing us to gather features key to establishing attribution. We have developed a number of cutting-edge feature extraction techniques and have been able to frame the problem uniquely to identify new avenues for correlation and integration with actor modeling efforts. In 2010, we are rapidly making progress on the normalization task and have identified the cross-domain correlation component as one of the keys to success in 2011. The technical achievements to date contributed to our selection to run a major government-wide workshop in the summer of 2010. Whether the final research objective is achieved or not, we will be able to have a major impact in the area of threat awareness.

Significance

The difficulty in applying attribution to malicious computer network behavior is one of the primary limiting factors in current security models. This research will contribute to our ability to understand the threat space, providing insight into who our adversaries are and what capabilities they possess. It also provides a basis for appropriate response to malicious activity. Success in this effort will benefit cyber security and information protection needs of DOE, DHS and DoD.

Next Level Technology Development for Satellite Based Processing Architectures

130720
Year 2 of 3
Principal Investigator: J. L. Kalb

Project Purpose

Sandia is currently developing new satellite payload processing and data communication architectures that are integral to providing intelligence about worldwide threats to our nation's security. These architectures focus on increasing mission flexibility, accommodating enhanced sensor performance, and optimizing payload size, weight, and power consumption. The focus of this effort is to define a network-based architecture that is scalable, reliable, and reusable. By leveraging internal investments and Work for Others projects, Sandia has been able to make significant progress in the specific architectural areas of network communication, model-based design, sensor data processing algorithms, and reconfigurable computing. In the area of network communication, much progress has been made evaluating high-speed serial protocols and potential topological configurations, developing tools to easily automate communication performance modeling, and evaluating communication performance once recovery from faults has taken place. Results from prior analysis indicate two major findings that affect the system communication design and performance, both prior to and after fault scenarios. These findings are that node placement and routing algorithms are important to communication performance.

These architectures are based on two fundamental components: network communication and reconfigurable field programmable gate arrays (FPGAs). Several areas relating to these fundamental components pose technical challenges that need to be addressed in order to effectively implement these architectures. These challenges include mitigating single event upsets (SEU) in Static Random Access Memory (SRAM)-based FPGAs, reducing the large size of FPGA configuration bit files, placing processing nodes in a distributed, network connected architecture, and recognizing and recovering from fault conditions. The objective of this work is to investigate efficient approaches to SEU mitigation and device configuration and to design methods to optimize architecture topologies for communication performance and fault detection and recovery.

Summary of Accomplishments

In the area of node placement optimization, we developed an implementation of a fault tolerant node optimization algorithm and implemented it using the GAMS (General Algebraic Modeling System) software package. These simulated topologies were compared to results from a previous project and initial results displayed a 30-40% improvement of optimally placed networks versus "intuitively" placed networks.

Investigations into quality of service and fault detection parameters started with services provided by the Consultative Committee for Space Data Systems Spacecraft Onboard Interface Services standards. From these services, we determined a set of metrics for which a network manager would be responsible. Also investigated were the types of network protocols that mitigate these failures through hardware. One promising area is the new plug-and-play standard for the SpaceWire protocol being developed by National Aeronautics and Space Administration at Goddard.

Bit file compression activities completed evaluation of compression algorithms. We identified two algorithms and obtained commercial Internet Protocol evaluation licenses for comparison. We collected an industry-standard file set to benchmark the compression products and made a selection. This has been demonstrated in

hardware and will be on the eighth *Materials on the International Space Station* Experiment.
In the area of partial reconfiguration, we performed a trade study for using SelectMAP vs. Internal Configuration Access Port for space applications. We demonstrated a reconfiguration concept, by loading a soft core processor application over the SpaceWire network into a partially reconfigured region of the FPGA.

Progress to date has been focused on leveraging test resources from the Xilinx Radiation Test Consortium to qualify and characterize elements of the SEU Immune Reconfigurable FPGA (SIRF) device. One area is to mitigate the processors in the SIRF. These processors cannot be mitigated using traditional triple modular redundancy. One method is mitigating the instruction and data caches. This was successfully implemented and verified in beam tests.

Significance

Sandia's space-mission communications program is an integral part of its national security mission, and also of importance to DOE's nonproliferation programs in addition to DHS. To keep pace with new emerging threats, we must continually advance the capabilities of our intelligence systems. The availability of this architecture can address the challenges of design complexity, design reuse, bandwidth, and redundancy so that future design resources can be better spent developing capabilities to meet the needs of our national security.

Phase-Based Geolocation

130725
Year 2 of 2
Principal Investigator: J. J. Mason

Project Purpose

The geolocation of radio-frequency (RF) emitters is a crucial element of many electronic systems used in national security. These systems include overhead systems for signal collection and location, systems for recovery of distressed personnel, and systems for force or asset tracking. RF emitter geolocation is becoming ubiquitous as systems are more routinely expected to provide not just signal content but location of the signal source. An example of this is the forthcoming location capability mandated for wireless phones (E911).

Most RF emitter geolocation systems use time of arrival (TOA) measurements. A limitation of this approach is that the accuracy of the location estimate is proportional to the signal bandwidth so that narrowband signals like voice (e.g., two-way radio) can typically be located to within only a few kilometers. Narrow bandwidth signals can also be located with moving collection platforms using frequency of arrival (FOA), but again, a typical FOA fix is a few kilometers. Another physical observable is carrier phase, and it is sensitive to emitter location variations of centimeters or millimeters depending on RF wavelength. This indicates that phase measurements have the potential to provide the basis for very accurate geolocation. This project sought to develop and demonstrate new approaches to the use of carrier phase measurements to accurately locate an RF emitter.

Summary of Accomplishments

Two new phase-based geolocation techniques were developed and investigated. The first approach is a generalization of the frequency difference of arrival (FDOA) technique that we called phase difference of arrival (PDOA). It has the potential to be more accurate than FDOA, but in applications with relatively smooth platform motion, the two approaches perform similarly. This is the case for satellite based sensors and the PDOA and FDOA approaches were both demonstrated to perform similarly.

While searching for a better performing approach, a relative positioning technique was investigated and found to be capable of much better accuracy than other approaches. This technique uses phase differences between the emitter being located and a nearby reference emitter. We call this approach differential (or relative) emitter geolocation.

Significance

Our research has shown a way to greatly improve the performance of some existing Sandia tracking, tagging and locating systems. We hope to be able to demonstrate the relative localization technique on one of these systems in the near future. This approach will hopefully be of interest to other government agencies involved with global awareness and national security. Specifically the technique could be used to locate and track red or blue forces or assets, recover distressed personnel, both civilian (e.g.,Search and Rescue Satellite-Aided Tracking and military (e.g., Joint Personnel Recovery Agency), or locate targets of national interest.

Silicon Microphotonic Backplane for Focal Plane Array Communications

130727
Year 2 of 3
Principal Investigator: A. L. Lentine

Project Purpose

Future large focal plane arrays (FPAs) (~10^8 detectors) will have on and off-chip bandwidth requirements exceeding 1 Tb/s. Furthermore, many FPAs must operate at low temperatures in a cryostat with a few percent cooling efficiency. Hence, each watt of dissipation on the FPA causes 20–30 W of additional cooling system dissipation. Electrical communication from an FPA, while the standard, is undesirable because of its relatively high power dissipation, increased thermal conductance caused by conductive electrical lines, and innate susceptibility to electromagnetic interference. Existing optical transceiver solutions require large, complex mechanical assemblies, have significant scaling limitations, and dissipate even more power. Here, we propose silicon microphotonic communications to enable massive on and off chip bandwidths (>1 Tb/s) on a FPA. A silicon microphotonic backplane will be developed that will fit into the current FPA electrical backplane solution developed by the FPA Grand Challenge LDRD project. All data will be transferred on and off chip with a single optical fiber, thereby simultaneously minimizing thermal conductance and susceptibility to electromagnetic interference. Further, the silicon microphotonic backplane can dissipate 100× less power than electrical or competing optical solutions and the optical source will be located off-chip and outside the cryostat.

Summary of Accomplishments

- Over the past year, we have reduced our modulator power consumption to under 10 fJ/bit, representing a new record in ultralow power modulators.
- We integrated heater elements and temperature sensors directly into our modulators, and we have demonstrated the ability to hold the resonant frequency of our modulators stable across a 55 °C temperature excursion, another first for silicon photonics.
- We demonstrated both direct integration of silicon photonic devices with complementary metal oxide semiconductor 7 (CMOS7) radiation-hardened electronics operating at 2 Gb/s, limited by the CMOS7 transistor performance.
- We have also demonstrated hybrid integration of our silicon photonics modulator with an IBM 90 nanometer technology node driver circuit, demonstrating high speed performance to 5 Gb/s, limited by the electrostatic discharge pad protection devices on the IBM circuit.
- We have matured fiber-attach mechanisms and demonstrated germanium detectors on silicon, so that we can have both detection and modulation on the same circuits.

Significance

The results of this effort will be applicable to many DOE and DoD areas of interest. This silicon microphotonic communications platform will be important in the advancement of high-performance (HPC) and embedded computing applications in addition to the scaling of very large, high-speed digital imagers. HPC is critical to maintaining a nuclear deterrent and very large, high-speed digital imagers are critical to minimizing the proliferation of weapons of mass destruction, two stated goals of the DOE strategic plan.

Velocity Independent Continuous Tracking Radar

130729
Year 2 of 3
Principal Investigator: D. W. Harmony

Project Purpose

The thrust of this project is to develop techniques and algorithms for following a mobile high-value target with radar by combining VideoSAR (synthetic aperture radar) and azimuth mono-pulse ground moving target indication (GMTI) processing methods. The effort merging these techniques into a new radar mode for continuous tracking is divided into six main tasks: clutter attenuation, azimuth location measurement, tracker development, antenna guidance, image formation, and mover focusing.

Existing radars are severely limited in their ability to follow individual vehicles over typical velocity changes experienced while maneuvering in traffic. All GMTI radars rely on the vehicle's motion for detection against ground clutter. When a vehicle slows or stops, tracking becomes difficult and is virtually impossible for present systems. If successful, the research proposed here would permit continuous tracking through all phases of motion, including full stops.

Summary of Accomplishments

The effort this year has been directed to preparations for data collection flights with a rebuilt Ka-band radar to evaluate the signal processing algorithms developed so far and to collect additional data to support algorithm extensions. Several improvements were made this year to the mono-pulse calculation and tracking algorithms to support real-time operation. While early testing of the initial algorithms in the actual radar system showed they were too slow, improvements made this year now enable real-time functionality. Fortunately, these improvements were accomplished mainly by isolating and restructuring computational inefficiencies and not by utilizing the available graphical processing unit (GPU). The GPU remains available for any future algorithm needs. Improvements to the tracking algorithms were also made that demonstrate track continuity through move-stop-move scenarios.

Significance

Sandia's national security partners are relying more heavily upon monitoring mobile targets. DOE proliferation detection goals have explicitly stated the strong need for continuous tracking of a single high-value vehicle. Our army, navy, and air force have expressed a similar need for their applications. The research proposed here is the best approach for meeting these needs.

Wavelength-Division-Multiplexed (WDM) Free Space Optical Communication Using a High-Repetition-Rate Coherent Broadband Short-Pulse Laser

130731
Year 2 of 3
Principal Investigator: J. Urayama

Project Purpose

Rapidly increasing data generation capabilities in situational awareness operations demand high transmission rates and high-level security. Imagery based activities in remote areas are specific applications for which high-bandwidth communication would provide solutions for existing communication obstacles. As an alternative to conventional radio-frequency and fiber-optic links, this project will pursue free space optical communication (FSOC) using line-of-sight atmospheric delivery of encoded broadband laser beams offering high channel capacity and operational flexibility for secure communication. FSOC using short pulses increases the transmission bit rate through the generation of parallel wavelength-division-multiplexed (WDM) channels in the associated broad bandwidth of the high-repetition rate laser source.

Secure transmission can be achieved through the selective use of the optical encoding and decoding techniques incorporating amplitude and phase control using optical pulse shaping. This coded information is less susceptible to intercept and detection also enabling possible applications for secure key distribution. Because both the high-speed and security capabilities rely on the broadband spectrum of the femtosecond laser, source development and propagation efforts will emphasize the generation and delivery of phase-preserving broadband spectra. Challenges in the optical shaping of the broadband source and those in the atmospheric propagation involving wavelength-dependent scintillation effects will be addressed. Also, encoder and decoder schemes will require high-speed, multi-element modulation technologies adhering to strict operating parameters. Advanced signal processing techniques will be implemented to enhance the high-fidelity transmission of data in challenging environmental conditions. Combined, the effort will be dedicated to achieving the right balance of modulation rates, channel generation, beam delivery, and security for a proof-of-concept high-speed FSOC link. This technology is in its infancy, with associated high risks with regard to level of performance.

Summary of Accomplishments

The effort in FY 2010 focused on the design, implementation, and proof-of-concept testing of the broadband, hybrid time- and wavelength-division multiplexed (TDM-WDM) FSOC approach in the laboratory. We decided to use a broadband fiber laser centered near 1.55 nm to exploit availability of commercial off-the-shelf (COTS) lithium niobate modulation technologies and advantageous atmospheric transmission. Upgrades on the amplitude and phase modulated TDM-WDM transmissions in the C-band produced bit rates above 1 gigabits per second per modulator measured against metrics such as Q-factors and bit error rates. These tests showed the limitations of the existing hardware and the requirements for the next upgrade for a robust working unit. Within the phase encoding scheme, we devised a new approach, in the form of interferometric phase shift keying, as a means to increase the level of communication security and to mitigate impact of atmospheric turbulence. This technique was constructed and shown to be successful in a proof-of-concept test. Laboratory tests for free space propagation were also conducted using turbulence-simulating phase plates. By propagating the communication beam through the rotating phase plates, we found that for atmospheric structure constants of 10^{-15}, the link could be well maintained. Both the amplitude and phase-encoded beams were transmitted over free space in the laboratory to test for link performances and to evaluate hardware needs for both the transmit and receive optics.

The free space performance over short distances in the laboratory generated bit rates similar to those reported above for in-fiber tests. We also pursued broadband pulse-shaping technology to give yet another phase-based option for secure communication. Subnanometer optical resolution of the pulse shaper and a spectral coverage of tens of nanometers were determined to be useful for phase control.

Significance

The DOE/NNSA program lists, as high priority in its FY 2010 call, data exfiltration from areas of denied access toward which burst-mode operation of FSOC could contribute significantly. Other known programs also deem high priority the capability to increase image data transmission beyond the rates demonstrated by existing technologies for national security missions. The high-speed and secure transmission of the FSOC link would directly enhance communication capabilities to these ends.

High-Frequency RF Effects

131503
Year 2 of 3
Principal Investigator: L. D. Bacon

Project Purpose

Satellite communications provide an important capability to military/civilian operations. Today, the loss of a small number of satellites could greatly influence the global economy as well as reduce the US military's ability to exert its influence around the globe. We are conducting an effort composed of theoretical, numerical, and experimental work to understand the potential of extremely high-frequency radio-frequency (EHF RF) to disrupt satellites or other electronic systems. It is our understanding that previous electronics requirements and testing may not have uncovered all of the effects that may be enabled by modern equipment. The primary goal is to understand the fundamental mechanisms of effect and their scaling. Achievement of this goal will provide the information needed to determine if an adversary can design and build a system to disrupt our critical electronic systems. Public domain literature indicates that high-powered HF RF systems that might be able to achieve previously unstudied effects may be due for implementation in less than a year.

An inherent difficulty in the measurement of high-frequency effects in electronics is interfacing such electronics with test and measurement equipment operating at frequencies far outside of the intended bands of operation. Extant device and circuit models are also intended for lower frequency regimes and will have to be extended for validity at the high frequencies of interest to this project. This project will have to develop unique and innovative measurement techniques, as well as advanced models and codes to enable the understanding of the fundamental physics of EHF RF effects on electronics. The unique measurement data generated in this project will be used to validate the codes and establish the level of certainty in the success of the codes and understanding of physical mechanisms at high frequencies.

Summary of Accomplishments

As the "hydrogen atom" of electronics, the first subject device of our study of RF effects is the p-n junction diode. Diodes are also frequently found deployed as transient voltage suppression (TVS) input protection for other devices. We have selected the ubiquitous type 1N914 switching diode to analyze. Our study employs the Agilent IC-CAP/ADS (Integrated Circuit Characterization and Analysis Program/Advanced Design System) circuit characterization/analysis system. The harmonic generation from the diode under RF drive is measured and compared to the ADS simulation, which feeds the data back to IC-CAP for iterative model fitting and optimization. Semiconductor device physics models have been developed and compared to measurements and analytic solutions.

We are characterizing the EHF RF response of the uA741 op-amp, one of the oldest and most popular general-purpose amplifier devices. The 741 and its very similar more modern incarnations are so ubiquitous that it is an appropriate choice as an important component to include in our study of RF effects. We have measured its offset bias under EHF drive.

We are characterizing the effects of free-field illumination of the 741 amplifier printed circuit board (PCB) circuit at 95 GHz. To detect the response of the amplifier to the 95 GHz, we employ lock-in detection and the amplitude modulation of the 95-GHz source, enabling this measurement to be done with extremely high sensitivity. The 95-GHz response of the amplifier as a function of AM frequency tracks the baseband frequency response of the amplifier, indicating the primary 95-GHz interaction is occurring at the input and is too fast (100 KHz) to likely be a thermal effect. To analyze coupling, we have completed measurements of this response as a function of incidence angle, for both surface normal and end-fire geometries, and horizontal and vertical polarizations. This data will be used to guide electromagnetic modeling of the coupling through the PCB to the op-amp.

Significance

DOE, DoD, and other federal agencies rely on satellite communication systems for day-to-day and special operations. Loss of these systems would compromise the ability of the US to defend itself and compromise the ability to extend its influence around the globe, leaving assets at risk. Determination of vulnerability will enable efforts to protect valuable electronic assets. High-power RF sources are rapidly becoming widely available to those who would desire to exploit these vulnerabilities.

Security Through Unpredictability

131541
Year 2 of 3
Principal Investigator: M. Berg

Project Purpose

Information system defense is currently engaged in an unfavorably asymmetric struggle with sophisticated adversaries. Standardized instruction sets, protocols, and hardware interfaces make our systems too uniform and predictable, allowing our adversaries to exploit these systems en masse using minimal reconnaissance. Today's defense systems do very little to directly address this asymmetry, relying instead on reactive technologies such as signature matching and patching. Truly effective information security measures must focus on eliminating the attacker advantage intrinsically.

This research will develop diversity technologies that eliminate certain classes of security vulnerabilities from information systems. For example, we will develop randomized instruction sets that can hinder propagation of malicious code. These technologies will be based on fundamental theories of information system security (being developed as part of this research), allowing us to scientifically determine where and how to incorporate diversity for the greatest security impact.

Summary of Accomplishments

We have written a draft report describing a new way of scientifically reasoning about vulnerabilities, the root causes of those vulnerabilities, and the effectiveness of potential security solutions — including the effectiveness of various randomization approaches. Our approach maps information system design to a hierarchy of nested universal Turing machines. Design patterns are repeated at each layer of this hierarchy with the repeated indirections (abstractions or mappings) at each layer being the root causes of security vulnerabilities. By studying the indirections that cause vulnerabilities, techniques for mitigating the vulnerabilities can be evaluated and reapplied at other layers in the hierarchy of nested universal Turing machines. We have been able to prove that certain security protections do not propagate across layers of this Turing machine hierarchy and to calculate upper bounds on the effectiveness of certain security protections.

We have modified both the GNU assembler (commonly known as "Gas") and the ld86 assembler to generate randomized instruction sets. We have modified the QEMU machine emulator and the basic input/output system (BIOS) used by QEMU to support our randomized instruction set. The randomized instruction set BIOS is successfully booting in 16-bit real-mode in our modified QEMU. We are currently debugging a few randomized 32-bit protected-mode instructions before booting a 32-bit protected-mode Linux kernel and applications that have been built with the randomized instruction set assembler.

Significance

New techniques for building secure systems will be invaluable in helping Sandia fulfill its mission of developing high-assurance systems and in satisfying our country's cyber security needs. Sandia is pursuing information assurance as a core capability as a result of recently expressed national need. This research aligns with Sandia's cyber security initiatives and is threat-informed.

2D Tracking of Maneuvering and Closely Spaced Targets and Fusion into 3D Tracks

141541
Year 1 of 3
Principal Investigator: T. J. Ma

Project Purpose

The purpose of this project is to develop algorithms to improve tracking of closely spaced objects (CSO), maneuver objects, and the ability to fuse tracks from multiple sensors to produce 3D tracks.

In high-consequence and time-critical tracking problems, one or more moving objects may be observed by multiple sensors. The sensor data are processed in real-time, with the goals of discriminating the separate target objects, tracking their progress in each sensor's dynamic field of view, and combining information across sensors to estimate 3D object positions as a function of time. Two of the most difficult scenarios encountered in such applications are closely spaced targets and maneuvering targets. When multiple moving objects are located very close to one another, many of the standard solutions for building and maintaining tracks are prone to failure. Multiple hypothesis trackers (MHTs) are theoretically appealing for this scenario but can induce exponential growth of the hypothesis space, rendering real-time solutions infeasible. Rather than computing every possible hypothesis formation, our approach only requires computation of small sets of "good" hypotheses and selects the best one based on their likelihood score. Also, when a large number of unresolvable objects are present, a cluster tracking technique is used in combination with an MHT to provide an efficient means for controlling the size of the hypothesis space.

The problem of tracking maneuvering targets, whose trajectories vary from those predicted by simple physical models, is also amenable to using MHTs in combination with interacting multiple model filters. Fusion of single-sensor, 2D detections and tracks into 3D position and velocity estimates is an additional challenge. Algorithms are needed to associate tracks of the same object from sensor to sensor, and to combine the associated 2D tracks into a single 3D track.

Summary of Accomplishments

In the area of 2D tracking, we have successfully developed a 2D MHT algorithm and implemented our solution to the (CSO) problem. We have demonstrated that if objects were detected as separated, we can track them as separate objects even if they are extremely close in proximity. We are able to track more objects with lower signal-to-noise ratio using our MHT tracker than a typical tracker using global nearest neighbor assignment. We also verified and validated our MHT tracker with operational real sensor data and demonstrated significant improvement in tracking CSO conditions. In addition, we are seeing improvement in track coverage, track density, and reduction of track fragmentation. Moreover, we demonstrated that our algorithm can run at real sensor frame rates.

In the area of 3D tracking, we have developed a 3D tracker that can initiate 3D tracks based on 2D tracks from individual sensors. Once a track is initiated, either the 2D tracks or 2D observations from individual sensors can be used to update the 3D track. Since many possible pairing of 3D tracks can occur under CSO conditions, we have developed a 3D MHT algorithm to form all possible hypothesis paring and a scoring mechanism to prune out unlikely candidates. We have developed a flexible test hardness to simulate all types of scenarios that we will use extensively in FY 2011 to further evaluate and refine these algorithms.

Significance

The general field of remote sensing plays an important role in Sandia's national security mission, with numerous divisions and centers involved in the design of novel sensor systems, manufacture and testing of components and hardware, and development of algorithms and software for sensor command and control, data collection, and data analysis. Real-time target tracking and multi-sensor fusion are always high priorities for the remote sensing community and active research areas in the S&T community. Accomplishments this fiscal year provide a state-of-the-art, real-time target tracking technology that is applicable to a broad spate of surveillance applications. Moreover, our 2D tracking algorithm has been verified and validated with real data and is sufficiently mature to move forward for potential transition into real world applications. In addition, this research can be summarized in a technical journal article and communicated through technical presentations shared with the remote sensing community.

Novel Techniques for the Geolocation of Sources Using Timing-Based Sensors

141542
Year 1 of 3
Principal Investigator: D. C. Jackson

Project Purpose

The purpose of this project is to develop algorithms and tools to geolocate sources using time of arrival (TOA) sensors in classically under-constrained scenarios. Algorithms for determining the three-dimensional location of a receiver when in contact with four standard emitters is well documented (e.g., global navigation satellite systems such as the Navstar Global Positioning System). Alternatively, one can determine the three-dimensional location of an emitter using four TOA receivers. In scenarios where fewer than four receivers detect a signal, a unique location cannot be determined. However, in some cases additional information encoded in TOA data can be used to geolocate sources using fewer than 4 receivers.

Summary of Accomplishments

We have identified a number of methods of acquiring additional information that can be used to contribute to TOA geolocation solutions but that are not routinely utilized.

- A number of these methods include processing TOA data as a time-series when the source emits multiple signals, rather than considering single events in time. Approaching data in this manner can result in constrained geolocation solutions using only one, two, or three receivers. This is possible by calculating changes in range between the source and sensors over time. Time-series analysis can also be used to generate synthetic multi-sensor detection, empowering users to apply standard many-sensor geolocation algorithms to scenarios involving fewer than four TOA sensors. Further, this method permits the generation of synthetic TOA data to provide increased detection capability in low-signal-to-noise and sparse sensor constellation scenarios.
- We have created algorithms that can be applied to multiwavelength TOA sensors capable of measuring propagation medium characteristics. These characteristics can be compared against ancillary global data measuring the same value to provide refined geolocation estimates.
- We have also constructed tools that compute visible regions of space from the sensor perspective that can be used independently or coupled with other techniques to generate geolocation estimates.
- Of key importance is coupling the aforementioned processing methods with measurements from one, two, or three TOA sensors that together can enable the determination of a unique geographic location.

Significance

The algorithms and tools we have created will provide users of timing-based sensors in civil and defense communities with the ability to geolocate sources using fewer than four sensors. The end products of this project will provide users with a significantly enhanced geolocation capability with no required changes to existing receiver constellations.

Air Delivered SIGINT Sensor System Study

141543
Year 1 of 2
Principal Investigator: H. D. Nguyen

Project Purpose

Part of the military's intelligence, reconnaissance, and surveillance mission is to collect information about enemy intentions and to determine the locations of specific targets. One way to obtain this insight is by finding and intercepting their electronic communications (SIGINT). Our adversaries guard against having their communications intercepted by using low-power, directional transmissions. Airborne and man-portable systems allow our forces to penetrate the adversary's rear-echelon battle space to better intercept these communications, but these methods entail a high amount of risk. Remote delivery of such systems (SIGINT Darts) would minimize these risks. Darts could be placed in multiple, hard to reach locations that are both near and directly in the path of low-power, directional communications; thus maximizing our ability to intercept our adversaries' communications. The small, visible profile of the sensor dart minimizes the likelihood of it being detected. We envision the key R&D focus of this project will be the following: 1) to determine what information must be gathered to accurately snapshot the background spectra; 2) to determine to what extent on-board signal-analysis will be required to accomplish the conduct of operations; 3) to develop a design for a multiband antenna that is capable of telescoping into the sensor dart; and 4) to integrate sensors and electronics packages into a single, compact and g-hardened system.

Summary of Accomplishments

We have completed our original discovery milestones for this year. We have our team in place and have developed concept design approaches. We have developed high-level system requirements that will drive our design concept. One particular area that drives both power and deployment design is the information spectra that we are targeting to monitor and exploit. In order to bound our design approach we took two paths. The first path was to seek out potential users in the community who could help identify spectral regions of particular interest. The second approach was to select canonical problems, such as current communications that could be mapped to many scenarios based on our understanding of end user needs. Our second approach has yielded a concept design that will incorporate a zero-power radio-frequency device that will be used to extend system life to make it more applicable to many missions. We have chartered Center 1700 with the creation of these devices and initial units have been delivered and are under test. Integration experiments with other system electronic boards is scheduled for FY 2011. Potential users have also been contacted and technical exchange meetings are scheduled to discuss user needs, establish useful performance envelopes, and discuss key technology areas. This will provide a basis to refine our requirements and operational space as the project moves forward. We are on-schedule to meet our milestones.

Significance

The military is constantly in search of methods of completing their missions while minimizing risk to personnel and equipment. The integration of SIGINT systems onto the sensor dart platform minimizes both these risks.

Application of Non-Coherent Processing for Added Link Margin and Lower Profile Signaling

141586
Year 1 of 1
Principal Investigator: D. A. Wiegandt

Project Purpose

There are two distinct requirements for outcomes within the tagging, tracking and locating, and low-profile communications communities: 1) low-power, micro-sized electronics, and 2) low probability of intercept, probability of detect, and probability of exploitation (LPI/LPD/LPE) signaling. In addressing the second requirement, significant work has been done at Sandia and in industry in the area of featureless waveforms. These solutions often require power-hungry processors and larger form-factors to accommodate power and processing considerations, and therefore, begin to push back on the first requirement. Many systems that are currently deployed address requirement 1 by applying low-power, micro-sized, commercial-off-the-shelf (COTS) parts. These parts have the advantage of significant investment in their size and low-power designs because of mass commercialization, but as a consequence, employ signaling that pushes back on requirement 2 because of their more standard communications approaches.

Numerous techniques of communicating only when prompted, or only at prespecified times have been attempted to mitigate this issue, but do not accommodate systems with more dynamic requirements, or those with "any time" needs. This project leveraged recently proven non-coherent, low-complexity data encoding/decoding and developed LPI/LPD/LPE approaches through use of COTS radios. The resulting method addresses LPI/LPD/LPE concerns by: 1) significantly reducing the per-burst time on channel; 2) randomly spacing the transmitted bursts; 3) reducing transmit power per burst, and 4) exploring use of dynamic modulation, data rate, and frequency manipulation. The resulting capability enables Sandia to produce an overall design that has a lower channel signature, small form-factor, and low-power consumption and transmit power.

Summary of Accomplishments

We proved that non-coherent processing gain can be added to COTS parts, and we discovered the boundary conditions that limit the ability to continue to observe gain through added sequence length. By using the methods implemented, we devised a robust method for enabling hopping in the signaling. Based on these results, the objective of creating nonstandard signaling was successfully implemented and proven.

Significance

The proposed work will position Sandia and DOE with a unique capability to design and develop wireless tagging and communications systems that address the main needs of micro-size and low-profile signaling. Within these applications, size and receiver sensitivity are critical. This strategy is immediately applicable to current tag and special communication systems within Sandia and useful to numerous communities we support.

Augmented Cognition Tool for Rapid Military Decision-Making

141587
Year 1 of 2
Principal Investigator: M. L. Bernard

Project Purpose

According to the Rumsfeld Commission, 25 nations have or are acquiring weapons of mass destruction (WMD). Several of these have or are acquiring long-range missiles. The Prompt Global Strike (PGS) program is seeking to counter these threats by permitting deployment of military assets within hours. Thus, PGS decisions on whether to act or not must be made with all available data and within a very short time window. Systems that mimic the neurocognitive processes through which humans automatically uncover and link disparate information to detect co-occurrences and associations would make it possible to incorporate and process relevant decision information faster and more accurately. Accordingly, we propose to leverage Cognitive Science and Technologies (CS&T) LDRD-generated capabilities to produce an augmenting capability that would filter through a corpus of all-source data to uncover relevant associations in order to auto-associate episodic (what, where) and semantic (meaning) concepts permitting potentially more efficient and accurate processing of information. The human analyst's ability to extract evidence and test hypotheses across large data sets would be augmented through interface with an engineered system. This capability is intended to support PGS and intelligence community needs by creating a system that will extract evidence from HUMINT (HUMan INTelligence), SIGINT (Signals intelligence), or IMINT (Imagery Intelligence) information sources to piece together conceptual elements identified from the input information to improve analyst efficiency, awareness, and knowledge discovery.

Summary of Accomplishments

For FY 2010 we have accomplished the following:

1. Identified Analyst Notebook (AN) to be the visualization platform for the prototype system. The AN is an industry standard for visualization of intelligence information and will enable detailed visualization of associations between individuals, objects, and locations.
2. Integrated AN with STANLEY (Sandia Text ANaLysis Extensible library), a Sandia-developed statistical analysis tool that will pre-process textual information for later associations.
3. Begun integration of AN with the Sandia developed, multidimensional association engine using multiple sensory activation neurocomputational architecture that is based on the associative properties of the hippocampal region of the brain.
4. Identified an intelligence use-case to train the system. The SoC intelligence assessment training scenario will be used as the use-case scenario during development of the system. The SoC was developed by the Joint Military Intelligence College to train intelligence analysts. This case study is both challenging and realistic.
5. As a means of comparison, we have begun to manually construct SoC scenarios in AN. The manually created scenarios serve as a baseline against which PGS system performance may be quantitatively assessed.

In its current state, the prototype system can extract formatted textual information, identify statistical relations between entities via STANLEY, and display those relations in AN.

Significance

If successful, this capability will benefit military technologies and systems capabilities within the DoD, as well as benefit nonproliferation and assessment of nuclear weapons within the DOE. This work will enable progress in the ability to assist human decision-makers in the task of filtering and incorporating large amounts of data to generate associations between people, events, and organizations.

Developing an Architecture for Leveraging Information between Heterogeneous Modeling and Simulation Tools to Provide Critical System-of-Systems Analysis Capabilities

141588
Year 1 of 2
Principal Investigator: N. E. Miner

Project Purpose

As the intricacy and scale of current and future net-centric System-of-Systems (SoS) increases, the existing ability to measure the effectiveness of these SoS significantly diminishes. The primary objective of this project is to develop an architecture and methodology that enable the impacts of network communications and combat effects to be assessed at an SoS level that cannot be currently accomplished. The project will demonstrate these new capabilities by implementing the methodology and performing analysis of problems of interest to decision-makers about policy, technology acquisition and deployment strategies. Finally, the project will extend and generalize the approach for use with a wider range of modeling and simulation (M&S) tools.

The complexity of net-centric SoS being fielded today has the DoD leadership increasingly dependent on M&S tools such as SoS analysis, force-on-force (FoF), and network communication. These M&S tools however have vastly different computational fidelities (minutes to months) and system scales (tens to thousands of platforms), and thus, current approaches using direct information transfer cannot provide cohesive analysis for today's large, complex SoS problems. This research will address the gaps left by previous approaches by developing an architecture and methodology for utilizing information between diverse M&S tools. The cutting-edge approach is to identify key performance features, or measures-of-performance (MoP), of the simulated information, and transform the MoPs into a context that is useable by the larger-scope SoS tool. The primary risk is that we oversimplify the data, losing essential information, or that the MoP transformations cannot be identified. Our innovative approach mitigates these risks through the use of well-established mathematical and statistical methods, preliminary research into transformation methods, and the high-level of expertise of our team. This capability will benefit a wide variety of parties throughout the DOE and DoD.

Summary of Accomplishments

We made significant progress toward project goals and milestones during FY 2010. Accomplishments toward the goal of developing an initial set of performance measures include the following. 1) We completed problem scoping and definition phase, including development of a problem scope definition document . The team clarified the problem definition and established common goals. 2) We completed an initial background literature review and annotated bibliography. This task confirmed our postulates that this problem is of significant interest to the M&S community, that the problem has not yet been solved, and that there is a large agency base interested in the solution. 3) We identified salient information, key performance metrics, and candidate performance measures at different model levels for communications-to-SoS and FoF-to-SoS.

Accomplishments for the goal of defining transformation methods include the following: 1) We identified mathematical transformation methods for use within the surrogate model. These methods are the primary candidates for use within the surrogate to encapsulate the high-fidelity data. 2) We developed an initial approach definition. 3) We documented the approach in an Institute of Electrical and Electronics Engineers MILCOM (Military Communications) 2010 full paper submission.
Accomplished milestones include the following:

- Development of proof-of-concept architecture design including development of process flow document
- Implementation design for proof-of-concept architecture for FoF-to-SoS
- Database design and generation of initial, notional FoF simulation data library (presented at MAES [Society of Mexican American Engineers and Scientists] conference
- Implementation of: FoF-to-SoS proof-of-concept architecture, surrogate builder, graphical user interface, database and FoF-to-SoS surrogate software

Finally, we carried out preliminary integration and testing of the proof-of-concept approach and architecture, and submitted a Sandia invention disclosure. We began formation of an external advisory team, and pursued business development efforts toward establishing a transition partnership, with the most likely transition partner, DoD, specifically, the Army's Program Executive Office of Integration.

Significance

Consistent with DOE's National Security Mission, the proposed research addresses SoS M&S for evaluation of integrated systems inherent in DoD and Homeland Security programs such as the Army's Future Combat Systems and current force transformation, missile defense, coast guard, and other national security operations. This work addresses the challenges of improved global awareness and strategic information operations as well as DoD transformation to net-centric operations. Development of these capabilities will enable Sandia to maintain a leading-edge SoS assessment capability and maintain its position as a preferred supplier for system sustainment tools. This work will bring a new level of SoS analytic capabilities to DoD decision-makers. Ongoing war-fighting advances outpace our current ability to effectively analyze the capabilities and performance characteristics of such advances. Identifying the operational characteristics of an SoS is key to avoid catastrophic failures and to obtain the greatest benefit from SoS operations. Success in this project will position Sandia in providing a unique SoS analysis capability to make precision decisions in a cohesive, SoS-level that does not exist today. This capability will benefit a wide variety of agencies including all DoD branches, the missile defense agency, space agencies and coast-guard operations. Furthermore, the resulting R&D will be fed back into Sandia's M&S community to enable other Sandia programs to remain on the cutting edge of the M&S field. Key R&D accomplishments of completing the proof-of-concept methodology and architecture design for linking diverse M&S tools through information sharing is a unique and novel approach to a widespread S&T problem. Publication of this approach will ensure that the general S&T community benefits from the results of this research effort. Furthermore, the key accomplishment of completing a FoF-to-SoS proof-of-concept implementation of the approach is a major step towards validating the methodology and being able to apply this research to analysis of real-world problems. Socialization of this research to potential agencies has resulted in serious discussions toward establishing transition-partnerships for the results of this project.

Development of 3D Tools for Threat Signatures

141589
Year 1 of 2
Principal Investigator: J. L. Powell

Project Purpose

Improved sensors are needed to detect radioactive threat sources such as nuclear weapons (NW) and radiological dispersal devices (RDD), as well as radioisotopes used in nuclear medicine and other industries. The dominant software tools used to predict the instrument response of a detector uses the gamma flux computed by a 1D radiation transport code that assumes spherical symmetry. The detector response is computed using this flux and parametric models derived from measured spectra of radioactive calibration sources. This approach works well in many scenarios, particularly when the source-to-detector geometry is well known, such as in a portal-type detection system. However, the approach can be insufficient for detection scenarios involving small sensors (a few cubic inches) and operating scenarios where the radioactive source can no longer be modeled as a point source, making it difficult to properly relate the 1D simulation to the real 3D world.

We theorize that the use of 3D, physics-based end-to-end simulations can overcome these limitations and enable the development of improved detectors. In this project we propose to use Sandia's high performance computing resources in conjunction with computer aided design (CAD) tools and high-fidelity radiation transport codes to develop a capability that addresses scenarios of interest. The focus of the project is the ambitious task of developing a physics-based 3D detector response function, given that it is the key to designing optimal radiation detection systems. In this effort, we will develop and validate a detector response model using experimental data. Subsequently, we will compare the 3D results to those from the 1D calculation and discuss the observed performance improvements.

Summary of Accomplishments

We designed and executed validation experiments intended to validate the results of the 3D detector response algorithm under development. The initial validation test campaign was designed to simulate a low-scattering environment in which the scenario is essentially a 1D problem and increase the scattering until the problem essentially becomes a 3D scenario with a higher degree of scattering. We clearly demonstrated 3D effects in these experiments. We designed and executed a validation experiment in which radioactive sources were placed in a target object to measure emitted spectra as a function of position around the object. This measurement configuration gave us the ability to demonstrate the 3D nature of a realistic scenario, such as a threat source inside a commercial shipping container.

We designed the process for developing input into the 3D instrument response function to consist of three fundamental steps: 1) define the operating scenario using CAD, 2) perform high-fidelity radiation transport simulations, and 3) generate gamma radiation flux map. We developed the algorithm for the detector response function, which computes the actual gamma ray detector response to the incident flux, and began writing code to implement this algorithm. We verified that the radiation transport calculation alone does not accurately model material-specific properties of scintillation crystals, such as energy-dependent scintillation efficiency or surface effects. We began analyzing the best approach to account for these effects.

Significance

This capability will enable Sandia to respond rapidly to requests to design radiation detection systems that address a wide variety of custom missions. The ability to model complex transport environments will enable detection systems to be designed and optimized for a particular application. It will also increase the confidence of detection and improve the interpretation of results collected in the field.

This project develops a unique toolkit to enable design and analysis of complex 3D radiation detection scenarios. This capability is fundamental for further development of tools that enable the direct analysis of the response of radiation detection systems in a specific operational environment and to specific threats. The development of this toolkit will also allow Sandia to perform quality assessments of analysis software currently in use and create more robust methods for Sandia applications.

Explosively Driven High-Power Microwave Source

141590
Year 1 of 2
Principal Investigator: L. R. Shapnek

Project Purpose

Electromagnetic pulses of proper frequency and amplitude have demonstrated the ability to disrupt, disable, or destroy electronic systems. These systems can generate extraordinarily high effective radiated power (ERP) but typically require large power supplies such as capacitor-based Marx Banks that are difficult to miniaturize. An efficiently designed single-shot system that leverages the greater energy density of explosives for its power source, such as a Flux Compression Generator (FCG), has the potential to deliver the same power to an antenna in a smaller system volume.

A general concept design for an FCG-based high-powered microwave (HPM) source is relatively simple. It consists of an FCG, an impedance matching section, and an antenna. The great advantage of such a system over conventional HPM sources is that the energy stored in explosives ($\sim 10 \times 10^3$ J/cc) is much higher (50,000 times higher) than the energy density stored in high-voltage, low-impedance capacitors (0.2 J/cc). The great disadvantage of FCG-based HPM devices is that the FCG themselves have sub-1 Ω (0.1 Ω, for example) impedance and the RF antenna's impedance is ~100 Ω. For this example, the ratio of the power radiated unmatched versus matched is 4×10^{-3} mostly negating the gains of having higher energy density. This project will demonstrate a better impedance matching section for FCG-based HPM devices.

The availability of legacy FCGs allowed us to conduct this project with relatively low risk in the FCG itself. This, together with our extensive experience in the design of radio-frequency (RF) pulse generators (HPM) allows realistic project goals. Because the FCG design is fixed, efficient handling of the electrical power within the transformer and inductive capacitive oscillator (LCO) sections is the high-risk area of this project.

Summary of Accomplishments

We began characterization of the existing FCG devices by static output impedance calculations for the FCG structure. Next, we designed and fabricated an instrumented load (i-Load) to facilitate collection of output waveform data (during dry-run and live explosives tests) leading to an understanding of the dynamic output impedance of the device. A few iterations of this load were required, with different physical configurations of sense resistors.

We then conducted live explosive shots, with different combinations of i-Loads, inductances, and drive current levels. All tests were successful, and yielded useful data including broadband RF measurements (to establish background) and high-speed video (shock wave characteristics). The FCG performance parameters were then fed into circuit models and are being used to support transformer and pulse generator design for use in electrical characterization of the matching circuits and loads (oil tank tests) as a lead-up to open set-up explosives tests. Challenges did occur in understanding the FCG/i-Load performance and instrumentation behavior. We recruited new resources to help us understand the data and now have transformers in fabrication. Also, fabrication of the pulse generator, LCO and test tank is underway.

During FY 2010, we also supported (under separate funding) another project using the same FCGs. In those tests, we were able to successfully operate the FCGs at higher levels, into higher impedance loads than the original FCG specifications would have recommended. With this knowledge, we may be able to design the balance of the HPM system in this project to use this higher demonstrated power for improved efficiency, margin or performance.

Significance

These successes position Sandia to provide a leadership role for addressing the many areas in which there is a pressing security need for such a solution (such as Defense Systems and Assessments and Homeland Security and Defense).

Generalized Code Obfuscation

141591
Year 1 of 2
Principal Investigator: A. R. Chavez

Project Purpose

Protecting the software that executes on critical government systems from adversarial understanding and manipulation is key to national security. Reverse engineering and malicious manipulation of critical algorithms are threats to our nation because they are among the primary means that adversaries leverage to attack US systems. Prior LDRD project research has demonstrated the feasibility of obscuring a simple state machine in a way that makes it provably cryptographically secure. This new research is aimed at the much more difficult challenge of obscuring arbitrary software code written in a commodity programming language with the same degree of security. Unlike previous research efforts, this work will result in an obfuscation system that allows generalized software code to remain obscured during execution. The tools that result from this research will offer a new degree of protection for critical government systems.

Summary of Accomplishments

Our major accomplishments for the first year have been our implementation of the Turing Machine and TOY obfuscation algorithms we developed. Our initial pass of implementing the Turing Machine obfuscation routines was a major accomplishment because it proved that we could obfuscate any computer algorithm. Although we achieved a major accomplishment, there were some initial performance concerns about the algorithms because they were highly inefficient. To address this problem, we modified the algorithms to significantly improve the performance of our obfuscation routines. The performance increase was geared towards computer programs using a static amount of memory, to which all programs can be translated. These improvements have made the technology usable when obfuscating Turing Machines algorithms. The major difficulty of this task was developing and testing the algorithms based on reviewing and enhancing our prior research results. The development and implementation of the TOY assembly instruction set has also advanced our technology in terms of usability, efficiency, and scalability. Although TOY is a simplified assembly instruction set, the concepts necessary to securely obfuscate an assembly instruction set can be applied towards our next steps of obfuscating more ubiquitous instructions sets such as the ARM (Advanced RISC Machine) and x86 (based on the Intel 8086 CPU) instruction sets. A major accomplishment in advancing our Turing machine algorithms to the TOY assembly instruction set was the incorporation of memory and registers into our algorithms. This accomplishment has now provided us with clear a path forward on how we would further advance our technology to the ARM and x86 instruction sets.

Significance

The tools we have developed provide a new set of security functions for our most critical algorithms that must be protected against reverse engineering. Our R&D results provide a game-changing technology that can be applied towards a variety of scenarios for which we can now develop security functions that defy analysis and manipulation by even the most sophisticated adversaries. This technology holds the promise of creating significant risk and cost to adversaries who seek to exploit and attack US government systems.

High-Contrast Decoration of De-Layered Integrated Circuit Surfaces Using Molecular Markers

141592
Year 1 of 1
Principal Investigator: J. J. Sniegowski

Project Purpose

The intent of this project was to address the deficiency of available tools for acquisition of circuit information from high-density integrated circuits (ICs) for failure analysis, design verification, or circuit debugging. The essence of this work is to add contrast enhancement to the surface of an IC that subsequently allows the use of high-speed data acquisition techniques that otherwise cannot see the surface features of interest. Inspiration for this work is derived from nano-assembly techniques, and biomolecular markers used to tag specific proteins, cells, and cell locations. The original expectation was that the electrostatic state of an IC's individual device element might preferentially influence the attachment of a marker molecule or nanoparticle to its location. Once the markers attach, high-speed optical or electron imaging can be used to rapidly acquire data from the IC surface. The key obstacles anticipated were the sufficiency of the electrostatic state on the IC to accomplish electrostatic attachment, and development of an IC preparation technique that does not mask or quench the local surface state. The key obstacles encountered involved subtleties of the experimental setup and control of the attachment process. The effort concentrated on nanoparticle attachment to accommodate sub-100 nm node technologies with ultrahigh circuit densities, and the need for rapid, whole circuit acquisition. There has not recently been a novel breakthrough in imaging methods for sub-100 nm, high-density circuits.

Summary of Accomplishments

We have demonstrated relatively "routine" attachment of various nanoparticles to control surfaces that may be relevant to ICs. These successful decoration techniques demonstrated on control samples were accomplished using both dry and wet chemistries, also with a variety of nanoparticle sizes and materials. Examples include:
Dry Attachment Trials:

- Fe_3O_4, <50 nm (ultrasonic dispersion)
- ZnO, <50 nm (ultrasonic dispersion)
- Carbon nanopowder, <500 nm (ultrasonic dispersion)

Liquid Attachment Trials:

- Fe_3O_4, <50 nm in FC-77

Although not part of the original scope of this project, we gained a rudimentary understanding of various potential field configurations emanating from the surface and their effect on attachment. This provided insight into the experimental setup and approach, and somewhat explained the difficulties of obtaining good selective attachment.

Significance

Sandia has a strong and leading presence in the field of failure analysis of ICs. As IC technology continues to shrink, this project developed a novel path to ensure the continued ability to gather information from high-density ICs for failure analysis. This effort provides Sandia with the basis for a unique capability by clearly delineating a path to its development. This nanoparticle contrast enhancement project allowed us to gain significant knowledge and fundamental facilities towards such competence. The tools and knowledge gained are immediately available for use by ongoing projects to more fully develop this capability.

High-Efficiency High-Power Laser for Directed Energy Application

141593
Year 1 of 2
Principal Investigator: K. L. Schroder

Project Purpose

The purpose of this project is to develop a novel laser architecture that integrates spectral beam combining (SBC) with spectral compression of the beam combiner output using a Raman fiber cavity. SBC combines multiple laser beams of different wavelengths into a single spatially coherent, multicolor beam. The number of beams that can be combined is typically limited by the resolving power of the grating, the gain bandwidth of the active laser medium, the emitter fill factor, and the size of the system. This spectral beam combining and compression (SBCC) approach can potentially overcome the limitations on the number of beams that can be spectrally combined using SBC alone. The output of a spectral beam combiner is coupled into a Raman fiber cavity formed in passive fiber with a broadband high reflectivity fiber Bragg grating (FBG) on the input end and a narrowband (relative to the input beam spectral range) partially reflective FBG at the output end. Each of the SBC output wavelengths undergoes stimulated Raman scattering (SRS) in the Raman fiber cavity to a Stokes shifted output wavelength that is determined by the output FBG. Success of the project requires maintaining high coupling efficiencies through the beam combiner and into the Raman fiber laser, high Raman conversion efficiency, and mitigation of nonlinear wave mixing and other nonlinear processes that compete with SRS.

Summary of Accomplishments

1. We increased the output power and number of spectral channels in a fiber-amplified spontaneous emission (ASE) source developed in a previous LDRD project, and then used this to conduct low-power (10 W) Raman compression experiments in a Raman fiber cavity, designed for a low Raman threshold, but not otherwise optimized. We achieved a 75% slope efficiency for Stokes power conversion and observed spectral broadening due to nonlinear four-wave mixing that would need to be mitigated for higher power.
2. For power scaling, we are conducting Raman fiber laser experiments pumped by a non- polarization-maintaining (PM), 100-W broad (5-nm) line-width fiber laser provided by the University of Central Florida (UCF). After a PM isolator, cutting the non-PM power into less than a half, the actual pump power is ~45 W. The Stokes power is thus expected to be ~40 W.
3. We have created an SBCC system model in the form of a spreadsheet and have used it to establish goals for coupling efficiency, Raman compression efficiency, and spectral line-width of the compressed output, and to prioritize future work.
4. We developed a rigorous stochastic model, incorporating comprehensive nonlinear processes, for incoherent continuous-wave light and its spectral broadening in fiber. A comparison of the numerical simulator based on the stochastic model and results from a carefully conducted Raman fiber experiments shows excellent agreement. Systematic study has been conducted, showing the effect of the dispersion in mitigating spectral broadening, with a striking feature of rollover and reversal of the broadening through fiber dispersion. We derived an analytical expression of the ensemble-averaged spectral power density that clearly reveals the physics. The model can be used to optimize the Raman fiber laser for SBCC.
5. Our UCF contract partner is currently conducting an SBCC experiment for multi-channel coupling. The demonstrated coupling efficiency of single channel to single fiber was 83%.

Significance

The outcome of this project will benefit the military's needs of developing high-energy lasers for directed energy applications. This project will yield a much more operational alternative to the Chemical Oxygen Iodine Laser for the Special Forces Advanced Tactical Laser for use against ground targets in urban areas. This technology is also aligned with the DOE mission for improving energy efficiency by reducing power usage of high-energy lasers in material processing.

This laser architecture can also benefit the DOE/NNSA program in nonproliferation. High-energy lasers could potentially be used for tagging tracking and locating (TTL) of important items, it could be used in remote detection of illicit activities, or could be used for processing aerosols or materials to assist in collected sample analysis. The development of a compact and efficient system could lead to an airborne system for practical field use.

Finally, high-energy lasers are also used for material processing in the commercial community. The energy consumed to power such lasers is a major operational cost. DOE promotes the use of efficient processes to minimize energy waste. The efficient architecture promoted by this concept could significantly reduce that cost.

On the scientific front, the rigorous stochastic model, numerical simulation, and analytical expression for spectral broadening that were developed for this project have application to a wide range of applications in which spectral broadening of light in fiber is important.

Refereed Communications

D.B.S. Soh, J.P. Koplow, S.W. Moore, K.L. Schroder, and W.L. Hsu, "The Effect of Dispersion on Spectral Broadening of Incoherent Continuous-Wave Light in Optical Fibers," to be published in *Optics Express*.

High-Performance, High-Density Interconnect Technologies for Next-Generation Satellite Systems

141594
Year 1 of 2
Principal Investigator: S. E. Garrett

Project Purpose

We propose to develop and qualify high-density interconnect (HDI) technologies currently used in commercial graphics processing applications for next-generation, high-consequence space applications. Designs for current data processing satellite applications utilize commercial, advanced field programmable gate array (FPGA) components with 1-mm pitch and 1752 Input/Output (I/O). These components require advanced printed circuit board (PCB) designs that challenge standard PCB fabrication technologies. Subsequent yields are low with high costs and lengthy delivery times. Future advanced components will certainly have higher I/O counts and finer device pitches. Current PCB technologies will not support commercial components with pitches less than 1 mm. In order to support next-generation space applications, we must begin development and qualification of HDI technologies that will be compatible with future commercial components.

As components and technologies continue to evolve, Sandia must be prepared to adapt these HDI technologies, compatible materials, and on-shore vendors to meet requirements for next-generation space applications. New technologies and materials must support program objectives of reducing size, weight and power while improving high-speed, high-frequency performance. Aspects that will be addressed are 1) fabrication process capability, 2) materials compatibility 3) thermal management and power dissipation, and 4) improved reliability.

The proposed technologies will produce products with improved performance and reliability with shorter delivery times and lower costs. Developing multiple vendors will ensure that future programs, even export-controlled information programs, will be supported. The objective of this project is to deliver high-complexity, high-mix and low-volume products for space applications in two years. Presently, this technology has not been demonstrated to be adequate for Sandia high-reliability applications. This project will provide an initial demonstration of this technology that could support a wide variety of applications at Sandia.

Summary of Accomplishments

1. We evaluated the initial HDI design and fabrication process (from a previous LDRD project) and completed a "lessons-learned" review with the designer and fabricator. This review identified areas for improvement in the HDI design layout. These improvements will be documented in an initial "HDI for PCB Design Guideline." Furthermore, the review revealed additional manufacturing issues that are being addressed in Phase 1.
2. This review was beneficial in establishing an initial understanding of issues related to design, vendor selection, and manufacturing. It also emphasized the importance of utilizing test coupons in addition to functional PCBs, in order to assess the capability of individual vendors and to determine the integrity of the HDI design features.
3. We postponed initial assembly of the NADP-20 design because an opportunity exists to improve the HDI layout with a revised NADP-10 design. This postponement avoids the use of costly components during the first phase and enables more HDI vendors to be investigated. The postponement should not prevent any major objectives from being completed.
4. We created an HDI test-panel design, and it is presently being fabricated. This design enables Sandia to

evaluate vendor technologies in several areas; via reliability, fine-line and space imaging, layer-to-layer registration, and laminate integrity. The principle of the test coupons is to have incrementally more-complex features on the test-panel. This enables Sandia to evaluate vendor technologies and perhaps the limitations of the HDI technology.

5. We identified on-shore HDI vendors and conducted initial discussions in order for Sandia to down-select a list of vendors that had the potential to fabricate HDI technology PCBs. We selected seven vendors from a field of twelve. Four of the seven vendors are currently fabricating the HDI test panel.

Significance

One critical enabler of advanced electronic systems is high-bandwidth electronics. As design complexity increases, we must look beyond standard PCB technology to find suitable alternatives for the future. Future high-bandwidth electronics will require circuit miniaturization beyond the capabilities of standard PCB technology. This project will position Sandia to support applications requiring complex high-speed data processing from space. High-reliability HDI technology developed by this project will potentially support a variety of missions such as: 1) DOE nuclear weapons nonproliferation, 2) DHS programs that detect or prevent radiological, biological or chemical attacks against the United States and 3) DOE efforts to detect global warming trends from space.

This project directly supports future GPS-III and Advanced Space Electronics (ASE) programs and will develop robust, technologies that deliver high performance and reliability. Use of HDI technology will enable substantial reduction in size, weight, and power of space assemblies resulting in significant improvements in quality, performance, cost, and schedule. These project objectives align with key ASE requirements such as extensive use of high-performance commercial components, maximum exploitation of commercial suppliers, and highly adaptable and scalable designs for multiple payloads. Other programs that could benefit by using HDI technology are Synthetic Aperture Radar and Missile Defense Agency applications.

Hybrid Femtosecond/Nanosecond Pulsed Laser Machining

141595
Year 1 of 3
Principal Investigator: B. H. Jared

Project Purpose

There is an existing demand at Sandia for versatile micromachining techniques that precisely and rapidly section composites of different known and unknown stoichiometry. Such materials, which may include metals, dielectrics, semiconductors, and organics in the same volume, are not adequately addressed with conventional methods due to a distinct lack of material selectivity or other limitations. While laser-based micromachining methods involving a single pulse duration have been pursued as a viable alternative to mechanical and chemical sectioning, no single laser source provides the combination of rapid processing, material selectivity, and material versatility required for successful processing of all composites. To address these issues, we propose researching and developing a hybrid pulsed laser technique with in-situ chemical characterization, for high-throughput, feedback-controlled processing.

Summary of Accomplishments

Project progress against milestones has been consistent and on schedule throughout FY 2010. We have accomplished spatial overlapping of the femtosecond (fs) and nanosecond (ns) pulsed laser systems as the integration of optical and electrical hardware, and completed the development of alignment procedures. We have quantified machining rates for materials of interest using the ns laser and fs lasers individually and then combined spatially. While spatial overlapping produced a rate increase for some organic materials, we observed that it inhibited the processing of other materials where debris appeared to be sintered in place, such that surface swelling occurred instead of ablation. Such results were unexpected, but indicate that temporal control of the fs and ns pulses may be necessary to observe significant removal rate gains. We have also begun to develop a database of laser-induced breakdown spectra useful for closed-loop processing. Spectral data has been collected for each of the materials examined in the rate studies as primary material constituents in each material have been identified. While we have observed that the complexity and signal levels of molecular material spectra are very different from those of elemental materials, the feasibility of in-situ signal differentiation has been demonstrated.

Significance

Sandia is a leader in developing advanced materials engineering and analysis techniques that allow us to provide leading-edge capabilities in microelectronics, microelectromechanical systems, and photovoltaics, etc., for DOE. The development of hybrid laser sectioning methods that address a large variety of materials, including composites, will enhance our ability to address future DOE needs, as well as advance the mission of scientific discovery and innovation.

Investigating Payloads and Missions for CubeSat Systems

141596
Year 1 of 3
Principal Investigator: R. C. Ormesher

Project Purpose

Access to space enables many missions that are critical to national security. However, current satellite development requires funding on the order of $200 M to more than $1 B and many years to deliver. Many users need space access for their missions but are denied due to the high cost and limited availability of current satellites. Our goal is to develop satellite systems that can be quickly designed to meet specific mission needs, can be rapidly deployed, and are low cost, thereby enabling satellite development for unique and time-critical missions. Our approach is to utilize recent advances in small satellites called CubeSats to show the potential for mission utility in a very small form factor. Current CubeSats are designed mainly for science experiments, and therefore, have a short operational life and poor reliability. Leveraging ongoing work, we will develop a CubeSat payload carrier, or bus, that meets the environmental and reliability requirements needed to transition from an experimental to a mission capable platform. To demonstrate this operational capability, we propose to develop a radio-frequency (RF) transmitter that provides global coverage for a unique communication mission. A major technical challenge in developing this payload is the limited volume, power, and weight available for the payload. For the bus, we will invest in bus technologies such as energy harvesting, energy storage, attitude control, propulsion, and tele-command.

Summary of Accomplishments

During the first year of this project, we completed a comprehensive analysis of the CubeSat bus, payload, mission engineering, communications architecture, and system operations in support of system requirements definition and a high-level system design. We conducted research and trade studies on CubeSat buses to identify components and existing or emerging bus subsystems that could be leveraged for this project. We identified an industrial partner/supplier with recent advances in bus hardware to significantly reduce in-house development and provide a reliable bus and subsystem foundation on which to base our final CubeSat bus design. We completed payload power supply definition, and thermal analysis of the payload and bus is ongoing.

We conducted orbital studies to identify appropriate satellite orbits and investigate Doppler effects related to both the data infiltration mission and the iridium command and control link. We conducted initial studies to investigate coverage and handoff of a low earth orbit (LEO) CubeSat by the iridium constellation. We identified preliminary orbit and target altitude, and investigations of launch options are ongoing. In conjunction with these studies, we performed extensive analysis and development on transmit waveforms, link analysis, and operational parameters in support of defining the data link capabilities and RF payload requirements. Ground coverage and ground track uncertainty were accounted for in this analysis.

We identified key components for the RF payload, including initial firmware/software development and lab testing to confirm performance of example components. A suitable iridium modem for the command link was identified and acquired for testing. We developed and simulated antenna design concepts, including consideration of packaging and deployment options.

Significance

This development provides Sandia the potential to address the need for persistent communication from extended ranges to small receivers. We have identified this mission as one of intense national interest, as it fills an existing need for an under-served community. If successful in building this satellite system, we expect with high probability to secure Work For Others funding to launch and operate a demonstration mission. Success may evolve into a sustaining line of business for short burst data services.

Laser Characterization and Prediction for Silicon Sensors

141597
Year 1 of 3
Principal Investigator: S. S. Mani

Project Purpose

Laser illumination poses a threat to electro-optical sensors. We propose to understand the fundamentals of laser damage, the resulting degradation mechanisms in electro-optic sensors, and to discover and assess mitigation techniques that may be implemented during microsystem design and fabrication. To realize these objectives, we will develop a physics-based laser damage model of the most credible damage mechanisms and then verify that model against real-world destructive testing.

Historical work within other organizations has solely focused upon the empirical measurement of device damage thresholds for specific designs. Our differentiating approach, in contrast, will develop a basic physical understanding of laser damage mechanisms that will be used to advance mitigation strategies that can be applied to device synthesis. We postulate that a process analog to that for hardening against the effects of natural and nuclear burst radiation can be applied to hardening against laser damage. Specifically, we believe that through this strategy, a set of basic materials and processes can be implemented during the design of focal plane arrays (FPAs) and other electro-optical sensors to harden them against laser damage and, as importantly, provide an understanding of the limitations of this hardening. In order to meet our objectives, initial efforts will center on the development of a physics-based laser damage model of the most credible damage mechanisms including destructive testing. Further, in the second year, we will use the knowledge gained from this model to design devices and components that mitigate selected damage mechanisms. Subsequently in the final year, we propose to build and test devices that incorporate our newly developed "Laser Hardened By Design/Process" rules. Transition paths for this technology are staring and scanning electro-optical systems. Therefore, in parallel, we propose to address both an evaluation (testing) and modeling capability to assess vulnerabilities in silicon-based sensors.

Summary of Accomplishments

We identified two candidate code tools, namely ANSYS and EMW/Device (EMW is a module that is called-up by the Device code). ANSYS has sophisticated thermal modeling capabilities that include mechanical behavior but does not include optical heating on short timescales. EMW/Device, owned by Sentaurus, is a technology computer-aided design device simulator. It includes detailed solid-state physics processes including high-energy and short-timescale phenomena such as the capability to monitor independent carrier and lattice temperatures. The Bartoli group (Bartoli is an expert cited in this area over last few decades, his research group originally located at the National Renewable Energy Laboratory) analyzed semiconductor heating in the Device code, accounting for the dependencies of the material parameters on temperature and optically excited carrier density. Simplifying assumptions were required to solve the derived equations. The simplification was a reduction to one-dimension, with the heating depth being the primary calculated parameter. Device can even take into account the temperature-dependence of the optical parameters, but only for the simple geometries where finite-difference time-domain optical simulation is not required. We are using Device and ANSYS to pursue our simulation efforts. We have demonstrated preliminary results using both ANSYS and Device for existing experimental data

We performed software evaluation with two primary goals: 1) Reproduce, via simulation, experiments performed by Ball Aerospace on two related Sony charge coupled device chips; 2) Gain a better understanding of the physics of laser heating. Our Rev A chip was much more resistant to laser damage than our Rev B chip. Simulations were performed using the coupled electromagnetic/diffusive-thermal simulations in an older version of EMW. When light was focused on the sensor area of the chips, only small differences were seen between Rev A and Rev B. However, when the light impinged on the light shield, the Rev B chip heated approximately four times more quickly than the Rev A chip. A group of simulations has already verified the importance of the thermal dependence of the optical constants (n, k) on temperature.

Significance

Sandia has programs that are directed at providing solutions to the capability for sensor operation in hostile environments. The technology developed in this project will harden future optoelectronics systems against laser threats. This effort would enable critical decisions for missions by predicting sensor performance under hostile environments. Successful completion of this work will position the Laboratories to provide laser-hardened next-generation FPAs to a variety of agencies. Laser hardening is a logical extension of our rich history in radiation hardening for both natural and manmade environments. We propose to merge our existing radiation and nuclear hardening knowledge with laser hardening intellectual property developed through this project. We believe that application of a complete hardening solution to the delicate, hand-crafted FPAs will provide Sandia with a clear competitive advantage for developing next-generation FPAs.

Remote Laser Location and Identification

141598
Year 1 of 3
Principal Investigator: L. R. Thorne

Project Purpose

Battlefield use of lasers has become ubiquitous and includes target designation and tracking, ranging and mapping, and point-to-point communication. Thus, identifying offensive laser use, intended purpose, and location provides critical defense assessment information. To address this issue, we are developing fluorescent materials that operate as real-time and/or delayed or memory laser detectors. The real-time detection materials will produce bright fluorescence when exposed to offensive laser radiation that can be observed remotely at long distances and at large off-axis angles to the offensive laser propagation vector. The location and spectral characteristics of this fluorescence can be used to infer the identity and location of the offensive laser. Quantum confined (QCM) or nanomaterials offer the possibility of engineering the optical properties needed for this application through control of particle size, shape, architecture, chemical composition, etc. Thus, producing and measuring the characteristics of candidate nanomaterials are the major goals of this project, together with using the measured values in a detection system model to estimate the performance of a battlefield laser detection system.

Although there is rapid development of nanomaterials, most current applications are applicable to wavelengths too short for most battlefield laser detection. Thus, we are using various approaches to generate nanoparticles capable of longer wavelength excitation including the following: 1) increasing the aspect ratio of fluorescent gold nanorods; 2) modifying the host matrices of lanthanide-doped nanowires and nanoparticles; 3) using long-wavelength sensitizers for silver iodide nanocrystals; and 4) developing narrow band-gap chalcogenide semiconductor quantum dots. Adding memory capability to the detector nanomaterials is a new approach that we are exploring; another is using the thermal transient nanoparticles experience when exposed to laser radiation to permanently alter their fluorescence properties, e.g., erasing fluorescent color centers by annealing, alloying two noble metals, two lanthanides etc.

Summary of Accomplishments

We determined detailed engineering-performance requirements for real-time and memory fluorescent nanoparticles, including excitation-wavelength (in the near infrared region) fluorescence quantum efficiency, chemical reactivity, geometric specifications and laser-heating rates. We developed a new, flexible chemical synthesis for nanowires of various lengths and elemental compositions and used it to produce GdYO nanowires doped with Er/Nd and GdTiO doped with Nd. All produce bright orange fluorescence when excited at 350 nm. We investigated YF_4 as a host matrix to enhance near-infrared absorption of lanthanide dopants. We developed a synthesis for high-aspect-ratio gold nanowires, which have long wavelength, transverse surface phonon resonances that we have extended into the near-infrared region. We observed that gold nanoparticles in decanethiol appeared to melt together near the boiling point of the solvent (285 °C), much lower than the melting point of gold. This low-temperature fusion of decanethiol-coated gold nanoparticles could be one means of enabling nanoparticle memory, in effect, making the memory particles sensitive to low-energy laser radiation that changes their fluorescence properties. We initiated the production of lanthanide-fluoride based nanomaterials as an alternative host matrix for the photoluminescent nanomaterials. The fluorescence properties of lanthanide-doped nanomaterials are influenced by the host material and a lanthanide fluoride host matrix could serve to shift absorptions to longer wavelengths. We produced protective nanoshells for fluorescent core materials composed of SiO_2 using tetraethyl orthosilicate and ethanol. This is a very flexible method for producing shells and will work for most of the nanomaterials produced in this project. We designed and assembled a fluorescence lifetime instrument that uses near infrared laser excitation at a wavelength near that of lasers we wish to detect. The instrument is capable of measuring nanosecond fluorescence lifetimes and multiple lifetimes. This capability does not exist elsewhere at Sandia.

Significance

The immediate goal of this project is to produce and test fluorescent materials for use in a large-area system for the real-time and memory detection of threat lasers on the battlefield. This type of detection system will be of obvious importance in generating actionable intelligence and increasing defensive options. In addition to this eminently practical application, the project will also advance the basic materials science of fluorescent nanomaterials by producing, for study, novel materials that can be excited from their ground electronic states to other electronic states by very long wavelength light, instead of by, more typically, short-wavelength (i.e., visible or ultraviolet) light. For most materials, electronic excitation by near-infrared light requires that the materials already be in an electronic excited state, so our approach places new requirements on the electronic properties of the fluorescent materials. Significantly, since most materials are in their ground states at room temperature and lower, this requirement means that most of the fluorescent centers will be excitable by the long wavelength light whereas, if the initial state of the excitation transition were required to be an excited electronic state only a small fraction of the centers could be excited. However, with ground state transitions accessible by long-wavelength, near-infrared light, these new and unusual materials will undoubtedly find widespread, innovative application in electronics (e.g., metamaterial or regular arrays of quantum detectors); medicine (e.g., functionalized contrast agents for the emerging field of long-wavelength, near-infrared imaging, focal, photothermal therapies, and in the rapidly developing area of optical coherence tomography); telecommunications (fiber amplifiers and saturable absorbers for near infrared communications bands), etc. This project will also produce fluorescent nanomaterials that will store information that they had previously been exposed to laser radiation. These materials will be engineered so that one or more of their fluorescence properties will be permanently altered by battlefield laser exposure. These altered fluorescence properties will permit their memory state to be interrogated remotely using suitable laser excitation and appropriate fluorescence detection hardware. Since their response to laser radiation can be thermal, photochemical, or some other laser-induced phenomena, their engineering requirements are less restrictive than if long-wavelength light is required to produce fluorescence directly. Significantly, these materials could have important applications in various types of diagnostics and dosimetery, and because their memory state can be read remotely by means of their altered fluorescence (noncontact interrogation), these nanomaterials could be located in very small volumes.

Refereed Communications

L.R. Thorne, “An Innovative Approach to Balancing Chemical-Reaction Equations: A Simplified Matrix Inversion Technique for Determining the Matrix Null Space,” *Chemical Educator*, vol. 15, pp. 304-308, July 2010.

Low-Level Control Systems Assessment

141601
Year 1 of 2
Principal Investigator: J. Trent

Project Purpose

Supervisory Control and Data Acquisition (SCADA) networks are currently used to automate all major utilities throughout the world and to control security and heating, ventilating, and air conditioning (HVAC) systems on significant sites, including military bases and government laboratories. Sandia has spent a great deal of effort to become intimately familiar with the hardware architectures of computers and information technology network devices, but our familiarity with the hardware of control system devices in SCADA networks is far less mature. The ability to compromise SCADA networks has been demonstrated through several high-profile events. Sandia does not currently possess the low-level analysis capabilities required to study these architectures. Solutions in the problem area will lead to a better understanding of the threat that the US Critical Infrastructure faces. This work proposes to study these systems, the state-of-the-art in vulnerability assessment, perform a red-team assessment against a device, and develop a compelling demonstration of the threat that US infrastructure faces.

Summary of Accomplishments

We wrote a report describing the state of the programmable logic controller (PLC) industry. Additionally, we performed an in depth assessment of a particular PLC device.

Significance

The PLC report can be used to allow cyber security professionals to understand a new class of devices and why they need additional security analysis. The report also describes a method that can be used for performing a detailed supply chain analysis of embedded electronics. Additionally, the in-depth assessment of a particular PLC device will enable future forensic capabilities.

Low Probability of Detection, Directly Synthesized, Digital UltraWide-Band Communications

141602
Year 1 of 2
Principal Investigator: C. L. Gibson

Project Purpose

The purpose of the project is to demonstrate a low probability of detection and multipath resistant ultrawide-band (UWB) communication system for the warfighter. To attain this level of performance, novel signal processing is being employed in state-of-the-art field-programmable gate arrays with custom low time-domain distortion antennas and ultrastable chip-scale atomic clocks (CSACs). Custom algorithms will mitigate power consumption with field applications in mind.

Summary of Accomplishments

We have designed and tested a low dispersion UWB antenna that is sufficiently compact for the warfighter communications application, outperforming commercially available UWB antennas. We have also successfully implemented a Walsh transform for determining the amount of delay in a transmitted message, as well as a tracking loop to account for system drift and physical movement.

The general hardware system architecture has been designed with some hardware implemented. The general software system architecture is nearly complete with much of the software implemented and tested. Finally, we have determined that a GPS fiduciary is unnecessary, simplifying the system, and guaranteeing operation in GPS-denied environments.

Significance

Undoubtedly, the system as a whole would benefit both the military and national security agencies by offering improved low-probability-of-intercept/low-probability-of-detection communications.

The antenna offers a true time-domain design perspective that is key to performance in a low probability of detection and multipath resistant system that is simultaneously ultrawide-band. This design could be leveraged in other UWB efforts as sufficient commercial off-the-shelf solutions appear to not be available.

Once the CSACs are available, our experience with using them will be beneficial to any project requiring ultrastable independent clocks.

Model Checking for Latent Vulnerability Detection in Source Code

141603
Year 1 of 2
Principal Investigator: D. Bueno

Project Purpose

The purpose of this project is to demonstrate practical use for formal methods, and along the way, develop recipes and experience to assist in using formal techniques for vulnerability assessments. The field of formal methods has recently become a practical means for obtaining precise analysis. In contrast, methods using more traditional data flow analysis suffer from a lack of precision.

Formal methods is a broad area, encompassing theorem proving, decision procedures, and model checking. We are investigating satisfiability-based (SAT-based) symbolic execution for deep and precise code analysis. This involves translating program code and code safety properties into propositional logic constraints. In order to check code safety properties, the constraints are then solved by a SAT solver.

There are but a few symbolic execution systems, and we have been examining and extending one of those systems, Klee. In order to demonstrate the practical use of Klee, we have been extending its reasoning capabilities in order to be able to analyze software more quickly.

Summary of Accomplishments

1. We have developed understanding of the Klee architecture and discovered some of its key weaknesses.
2. We have implemented a new reasoning engine for Klee which gives significant speedups on some benchmarks.
3. We have designed new optimizations for Klee's reasoning that we intend to implement next year.

Significance

We are enabling a new level of precise code analysis at Sandia. Our tools can be used to aid a software vulnerability assessment. Our advancements allow those tools to scale to code that was infeasible to analyze beforehand.

Optimization of Time-Critical Constellation Scheduling

141604
Year 1 of 2
Principal Investigator: T. P. Fielder

Project Purpose

Evolving threats and growth in complexity of heterogeneous space-based sensing systems prove too difficult for humans to efficiently and effectively manage. Optimizing collection coverage for automated time-critical response to developing situations requires sophisticated constellation resource allocation and scheduling algorithms. Greedy solutions or other naive heuristics often do not provide good results. The goal of this project is to develop algorithms that maximize coverage and minimize tracking error of a set of targets using limited sensors in a real-time setting in the face of multiple dynamically varying cost functions, such as situations in which a target's position and velocity uncertainty grows over time. In this project, we are developing schedules based on local search algorithms, specifically variants of Tabu search and variable neighborhood search. These algorithms have achieved dramatic improvements in manufacturing settings. Extending robust optimization to real-time applications and developing real-time optimization heuristics is a new area of research. We are also pursuing other algorithmic approaches including a mixed integer linear program. We will also explore implementing our algorithms using multicore and graphical processing units technologies to make real-time performance more practical. We will evaluate scheduling algorithm performance against simulated time-critical scenarios, the merits of alternative command and pointing architectures, sensitivity to update frequency of time-varying costs, significant challenges and tradeoffs, and the benefits of the developed algorithms to a range of real-time missions. This work will reduce the latency over human scheduling, and we expect to significantly reduce the number of target leakages and target location uncertainties as compared to existing techniques.

Summary of Accomplishments

We have met all our milestones to date, and are making significant strides on upcoming milestones. The VEGA (Vehicle EnGagement Analysis) simulation has been up and running on our development environment. Additionally, we have designed and implemented a "projection" capability, which will allow schedulers to project tracking error into the future to estimate the quality of candidate schedules, which is a key component of local search techniques. Based on this, we have implemented a Tabu Search and are in the process of running simulations and analyzing the results. We have designed a test harness enabling us to quantify our results, in a meaningful way. Additionally, we have implemented a visualization capability based on NASA WorldWind that will enable us to understand the behavior of the simulation and algorithms by replaying the system results and comparing the behavior of various runs. We analyze collected information to determine presence of outliers or inability of the system to maintain desired performance. We have made significant progress towards a new milestone of codifying the analytic optimization model, which requires a thorough understanding of the ballistic target tracking state estimation problem. This new milestone will feed back into our algorithm development and our projection capability, and will also facilitate our original milestone for FY 2011 of finding optimal solutions for evaluation scenarios. Currently, we are optimizing the simulation and search algorithm to allow us to examine more candidate solutions. This milestone of examining ways to speed up implementation is scheduled for completion in Q2 FY 2011, but this is really an ongoing effort that must be started early, as high-speed evaluation of candidate schedules is important for successfully applying local search techniques.

Significance

Budget and resource constraints will place increasing pressure on remote sensing resource utilization in the years to come. Whenever there are limited sensor and ground assets and multiple time-critical areas of interest to be observed, the problem of finding a feasible schedule in limited time that has optimal or even sufficient coverage can be very challenging. These complex real-time scheduling problems occur frequently in remote sensing applications across a wide array of application domains. Scheduling techniques that provide rapid electronic cueing or enhanced human-in-the-loop decision-making responsiveness, improved coverage, and a low percentage of missed targets ensure the greatest return on investment for sensor assets.

Sandia's Space Mission and Remote Sensing program is a critical part of the national security mission and intelligence arena. As such, improving our understanding of resource utilization will better position Sandia to address the growing threats of the future. Challenging issues facing the national security community include the need for improved capabilities for global and theater situational awareness. This study can provide Sandia with constellation scheduling algorithms and simulation capabilities for time-critical response to developing situations for use in existing and future systems. This project will integrate the various scheduling algorithms into an established framework, VEGA, that has been used in various studies for simulating satellite constellation behavior. This new modeling and simulation capability will allow us to model the response of US satellite assets to a variety of real world threats.

Remote Sensing of Greenhouse Gases by Means of Gas Filter Correlation Radiometry

141606
Year 1 of 3
Principal Investigator: J. A. Mercier

Project Purpose

The purpose of the project is to investigate gas filter correlation (GFC) radiometry as a technique for optical remote sensing of a suite of gases that are of special interest for Sandia's Remote Sensing and Verification Program (RSVP). The primary gases are carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4). All of these gases have absorption features in the shortwave infrared (SWIR) spectral range from 2.0 to 2.5 microns. The major objectives are to model the performance of airborne and space based GFC imaging radiometers and to design a dual-use optical sensor that measures both nonproliferation relevant effluents as well as CO_2, CO, and CH_4 to verify compliance with treaties that might eventually regulate greenhouse gas emissions.

This work presents several unique challenges. CO and other effluents have spectra that consist of very narrow, widely spaced lines. Very high spectral resolution is required to isolate absorption by these lines. CO_2 and CH_4 are relatively uniformly distributed around the globe and therefore concentrations of these gases must be measured with very high precision in order to draw useful conclusions about local sources. GFC radiometry combines high spectral resolution with high throughput and high signal-to-noise ratio to meet all of these demands. However, scene clutter and interference from water vapor remain as significant issues for this approach. While GFC radiometry has a rich heritage of remote sensing of atmospheric trace gases in the stratosphere and mid-troposphere, the difficulties of working in the SWIR solar reflective range and measuring gases in the lower troposphere have not previously been overcome. By tackling these issues this project will enable the RSVP program at Sandia to meet mission needs for the Department of Energy and other government organizations.

Summary of Accomplishments

An initial 1-Dimensional radiometric model of scene plus sensor that covers absorption bands of CO_2 and CH_4 at wavelengths < 3.0 micron has been developed in MATLAB. In addition to the model development, we designed a software algorithm to optimize the spectral pass bands that should be used for observation of the gases. Optimization means producing high sensitivity to the gas of interest while minimizing interference from water vapor, which is a ubiquitous absorber that is present in highly variable amounts around the globe. The model has been used for several single line of sight simulations to predict performance for hypothetical satellite sensors that could monitor CO_2 and CH_4 from space.

The major goal in the upcoming years is to extend the model to a full 2D time varying scene simulation model, to better represent both the spectral and temporal signals and noise sources. In order to extend the model, a 3D plume dispersion model is necessary to simulate the contribution from a release source. This year's research focused on the application of advances in computational fluid dynamics (CFD), as well as visualization and data processing methodologies for analyzing plume dispersal. To that effect, we have developed a Fuego CFD aerosol model for the dispersion of aerosols from a stack under a crosswind. The model has been used to simulate dispersion of aerosols with light molecular weight that are of current interest including CO, CO_2, and CH_4. Additionally, an extensible markup language (XML) script has been developed for the measurement of the aerosol concentration across multiple rays that traversed the plume. The rays can emanate from a ground observer or from a sensor in space. This is the first step to integrating the results of the plume dispersion into the radiometric model.

Significance

The primary focus is to investigate a dual-use optical remote sensing technology to measure indicators of nuclear proliferation activities and to measure CO_2, CO, and CH_4 to verify compliance with treaties that might eventually regulate world-wide greenhouse gas emissions. Space based operation would allow these measurements to be made globally, including over denied territory. These capabilities would be very significant for DOE, NNSA, the Department of State, and the Intelligence Community.

While GFC radiometry has been used for remote sensing of atmospheric trace gases in the stratosphere and mid-troposphere, it would be a unique application to use the technology as a global facility monitoring technique in the short-wave infrared solar reflective range measuring gases in the lower troposphere. In order to more appropriately characterize the sensor performance against specific facilities, it is important to develop accurate source modeling capabilities. One major success of this research will be to leverage all of the extensive capabilities of Fuego for detailed mission assessment. Fuego is a Sandia developed, massively parallel CFD code that addresses plume transport and mixing at a far finer scale and with far more detail than any existing Gaussian or puff-based transport models. Fuego is a 3D, reactive flow code that includes laminar, buoyancy, and turbulent flow models, combustion models, and conjugate heat transfer.

Fuego includes state-of-the-art turbulence models such as Reynolds-averaged Navier-Stokes and large eddy simulation turbulence models. For the initial plume dispersal calculations, the 3D turbulence and mixing used primarily the dynamic Smagorinsky, and time filtered Navier Stokes models as they are considered the most adequate. Merging these extensive simulation capabilities with the sensor design expertise within the monitoring systems center will certainly put Sandia in a uniquely advantages position within the remote sensing community.

Finally, an additional goal of the first year was to identify other gasses that have environmental monitoring or nonproliferation significance. A more specific list of gases to investigate has been created. The original list consisted of CH_4, CO_2, and CO. Nitrous oxide (N_2O) along with several other effluents have been identified as additional gases of interest that are compatible with the GFC technique. N_2O is another greenhouse gas, and therefore, fits well with the original scope of the project.

Hybrid AI/Cognitive Tactical Behavior Framework for LVC Simulations

141607
Year 1 of 2
Principal Investigator: P. G. Xavier

Project Purpose

Exploiting its 3D embodied agent simulation technologies, Sandia is delivering force-on-force (FOF) simulation-based tools to DoD and DOE. However, because the simulated human entities lack understanding of combat tactics, setup and debugging of scenarios is time intensive. This hampers using Sandia's analysis tools in rapid, precision decision-making and limits scenario scale, complexity, and realism. Sandia's Live-Virtual-Constructive (LVC) simulation technology is also being used to address DoD and DOE challenges. This technology is class-leading in its ability to combine live and constructive. Competent and realistic constructive-simulated human entities will enable the participatory use of LVC systems for training, analysis, etc., without efficiency-sapping numbers of humans playing supporting roles. Furthermore, LVC systems can be used to test and validate the behavior of constructive entities and to capture data from human participants to speed construction of behavioral models. This potential synergy is impeded by lack of scalability of the current version of our LVC framework with respect to constructive entities whose computational demands compete with the realtime update needs of live and virtual elements.

This project seeks to overcome these limitations, especially within tactically intensive 3D scenarios. We will develop, implement and demonstrate a framework for behavior models that builds upon state-based, artificial intelligence and 3D algorithmic techniques and enables appropriate insertion of cognitive modeling, for example, to account for factors such as emotions, stress, and human memory performance. The framework will enable further insertion of cognitive modeling as that technology advances. Concurrently, we will revise our LVC framework to improve its scalability, to support the behavior framework and its rich set of simulation (sensing/perception, actions, etc.) needs. We will consider shared-memory multiprocessing and distributed simulation approaches. Tactically enabled behavior models will be exercised and demonstrated in LVC simulations featuring live human and robotic elements.

Summary of Accomplishments

To begin, we analyzed behavior and LVC simulation component technologies and their interdependencies and completed an engineering analysis and project scoping. For the initial spiral of behavior model architecture development and initial spiral of revision of Sandia's LVC framework, we began by identifying elements of behavior modeling according to response latency. This led to a hypothesis about how to exploit time constants of behavior to avoid compromises between behavioral competence and LVC scalability. We developed a conceptual architecture based on this hypothesis. In the initial spiral of behavior model architecture development, we implemented a demonstration of a team behavior applying tactical knowledge via a highly configurable path planner. This is proof-of-concept that our technology will accelerate how quickly users can specify team behaviors in a scenario. We then extended this capability to enable team members to dynamically update the team members' paths in a tactically coordinated way in response to updated perceptions. We demonstrated this capability.

Toward improving the scalability of Sandia's LVC framework, we initially focused on moving path-planning processing out of the simulation loop thread(s) so that the simulation loop will not stall during path planning. We have adapted our highly configurable path planner to dispatch planning requests to a thread pool, and we created a prototype version of the appropriate behavior component that uses this feature. We successfully demonstrated this software, and other projects have adapted and adopted it. More recently, we have been experimentally studying multithreading the module update loop of the underlying Umbra simulation framework. The results showed the significance of multithreading Umbra worlds, which model entity interactions, and provide us directions for continued progress. In addition, we have developed an algorithm that will enable the planner to simultaneously plan and handle terrain modifications.

Significance

This project develops technology for large-scale force-on-force simulations within live virtual constructive environments to enhance current training, and analysis tools for tactically intensive scenarios. Such tools are used to enhance our country's warfighting capabilities by enabling the evaluation of new technologies, techniques, and procedures in a virtual environment, obviating the requirement for building and testing. This is not only more cost-effective, but it also allows rapid spiral development and insertion into the current force.

Solid-State Replacement of Traveling Wave Tubes for Next-Generation SAR

141609
Year 1 of 2
Principal Investigator: R. B. Hurley

Project Purpose

A limiting factor for miniaturizing radar systems, including Synthetic Aperture Radar (SAR) systems, is the microwave power transmitter, which is located in the final stage of the radar front end before the antenna. Current Sandia-designed systems typically use tube-based technologies, such as Traveling Wave Tube (TWT) or TWT-based Microwave Power Modules (MPM). These tube-based amplifiers have low efficiencies and limited lifetime. The goal of this study is to develop a technology that allows the replacement of TWTs and MPMs with solid-state power amplifiers (SSPAs). A single solid-state device simply does not have sufficient power to generate the power output necessary for SAR applications (>100 watts), but there is the potential for combining a handful of devices to reach the 100 watt level. The challenge will be power-combining these devices in a low-loss, efficient, and thermally controlled design. If successful, this will enable solid-state devices to replace tube-based amplifiers in Sandia SAR applications, thus improving the reliability, cost, and size of the systems.

Summary of Accomplishments

We located, evaluated and procured an emerging GaN (gallium nitride) power device usable for demonstrating wideband combination of high power at Ku-band radar frequencies (30 W, 14-17 GHz). We successfully designed and demonstrated a four-way power combiner circuit (to provide 100 W of power) based on this device, which exhibited reasonable loss and isolation performance at frequencies of interest. Because of thermal issues, the GaN chip can only be operated in pulsed mode (i.e., not run steady state), so an external pulse modulator was located that allows enough current capacity for single-device characterization.

Based on thermal modeling, thermal expansion coefficients and heat conduction requirements, we chose a feasible heat spreading material (5/95 copper tungsten) to match characteristics of the silicon carbide substrate of the GaN die, thereby optimizing performance and reliability of the critical die-heat spreader interface. We evaluated his unplated heat spreader material for mechanical and packaging viability, and found it to be difficult (though not impossible) to machine and difficult to wet for soldering. However, we have successfully performed die attachment of mechanical samples to the unplated heat spreader using Diemat epoxy (a non-soldered approach) and successfully laminated the Arlon substrate used for the four-way power combiner test circuit to the spreader, allowing construction of initial test circuits for electrical evaluation.

Using external drain modulation, initial devices yielded only 5–7 W of pulsed power due to inadequate drive and stability issues, so design changes were initiated. A driver amp was added and verified in pulsed operation with the external pulse modulator, then looped in a SAR, a milestone that represents the first time a solid-state, drain pulsed amplifier was successfully looped with a Sandia SAR. Image evaluation showed no significant degradation of performance due to drain pulsing of the driver, proving feasibility of drain pulsing for this system.

Significance

To allow integration onto small unmanned aerial vehicles (UAVs), next-generation SAR needs to be smaller, lighter, and more reliable than predecessors. Traveling-wave tube TWT replacement by solid-state power amplifiers allows for further miniaturization and improved reliability for airborne radar applications (including SAR), in support of Sandia missions in nuclear security and nonproliferation (DOE).

The ability to successfully integrate just the driver amplifier in a looped SAR makes the implementation of an active phased array more attractive in this application. Where constant voltage amplifiers have power consumption characteristics that made integration in an active array unlikely, a pulsed amplifier that conserves power and does not significantly degrade SAR image effectively solves this problem and enables the potential for effective spatial power combining, leading to higher-efficiency antennas, extended ranges and perhaps smaller volumes. A project, attempting to address the active array design for Ku-Band radar, has already been pursued this year and leveraged from this project.

Although hampered by the prototype nature of our GaN devices, sufficient evidence exists that these devices can easily supply significant pulsed power and be improved with financial investment (i.e., another design run on the device) to improve overall electrical performance, providing a viable alternative to Ku-band tube technology. Even a "low" output of 5 W is still quite impressive and useful in near-range radar applications, such as those using drones or other ultrasmall UAVs.

Space Payload Flight Software Architecture

141610
Year 1 of 2
Principal Investigator: R. D. Hunt

Project Purpose

Sandia is currently developing the next generation of space payloads to provide intelligence about worldwide threats to our nation's security. These payloads will utilize new data processing and communication architectures for both flight and ground systems, and new payload software is needed to support them. With high development costs and long development cycles, there is a growing trend to build reconfigurable and reusable systems that have the flexibility and scalability to support new and evolving missions. The payload software must support this trend through a dynamic and reusable design that can support both multi-mission and multi-program paradigms. A design of this magnitude requires a revolutionary approach and will lower the overall software development costs to all programs through code reuse and efficient resource utilization.

The focus of this project is to develop and demonstrate an operating system level of software that provides the platform for rapidly deploying new space-based payloads and the scientific algorithms used within them. Based on emerging technologies in both embedded software and communications, this software will provide a core set of frameworks, services and applications that will become the fundamental building blocks of any future payload software. We will standardize the way we control payloads and create an abstract environment where program-specific applications can operate in a distributed processing environment. It will complement existing research activities in the areas of node-based flight hardware, mission data processing, sensor development, and ground systems. This project allows a broader perspective of requirements to be considered, incorporating the needs of many programs, and positions Sandia to quickly respond to the needs of future programs.

Summary of Accomplishments

The tasks for FY 2010 consisted of gathering requirements at the program and payload levels, researching standards and technologies, identifying the main architectural components and beginning to elaborate on the design. The first task was to identify key functional requirements that would drive the design. An assessment was made of current and legacy payloads at Sandia as well as comparable payloads and satellites developed by industry. There have been several key technologies identified, as a result of researching new standards and technologies. The first was the identification of a communication service framework based upon developing standards from the Consultative Committee for Space Data Systems (CCSDS) called the Mission Operations and Information Management Services (MOIMS). The second technology provides an execution framework based on Active Objects (AO). The culmination of research at this point is the definition of a payload software architecture that consists of three main components: core applications, a communications framework, and an execution framework. The core applications provide the fundamental operating system services for controlling the payload and interfacing to ground systems. The communications framework provides the services and messaging formats for communicating between flight and ground system applications. The execution framework provides the modular interface for applications to operate and interact in a distributed processing environment. With the main components identified, we began to elaborate on the design, identifying specific technologies that could be used to realize it.

Significance

Sandia is currently developing the next generation of satellite payloads to provide intelligence about worldwide threats to our nation's security. This software architecture will enable the success of a number of key technologies of the next generation of satellite payloads. Specifically, it complements the work being performed in the areas of node base architectures, mission data processing architectures, sensor development, technology development, and ground system architectures.

Tightly Coupled Navigation and Targeting

141611
Year 1 of 2
Principal Investigator: J. T. Spooner

Project Purpose

Within this project a new tightly coupled navigation and targeting approach will be developed to improve geolocation and target trajectory estimation given one or more assets. While this approach has numerous applications, for the sake of brevity, it is described here in terms of space-based trajectory estimation problem. When target detection is made by a satellite, the LOS (Line Of Sight) vector to that target from the spacecraft is calculated along with the direction uncertainty. If a star tracker provides the primary attitude reference for the spacecraft (e.g., the mission payload has a narrow field of view and wavelength not appropriate for reliable stellar detection), then the mounting uncertainty between the payload and star tracker will cause target LOS uncertainty. If this uncertainty is not later compensated, it will subsequently affect trajectory estimate accuracy. Within this project, a data fusion engine will be designed to not only estimate the target trajectory but will also be expanded to enhance the attitude estimate of each asset in play so that the payload mounting uncertainty may be compensated, potentially achieving much more accurate position and velocity estimates of the target.

Accurate target position estimation will directly impact the ability to provide a useful handoff to other assets and associate detection data with a particular target. In addition, if the solution is made to converge more quickly, one may reduce the number of observations required or provide a handoff earlier. This not only improves the performance of current assets, but may allow one to relax design requirements on future assets, affecting cost and schedule of development programs.

Summary of Accomplishments

During the first part of this project, we enhanced software tools for use in the modeling and performance evaluation of the tightly coupled navigation and targeting algorithms. During the scope of this project, we will investigate several applications, hence, a flexible Sandia-developed modeling tool called VEGA (Vehicle EnGagement Analysis) is being used. Several enhancements have been made to VEGA in support of this project including the following: 1) more general framework for diverse vehicle types (e.g., original version did not consider unmanned aerial vehicle applications); 2) enhanced earth visualization for airborne and ground-based vehicles; 3) enhanced dynamics modeling including gyro and accelerometer models for input to navigation systems; and 4) automatic generation of targets for algorithm evaluation.

We have also identified a sparse multi-pass filtering approach that appears well suited for this application. This approach has the advantage that it preserves a sparse structure within the EKF (Extended Kalman Filter) framework, allows for targets to be included or rejected on the fly, and retains the dominant interaction between the targets and the navigation system. An initial implementation of this algorithm has been completed and shown to be able to form tracks of the target trajectories given satellite observations.

Significance

Sandia has developed world-class satellite payloads. This project is intended to enhance Sandia's capabilities in geolocation and targeting using these and future assets. Benefits include the following:

- Accurate trajectory position and velocity estimates
- Help preventing over-designing future satellites due to overly restrictive attitude knowledge requirements
- Quicker convergence of the trajectory estimate allowing for earlier target engagement

Tools for Evaluating Embedded Wireless Devices

141612
Year 1 of 2
Principal Investigator: R. A. Jung

Project Purpose

The purpose of this project is to create tools and processes useful for characterizing the security properties of Universal Mobile Telecommunications System (UMTS) and Global System for Mobile Communications (GSM) enabled mobile devices. There is a clear need for such capabilities in this area that are flexible in supporting all mobile devices. In addition, there is a need for automation of such an approach, in order to conduct vulnerability assessment (VA) work in a timely fashion because the technology is evolving rather quickly and new devices are continually introduced into the market. Current tools, commercial and otherwise, in this area, for the purposes of VA are extremely limited.

In order to meet these needs, this project will leverage the current state of the art in cellular network simulation using commercial-off-the-shelf (COTS) elements, where we are able to create vulnerability assessment capabilities that are completely external to mobile devices. In so doing, this project will create fully automated assessment tools that are compatible with all devices conforming to the previously discussed cellular standards that can easily be used in an automated fashion.

Summary of Accomplishments

We demonstrated an initial implementation of a fully automated testing framework useful for conducting vulnerability analysis on GSM- and UMTS-enabled mobile devices. After pursuing several other approaches in this area, we built an understanding of the pros and cons in several potential software fault analysis approaches and their fitness for this particular area of system assessments. While several of these approaches were proven infeasible for the goals of this project, they were necessary steps in order to fully understand the tradeoffs. In addition, this process was necessary to arrive at the currently chosen path of VA through cellular network simulation.

Significance

This research has created an assessment framework that allows leveraged security researchers to conduct VA work on GSM and UMTS mobile devices. Because there are ever-increasing needs for wireless capability as the technology proliferates, this is incredibly important.

At this project juncture, after purchasing a few key COTS parts for network simulation, combined with this project's assessment framework, any organization can use the software and tools created for this work for VA project work. The focus of our second year, FY 2011, will be making the VA framework more complete in both breadth and depth of the protocols supported. In addition, there is currently much to be desired in terms of documentation, both in terms of example source code and user manuals.

Use of Phase Conjugation in High-Energy Laser Systems

141613
Year 1 of 3
Principal Investigator: D. E. Bliss

Project Purpose

The purpose of this project is to understand how phase conjugation by stimulated Brillouin scattering (SBS) can be used to correct for optical aberrations in high-power laser beams. Systems that propagate high-energy lasers through high thermal turbulence regimes would benefit from delivering more energy on target. Beyond building bigger lasers, higher intensities are achievable by combining beamlets from multiple sources and correcting for aberrations. Simple beam combining methods using passive optics do not ensure mutual coherence, resulting in a beam with a non-ideal wavefront and poor Strehl ratio. Scientists have claimed that multiple high-energy laser beams (>100 kJ) can be phase conjugated (PC) and coherently combined using SBS to create a single beam with an exceptional Strehl ratio. However, results are not clearly documented in the open literature. If true, these claims mark a major breakthrough in extending the energy limit for propagating laser beams through turbulence. To verify claims and develop this technology for Sandia programs, we will experimentally investigate phase conjugation of aberrated beams using an SBS cell. Once we understand the trade-off between the maximum attainable energy and best possible wavefront, we will test a PC SBS cell in collaboration with the Air Force Research Laboratory's (AFRL) Davis Laser Lab to establish the practical physics limits and opportunities for inserting this technology into Sandia programs.

Summary of Accomplishments

We completed the installation and testing of the laser and diagnostic suite for the laboratory based experiments. The laser is 4 J at 10 Hz and can be operated both as multimode oscillator/amplifier and a seeded single-longitudinal mode laser. Functioning diagnostics now include a wavefront sensor, photodiode, far field camera, and simple phase conjugate fidelity ("energy in a bucket") monitoring. The SBS cell has been designed and assembled and the associated pressure safety data package has been completed. We are awaiting a hydrostatic pressure test of the cell, before pressurizing it with xenon and starting laboratory tests.

Two organizational meetings have occurred between Sandia and AFRL staff to coordinate our collaboration on the AFRL Davis Laser Laboratory's chemical oxygen iodine laser. We met with AFRL management to reach an understanding about the importance of joint research between the two laboratories in the future. We also worked with the AFRL technical staff to investigate testing alternatives and initiated the test design for the full-scale phase conjugation tests to be conducted at the AFRL Davis Laser Laboratory in FY 2011. The preliminary test design will be completed in this quarter of fiscal year 2011.

Significance

Understanding the capabilities and limits of SBS for phase conjugating optical aberrations in high-energy laser systems will benefit Sandia missions such as laser production of x-rays for photo-lithography and inertial confinement fusion high-resolution laser imaging, material processing, and space debris removal.

Micro-Optics for Imaging

148901
Year 1 of 1
Principal Investigator: R. Boye

Project Purpose

Producing high-quality imagery becomes increasingly more difficult as the size of a system is reduced. For very small form factors (efl <1 mm), it is essential to develop a system that takes advantage of post-processing techniques to fully leverage all the information available. Unfortunately, post-processing cannot fully recapture information lost due to poor quality optics. Additionally, the constraints imposed by the reduced form factor make the fabrication of image forming optics a challenging problem. An approach that considers how the optics transfer information as opposed to forming an image may provide an avenue to a more successful system. The combination of an annular design with a phase coded pupil and post-processing can enable the realization of a micro-optical imaging system.

A project utilizing simulation tools can provide a determination of the increased value of this approach. Optical design software can accurately predict the output of the physical lens. These outputs can then be post-processed in the same way real imagery would be handled. The increase in image resolution, or information content, can be quantified in this way.

Summary of Accomplishments

This project investigated the fundamental imaging capability of an optic with a physical thickness substantially less than 1 mm. The analysis assumed that post-processing can overcome certain restrictions such as detector pixel size and image degradation due to aberrations. A first-order optical analysis quickly revealed the limitations of even an ideal thin lens to provide sufficient image resolution and provided the justification for pursuing an annular design. Some straightforward examples clearly showed the potential of this approach. The tradeoffs associated with annular designs, specifically field-of-view limitations and reduced mid-level spatial frequencies, and their impact on the imaging performance were evaluated using several imaging examples. Additionally, issues such as detector acceptance angle and the need to balance aberrations with resolution were included in the analysis. With these restrictions, the final results presented an excellent approximation of the expected performance of the lens designs assessed.

Significance

This novel form factor imaging system allows integration into many systems and applications. It will be a versatile sensor with direct utility for Defense Systems and Assessments, Energy Resources and Nonproliferation and Homeland Security and Defense missions. The concepts proposed here would allow for a variety of applications of interest to proliferation assessment activities. This project will result in a flexible architecture that can be optimized for specific applications.

Polymer Adaptive Lens Athermalization

149211
Year 1 of 1
Principal Investigator: M. Baker

Project Purpose

Sandia has been integrating variable focal length polymer lenses for application in adaptive optical systems. This effort has included work in finite element modeling and material development. One undesirable attribute of using polymer lenses is the dependence of focal length on temperature. To apply these polymer lenses to tactical optical systems, it is necessary to compensate for the effects of temperature variation.

Summary of Accomplishments

We have successfully demonstrated compensation approaches for temperature effects through finite element modeling of the complex interactions between the expanding fluid, the elastic membranes, and the outer housing material of the lens core.

Significance

This work ties directly to the mission of Defense Systems and Assessments in the Military Technologies and Systems strategic program area through the potential application of an advanced electric zoom rifle scope and a compact pan-and-zoom surveillance system. These technologies would provide real and immediate benefit to the warfighter through new weapon systems and improved optics on existing rifles.

Demonstration of High Current Device

149406
Year 1 of 1
Principal Investigator: J. A. Alexander

Project Purpose

A number of government agencies (DoD,DHS,DOE) have an urgent need to have a compact device that effectively stops vehicles in a nonlethal manner. Sandia has demonstrated that a high-power short electrical pulse driven directly into a vehicle body can safely and effectively disable many of the electronic systems and cause the vehicle to cease functioning. This is easily accomplished by discharging a modest capacitor bank into the vehicle body. An efficiently designed single-shot system that leverages the energy density of explosives (>1000 times that of a capacitor) for its power source, such as a compressed flux generator (CFG), has the potential to deliver the same high power to an vehicle in a system volume 1/100 the size or less than a system that uses a capacitor bank. Sandia has a number of legacy CFGs on hand. This project will demonstrate that these very small CFGs can have their electrical output coupled to a vehicle body and disable the vehicle via the same electrical direct drive mechanism demonstrated with capacitors. We will operate the legacy devices at less that full output to show that a follow-on design would require much less explosive to disable a vehicle.

Summary of Accomplishments

Although the test failed to stop vehicles on 4 of the 5 shots, we learned many important lessons from the testing. A much better understanding of the legacy CFGs was obtained. The nominal operating parameters (seed current) from the legacy data could exceeded by a factor of three without voltage breakdown. This will aid us in using these devices in the future. We are now relatively certain that the current rise time (di/dt) is a very important parameter for direct driving vehicle bodies for electronic damage or upset. If voltage induced due to di/dt were the only factor effecting the result, then one would expect to require ~15 times greater peak current from the CFG to overcome the slower pulse. The fifth shot's result indicates that we are not far from the required waveform using CFGs. CFGs optimized to give a faster rising waveform are a promising technology for addressing the vehicle stopping need. Although it was not demonstrated by either this test or the 2005 tests, it is understood that pulse width/energy will have a threshold value for producing damage. CFGs do certainly have the energy required to address that concern. Further investigation of this technology is warranted. The use of passive peaking elements on the output of the legacy CFGs may be all that is required to achieve positive reliable results.

Significance

DoD, DHS and other agencies will benefit from compact power supply design experience.
Also, border patrol is very concerned about stopping vehicles via nonlethal means and has, in the recent past, approached this strategic management unit for solutions and, as highlighted by current events (i.e., piracy) we believe that the Coast Guard and Navy would have interest in stopping watercraft using such techniques. Expansion of the suite of demonstrated power sources will allow more flexible use of these types of systems in future.

Exploration of THz Phenomenology for THz Imaging

149407
Year 1 of 1
Principal Investigator: M. Wanke

Project Purpose

Terahertz imaging has the potential to be useful in a variety of national security applications, such as package inspection, nondestructive evaluation, or personnel inspection at checkpoints. Often, the detailed phenomenology needed for various applications is not well understood and efforts to field a system are therefore unsuccessful either because the materials being studied do not have appropriate optical properties or the because the wrong technology is chosen. This project will explore the THz phenomenology of materials for a THz tomographic imaging application, determine whether THz radiation could meet the imaging needs, and provide requirements that an imaging system would need.

This project was not aimed at demonstrating a usable imaging system but instead focused on exploring the contrast mechanisms and the transmission/reflection phenomenology, to provide the scientific foundation necessary to build an imaging system.

Summary of Accomplishments

We measured the transmission of the background material of interest for the application over the frequency range of 1–17 THz. At the low end, the transmission was greater than 10% for a typical material thickness, but for most of the frequency range the transmission was approximately 1% or less. The contrast between the background matrix and embedded objects on the other hand appeared to increase at higher frequencies, but never exceeded 15% and was usually close to 5%. These data make potential tomographic imaging difficult but not impossible.

We also discovered a large inhomogeneity of the transmission and reflection from the background matrix. This inhomogeneity resulted in transmission/reflection fluctuations on the order of 50% or more. Adding this effect, makes imaging based on simple transmission of reflection highly unlikely to succeed.

Significance

Over the past few years, there have been significant investments in THz imaging to solve a particular imaging application. However, these investments focused on building an imaging system before the material phenomenology was determined. Measuring the phenomenology demonstrated that simple approaches of using THz radiation for tomographic imaging in this particular application are unlikely to succeed. More phenomenological studies are required to explore whether more sophisticated imaging techniques may be worth exploring. However, any potential system must ultimately solve the problem of the spatial inhomogenities present in the background matrix materials.

Robust High-Sensitivity EEG Data Analysis Tool

149408
Year 1 of 1
Principal Investigator: E. Akhadov

Project Purpose

With the emergence of electroencephalography (EEG) as a neuroimaging technique in commercial off-the-shelf (COTS) devices, there is a need to process the data in an expeditious and robust manner. Currently, real-time analysis of EEG is typically done by partitioning the EEG into frequency bands and measuring the relative power of the EEG in the alpha, beta, and gamma bands. Another widely-used analysis technique is to time-lock the EEG signal to the presentation of events of interest and to average the discrete, time-locked segments of EEG together. This technique produces components called event-related potentials (ERPs). ERP analysis reveals valuable information about brain activity that cannot be observed from frequency band analyses. However, it is typically performed off-line, using high numbers of trials to achieve a robust analysis (high signal-to-noise ratio).

Here, we use a multivariate statistical analysis (MVSA) technique pioneered and established at Sandia for materials science applications for high-sensitivity and robust ERP signal discrimination and detection. Conventionally used for discrimination between similar and dissimilar phases, microstructure, elements, etc. MVSA is the technique of choice for high-sensitivity measurements. Instead of manually (and subjectively) analyzing a large number of observations on an individual basis, this multivariate approach reduces a large set of individual patterns into a core set of statistically derived components that can be sequentially indexed. Our hypothesis is the following: a single experimental ERP waveform can be treated as linear combinations of spatially simple components and analyzed using MVSA, yielding a series of signatures consisting of relative intensity and presence of other contributing peaks.

Summary of Accomplishments

This project has demonstrated the effectiveness of MVSA as a new tool for EEG and ERP analysis. In particular, the MVSA method accurately indentifies electrode response distributions and ERP signal peaks. This new approach to ERP analysis provides additional information about the spatial distribution of cognitive activity by providing more detailed electrode response distributions and ERP peaks than those anticipated by ERP analysis experts. This new tool represents a significant step forward in ERP analysis that enables new applications of EEG technologies in operational environments. To more fully demonstrate the applicability of the MVSA method to operational environments (in particular for augmenting cognition), we recommend the following work products:

1. Apply the MVSA method to data available from an additional 10 subjects in the Analogy EEG study.
2. Compare MVSA factors to grand average ERP signals with particular attention to inter-subject variability.
3. Test the effectiveness of MVSA for classification of single-trial ERP signals that have not been used to develop the MVSA factors (true, forward prediction of unknown samples).
4. Determine if differences in peak locations are a result of the MVSA method identifying underlying peaks that are combined by the grand averaging method.

Significance

Many DoD missions have a need for fast, reliable analysis of analysts'/soldiers' cognitive state for augmenting their cognition in real time. Current analysis techniques require large numbers of observations because of poor signal-to-noise ratio. This work opens up a new class of capabilities for augmenting cognition in operational environments.

A Generalized Subgrid Fragmentation Capability for Hydrostructural Simulations

149565
Year 1 of 1
Principal Investigator: J. Hollenshead

Project Purpose

Optical sensors and radars provide critical information used to perform real time hit and kill assessment from ground, airborne, and/or space-based sensors. This information yields insight into the target type, resulting debris mass distribution, and quantity of high-explosive materials detonated. These factors influence the optical and radio-frequency emissions and the observed post-impact debris cloud characteristics, composed of material masses ranging from sub-gram to many kilograms.

Current methodologies for predicting radar cross-sections (RCS) and range time intensity (RTI) plots are calibrated using the larger debris pieces, where there is greater confidence in model predictions. The characterization of small debris (< 0.1 gm) has received less attention. However, small debris can be important in both radar signatures, where it affects the brightness and radial spread of the RCS/RTI tracks, and in optical signatures, where it is expected to play an important role due to its anticipated higher temperatures and velocities, when compared to the larger debris. Recent flight test analyses comparing observed emission data with predictions have illustrated differences that may originate from the influence of small debris. Thus, well-characterized small debris may be a key factor in properly predicting post-intercept debris emission.

Our analysis codes are based on discretization of the mass, momentum, and energy conservation equations. The smallest computed debris is limited by the size of the smallest computational element (around 1 millimeter). Hypervelocity impacts can produce fragments as small as a micron. Thus, certain subscale physics that affect debris size are not completely represented in the current analysis. The computational approach to characterize post-intercept debris for radar and optical sensors must be capable of accurately representing both large and subgrid sized debris. This study investigates the implementation of a subgrid fragmentation capability for hydro-structural simulations and involves both basic research and model implementation.

Summary of Accomplishments

Utilizing the Sandia shock physics code, CTH, and starting from the current CTH Grady-Kipp (GK) fragmentation model, we have implemented the GK fragmentation model in Zapotec, a coupled Eulerian (CTH)-Lagrangian (Pronto3D) code. We proposed a new compact data set (CDS) representation for relaying subgrid fragmentation data with technical partners, and we presented the technique used to incorporate this methodology into the current post-engagements analysis toolkit. We have made key advances that increase our capability to deliver subgrid fragmentation data for hydro-structural simulations of MDA engagements. Additionally, we have investigated and addressed several fundamental questions. These included generalization of conditions under which CTH evaluates Grady-Kipp fragmentation and handling of fragment size predictions at low strain rates. Finally, we explored the sensitivity of predicted fragmentation characteristics to impact velocity, computational grid resolution, and variation in the damage volume fraction threshold.

An opportunity arose to compare predictions with experimental data. Although initial attempts were unsatisfactory, the final predictions led to predicted radar metrics that were all within reported experimental uncertainty. This success provides a key measure of the accomplishment of the current work.

Significance

The principal tie to the DOE mission is by way of the connection to the Strategic Plan Nuclear Security goal. This work directly supports Goal 2.2. The technology developed here will enhance deterrence and counter-proliferation of weapons of mass destruction. A secondary tie to the DOE mission is science based stockpile stewardship. The technology developed here has dual use potential and could be used to describe complex phenomena involved in nuclear weapons safety and transportation.

A Novel Experimental Approach for Quantum Information Sciences

149566
Year 1 of 1
Principal Investigator: T. D. Tarman

Project Purpose

Quantum information science (QIS) holds the potential for dramatically improving information processing tasks such as data acquisition, data processing (computing), and communications. These improvements are a result of two unique properties of quantum information (stored in quantum bits, or qubits), which lead to quantum parallelism:

- Quantum superposition

This property allows a qubit to be configured to assume a state between 0 and 1, inclusive, and allows a register of qubits to be configured to represent all values between 0 and $2^{(n-1)}$ simultaneously.

- Quantum entanglement

Entanglement correlates two or more qubits in a manner that allows operations on one qubit to affect other qubits.

A barrier to QIS is the experimental realization of a system that demonstrates these properties and is effectively isolated from noise sources that cause qubit decoherence (e.g., nonuniform magnetic fields from neighboring particles with non-zero spin). This project proposes to pursue an idea for realizing qubits using conventional fabrication techniques and is distinct from current approaches (e.g., donors-in-silicon and quantum dots). If successful, this technique would find immediate application that broadens Sandia's QIS thrust into quantum sensing and communications.

Summary of Accomplishments

We surveyed alternative approaches to the quantum circuit model of computation and analyzed the deterministic quantum computation with one pure qubit (DQC1) model. This model of computation relaxes the requirements for high-fidelity initialization and read-out for most qubits in a quantum system, which makes this model attractive for future experimental realization of small quantum circuits.

Significance

Sandia is engaged in basic quantum information sciences research in support of Sandia and DOE missions (e.g., materials simulations for nuclear weapons missions, secure communications in support of DOE programs, etc.). This research is motivated by advanced computing architectures and the fact that future engineered systems will require increased understanding of quantum effects.

Indigenous Surveillance and Reconnaissance Platform

149569
Year 1 of 1
Principal Investigator: J. Whetzel

Project Purpose

As US military engagements focus on combating a decentralized, embedded enemy, the tactics for surveillance and reconnaissance must become more agile. Instead of relying on traditional C2 hierarchies and networks, we propose to develop a mobile software platform that leverages indigenous infrastructures and enables decentralized decision-making to match the threat.

In the past five years the sensor suite on smartphones (e.g., iPhone, Android, Blackberry) have expanded tremendously. The intent of this project is to use this ubiquitously deployed hardware to develop tools for the collection and sharing of surveillance and reconnaissance information, both within the traditional C2 hierarchy and between operators. It is in the "horizontal" sharing of information that the greatest potential exists — empowering deployed operators to quickly develop situational awareness, and shift assets appropriately for precision tracking, locating, and data-collection on elusive human subjects.

This software platform will be, first and foremost, designed to address the immediate needs of operators. This proof-of-concept will provide a strong basis for follow-on development efforts, which fully exploit Sandia's expertise in sensor fusion.

Summary of Accomplishments

Our primary goal for this project was to develop a smartphone-based tool that would immediately meet the needs of operators to defeat low-contrast, embedded enemies. At the onset of the project, we formed a relationship with subject matter experts (SMEs) from NEK Advanced Securities Group, who specialize in training US personnel on Intelligence, surveillance, and reconnaissance (ISR) tactics. These SMEs volunteered their time to ensure our work fit within the day-to-day tasks of ISR teams.

Based upon our vetted designs, we constructed a three-part system to serve as the Indigenous Surveillance and Reconnaissance Platform (ISRP). The first part, colloquially known as C1, is an Android-based smartphone application. C1 allows an operator to collect and share various media (e.g., notes, photos, videos, audio), with all media time-stamped and geo-spatially tagged. Furthermore, C1 also encompasses functionality needed by ISR teams to better coordinate efforts (e.g., sharing GPS location, storing past tracking routes).

The second part of ISRP is a data repository accessible through a secured web service. The web service follows the representational state transfer (REST) schema popularized through many other social networking applications. Using this protocol provides an extensible environment where other applications may be constructed to utilize this database.

The third part of ISRP is a website, known as C2, to assist team leaders in tracking and sorting information collected from operators. The website also provides a team leader with near-real-time positions of operators, allowing leaders to orchestrate their operators based upon incoming data.

Our demonstration of the completed ISRP prototype to our SMEs yielded an enthusiastic response and feedback for moving forward with development. We are securing a copyright of the ISRP software to allow for licensing and shared development with external sources, once we secure follow-on funding through Work-For-Others (WFO) sources.

Significance

This work supports Sandia's role in developing innovative, technology-based system solutions to the most challenging issues facing national security. According to the report, *Fixing Intel: A Blueprint for Making Intelligence Relevant in Afghanistan*:

"…the intelligence apparatus still finds itself unable to answer fundamental questions about the environment in which US and allied forces operate in and the people they are trying to protect and persuade."

The report has a recommendations call for lateral sharing of information between individuals, based upon geographic or regional mission needs (not necessarily organizational affiliation). Smartphone technologies provide a low-cost, ubiquitous method to quickly digitize and disseminate surveillance and reconnaissance from human sensors on the frontlines. Through development of this platform, we will provide capability for operators to quickly develop situational awareness and adjust combat strategy.

The need for this capability and the lack of existing solutions has been identified in past and recent interactions with operators performing and training these activities. This project represents an opportunity to create a new capability area of discriminating expertise for the Defense Systems and Assessments strategic management unit, in a secure environment, which will directly benefit the surveillance and reconnaissance program area. In addition, once a capability is demonstrated, it has a high potential to lead to externally funded work and directly impact the current conflict.

Furthermore, ISRP provides a research environment for studying problems that leverage Sandia expertise in the areas of sensor fusion, network analysis, and augmented cognition. Potential research areas that have been discussed with our SMEs include: analyzing phone usage of team members to detect possible uncooperative behavior and correlating incoming data streams to cue team leaders about a particular information pattern(s) to assist in identifying critical events unfolding in this dynamic environment.

Neurophysiology-Based Bilateral Asymmetry: A Face in Conflict as a Standoff Biometric Signature of Hostile Emotion or Malicious Intent?

149572
Year 1 of 1
Principal Investigator: I. Dubicka

Project Purpose

The purpose of this feasibility study is to explore the leading-edge neurophysiological concept of using bilaterally asymmetrical facial expressions as a noninvasive indicator, at security checkpoints, of hostile emotions such as contempt, anger, disgust, and/or fear. We will compare published photographs of expressions in right versus left corners of mouths in negative/conflicting cognitive states of individuals in neutral versus booking mugshot scenarios. Distinctive results would provide a remote standoff behavioral indicator of hostile emotions or malicious intentions in potential adversaries within next-generation multimodal biometrics. Further quantification and automation of analytical methods would improve surety against intruders and/or other harm-intending actors at weapon storage facilities, airplane boarding areas, border inspection stations, and/or battlefields. There is currently no dedicated 2D facial-processing laboratory capability at Sandia. Furthermore, imaging sensor exploitation of negative emotional facial expressions for biometrics is not funded at this time.

Functional asymmetries of complex cortical processes are commonplace in the human brain, including differing contributions of the two hemispheres to governance of emotion. Emotionality is more lateralized in the right cerebral hemisphere, particularly the temporal lobe, which dominates the expression and comprehension of the affective aspects of speech. Bilateral hemispheric asymmetry related to emotional expression is observable in individuals confronted with conflicting situations, such as those that pit their (involuntary) feelings against their controlling thoughts and intended public demeanors. Individuals typically express their spontaneous emotions more intensely with their left facial musculature than with the right because the right hemisphere contralaterally controls the left lower face (and vice versa). Right-sided facial musculature more typically represents the posed, cerebrally regulated, and intentional (and possibly deceitful) public display. We can exploit these deltas by having individual faces act as their own experimental controls, and also compare them to neutral (enrolled) passport, badge, or department of motor vehicles photos.

Summary of Accomplishments

We discovered that there are huge differences between neutral images found by using the keyword “face” with the Google search engine and those published as booking mugshots. Mixed expressions, particularly contempt (with a one-sided lip curl) and disgust, as well as combinations of anger and fear with polite smiles or neutral expressions were several orders of magnitude higher in the booking mugshots, some persistently so (such as intense anger throughout three photographs of one female individual over many hours). These findings indicate that conflicted states, with a left-sided (right-hemisphere) negative emotional expression, are much more prevalent in law enforcement environments than those randomly posted to the Internet. Facial cuing by means of such persistently negative or mixed emotional states may be useful in border and airport security checkpoints, as these behavioral indicators can be helpful in behaviorally tagging individuals for follow-up by secondary inspection or further questioning. This newly detected and indentified “Face in Conflict” (FIC) phenomenon of mixed polite smiles with intense negative emotions on one face provides a way of identifying individuals who are not on any watch lists and do not have any prior arrests or detainments on record. Furthermore, behavioral measurements of emotionality on the right versus left sides of the face offers a more scientifically based alternative to national or racial profiling. This study provided theoretical and neuroanatomical validation of the

FIC effect. Further validation and verification work via experimental human studies with university partners and collaborators is proposed for follow-on work in an environment that is more similar to a security checkpoint, where one would expect adversaries to be attempting to escape scrutiny, evade capture, and disguise violent or otherwise harmful objectives against the US.

Significance

Use of remote sensor data on conflicted facial expressions in next-generation biometrics is directly applicable to the DOE national security mission, in that this science and resulting technology could enable some automated surveillance for discovery, detection, identification, and quantification of malevolent emotions — and for related hostile intent. This is an emerging option for eventual data fusion with state-of-the-art iris or facial recognition, facial thermography, vascular pattern, palm geometry, and/or odor typing. Furthermore, some biometrics systems being operationally tested in the field already incorporate remote video camera equipment, particularly for iris detection or enrollment, which could be dual-purposed for detecting and identifying facial emotional expression. Some smartphones already have rudimentary facial and emotional recognition capability, so it would be useful to study these relatively inexpensive technologies and assess their capability for field use in combination with other higher-technology equipment that is already in place. We have the computational capability at Sandia to develop and process algorithms for comparing neutral (enrolled) facial expressions by salient features against right and left and upper and lower hemifaces, in order to compute the deltas and analyze them. Such a set of actual behavioral measurements in individuals transiting security checkpoints would be a useful adjunct or alternative to profiling based on national origin or other static data. Finally, a dynamic measurement of a persistent facial behavior such as negative or conflicted emotional state while walking through a whole-body scanner or being patted-down by a security officer, could provide a potential indicator of malicious intent in individuals who have not been watch-listed or identified in any other way as potential bad actors. This would provide a more objective cue for detaining that individual for secondary questioning or inspection.

Video SAR Compression

149580
Year 1 of 1
Principal Investigator: B. G. Rush

Project Purpose

Synthetic Aperture Radar (SAR) applications are beginning to implement a new operational imagery mode called VideoSAR. VideoSAR movies contain thousands of large SAR (rather than optical) images captured over a few minutes. This VideoSAR mode creates a tremendous amount of data that is a problem to store as well as disseminate from an airborne system to the ground in real time. Also, the success of a VideoSAR product depends on maintaining shadows within the SAR images. We propose compressing the data with a compression scheme that does not degrade the shadow content. This project addresses the precision knowledge area of the Defense Systems and Assessments (DS&A) mission, in terms of performing initial R&D in advanced methods of image processing for sensor systems and supporting technologies. Ultimately, the follow-on technology would be transitioned to a fielded airborne system.

Summary of Accomplishments

The project showed how pre-processing such as speckle filtering and scene rotation removal allows an increase in compression with minimal image degradation. In addition, image quality metrics were developed/implemented such as structural similarity and shadow preservation.

Significance

This activity supports the DS&A's precision knowledge thrust by developing a capability to support our military and the DOE. Sandia currently has several radar programs with deployed systems that would benefit from this image processing scheme.

Co-evolutionary Approach to Countering IED Threats

149654
Year 1 of 1
Principal Investigator: M. E. Senglaub

Project Purpose

The purpose of this project is to demonstrate the foundations of a “what-if” capability that would deal with one aspect of the improvised explosive device (IED) threat. The nature of counter-IED efforts is a very complex co-evolutionary process. A co-evolutionary process is one in which an opponent reacts to actions taken by a protagonist. The Irish Republican Army (IRA) bombing campaign which started in the 1970s is a prime example of a co-evolutionary process: the IRA continually developed new tactics and technologies which required new responses on the part of the British military to mitigate their effectiveness, forcing another cycle of innovation on the part of the IRA. The roots of co-evolutionary analysis are in the field of economics, in which actions taken by an agent must take into consideration the unknown and unpredictable responses of other agents in the system. In countering the IED threat, lacking proper tools or the application of those co-evolutionary tools puts us operationally in a reactive mode that can be costly in terms of men and material. Building on a core in-house capability, called Peircean Decision Aid (PDA), the project demonstrated the foundations of a co-evolutionary “what-if” capability that deals with one aspect of the IED threat. It combined this core capability with in-house subject matter expertise in homemade explosives (HMEs) into a co-evolutionary decision aid for addressing dynamic problems in countering IEDs. Ultimately this capability can be incorporated in a full-scale co-evolutionary environment with embedded reasoning capabilities to deal with complex, dynamic counter-IED problems. The ultimate goal is to provide a capability to anticipate an adversary’s response to counter-IED measures and to mitigate the effectiveness of IEDs as weapons of strategic influence.

Summary of Accomplishments

We discovered that a hierarchical knowledge base holds promise for providing a representation of the homemade explosives process that is easily extensible as new knowledge is gained.

The front-end for the PDA was successfully developed for “bottom-up” analyses. A bottom-up analysis poses questions such as, “If I see X in the environment, what might the adversary be doing?” In this analysis, X might be “blue chemical storage barrels” or “chemical A associated with chemical B.” Such questions have obvious applications to the counter-IED problem.

In addition and unexpectedly, we discovered that it was relatively straightforward to implement an additional capability: the framework for a capability to perform “top-down” analyses. A top-down analysis poses a question like, “I want to attack X; how should I attack it?” X in this case might be a military convoy or an unmounted squad of warfighters. This type of analysis has application to problems involving protecting our warfighters in the field. It also has applications to homeland defense strategies, if X is visitors at a sports stadium or passengers on a train.

Once the front end was implemented to the PDA, a variety of bottom-up and top-down “what-if” scenarios were analyzable using the hierarchical knowledge base for the HMEs selected.

Significance

Using a decision aid has significant advantages in countering the IED threat. It enables the analyst’s experience to be captured in a way that is then easily accessible by other analysts. The PDA then generates all valid hypotheses from the knowledge base. This avoids human biases and foibles and also provides options that are outside the analyst’s experience.

The improvements made in the PDA in this project provide a number of important new capabilities for countering the IED threat. The improvements enable the exploration of tactical responses by both the Red Force and the Blue Force. For example, what if the Blue Force restricted the supply of a critical HME component? How might the Red Force respond? Would the IED threat in a specific theater increase or diminish based on the Red Force response? The improved PDA can explore the answers to such questions. The improvements enable the prioritization of Blue Force investments in counter-IED technologies. What if the Blue Force could detect illicit use of a critical IED component that was previously undetectable? Would this increase or diminish the IED threat? Would this then be a good investment? The improved PDA can be used to explore the answers to these questions.

The results of the work demonstrate the utility of co-evolutionary approaches at varying levels of sophistication. These co-evolutionary approaches can move us from reacting to an adversary’s actions to being better able to anticipate an adversary's next moves and act appropriately, reducing the IED threat and helping to mitigate IEDs as weapons of strategic influence.

3D Precision Decision Analysis

150113
Year 1 of 1
Principal Investigator: F. J. Oppel, III

Project Purpose

Experience with military analysis for in-theater operations has shown there are a lack of tools for understanding complex scenarios and analysis of terrains (land, buildings, etc.) that allow quick tactical desktop analysis and what-if scenario exploration. Difficult critical questions being asked include: where adversaries would hide; best places to observe and attack a point (installation), road (convoy), or area (gathering location); and best locations to place sensors. Most of these questions are dependent on multivariant conditions of speed, stealth, intent, strategy, and ability to traverse terrain. In addition to physical constraints, operations are dependent on ephemeral issues such as communications, information, sensing modalities (optical vs. radar vs. ground sensors) and intelligence. Recent technology developments in path planning and viewshed computation have exposed the possibility of a new generation of planning and analysis tools that enable rapid precision decision-making. We must still investigate a number of analysis techniques to enable a new generation of tools. These include the ability for planning multiple units, understanding needed expressiveness of tools for this type of military analysis, inclusion of dwell time in path-cost estimation, approaches for dealing with more general time-dependence in multi-objective planning, and overlaying communication and information effects on the mission space that would enable more complex viewshed and path planning for these tools. This project will enable more rapid decision-making in tactical mission operations.

Summary of Accomplishments

This research developed an intuitive analysis approach for discovery of mission operation insights in 3D spatial and temporal domains. This technology enables an analyst to locate vulnerable hiding areas and adversarial look-out locations along routes or facilities, to determine optimal sensor locations, and to evaluate sensor probability detection contours based on terrain surface. This work developed an application tool called OpShed (Operations ViewShed) that was built in the Umbra framework. This tool allows an analyst to interactively explore solutions to these questions by rapidly computationally steering the analysis. This research developed a unique situational awareness approach by combining modeling and analysis to anticipate vulnerabilities in order to mitigate risks in battlefields, at physical security sites, and in homeland public arenas. In addition, this research developed an optimization approach for sensor layouts in security design to reduce costs and improve operation accuracy. The optimization approach and the expressive path planner are both candidates for Sandia intellectual property.

Significance

This project will provide Sandia with a unique situational awareness approach and tool for gaps identified by the warfighter. It combines modeling and analysis to anticipate vulnerabilities in order to mitigate risks in the battlefield and in homeland public arenas. It addresses Sandia's strategic mission areas of Defense Systems and Assessment (particularly precision knowledge and precision decisions), Homeland Security and Defense, and relates to special operations forces needs.

Demonstrating Utility of Optical Tags by Considering the Tag/Interrogator System and CONOPS – What's Important?

150117
Year 1 of 1
Principal Investigator: S. A. Kemme

Project Purpose

This project seeks to test a proposed strategy of choosing an optical tag by considering not just the endpoint tag component, but also a larger system that includes the tag, the interrogator, the conduct of operations (CONOPS), and the fundamental photon properties we are sensing. This approach is intended to quantify the utility of optical tags, where radio-frequency (RF) tags are the traditional approach. Clearly, there are differences between these two approaches in terms of area coverage, packaging, and selectivity. Our approach in quantifying these differences is to combine the optical technology (design, fabrication, test, and delivery) expertise within Sandia's Microsystems and Engineering Sciences Applications (MESA) fabrication facility and the expertise in RF tagging tracking locating and CONOPS understanding within Sandia's synthetic aperture radar (SAR) unit to define and demonstrate a figure of merit for optical tags.

Currently, most tags utilize RF technology; optical tags are much less prevalent. We hypothesize that two factors promote this asymmetry: 1) there is no straightforward figure of merit to compare the utility of both technologies; and 2) proposed optical tags are often a combination of commercial off-the-shelf (COTS) parts. These two facts make optical tag technology too risky and ill-defined to encourage use. We will address the first factor by identifying each tag technology's fundamental, measurable parameters and considering them in real-use scenarios, including realistic loss budgets, size, weight, and power (SWAP) aspects. This last point elucidates the second factor that inhibits usage. If an optical tag configuration is limited to COTS components, then it will never be optimal in use or in SWAP. We will not limit our considerations to COTS, but can leverage Sandia's MESA fabrication facility expertise to particularly include optimal microsystems that can minimize SWAP and make optical tag technology more compelling.

Summary of Accomplishments

In this project, we have surveyed commonly deployed thermal infrared (IR) vision systems and optical tagging systems. We take these findings and developed an easy to use radiometric analysis that can be used to determine the performance of optical tags for comparison between different makes and types as well as for integration with RF tagging modalities. This model incorporates atmospheric losses and target properties like temperature and emissivity to determine the appropriate size and range the tag can be imaged with several modern infrared vision systems. Finally, we identify operation modalities in which RF tags can be combined with optical tags in the areas of line of sight communications, low-power applications, and data fusion methodologies.

Significance

This effort tested our proposed strategy of choosing an optical tag by considering a whole-link system, which includes the tag, the interrogator, the CONOPS, and the fundamental photon properties we are sensing. The simple radiometric model we developed allows for easy comparison between different optical tags. We also investigate power requirements of given infrared emitter technology, with an eye toward creating low-power optical signatures. We have identified how optical and RF tags can be compared and used together to obtain orthogonal sensing information. Results of this work will help to demonstrate the utility of this approach for DoD mission applications.

Lethality of Kinetic Energy Projectile (KEP) Warheads in Tactical Engagements

150226
Year 1 of 1
Principal Investigator: J. S. Ludwigsen

Project Purpose

Sandia has been a leader in the development of kinetic energy projectile (KEP) warheads for delivery from high-speed (hypersonic) strategic delivery systems. In these applications, the warhead detonates at reentry velocities and projectiles engage the target at velocities typically greater than 5,000 feet per second. Sandia has engaged the conventional weapons effects community to develop Joint Technology Coordinating Group on Methods and Effects-approved methodologies to assess the effectiveness of KEP warheads in these applications.

There is emerging interest from the DoD Services in employing KEP warheads at shorter ranges for tactical applications. In these engagements, the warheads will be delivered at much lower velocities. These lower velocity target engagements are not well characterized and potentially more difficult to assess. This project will employ state of the art simulation and analysis tools to characterize the KEP blast/fragment expansion behavior at these lower velocities and the KEP-target interactions, and develop simplified methodologies that can be employed by the weapons effects community.

Summary of Accomplishments

This report developed a methodology to assess the performance of a kinetic energy warhead against a range of targets when delivered at velocities less than 5,000 feet per second. A kinetic energy warhead is delivered to the target at high velocities where it deploys small kinetic energy projectiles (KEPs) that spread out and engage the target. The methodology developed in the effort can be used to assess the probability of killing the targets for a given total weight of KEPs and for different KEP sizes. Two targets were evaluated for this project, with one being a small and physically hard target and the other being a large and soft target. The probability of killing each target for different KEP sizes was determined as a function of detonation distance from the target, circular error probable and target location error. We showed that kinetic energy warheads can still be effective at lower delivery speeds if the proper KEP sizes are chosen and attention to the effects of the targeting errors are well characterized.

Significance

Strategic delivery of tactical systems employing KEP warheads enables the force projection mission of DoD (US Strategic Command). These systems potentially provide a capability against classes of targets that may not be effectively engaged by current or envisioned future systems. After development of a methodology to evaluate KEP performance in tactical environments, we anticipate that Sandia will be able to support an important area of growing national interest.

Tunnel Interface Response Modeling

150640
Year 1 of 1
Principal Investigator: S. R. Sobolik

Project Purpose

In attempting to map out underground facilities, be they large-scale hardened deeply buried targets or small tunnels for clandestine border or perimeter crossing, seismic imaging using reflections from the tunnel interface has been one of the better ways to detect and delineate tunnels from the surface. The large seismic impedance contrast at the tunnel/rock boundary should provide a strong, distinguishable seismic response, but in practice, such indicators are sometimes lacking. One explanation for the lack of a good seismic reflection at such a strong contrast boundary is that the damage caused by the tunneling itself creates a zone of altered seismic properties that significantly changes the nature of this boundary. We propose to examine the geomechanical changes caused by tunneling and the consequent effect on seismic velocities to determine whether this gives rise to the lack of strong seismic reflections. There are four potential mechanisms by which tunnel excavation may impact wave propagation in the host rock: creation of large fractures (or enhancement of existing fractures), rubblization of the host rock, localized desaturation of moisture into the tunnel, and significant stress/strain changes around the tunnel. As a first step, we conducted a literature search to locate experimental studies of damage around excavation zones, in particular, looking for evidence of any of these four mechanisms. Using data from the drift scale test at Yucca Mountain, and simulations using a seismic wave code, the development of a methodology for the case of tunnel construction damage will begin, focusing on calculation of damage zone thickness based on geologic medium and construction method, and correlation of these effects to seismic measurements. The cutting-edge aspect is the development of methodology to convert numerical predictions to an estimation of the extent of rock damage around an underground facility and its corresponding seismic velocity.

Summary of Accomplishments

We discovered that the excavation damage zone (EDZ) is, at most, 2 m from the tunnel wall, significantly less than previously thought; that the presence of the damage zone has negligible effect on the waves generated at the tunnel/air interface; and that the assumption of P-wave reflections as the primary wave phenomenon is incorrect, and that the wave form is a spawned wave (possibly a Stoneley wave) developed along the tunnel/air interface. It is important to develop a different methodology for integrating geophone data used to detect the presence of a tunnel; an example of such a method is provided in our report. These simulations specifically evaluated tunnels in good quality rock, for which excavation effects do not propagate great distances in the host rock. These simulations also evaluated tunnels at several hundred meters below the surface, which implies the use of low-frequency seismic wave pulses at the surface, whose wavelengths are larger than the tunnel diameter. Therefore, several potentially important variables were not evaluated: 1) the potential dewatering of the region around a tunnel on wave behavior; 2) the predicted behavior for tunnels in poor quality rock, which may enhance the extent and effect of the EDZ; and 3) tunnels at shallower depths, which would allow the use of higher-frequency waves which may be more affected by the presence of the EDZ.

Significance

The work is relevant to Defense Systems and Assessment /DHS missions requiring characterization of underground facilities and cross border tunnels. It enhances capabilities in detecting and characterizing underground facilities and better understanding damage zones at the air-rock interface. The facilities may differ in geologic media and construction methods. This work builds a methodology to determine the effects of damage zone around the facility on detection measurements, to ultimately lead to methodologies to refine our measurement capabilities and enhance underground facility detection.

Scalable, Broadband, High-Efficiency, Active Planar-Patch Array Antenna for Small UAV-Based SAR Applications

150776
Year 1 of 1
Principal Investigator: B. H. Strassner II

Project Purpose

Sandia is currently engaged in an effort to provide synthetic aperture radar (SAR) sensor technology combined with unique data processing and exploitation techniques to help detect improvised explosive devices. The Joint IED Defeat Organization and the Office of the Secretary of Defense recognize Sandia's contribution as a vital element in this critical effort.

The Copperhead (CH) and Radiant Falcon Ku-Band (RFK) programs at Sandia have developed advanced radar and exploitation systems with the sensor technologies based on the Sandia miniSAR prototype radar. As is expected, the needs of the applications have pushed the limits of some key technologies used in the CH and RFK systems. The antenna and RF front-end electronics is a prime example.

The antenna used in CH and RFK is a refinement of a planar patch array antenna developed at Sandia specifically for the miniSAR suite of potential applications. Strengths of the design include wide bandwidth (essential for fine-resolution SAR), low cost, ease of fabrication, good side-lobe performance, and small size and weight. The major disadvantage of this design is its low radio-frequency (RF) efficiency.

For the stated application, near-future systems must continue to improve major data collection parameters such as swath width (area coverage) and longer ranges. Such requirements erode the radar's critical signal-to-noise ratio budget resulting in unacceptable or substandard data product. With patch array radiation efficiencies on the order of 25% to 35%, the need to overcome this problem is warranted.

The advantages of the extant planar array are too vital to ignore. Therefore, we propose an active sub-array approach that introduces solid-state power devices into the array's RF distribution network to overcome the bulk of the RF losses currently tolerated by the CH and RFK sensors. In addition, migrating from the current traveling wave tube amplifier to solid state technology will increase reliability and will eventually decrease unit cost.

Summary of Accomplishments

This study describes a 200-element array that is constructed for 52 transmitter/receiver (T/R) modules. Each T/R module has a power amplifier in the transmit path and a low-noise amplifier in the receive chain. The array uses a radially symmetric arrangement having weights based on efficiency-reduced multiples of 0.0625 to produce better than 30 dB side-lobe levels over an 18% fractional bandwidth. This aperture arrangement from a design standpoint is somewhat straightforward and can be applied to both passive and active array designs. Fourier analysis is done to predict the array's patterns.

This topology allows for the existence of 52 T/R modules within the aperture that provides essentially a doubling of range versus the passive/MPM system. The DC power draw for 52 TGA2508-SM 1 W parts is 157.6 W. If the drains are pulsed at a 35% duty factor, the DC power requirement becomes 55.2 W. The 55.2 W of DC power represents 18.4% of a Class III unmanned aerial vehicle's total onboard DC power. This is a reasonable amount of power to be diverted to the antenna. This drain pulsing has also been done as part of this project. Drain pulsing also reduces the heat that must be dissipated.

Significance

This project attempts to address some of the performance shortcomings inherent within the patch arrays that are used in various SAR systems at Sandia. There is a desire to increase the standoff operational distances for several of the miniSAR-based SAR systems. These systems are imagining radars used in surveillance and reconnaissance mission in hot spots around the globe. This project has examined how active amplification can be integrated into the antennas to realize increased operational spaces.

ENERGY, RESOURCES, AND NONPROLIFERATION INVESTMENT AREA

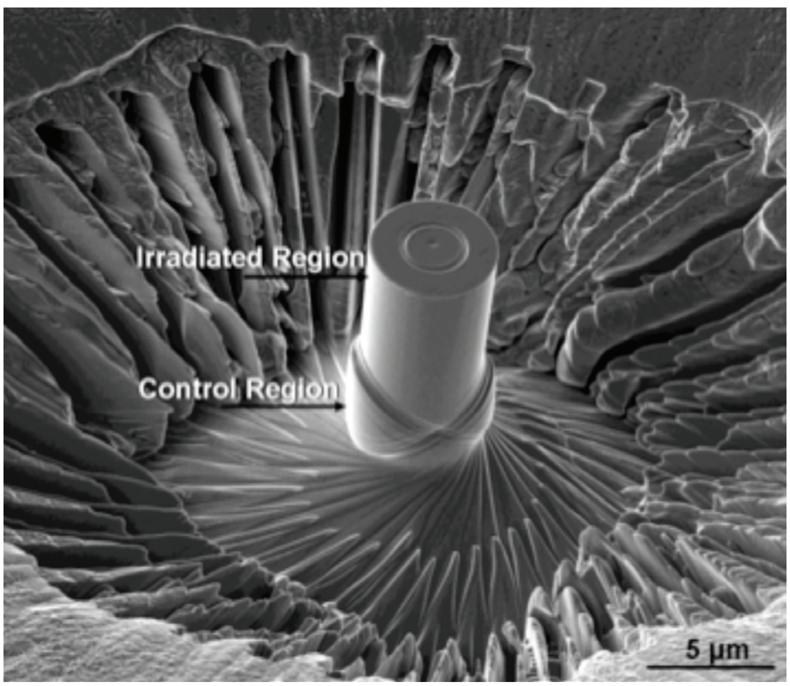
This investment area funds research initiatives in energy S&T, such as solar thermal and photovoltaic, nuclear power and the nuclear fuel cycle, biofuels, liquid transportation fuels and carbon dioxide recycling, the hydrogen economy, and other areas at the cutting edge of domestic and global energy challenge. In addition, the IA addresses diverse issues in nonproliferation of special nuclear materials (SNM) and other materials whose proliferation is potentially a threat to national and global security.

An Ion Beam Platform for Screening and Studying Materials for Use in Fast Neutron Environments

Project 130744

Reviving fast neutron reactor technology is a key element in creating a viable nuclear energy future. Producing materials tolerant to extensive high-energy irradiation is a requirement for any advanced reactor, but there are no currently operative fast neutron reactors in the US

To address this issue, this project is employing high-energy (MeV) ion irradiation combined with a suite of novel, microscale techniques to characterize the thermomechanical behavior of advanced cladding materials as a function of composition, stress, temperature, and irradiation damage level. For example, the project has developed micropillar compression capabilities for micrometer-sized irradiated volumes. Various other types of experimentally based simulations are also being performed. Ultimately, the aim is to clarify the fundamental science behind irradiation damage and mechanical behavior in metallic alloys that will be vital to nuclear fuels modeling efforts and to provide a rapid screening capability for identifying promising new alloys for this extreme environment.



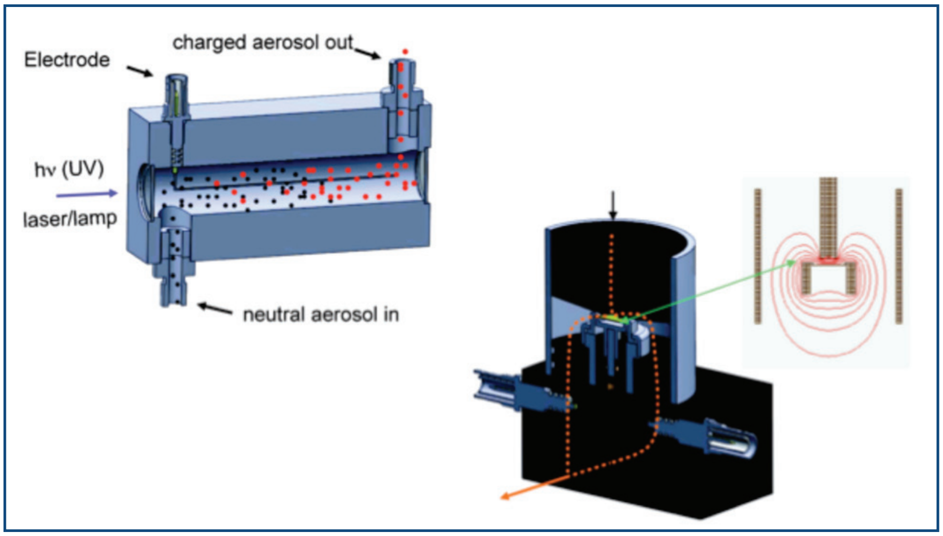
Electron micrograph of a self ion irradiated Cu micropillar produced by focused ion beam milling.

Innovative Control of a Flexible, Adaptive Energy Grid

Project 105865

Very small aerosol particulates are difficult to trap and detect, particularly against the atmospheric background. Examples of important particles include toxic soot aerosols from diesel combustion (typically in the 150 nm size range), trace quantities of uranium in aerosols (potentially indicative of proliferation activities), and biological aerosols possibly connected to bioterrorism.

In order to utilize various techniques (e.g., laser-induced breakdown spectroscopy, mass spectrometry) to diagnose the composition and potential significance of such aerosols, these very fine particulates must first be segregated from background. This project has devised a method for such segregation, using ultraviolet (UV) light to photoionize particles, such that the resulting charged particles can then be trapped in an electric field for subsequent analysis. Careful selection of the exact wavelength and intensity of the UV light source has enabled separation of several types of particulate aerosols.



Drawings of basic design for a device that uses ultraviolet (UV) light to ionize intake aerosol particles, such that they can be separated in an electric field for subsequent analysis.

ENERGY, RESOURCES, AND NONPROLIFERATION INVESTMENT AREA

Phenomenological Basis for Safety Assessment of Nuclear Process Facilities

117791
Year 3 of 3
Principal Investigator: D. A. Powers

Project Purpose

The objective of the project was to identify the generic phenomenological models that would be needed to support a probabilistic risk assessment of a facility for aqueous reprocessing of nuclear fuel. The project focused on the phenomenological threats that arise from fire or energetic interactions in the process stream including hydrogen generation from radiolysis, runaway reactions of hydroxylamine nitrate, radiolytic formation of tributyl phosphate adducts, metallic azides, and the formation and transport of ammonium nitrate in facility ductwork.

Summary of Accomplishments

In the course of work with ammonium nitrate transport, we found that currently available computer codes could not handle expected bounce and breakup of fractal aerosol particles. We therefore developed an innovative method to allow simulation of the formation of fractal aerosol particles by a variety of mechanisms and investigate the response of these particles to impact with solid surfaces. We likewise developed a reaction set for the modeling of water radiolysis and hydrocarbon radiolysis.

Significance

We have identified phenomenological models that must be available to support a risk analysis of reactor fuel reprocessing facilities. Development of risk analysis capabilities for fuel reprocessing will complement existing capabilities for risk analysis of operating reactors and spent fuel repositories. We have also developed a generic tool for the analysis of fractal aerosol formation and impact that will be of use for the analysis of accident phenomena in existing reactors and nuclear fuel cycle facilities. This new tool expands on existing capabilities for analysis of aerosol particle growth by agglomeration. It will allow refinement of existing correlations of aerosol deposition processes to include the potential effects of aerosol bounce and breakup.

The new aerosol tool is being used to assist in the definition of aerosol experiments sponsored at the Paul Scherrer Institut by the US Nuclear Regulatory Commission to investigate radionuclide release during risk dominant steam generator tube rupture accidents in existing reactors. The tool is also being considered for use in the definition of a licensing source term for the Next Generation Nuclear Power Plant, a gas reactor.

The US Nuclear Regulatory Commission has approached Sandia about providing technical support for the efforts to license any proposed facility for the aqueous reprocessing of spent nuclear fuel.

Development of a New Generation of Waste Form for Entrapment and Immobilization of Highly Volatile and Soluble Radionuclides

117792
Year 3 of 3
Principal Investigator: Y. Wang

Project Purpose

The US is planning to revive its nuclear power industries through the Advanced Fuel Cycle Initiative. One of the key components of this initiative is the safe disposition of various waste streams to be generated in spent fuel reprocessing. Immobilizing these waste streams into durable waste forms for long-term disposal is a great technical challenge. The existing waste forms are unable to meet such needs. Disposition of iodine (I-129) and technetium (Tc-99) are particularly problematic, because of their long half-lives and mobility. During fuel reprocessing, a majority of ^{129}I will enter the dissolver off-gas stream, and it is highly desirable to develop a material that can effectively entrap gaseous iodine during the off-gas treatment and then can be directly converted into a durable waste form for long-term disposal. We propose a completely new concept for developing a new generation of waste forms based on nanoscale radionuclide immobilization and encapsulation. We first engineer a suite of nanostructured materials that are able to effectively sequestrate a specific radionuclide and form nanometer precipitates of that radionuclide inside nanopores. The radionuclide precipitates are then be encapsulated by a glass matrix or a crystalline mineral phase so that they are effectively isolated from any contact with outside moisture or liquid water. The resulting waste form is expected to have an unprecedented flexibility to accommodate a broad spectrum of radionuclides, especially volatile or highly mobile ones, with high waste loadings and extremely low leaching rates. In this project, we plan to focus on I and Tc. Success of the project will open a new avenue to the development of new generation of waste forms that can significantly improve waste isolation, expand the waste envelope, and reduce costs related to waste disposal.

Summary of Accomplishments

More than 350 nanostructured materials have been synthesized. These materials have been characterized with x-ray diffraction (XRD), BET (Brunauer, Emmett, and Teller) method, and transmission electron microscopy (TEM). In FY 2010, we have focused on, 1) further optimizing material structures and compositions for the sorption of iodine and noble gas radionuclides, 2) communicating the project results to both scientific community and DOE, and 3) exploring new applications of the synthesized nanostructured materials. We have systematically studied the effect of material chemical composition on radionuclide sorption. We have found a new category of inorganic materials that have an extremely high sorption capability for gaseous iodine uptake, and the related invention disclosure is in preparation. We have also engineered a set of carbon-inorganic nanocomposite materials that have high sorption capabilities for noble gas radionuclides (e.g., Kr and Xe), and the related patent application is ready for submission. A sufficient quantity of nanostructured materials have been synthesized and shipped to Idaho National Laboratory and Oak Ridge National Laboratory for further testing. The results of this project have been presented at various national and international conferences.

Significance

Amid the issues of global warming and energy security, the US is preparing to revive its nuclear power industry. Development of appropriate waste forms for spent fuel reprocessing and disposal is a necessary component for an advanced nuclear fuel cycle. Success of the project has opened a new avenue to the development of new generation of waste forms that can significantly improve waste isolation, expand waste envelope, and reduce costs related to spent fuel reprocessing and waste disposal.

Refereed Communications

Y. Wang, H. Xu, E. Merino, and H. Konishi, "Generation of Banded Iron Formations by Internal Dynamics and Leaching of Oceanic Crust," *Nature Geoscience*, vol. 2, pp. 781-784, October 2009.

Metal Fires and Their Implications for Advanced Reactors

117793
Year 3 of 3
Principal Investigator: T. J. Olivier

Project Purpose

The proposed work aims to establish a general metal-fires expertise, experimental capability, and analysis capability at Sandia to address a key safety issue for the next generation of nuclear reactors. The anticipated nuclear power renaissance hinges on public acceptance and the resolution of safety issues. For example, a cornerstone of the DOE Advanced Fuel Cycle Initiative is the Advanced Burner Reactor. Fast-reactor designs being considered for this and other reactor applications commonly use liquid sodium as the primary and secondary coolant. Some reactor concepts are also based on the use of metallic-form fuels rather than metal oxides. These reactor concepts introduce a unique risk; namely, metal fires. Fire is a dominant contributor to total plant risk even for current generation reactors. Given "passively safe" advanced reactor designs, some elements of plant risk will diminish substantially. Unless the metal fire hazards are mitigated as an integral part of plant design, fires may represent the dominant risk contributor. Metal fires have unique characteristics such as very high temperatures and fire suppression challenges. An enhanced understanding of metal fire behaviors and the availability of appropriate analysis tools will be needed to achieve and demonstrate the mitigation of metal fire hazards. The objectives of the research are to establish a path forward for the treatment of metal fires. This project will advance Sandia's expertise in the science and safety/risk aspects of metal fires, and will establish and demonstrate a metal-fires predictive modeling capability to supplement existing Sandia fire-modeling capabilities. The work will also establish the foundations of a metal-fire experimental capability and will demonstrate that capability through a set of sodium-fire discovery experiments focused on key phenomena of interest. A working collaboration with Japanese researchers will also be pursued to complement existing agreements between Sandia and the Japanese in areas of advanced reactor design and safety analysis.

Summary of Accomplishments

This project addressed some of the significant challenges associated with the use of liquid metal coolants, primary among these being the extremely rapid oxidation (combustion) that occurs at the high operating temperatures in reactors. The project has identified a number of areas for which gaps existed in knowledge pertinent to reactor safety analyses. We developed experimental and analysis capabilities in these areas to varying degrees. In conjunction with team participation in a DOE gap analysis panel, focus was on the oxidation of spilled sodium on thermally massive surfaces. These are spills onto surfaces that substantially cool the sodium during the oxidation process, and they are relevant because standard risk mitigation procedures seek to move spill environments into this regime through rapid draining of spilled sodium. While the spilled sodium is not quenched, the burning mode is different in that there is a transition to a smoldering mode that has not been comprehensively described previously. Prior work has described spilled sodium as a pool fire, but there is a crucial, experimentally observed transition to a smoldering mode of oxidation. A series of experimental measurements have comprehensively described the thermal evolution of this type of sodium fire for the first time. A new physics-based model has been developed that also predicts the thermal evolution of this type of sodium fire for the first time. The model introduces smoldering oxidation through porous oxide layers to go beyond traditional pool fire analyses that have been carried out previously in order to predict experimentally observed trends. Combined, these developments add significantly to the safety analysis capabilities of the advanced-reactor community for directly relevant scenarios. Beyond the focus on the thermally interacting and smoldering sodium pool fires, experimental and analysis capabilities for sodium spray fires have also been developed in this project.

Significance

Previous experimental data (> 30 years old) does not have well-defined boundary conditions needed for the development of predictive fire models. The experimental results have demonstrated new behavior that has not been mentioned previously in the literature. These results will advance Sandia's expertise in the science and safety/risk aspects of sodium fires. The results have established and demonstrated metal fire predictive modeling capability that supplements the existing Sandia fire modeling capabilities.

Ensuring safe secure energy is a central DOE mission. Development of advanced reactors is key to our energy future. Acceptance of new reactors hinges on their assured safety, and metal fires present a unique hazard to future reactor design concepts. This project will directly impact reactor safety assurance benefiting DOE by establishing Sandia's expertise in metal-fire issues and physical phenomenology, a key step in the development of a safety case for various advanced reactor designs.

Design and Evaluation of Border Management Systems

117794
Year 3 of 3
Principal Investigator: H. A. Smartt

Project Purpose

Sandia studied the design and evaluation of border management systems in the context of radiation and nuclear detection along frontier borders in the United States. Sandia completed a baseline report in 2006, in which they identified existing infrastructure on the border, identified technology gaps, and proposed technology improvements. Much has changed regarding the stability of domestic border regions since then, and there are several aspects that the 2006 report did not discuss, emphasize, and/or anticipate. Moving forward from this previous analysis, this report is a 2010 investigation of the current border security situation in the United States, including essential background information, political developments and security updates. Analysis was also performed on existing border security infrastructure and border-localized radiation and nuclear detection technologies. Furthermore, this report presents new technologies that could support future border security work.

Summary of Accomplishments

In year 1, we developed a reference framework to decompose this complex system into international/regional, national, and border element levels covering customs, immigration, and border policing functions. This generalized architecture is relevant to both domestic and international borders. We also developed a set of associated analysis questions for each level to examine a country's border management system as part of an overall engagement strategy toward capacity building. In year 2, we surveyed the technologies and tools that could be used to aid and support the analysis of border management systems and for optimizing the design of enhancements. We also determined some relevant relative measures to better understand border management performance. In year 3, we performed a baseline analysis of the policy, political situation, and the technology used for barrier and intrusion detection. We were able to identify improvements in technology, especially for tunnel detection. We learned (and concluded) that the security situation continues to deteriorate and that technological improvements are necessary to rectify the situation.

Significance

This project supports the following missions: the NNSA mission to detect nuclear and radiological materials and related equipment; the United Nations Security Council (UNSC) mission in meeting the requirements of UNSC regulation 1540; DHS Prevention and Service Objectives; and Department of State agendas for defeating global terrorism, defusing regional conflicts, and cooperative actions. This work uniquely positions Sandia within the complex as the leader in formal border management methodologies and technology development to solve the difficult challenges.

Computational and Experimental Platform for Understanding and Optimizing Water Flux and Salt Rejection in Nanoporous Membranes

117795
Year 3 of 3
Principal Investigator: S. Rempe

Project Purpose

Lack of potable water plagues half the world's population, causing death, disease, and international tension. Furthermore, energy and water are inextricably and reciprocally linked, with production of one requiring use of the other. The best current solution to clean water lies in reverse osmosis (RO) membranes that remove salts from water with applied pressure, but this technology is mature and expensive. Incremental improvements, based on engineering solutions rather than fundamental changes to the materials, have yielded only modest gains in performance over the last 20 years. In order to progress, a breakthrough in materials research is needed. We propose to achieve a potential breakthrough with a fundamental research and development effort that exploits and extends recent advances by our team in theory, modeling, nanofabrication, and platform development. A combined theoretical and experimental platform will be developed to understand the interplay between water flux and ion rejection in precisely defined nanochannels. Inspired by protein channels in biological membranes, we seek to understand the molecular design principles of natural systems that filter water far more efficiently than conventional RO membranes, transcribe them into robust synthetic porous membranes, and optimize them for industrial working conditions. Scientific insight gained by establishing structure/transport property relationships in nanopores will inform new membrane processing strategies amenable to economic large-scale manufacturing. With guidance from worldwide experts in macroscopic membranes, our microscopic membranes will have the potential to be scaled up into practical systems that could enhance the quantity of fresh water supplies at an affordable cost for the nation and the world, thus directly furthering Sandia's commitment to water, energy, national security, and public health issues.

Summary of Accomplishments

We developed a combined theoretical and experimental platform to understand the interplay between water flux and ion rejection in precisely defined nanochannels. Investigations of ion selectivity in biological systems have helped elucidate the principles of ionic selectivity encountered by natural water conducting and ion-selective channels and generate possibilities for their translation into synthetic pores. Based on our achievements in atomic layer deposition and molecular imprinting techniques, we have constructed structures that mimic biological pores in dimensions and exposed functionality. Their atomic-scale was demonstrated using gas molecule size selectivity, and several have been shown to possess improved salt rejection and water permeability. Significant accomplishments have been made toward developing a science-based understanding of the principles for optimization of water flux and select salt rejection in membranes. Both equilibrium and nonequilibrium desalination energy requirements were derived in a form suitable for application to industrial processes, revealing the critical impact of membrane water permeability on overall process energy requirements and the potential ~25% decrease on total energy consumption that could be made possible through future improvements in membrane technology.

Significance

Affordable clean water is critical to global and national security: lack of it can cause death, disease, and international tension. Furthermore, efficient water filtration reduces the demand for energy, another national issue.

Refereed Communications

D. Asthagiri, P.D. Dixit, S. Merchant, M.E. Paulaitis, L.R. Pratt, S.B. Rempe, and S. Varma, "Ion Selectivity from Local Configurations of Ligands in Solutions and Ion Channels," *Chemical Physics Letters (Frontiers Article)*, vol. 485, pp. 1-7, January 2010.

Z. Chen, Y.B. Jiang, D.R. Dunphy, D.P. Adams, C. Hodges, N. Liu, N. Zhang, G. Xomeritakis, X. Jin, N.R. Aluru, S.J. Gaik, H.W. Hillhouse, and C.J. Brinker, "DNA Translocation Through an Array of Kinked Nanopores," *Nature Materials*, vol. 9, pp. 667-675, 2010.

K. Leung and S.B. Rempe, "Ion Rejection by Nanoporous Membranes in Pressure-Driven Molecular Dynamics Simulations," *Journal of Computational and Theoretical Nanoscience*, vol. 6, pp. 1948-1955, August 2009.

K. Leung, S.B. Rempe, and A. von Lilienfeld, "Ab Initio Molecular Dynamics Calculations of Ion Hydration Free Energies," *Journal of Chemical Physics*, vol. 130, pp. 204507-204518, 2009.

K Leung, I.M.B. Nielsen, and L.J. Criscenti, "Elucidating the Bimodal Acid-Base Behavior of the Water-Silica Interface from First Principles," *Journal of the American Chemical Society*, vol. 131, pp. 18358-18365, 2009.

S. Moghaddam, E. Pengwang, and Y.B. Jiang, et al., "An Inorganic-Organic Proton Exchange Membrane for Fuel Cells With a Controlled Nanoscale Pore Structure," *Nature Nanotechnology*, vol. 5, pp. 230-236, February 2010.

C.D. Lorenz, M. Tsige, S.B. Rempe, M. Chandross, M.J. Stevens, and G.S. Grest, "Simulation Study of the Silicon Oxide and Water Interface," *Journal of the Computational and Theoretical Nanoscience,* vol. 7, pp. 2586-2601, December 2010.

S. Varma and S.B. Rempe, "Multi-body Effects in Ion Binding and Selectivity," *Biophysics Journal,* vol. 99, pp. 3394-33401, November 2010.

L. Zhang, S. Singh, C. Tian, Y R. Shen, Y. Wu, M.A. Shannon, and C.J. Brinker, "Nanoporous Silica-Water Interfaces Studied by Sum-Frequency Vibrational Spectroscopy," *Journal of Chemical Physics*, vol. 130, p. 154702, 2009.

S.B. Rempe and K. Leung, "Ab Initio Molecular Dynamics Calculation of Ion Hydration Free Energies," *Journal of Chemical Physics*, vol. 133, p. 047104, 2010.

Development of Efficient, Integrated Cellulosic Biorefineries

117796
Year 3 of 3
Principal Investigator: C. R. Shaddix

Project Purpose

Cellulosic ethanol, generated from lignocellulosic biomass sources such as grasses and trees, is a promising alternative to conventional starch- and sugar-based ethanol production in terms of potential production quantities, CO_2 impact, and economic competitiveness. In addition, cellulosic ethanol can be generated (at least in principle) without competing with food production. However, approximately one-third of the lignocellulosic biomass material (including all of the lignin) cannot be converted to ethanol through biochemical means and must be extracted at some point in the biochemical process. Current biochemical biorefinery design utilizes this lignin residue as boiler fuel to generate the extensive steam heating requirements for the pretreatment and ethanol distillation steps. However, efforts to reduce the energy consumption of these process steps, for example through implementation of membrane-based ethanol distillation, should allow the lignin residues to be largely available for use in thermochemical conversion processes (such as pyrolysis or gasification) for production of additional liquid fuel. In this project we aim to gather basic information on the prospects for utilizing this lignin residue material in thermochemical conversion processes to improve the overall energy efficiency or liquid fuel production capacity of cellulosic biorefineries. The volatilization and combustion and gasification reactivities of characteristic lignin residues will be measured, and "exergy" analysis of canonical thermochemical and biochemical biomass processing systems will be analyzed to determine the most inefficient process steps.

Summary of Accomplishments

Two existing biomass pretreatment approaches, soaking in aqueous ammonia and the Arkenol (strong sulfuric acid) process, were implemented at Sandia and used to generate suitable quantities of residue material from corn stover and eucalyptus feedstocks for subsequent thermochemical research. A third, novel technique, using ionic liquids (IL) was investigated by Sandia researchers at the Joint Bioenergy Institute (JBEI), but was not successful in isolating sufficient lignin residue. Additional residue material for thermochemical research was supplied from the dilute-acid simultaneous saccharification/fermentation pilot-scale process at the National Renewable Energy Laboratory (NREL). The high-temperature volatiles yields of the different residues were measured, as were the char combustion reactivities. Surprisingly, the residue chars showed comparable reactivity to high-rank (i.e. relatively unreactive) coal particles. Exergy analysis was applied to the NREL standard process design models for cellulosic ethanol production from a dedicated thermochemical process (utilizing an indirect gasifier) and from a dedicated biochemical process. The thermochemical system analysis revealed that most of the system inefficiencies are associated with the gasification process and subsequent tar reforming step. For the biochemical process, steam generation from residue combustion, providing the requisite heating for the conventional pretreatment and alcohol distillation processes, was shown to dominate the exergy loss. An overall energy balance with different potential distillation energy requirements shows that as much as 25% of the biomass energy content may be available in the future as a feedstock for thermochemical production of liquid fuels.

Significance

This work aims to substantially improve the ability of the US to efficiently and cost-effectively use biomass feedstocks for production of liquid transportation fuels and other high-value commodities. The US can produce over 1 billion tons/yr of lignocellulosic biomass and through efforts such as that proposed here can significantly reduce the need to import crude oil. This work will also reduce emissions of CO_2 that contribute to global climate change and related geopolitical instabilities. This project's work has significance for the science and technology community, especially with regard to development of advanced biomass pretreatment approaches (i.e., ionic liquids). The new information gathered on the volatiles yield and combustion/gasification reactivity of biochemical process residues will aid computational fluid dynamics modeling of pyrolyzers, combustors, and gasifiers that utilize such residues for generating process heat (steam) and/or liquid fuels in integrated biorefineries. The exergy analysis explicitly implicates the low-temperature gasification process and the combustion of lignin residues for steam generation as the primary sources of inefficiencies in thermochemical and biochemical processing of biomass, respectively. This new insight should assist Sandia and DOE research in improving the efficiency and cost-effectiveness of lignocellulosic biofuels production.

Refereed Communications

D.C. Dibble, C. Li, L. Sun, A. George, A. Cheng, O. Cetinkol, P. Benke, S. Singh, and B.A. Simmons, “Ionic Liquid Pretreatment With Gel-Free Precipitation and IL Recycling Utilizing a Phase-Switchable Solvent System,” to be published in *Green Chemistry*.

K.Y. Teh and A.E. Lutz, “Thermodynamic Analysis of Fermentation and Anaerobic Growth of Baker’s Yeast for Ethanol Production,” *Journal of Biotechnology*, vol. 147, pp. 80-87, May 2010.

Intelligent Power Controllers for Self-Organizing Microgrids

117798
Year 3 of 3
Principal Investigator: S. V. Spires

Project Purpose

Increased energy security, decreased dependence on fossil fuels, and reduction of CO_2 emissions are primary drivers for future DoD/DOE military installation and civilian infrastructures. These goals suggest decreased dependence on 1) fossil fuel-based electricity generation technology, and 2) the traditional centralized architecture of electricity infrastructure. Instead, greater reliance on distributed energy resources (DERs), particularly those utilizing renewable energy, is indicated. A microgrid is a collection of one or more DERs serving one or more loads that can operate autonomously in standalone mode when required. To achieve maximum energy reliability, modularity, and security, the DERs must function as part of an "intelligent" microgrid that can self-configure to meet a diverse set of generation requirements. Most DERs are connected to the grid via power conversion systems (PCSs) to maintain both the electrical stability of the generation/storage sources as well as controlling their operation to maximize some economic or operating benefit.

When a microgrid is built from multiple small DERs, no single DER has control over the entire system; they must work cooperatively to share load and maintain system stability. Today's commercially available PCSs do not have this capability. The technical challenge is to make the PCS capable of implementing distributed control architecture.

This project proposes to tie together Sandia's considerable research base in microgrid technology and distributed agent-based control architectures.

Summary of Accomplishments

We have built three 1000-Watt inverters that can accept 12–200 V_{DC} inputs and produce 120 V_{RMS} single-phase output. Each has complete control and monitoring of every aspect of its operation in software, at every time scale necessary.

We have proven that multiple layers of control and abstraction — from very low-level C device drivers running in real time to very high-level Lisp code running agent software — can work together simultaneously to control power conversion systems while networked communication is taking place. This software environment is quite facile and changeable on the fly.

We have determined the information-processing hardware capability that is necessary to support the above software, having tried several different platforms. This control hardware is modular and can be changed out for hardware of equivalent capability while leaving the power electronics intact, or vice-versa: We can leave the control hardware intact while changing just the power electronics.

We have a library of models of the inverter's operation, including average-value models and switching models in both Matlab and Lisp. The models use the same code as that in the actual inverter, so we can use the models to experiment with new microgrid control algorithms, then immediately test them on real hardware. In addition, we will be able to simulate large microgrids with hardware in the loop.

We conducted numerous experiments on this platform. The rate of generating knowledge of control mechanisms (especially low-level and very low-level ones) has been high, e.g., sigma-delta vs. pulse width modulation, software fault detection, bus sensing for connection/disconnection with automatic time delay discovery.

We have tested the inverter system at Sandia's Distributed Energy Technology Laboratory to benchmark it against commercial inverters. Although "building a better inverter" was not a primary goal of the research, the inverter does perform as well or better than most commercial inverters.

Significance

This project specifically addresses DOE's strategic theme of Energy Security. The results of this project move us forward toward three DOE Goals: Goal 1.1: Energy Diversity, Goal 1.2: Environmental Impacts of Energy, and Goal 1.3: Energy Infrastructure.

We now have a durable hardware and software research facility that validated the idea of software PCS and microgrid control at various levels. This provided us with our first capability to evaluate mechanisms for advanced decentralized control of microgrids. Other ongoing projects will use this facility and expand upon it to develop advanced decentralized control of larger-scale microgrids, with the goal of making electricity generation, transmission, and distribution more robust, more efficient, and less dependent on fossil fuels.

Biosafety Risk Assessment Methodology (Biosafety-RAM)

117805
Year 3 of 3
Principal Investigator: S. A. Caskey

Project Purpose

Laboratory biosafety includes the facility, equipment, and practices used in bioresearch to protect against the risk of accidental exposure to an individual or the community. The biological properties of agents, pathogens, and toxins coupled with the laboratory procedures define the necessary biosafety measures for safe manipulation of an agent. Biosafety experts have historically provided institutions with biosafety recommendations based upon their expert opinion and experience. These recommendations are valuable, but there is no formal methodology on which they are based. This can lead to an inability to explain the recommendations or to assess situations where multiple recommendations may be contradictory.

Sandia is an international leader in understanding biological risk, and has developed a standard methodology and software tool for conducting biological security risk assessments. This project continues the creation of a biosafety methodology than can be shared with the biosafety community and will establish a standard approach to biosafety risk assessment. The project will continue the development of a software tool that can quantify the biosafety risk for a facility, based on the site environment and the agents that the site studies.

Summary of Accomplishments

Ideally, a risk assessment scheme that defines specific frequency of exposure and infection as well as specific consequences of disease would be created. Currently, there is limited frequency data to define the probability of an infection or an exposure, which makes implementing a pure quantitative risk assessment for biosafety problematic. Likewise, there is limited data to quantify the consequence of disease in a host. This begs the question of how a structured systematic biosafety risk assessment might be conducted?

There are several key points to examine regarding biosafety; biosafety and infectious disease expert opinions are valuable and provide a great deal of information on the accepted potential of exposure and infection and can be used to define the consequences of disease. The risks associated with biosafety consist of multiple factors that include the properties of the biological agent, laboratory factors, and environmental factors. Not all of these factors will impact the risk in the same manner. Based on these key elements, this project has developed a biosafety risk assessment methodology and accompanying model that uses a multi-criteria decision analysis process to structure and provide a systems approach to assessing biosafety risks.

This methodology and model were developed by partnering with biosafety and infectious disease experts from around the world. This partnership was used to create the methodology, and specifically define and detail the models. The resulting models have undergone review by international laboratories working with a variety of biological agents and based upon the positive feedback from these laboratories; both the process and the detailed models appear to have been successful.

Significance

This project has formalized Sandia's role in the biosafety community — which allows better leveraging with biosecurity. This project has helped Sandia to better understand key elements of biosafety risk management and has also directly provoked Sandia's increased project portfolio with external agencies. This project is helping develop relationships with international laboratories of US concern and/or interest and has helped to strengthen the practices of biosafety and threat-reduction programs globally. The project has lead to the World Health Organization (WHO) becoming a strategic partner with Sandia, including Sandia's role leading the development of WHO training courses. WHO has also endorsed the methodology and model and aims to license it.

Novel Instrumentation for Selective Photoionization and Trapping of Fine Particles

117810
Year 3 of 3
Principal Investigator: R. Bambha

Project Purpose

The collection and in situ analysis of fine particles is a major challenge. One of the few available indicators of proliferation activities is trace quantities of uranium transported from production sites on fine particles; detection becomes the proverbial "needle-in-a-haystack" problem. In the energy sector, uses of petroleum diesel and important alternative fuels are severely limited by the generation of toxic aerosols that are notoriously difficult to measure. Better soot diagnostics would directly benefit development of clean-burning, highly efficient engines. Progress is hampered in other areas of aerosol detection and measurement (e.g., biological aerosols, chemical agents, explosives) because of problems associated with handling fine particles. Particles of interest can be highly mobile as a consequence of their small sizes (e.g., typical diameter of diesel soot is ~150 nm) and difficult to distinguish against a background of interfering particles (e.g., trace uranium particles among ambient aerosols). We performed efficient collection of nanoparticles and reduction of background interference using ultraviolet (UV) photoionization and electrostatic trapping. This powerful and flexible method of collection will allow us to convey the particles to a wide range of diagnostics (e.g., mass spectrometry, chemiluminescence, laser-induced fluorescence, absorption, and laser-induced breakdown spectroscopies) for real-time analysis. We exploited Sandia's expertise in compact high-energy lasers and nonlinear optics to generate narrow-band UV radiation. Selective fine particle trapping and concentration techniques coupled with miniaturized UV laser sources will allow the development of field-able instruments that are smaller, more sensitive, and more versatile than current state-of-the-art particle detectors. This project leveraged investments in fiber-laser development through a Grand Challenge LDRD and particle diagnostics through the Office of Science Basic Energy Sciences program and will have broad application to multiple areas. It culminated in the development of a High Efficiency Photoionization Controlled Aerosol Trap (HEPCAT).

Summary of Accomplishments

We demonstrated a powerful technique for separating fine aerosols on the basis of composition and arrival-time using photoionization. Having reduced the technique to practice, we have submitted a invention disclosure. We modeled the electron optics using SIMION ion trajectory software and built a variety of flow tubes for separating and trapping aerosols. We have implemented several methods for particle generation and have characterized them with a scanning mobility particle sizer (SMPS). We have used a burner to generate carbonaceous soot (carbon:hydrogen ratio of ~8) from ethylene and air and have installed an arc-discharge particle generator that uses graphite electrodes to generate pure carbon aerosol with controllable size distributions (20–200 nm). We used an atomizer to generate CeO_2 particles, which serve as a target particle. We have produced mixed aerosol streams using CeO_2 and soot, and using our technique we have demonstrated the selective trapping of soot from the stream allowing the CeO_2 to travel downstream to further diagnostics. Using a biased microbalance and SMPS, we have demonstrated trapping of photoionized soot and CeO_2 aerosols with mass measurement. Using a differential mobility analyzer, we have selected ~100-nm sized soot particles from a flame and have studied the number of charges per particle as a function of laser pulse energy, average power, and wavelength. We configured a tunable ultraviolet (UV) laser source using a Nd:YAG laser (1064 nm, 532 nm), dye laser (550-820 nm), and doubling (275-410 nm) and tripling crystals (198-273 nm). The system produces 1–10 mJ in the UV with an available UV wavelength range of 198–410 nm. We performed the proof-of-concept work for a compact laser source for HEPCAT using Nd-doped phosphate glass (lasing bandwidth

~20 nm around 1054 nm) and small tunable holographic mirror (0.25-nm bandwidth) to produced ~190 µJ/pulse, which can be efficiently converted to the UV.

Significance

This project addresses critical detection needs in global security and energy. By introducing a new tool for emissions characterization for alternative fuel development, this project will further efforts to reduce dependence on foreign oil. The techniques developed here will enable new methods for performing time-resolved measurements of soot formation from engines. Time-resolved diagnostics of soot formation will allow exploration of the transient engine conditions that lead to the formation of soot that will facilitate the use of alternative fuels such as biodiesel. By enabling detection of uranium enrichment, this project will facilitate identification of nuclear weapons proliferation activities. One potential application is the detection of fine aerosols escaping from filtration systems in uranium enrichment facilities. Fine particles can then be transported down-wind from the facility. Although these aerosols would be present in a large background of other ambient particles, they could represent strong evidence for weapons proliferation. Significant preconcentration would be required to detect these particles, and a method such as ours would be absolutely necessary. Concentrated samples could be analyzed for isotopic content, a potential "smoking gun" indicator of uranium enrichment. This project will position Sandia at the forefront of particle analysis technology. Our approach leverages Sandia's expertise in lasers, fiber optics, combustion, and detection for nonproliferation and will advance core S&T capabilities in all these areas. The photoionization technique also creates new possibilities for reducing false alarms in airborne biological agent detection by removing known interferences such as soot. The generality of our approach will also benefit applications in other key Sandia business areas including defense and homeland security. This effort brings together capabilities and expertise from both basic and applied organizations within Sandia.

An Ion Beam Platform for Screening and Studying Materials for Use in Fast Neutron Environments

130744
Year 2 of 3
Principal Investigator: K. M. Hattar

Project Purpose

The overall purpose of this project is to devise a rapid testing method to provide a first order validation method for potential cladding materials for Generation IV nuclear power plants. The three aspects associated with this process are: simulation of neutron irradiation using ions, small-scale mechanical testing, and validation of damaged structures by microstructural comparison. Heavy ion irradiation can obtain the 100–500 dpa damage level expected at the end of lifetime in Generation IV reactors within a few days, significantly less than the year time frame that is required in neutron test facilities. As opposed to neutron bombardment, the ion implantation is limited in volume, requiring the use of small-scale mechanical testing. This project has developed micropillar compression and nanoindentation testing parameters that are acceptable for both qualitative and quantitative differentiation of the mechanical properties of the irradiated region. The irradiated regions are then extracted and the resulting microstructure is compared with control samples of the same non-irradiated metal coupon exposed to the same thermal treatment. The radiation-induced defects formed in three stainless steels (316L, 409, 420F) irradiated at 400, 500, and 600 °C to displacement levels of 10, 40, and 100 dpa are compared to microstructures found in similar neutron irradiated samples up to the equivalent damage levels. The microstructural comparison will provide a first-order validation of the technique's applicability in simulating neutron damage. The project then hopes to apply the techniques developed to new alloy compositions and completely novel materials in order to provide an initial screening of potential cladding materials for advanced nuclear reactors. This combination of microstructural analysis, small-scale mechanical testing and ion irradiation will provide a rapid screening technique that should quickly address the materials needs for future nuclear reactors.

Summary of Accomplishments

We designed and implemented a rapid method to implant, mechanically test, and microstructurally analyze the 316L, 409, and 420F stainless steels. First, we designed a rapid testing protocol for the large-spot ion irradiation at well-controlled elevated temperatures to simulate the effects of slower neutron irradiation rates. We then investigated both micropillar compression and nanoindentations, as potential methods for small-scale testing. We found that the micropillars provided reliable information on both the change in hardness and the decreased ductility of the irradiated samples, but needed to be milled to unconventional sizes that were smaller than the irradiated region. The nanoindentation method only provided hardness and modulus information, but required no additional preparation after ion implantation. As a result of the extra time required for preparation of the micropillars, nanoindentation was chosen as the small-scale technique for a first-order comparison of potential cladding materials. In addition to the refinement of the testing technique, we discovered several interesting findings regarding the resulting microstructure produced during ion irradiation at elevated temperatures. We found that in the nanoindentation method for 316L samples, the regions irradiated at 600 °C for all damage levels were similar in hardness to the control region. This is in contrast to the significant difference in hardness reported in the samples irradiated at 400 °C and 500 °C. Transmission electron microscopy microstructural analysis revealed that there was a significant decrease of dislocation loops and other defect structures present in the structure irradiated at 600 °C; and localized compositional analysis revealed that solute segregation occurred in the alloy during ion irradiation at 600 °C, but not at 400 or 500 °C. In addition, we have developed diffusion couples of 316L and various refractory metals that will provide a combinatorial material set that will benefit greatly from the refined validation technique developed.

Significance

The success of this project will provide Sandia with a materials testing platform that will support the development and scientific investigation of structural materials for use in advanced fast-neutron burner reactors and generation IV nuclear energy activities. The DOE Office of Nuclear Energy (DOE-NE) is keenly interested in the support and success of programs such as the Fuel Cycle R&D and the Gen IV reactor development. This project addresses technical needs for these programs. In addition, this capability may be used for future programs involving other types of neutron irradiation, including materials for thermal neutron reactors and fusion reactors.

Cognitive Stakeholder Modeling for Resource Management

130745
Year 2 of 3
Principal Investigator: V. C. Tidwell

Project Purpose

A key national challenge is formulating policies that motivate needed changes in resource production, allocation and management. The difficulty lies in selecting policy options that achieve particular goals while minimizing the potential for conflict. Furthermore, the success of a policy decision can hinge more on human factors than on the technical merits of the policy. A priori analysis is largely beyond the reach of current policy tools because, 1) there is a lack of integrated modeling of human behavior and the environment in which they operate, and 2) collection of primary data for behavioral modeling is costly and time consuming. Our approach is to create a simulation environment that integrates behavioral models of stakeholders with traditional system dynamics (SD) models of resource constraints and economics, with advanced processes and tools (e.g., automated learning, gaming) for expedited data capture. The proposed technical approach expands modeling and data capture to include factors such as stakeholder desires, needs, biases, and influence. The resultant model will aid development of candidate solution sets to streamline negotiation processes by providing perspective to all parties about decision trade-offs and an early assessment methodology to identify potential conflicts. The benefit is assisted decision-making for partners in government and industry across a broad range of complex, uncertain, and potentially conflictive situations, including resource scarcity management, energy production, post disaster recovery, and nuclear waste storage. We will use water planning and management in the Upper Rio Grande basin as an exemplary application.

While component elements of this project exist individually (e.g., behavioral models, environmental models, and stakeholder engagement processes), they have yet to be assembled in an integrated and synergistic manner. A functioning tool linked to a case study with measureable results is necessary to move this concept from the point of research to a point of sponsored project.

Summary of Accomplishments

We have completed a stakeholder map identifying the multiple agendas at play and the groups and individuals that will be key for this project. Through attendance at public meetings, knowledge drawn from project subject matter experts, and perusal of the literature and public documents, we have developed preliminary profiles of each of the primary stakeholder groups, and are nearly finished designing agents for the “zeroth”-order model prototype. We have identified a path into most of the relevant communities and have identified individuals who will be key to entree. We have developed a draft human subjects board submittal, approval of which will allow us direct access to these stakeholders in other than public settings.

We have done research over the past year to determine the state of the art in descriptive decision models that attempt to capture the methods by which people actually make decisions as opposed to an ideal, normative way they “should” make decisions. Often people decide “irrationally” and these models (such as Prospect Theory) modify aspects of normative models to reproduce behavior observed in people. We have based our agent decision models on these descriptive models while also looking to incorporate “softer,” cultural and social impacts on their decisions. We are investigating methods by which to express these “soft” aspects in computational terms and also how to recover the parameters of those expressions through elicitation or other techniques with real stakeholders. We have implemented a general-purpose interface between EMPaSE (extensible multi-paradigm simulation environment) and the PowerSim modeling environment. We will leverage this general interface with PowerSim to connect the cognitive stakeholder models developed in this project to the PowerSim URGSIM (upper Rio Grande simulation) hydrology model of the Rio Grande basin. We have also developed a collaborative relationship with Intel Corporation to couple our decision-support modeling suite of capabilities with Intel's Opensim serious gaming environment.

Significance

While technical approaches to large-scale problem solving can successfully address the predictive components of resource management problems, these approaches largely ignore the impact of human influence on the outcomes. Developing processes and tools for integrating the human and technical elements in decision-support tools holds promise for bridging the gap between science and society. It also provides new insight into some of the most complex problems facing society today. The combined behavioral-environmental system model can foster an alternative approach to participatory thinking and dialogue capable of more effective integration of the affective and cognitive dimensions of policy decision-making. Our approach involves developing tools and techniques for constructing virtual cognitive stakeholders and integrating them with technical resource management models. This will involve the following components: stakeholder engagement, stakeholder behavioral modeling, resource planning and management modeling, and a unifying simulation environment.

The ultimate product of this work is an integrated decision-support platform that marries agent-based and systems dynamics modeling with advanced data capture technologies. While the system is developed for the particular problem of water allocation in the Upper Rio Grande, it can be adapted and transferred to other equally challenging resource management and allocation problems. By bringing the resources all together in one package, we are attempting to change the way stakeholder behavioral models are constructed. By connecting these tools to a serious gaming interface, we are attempting the change the way public-mediated decision-making is performed.

The work proposed advances foundational science and technology by "driving the future" in the realm of energy, resources and nonproliferation technology solutions. Our approach is to create a simulation environment that integrates behavioral models of stakeholders with traditional system dynamics (models of resource constraints and economics, with advanced processes and tools (e.g., automated learning, gaming) for expedited data capture. This combined set of tools and processes is designed to assist decision-making applications in government and industry across a broad range of complex, uncertain, and potentially conflictive situations, including natural resource allocation environmental management; military, medical, disaster recovery and emergency response; and infrastructure planning and coordination. This work is also synergistic with Sandia's Computer Aided Dispute Resolution effort. This multi-agency, multi-university collaboration focuses on open public involvement integrated with transparent, technically informed decision-support computer models to facilitate the negotiation of constructive agreements and win-win outcomes.

International Physical Protection Self-Assessment Tool for Chemical Facilities

130746
Year 2 of 2
Principal Investigator: C. R. Tewell

Project Purpose

The goal of the project was to develop an exportable, low-cost, computer-based risk assessment tool for small to medium size chemical facilities. The tool would assist facilities in improving their physical protection posture, while protecting their proprietary information. In FY 2009, the project team proposed a comprehensive evaluation of safety and security regulations in the target geographical area, Southeast Asia. This approach was later modified and the team worked, instead, on developing a methodology for identifying potential targets at chemical facilities. Milestones proposed for FY 2010 included characterizing the international/regional regulatory framework, finalizing the target identification and consequence analysis methodology, and developing, reviewing, and piloting the software tool.

Summary of Accomplishments

The goal of this work was to develop an exportable, low-cost, computer-based risk assessment tool for small to medium size chemical facilities. In FY 2009, the team completed an initial milestone, which was to create an approach for identifying and prioritizing potential chemical targets. These targets, when used maliciously, can lead to unacceptable consequences such as death, injury, as well as impacting the environment and the chemical industry infrastructure. Algorithms for categorizing chemical weapon agents or precursors, energetic chemicals or precursors, toxic chemicals and two categories of sabotage chemical targets were developed. In addition, work was initiated on methods to identify target categories from a facility chemical inventory using minimal information.

This work served to address a gap in the current list-based approach used by the regulatory community for identifying chemicals of interest. A prioritized list, on the other hand, is beneficial to small and medium-size chemical facilities with limited physical protection resources, such that their resources then can be applied to the targets with the highest conditional risk.

A logical next step would be to calculate a semi-quantitative risk value for each target. This calculation will provide a ranking of each target to identify where resources should be applied to achieve the greatest improvement in physical protection. Such a calculation requires both the likelihood of success of a malicious attack on a particular target as well as the potential consequence of that attack. Extensive analysis of attack methods and chemical plant vulnerabilities would need to be conducted. Ideally, a computer based risk assessment tool would include all of these elements and be customized for the end-user.

Significance

Weapons of mass destruction nonproliferation is part of Sandia's mission and encompasses biological and chemical threats. The objective of this project, reducing the risk from the malicious use of chemicals and chemical facilities, is well aligned with our national security mission.

Linking Ceragenins to Water-Treatment Membranes to Minimize Biofouling

130748
Year 2 of 3
Principal Investigator: S. J. Altman

Project Purpose

Biofouling impacts membrane separation processes for many industrial applications such as desalination, waste-water treatment, oil and gas extraction, and power generation. We propose to use ceragenins to create biofouling-resistant water-treatment membranes. Ceragenins are synthetically produced antimicrobial peptide mimics that display broad-spectrum bactericidal activity. They are simple to prepare and purify on a large scale and are amenable to broad usage because we anticipate that they will not engender resistance. Our goals are to determine the best attachment method of ceragenins to water-treatment membranes, the optimal density and configuration of the ceragenins without compromising the permeate flux, the impact of sustained releasing versus permanently attached ceragenins, and whether the ceragenins will effect the permeate water quality. We will evaluate three methods for attaching the ceragenins to the membranes. Testing the efficacy of ceragenins will include measurement of minimum inhibition concentrations and minimum bactericidal concentrations, measurement of bacteria attachment and an assessment of percentage of bacteria killed on the membrane surface, and measurement of biofouling (flux reduction and bacteria concentration on the membrane surface) in a high-pressure cross-flow system. We will collect relevant source waters (e.g., waters used for steam extraction of heavy oil, surface seawater used for desalination) and culture critical bacteria from these waters. Our testing will expand to controlled single- or multi-species cultures of these critical bacteria and finally, less-controlled tests on the actual source waters. Finally, we will test the permeate waters to determine whether the ceragenins will pass through the membranes. To date the research on the antimicrobial effects of ceragenins have focused on testing drug-resistant bacteria and studies with medical devices. The application of ceragenins to water-treatment membranes is novel. Creation of biofouling resistant membranes will assist in creation of clean water and energy with lower energy usage.

Summary of Accomplishments

We have progressed in our goals of determining 1) the best method of attachment of ceragenins to water-treatment membranes, and 2) the optimal density and configuration of the ceragenins without compromising the permeate flux. We have selected the ceragenin structure that we will be working with: CSA-113. We are pursuing two methods for attaching ceragenins to the membranes: amine-linking and UV grafting. We are testing three types of membranes: a brackish water reverse osmosis (BWRO) membrane and two seawater reverse osmosis (SWRO) membranes. Treated membranes are now being stained with ninhydrin and hyperspectral imaging visualizes CSA-113 distribution on the membrane. Membranes treated with CSA-113 have been tested for their biocidal activity under moderate shear conditions using a cocurrent downflow contactor (CDC) reactor.

Imaging has demonstrated that 1) ceragenins can successfully be attached to the membranes, 2) distribution of ceragenin attachment on the membrane surface could be much more uniform, and 3) UV grafting leads to better attachment than amine linking. Biocidal testing on the CDC reactor has demonstrated that 1) amount of biofilm on the membrane surface can be reduced by almost 80%, 2) trends between membranes are still not apparent, 3) correlation between the imaging and the reactor testing is not apparent. The one test run on the cross-flow system showed very little flux reduction (< 10%) in comparison to a flux decrease of 70% to 80% on untreated membranes tested under the same conditions. Future testing on the cross-flow system will continue.

In summary, results to date look quite promising for both attaching ceragenins to the membrane surface and also using ceragenins to decrease biofouling. However, we strive to have more consistent and better coverage of ceragenins on the membrane surface and also to reduce biofouling to a much greater extent.

Significance

"The continued security and economic health of the United States depends on a sustainable supply of both energy and water. These two critical resources are inextricably and reciprocally linked; the production of energy requires large volumes of water while the treatment and distribution of water is equally dependent upon readily available, low-cost energy." Through creation of biofouling-resistant membranes, this research will facilitate creation of more clean water with less energy use.

Membranes and Surfaces Nanoengineered for Pathogen Capture and Destruction

130749
Year 2 of 3
Principal Investigator: M. D. Nyman

Project Purpose

With increasing population and wealth, we are approaching a critical state with respect to producing enough potable water to sustain the human race. Consequently, radical alternatives such as wastewater treatment, by necessity, become more common. Pathogens in wastewater are amongst the biggest threats to the health of communities that rely on these challenged resources. We propose to design coatings for water filtration media (including membranes and sand) that can help address these issues via controlled capture, destruction and release of pathogens. The proposed coatings are complex nanocomposites that are effective for microorganism capture via chemical affinity, and controlled pathogen destruction/release via photocatalysis. Pathogen capture is accomplished by electrostatics, hydrophobicity, Fe-metabolism, and surface disorder/roughness. Photoactive species in the coating control pathogen destruction, initiated by ultraviolet (UV)-irradiation. Controlled release of water-soluble disinfection byproducts accompanies UV-activation. Characterization of nanocomposite coatings will identify the active components of the coating, and their collective characteristics such as super-molecular ordering and enhanced photo-activity. Collective coating features control efficacy of pathogen capture, destruction and release, and therefore will be identified and optimized. Efficacy of coatings will be tested by filtering contaminated water through the coated media. Pathogen populations on the filtration media and in the filtered water will be quantified. Pathogen destruction/release will be similarly quantified, following irradiation of contaminated filtration media. Attractive/repulsive forces between coatings and microorganisms will be investigated via advanced Atomic Force Microscopy techniques. The coatings developed in this work are foundational to a number of other practical problems in which detection, mitigation, capture or destruction of microorganisms is required.

Summary of Accomplishments

We are developing composite coatings for water filtration media (membranes) that can filter microbiological contaminants by chemical affinity rather than size exclusion, and self-clean by photocatalysis and/or charge-switching. Progress is as follows:

- Optimization of catalyst for photodecomposition of contaminants.

We focused on delaminated layered titanates as the photocatalysts because titanates are inexpensive, robust, and have known photocatalytic activity; layered materials are the ideal morphology for surface coatings. Photocatalysis experiments were carried out comparing layered titanates with standard TiO_2. The results of these studies are currently being written for submission to a peer-reviewed publication. From these studies, we found that all of the layered titanates were very effective photocatalysts at extremely low concentrations (20 micrograms/ml); and more effective than the standard TiO_2.

- Assembly and Atomic Force Microscopy (AFM) characterization of composite coatings and sorbed viruses.

Previously, we reported both inorganic and organic surface functionalization species that sorb MS2 bacteriophage (model virus for study). From these results, we chose an aluminum polycation (denoted GaAl12) to assemble multifunctional coatings. GaAl12 serves two purposes: to attach the photocatalytic layers to an anionic surface, and to render the titanate surface cationic to bind MS2. Using AFM, we imaged a variety of functionalized surfaces. We confirmed that the titanate layers do not adhere to the substrate unless it is initially treated with GaAl12. Likewise, MS2 does not adhere to either the substrate or the titanate layers without a coating of GaAl12. The height of the sorbed titanate layers above the bare substrate ranges from 1-2 nanometers, corresponding to a monolayer. Multiple alternating layers of GaAl12-titanate can also be assembled and imaged. We imaged MS2 phage sorbed onto a GaAl12-modified surface. The smallest spheres observed correspond with a single phage, approximately 25 nm in diameter, and larger spheres are clusters of several phages.

Significance

This research has potential for impact in disciplines including materials, environmental and interfacial sciences; thus contributing to DOE's goal to produce world-class research. Alignment with DOE's mission areas includes the environment and national security, based on potential applications involving mitigation, detection or destruction of pathogens. The research may be applied in DoD, field-based operations including water treatment and personnel protection against infectious disease.

Modeling of Advanced Nuclear Fuel Pins

130750
Year 2 of 3
Principal Investigator: T. J. Bartel

Project Purpose

The core of a fast neutron burner or breeder reactor during a transient event represents one of the most complicated environments possible for structural materials. The ability to simulate the change in the microstructure and the resultant change in mechanical properties of the materials in this environment is vital to predictive models for the safety and performance of the reactor as a whole. Current models can simulate microstructural evolution such as coupled grain growth and bubble migration, but are not directly informed by the mechanical stress and temperature fields. The evolution in microstructure and mechanical phenomena such as cracking, creep, and swelling are intimately related and must be included together for high-fidelity predictive simulations. This project will develop algorithms and capabilities to incorporate the necessary multiple, coupled physical phenomena into a code based on the material point method (MPM). Microstructural evolution such as grain growth and restructuring will be handled by a calibrated Monte Carlo (cMC) model, while plasticity will be handled by continuum crystal plasticity theory. Lower-length-scale physics, such as atomic species transport at interstitial sites, cluster transport and gas re-absorption, will be modeled using diffusion theory with the transport coefficient obtained from direct numerical simulation. These three major methods will be further developed to include new physics such as fission gas bubble at the mesoscale, solid mass transport and fracture. The core challenge of this project will be to combine cMC, diffusive transport and plasticity methods within a MPM-based code in a time consistent manner, to provide a detailed physics-based simulation capability of the thermomechanical behavior of a fuel pin, that is, both fuel and clad, to a transient thermal environment in a computationally efficient timeframe.

Summary of Accomplishments

We have established collaborations within Sandia and Los Alamos National Laboratory (LANL) density functional theory (DFT) groups, so that transport coefficients in actinide materials can be obtained. Unfortunately, DFT functions for the actinides are not well developed at the current time, which result in large uncertainties in the computed activation energies and therefore cannot reasonably predict absolute diffusion coefficients. Colorado School of Mines is working with Sandia and LANL to develop an advanced DFT capability for the actinides. We plan to use a semi-empirical approach to determine diffusion coefficients as a function of strain and temperature and use DFT results only to introduce the effect of strain to experimentally determined diffusion coefficients.

We performed a verification and validation effort of both the Monte Carlo and the gradient-based crystal plasticity models in MPALE (material point automated lagrangian eulerian). We developed a time-implicit strategy and partially implemented into the Lagrangian grid–based strategy in MPALE. We are using the Sandia Aztec parallel matrix solver library. We plan to finish this work this fiscal year. We have determined that the standard MPM algorithm does not satisfy the infinite sump condition for stability. We are investigating the accuracy of the pressure stabilization strategy that was implemented at Sandia into MPALE. We obtained the material properties (e.g., grain boundary energies, elastic coefficient, bulk energies) for UO_2 at high temperatures, implemented them into three crystal plasticity models in MPALE, and compared the results with the experimental data. We have initiated work to include the effects of fuel restructuring in the high temperature gradient of the fuel. Preliminary results show favorable agreement with experimental observations. We are now adding the coupling effects of the elastic mechanical stresses of the fuel and the pore gas pressure for the restructuring process.

Significance

Sandia has had a long-standing and well-established role in safety technologies for nuclear reactors. This computational capability will allow new, advanced fuel configurations and geometries to be analyzed for safety considerations for the Nuclear Regulatory Commission (NRC) and commercial vendors; it will also support Sandia transient fuel experiments and maintain our unique capabilities in this area. In addition, several NNSA technologies will benefit from this code capability (e.g., fatigue of solder joints and ceramics).

Refereed Communications

R. Devanathan, L. Van Brutzel, A. Chartier, C. Guéneau, A.E. Mattsson, V. Tikare, T. Bartel, T. Besmann, M. Stan, and P. Van Uffelen, “Modeling and Simulation of Nuclear Fuel Materials,” *Energy and Environmental Science*, vol. 3, pp. 1406-1426, 2010.

L. Zhang, T. Bartel, and M.T. Lusk, “Independence of Grain Boundary Mobility and Driving Force for Square-Lattice Monte Carlo Models,” *Computational Materials Science*, vol. 48, pp. 790-795, June 2010.

L. Zhang, T. Bartel, and M.T. Lusk, “Parallelized Hybrid Monte Carlo Simulation of Stress-Induced Texture Evolution,” *Computational Materials Science*, vol. 48, pp. 790-795, June 2010.

L. Zhang, T.M. Lusk, T. Bartel, and R. Dingreville, “Parallelized Hybrid Monte Carlo Simulation of Texture Evolution with Plastic Effects,” to be published in *Metallurgical and Materials Transactions A*.

Novel Radiation Detection Technology for Active Interrogation

130751
Year 2 of 2
Principal Investigator: M. A. Grohman

Project Purpose

Various government organizations are funding active interrogation (AI) techniques for substantially increasing the detection signal in numerous national security applications. While there is some small amount of funded effort in the detector systems for AI projects, the majority of current funded efforts are focused on the generation of the actual AI beam. It has been assumed in several government organizations that the existing passive radiation detectors could be used for this other application. However, AI systems involve the operation of detectors in very harsh environments for which they have not been designed.

Sandia has developed a novel microcapillary detector array based on tiny tubes filled with high-pressure helium-4 for fast neutron detection. Because of the miniature size of the individual elements, they are far less susceptible to upset and saturation caused by operation in the harsh environment of a generated radiation beam during AI. Furthermore, the inclusion of many detector elements in a precisely controlled array allows for both spectroscopy and imaging from scattering events, both of which are extremely important to separate the signal from the target with the signal from the beam. An additional benefit is that the inherently massively parallel nature of the devices can lead to very high dynamic range in terms of data rate.

A related issue with AI techniques being pursued today is the lack of understanding of the signal to be detected. Sandia is one of the world leaders in developing algorithms for radiation detection and can apply this vast expertise to the new AI focus area.

Such technology could have widespread national security applications, such as DOE nuclear nonproliferation, DHS nuclear detection, and DoD standoff detection to locate and track nuclear materials.

Summary of Accomplishments

We demonstrated the ability to use high-pressure helium-4 as a scattering mechanism for detecting fast neutrons. This is a vast improvement over the standard thermal neutron detection methods using scarce, expensive, and highly controlled helium-3. By using the Microsystems and Engineering Sciences Applications (MESA) micro-array technology based on modular silicon plate technology, we have demonstrated the ability to scale and fabricate inexpensive neutron sensors to any size.

We also analyzed the efficiency relationship of pressure (as well as many other parameters) with respect to sensitivity, and we further measured the sensitivity of impurities inside the gas to the response parameters. Finally, we demonstrated the ability of MESA micromachine plate technology to contain sufficient gas pressure for neutron detection. Thus, the eventual future of the technology will lie in using inexpensive 3-D pressurized silicon plate stacks instead of a bulky pressure vessel.

Significance

Radiation detection, location, and identification are keys to, and share common requirements with, a number of DOE/NNSA, DHS/Defense Nuclear Detection Office, and DoD/Defense Threat Reduction Agency national security missions. Because the range of detection using passive techniques is limited, all these agencies are funding active interrogation technologies. All such techniques will require detector schemes that are likely to be substantially different from detectors deployed today due to a significantly increased background from the AI source.

The technology demonstrated in this successful project will pave the way for a new future in nuclear materials detection based on modular, inexpensive fast neutron sensing.

Scalable Microgrid for a Safe, Secure, Efficient, and Cost-Effective Electric Power Infrastructure

130752
Year 2 of 3
Principal Investigator: A. L. Lentine

Project Purpose

Distributed renewable energy generation is a key element in transforming society from its reliance on fossil-fuel based energy to a carbon-neutral, sustainable, and secure energy infrastructure. A new power grid architecture is needed that uses information to enable real-time cooperative generation, intelligent metering, load management functions, and to provide decentralized coordination of potentially millions of generation sources and loads.

We propose a fundamental shift in the management and distribution of electricity at the home, local, regional, and ultimately national scale. This consists of developing a "micro-grid" that is scalable at multiple levels (i.e., homes/businesses, neighborhoods, cities, and regions). In this project we will,

- Develop a control architecture for the evolution from the current grid to the scalable microgrid approach, using the theoretical foundation from our team's work in physical and information exergy and multi-agent based control systems at the community, regional, and national scale.
- Apply innovative microsystems technologies to build a low cost, compact power management, sensing, and secure communications module to provide information for managing the microgrid.
- Demonstrate the use of this module for power management of a representative portion of the scalable microgrid at the Distributed Energy Technology Laboratory (DETL).

Summary of Accomplishments

- We have completed the comprehensive intelligent agent controls architecture. We have constrained ourselves to a 100% renewable energy system decoupled from the grid. The demonstration requirements are still being refined based on the evolution of our progress on hardware and the DETL facility's ability to accommodate the verification experiment. We have a preliminary test plan that highlights the scenarios that we wish to run, but will refine that based on simulation scenarios and results.
- We have developed the agent protocol and created a simulation environment on a cluster machine to evaluate grid scenarios using the agent controls.
- We are constructing a smart sensor/actuator that will be able to turn off loads based on sensed voltage and current information obtained either locally or globally in closed loop control. A data sheet has been assembled with complete "specification goals."
- The printed circuit boards have been received and preliminary hardware testing and embedded software development is underway. A test plan for the device is mostly complete.

Significance

Transitioning the electric grid from its current centralized structure to a distributed intelligent scalable grid is required to enable the transition of the US energy infrastructure from fossil-fuel-based energy to a carbon-neutral, sustainable, reliable, and secure energy infrastructure with reduced dependence on foreign oil. We propose key innovations in grid architectures, intelligent distributed controls, and microsystems information technology, all of which will play key roles in this transition.

Space Reactor Impact-Criticality Modeling for Launch Safety

130753
Year 2 of 2
Principal Investigator: R. J. Lipinski

Project Purpose

The purpose of this project is to develop the tools needed to analyze the risk from launch of a nuclear reactor into space. The National Aeronautics and Space Administration (NASA) is anticipating using fission reactors for lunar, Mars and deep-space missions. Launch approval for the reactor must be obtained from the executive branch. The codes used to obtain launch approval for radioisotope power systems (RPS) are well established and are used at Sandia for RPS launch approval, but none exist for fission power systems. Preliminary studies show that the safety requirements for a reactor launch would be easily met unless the reactor goes critical during a launch accident. Reactor criticality could occur at any stage of the deformation resulting from impact on the ground, or impact by large structures onto it. The main technical hurdles that must be overcome are, 1) modeling an impacting reactor with sufficient detail for criticality assessment without excessive computer run times, and 2) coupling the impact code results with a neutronics code to track the event with millisecond resolution. At the end of the project, Sandia would possess a key tool that could support DOE and NASA in future reactor launch safety analysis.

Summary of Accomplishments

We developed computer aided design models (SolidWorks) for an 85-pin reference space reactor, a 19-pin simpler reactor, and very simple single fuel pin test cases. We modeled the impact of a simple test geometry (one fuel pin) onto concrete at 40 m/s and a 19-pin core at 40 m/s with both Pronto3D and Presto. The bottom half of all the fuel pins deformed until they touched each other in the 19-pin simulation. We established a contract with the University of Wisconsin for assistance with the direct accelerated geometry Monte Carlo (DAGMC) code. (DAGMC is the base code that we are modifying to handle the criticality calculation using the deformed geometry output from Pronto3D or Presto runs as input.) We ported DAGMC to Sandia successfully and calculated the change in reactivity in one large fuel pellet. We discovered that the fuel density changed; therefore, correction factors were introduced to ensure conservation of mass. An impact simulation of an 85-pin reactor was performed. We discovered that shell elements, which are needed for timely impact simulations, need special handling in DAGMC. We performed scoping studies for an 85-pin reactor assuming the bottom half of all fuel pins deform until they touch using MCNP (Monte Carlo n-particle code) and found a 5% to 8% increase in keff (neutron multiplication). We wrote three papers for the *American Nuclear Society Topical Meeting on Nuclear Emerging Technologies for Space* and two SAND reports summarizing our results.

Significance

Sandia was assigned the lead role for nuclear launch safety analyses in 2004. Besides being cutting-edge research, this project is strengthening our core capability in safety analysis so that we can be prepared for any future mission that might use a reactor. The US has only launched one reactor and that was in the 1960s. Currently there are no missions planned that would use a reactor power source although periodically the topic is discussed. Consequently this work is anticipatory of a future need. This project helps Sandia prepare for future DOE needs so that when a mission is funded, the techniques can be implemented in a production code in a timely fashion to meet the launch schedule. While DOE would be expected to fund the development of any production code should the need arise, the work being done in this project is examining modeling options and is exploratory in nature.

Additionally, there are other applications of this technology. The techniques being explored in this project can be used to assess the criticality margin for the impact of shipping containers with nuclear fuel or impacts in the transport of small reactors. At present, such analyses are not performed because they are not feasible. Hence, this work offers the hope of developing techniques that can be used for multiple DOE applications.

Complex Adaptive Systems of Systems Engineering and Applications to the Global Energy System

134529
Year 2 of 3
Principal Investigator: R. J. Glass Jr.

Project Purpose

Complex adaptive system of systems (CASoS) are ubiquitous: they include cities, infrastructure, government, armed forces, nations — in short, systems that are socioeconomic-technical in nature. As a national laboratory with an engineering mandate, nearly every important problem that we confront is a CASoS or a component of a CASoS; problems include nuclear stockpile management, nonproliferation, energy surety, and critical infrastructure protection. We must recognize this CASoS context to properly pose and solve problems while not producing unintended consequences: that they are feasible solutions, robust to uncertainties, and enhance system resilience. Of essential importance to this engineering process is the actualization of the solution within the CASoS, a step that is often neglected. We will develop a general CASoS engineering framework for the definition, design, testing and actualization of solutions within CASoS, and a CASoS engineering environment for the implementation of the framework. This development must be done through focus on high-priority, specific applications while keeping an eye on the general. We choose the global energy system (GES) as our CASoS of application. The GES contains both complex earth and complex adaptive human systems including economic, socio-political, and technical systems. The GES is currently the nation's and humankind's highest priority, and the largest, most important CASoS. In context of the framework, we will first define and evaluate several critical issues of high potential impact within the GES. Based on this evaluation, two of these initial applications will be chosen for full implementation. These implementations include the application of cutting-edge CASoS modeling approaches that combine network theory, agent-based models (with both finite and continuous state machines) and uncertainty quantification that integrates verification and validation into the engineering process. The development of CASoS engineering for the GES and beyond to the myriad socioeconomic-technical problems within DOE/NNSA/DHS/national security missions is vital and cannot be accomplished within current programmatic context.

Summary of Accomplishments

This project has moved CASoS engineering at Sandia forward on many fronts. For example, we have accomplished the following:

1. Increased the number of applications considered as we build capability in CASoS engineering through the CASoS Engineering Pilot Phoenix (living manuscript).
2. Continued development of a CASoS engineering framework that addresses the unique aspects of CASoS activities, various strategies for engineering solutions for CASoS engineering processes, and possibilities to leverage efforts if multiple aspirations are undertaken for a given CASoS (living manuscript).
3. Continued development of a CASoS engineering environment that can accommodate emergent theory, algorithms, and tools, the rapid integration of new CASoS engineers and CASoS projects, and effective use of high-performance computing (living manuscript).
4. Set the context for our work in the Global Energy System (GES) with links to interdependent issues of climate and international interdependency.

5. Defined two GES CASoS applications that function synergistically: global energy surety with extended collaboration outside of DOE in the Department of State and international diplomatic community, and strategic energy intelligence with collaboration at DOE and the broader national intelligence community.
6. For the global energy surety CASoS application, we have built models for both a single detailed core economy and for a global network of interdependent nation-states. Each makes use of the same fundamental underlying architecture and uses a networked agent (or “entity”)–based CASoS approach. Model sensitivity and stability analyses to finite energy perturbations are in progress.
7. For the strategic energy intelligence CASoS application, we have designed a new architecture for large-scale life cycle analysis using CASoS principles, gathered required data and represented the energy policy legislation analysis for the American Recovery and Reinvestment Act of 2009 in compatible form. Final development and demonstration of the new life cycle analysis simulator is in progress.

Significance

DOE’s overarching mission is to advance the national, economic, and energy security of the United States. Energy and infrastructure assurance is a mission area for Sandia. The GES is the arena in which both DOE and Sandia carry out their missions. The GES is a CASoS, but it is rarely treated as such. Bringing CASoS approaches and techniques to analysis of the GES will improve Sandia’s and DOE’s ability to optimally perform their respective missions.

Advanced Battery Materials for Improved Mobile Power Safety

141614
Year 1 of 3
Principal Investigator: C. Orendorff

Project Purpose

The objective of this work is to develop abuse-tolerant inactive materials for lithium-ion batteries for transportation applications. While the electrolyte and separator materials of lithium-ion batteries are considered "inactive" materials because they do not directly participate in the electrochemistry of a functional cell, it is well understood that the electrolyte and the separator have significant impact on the abuse tolerance and thermal stability of these cells. The primary concerns with these materials include flammability of the electrolyte, degradation of the electrolyte to generate a large volume of CO_2, and incomplete separator shutdown at modest temperatures (<150 °C) leading to cell thermal runaway. Most conventional approaches to improving the abuse response of these materials include using additives in electrolytes (e.g., flame retardants, stabilizers, etc.) or coating polymer separators with ceramics. However, these approaches do not solve the fundamental problems associated with these materials. Our approach is to mitigate these potential hazards by shifting the focus to utilizing new materials. We have used electrolyte salts and solvent systems that 1) have no flash point and are inherently less flammable and 2) are more thermally stable to minimize the amount of CO_2 decomposition gas generated by each cell. We have also demonstrated the use of lithium-ion battery separators based on teraphthalate polymers that are more thermally stable than conventional poly(ethylene)/poly(propylene)-based conventional separators. This program is unique in that it utilizes innovation in materials science, materials processing/development, fundamental characterization and macroscale testing to develop and verify inherently safer battery materials for the transportation industry.

Summary of Accomplishments

The key accomplishments of the first year of this project include demonstrations of electrolyte thermal stability, reduced decomposition gas generation from hydrofluoroethers (HFE)/sulfonimide electrolytes, preliminary cell performance of electrolytes (voltage stability to 5 V [Li/Li^+]), development of new electrolyte flammability tests, fabrication of terephthalate-based separators, thermal stability of therephthalate separators, and performance of separators in lithium-ion cells. Calorimetry experiments to determine the thermal stability of the standalone electrolyte show an increase in electrolyte degradation temperature from 150 to 250 °C compared to a carbonate/ $LiPF_6$ control sample. Moreover, the total decomposition gas volume (calculated at STP) of HFE/sulfonimide electrolytes is 40-60% less than the carbonate/$LiPF_6$ control (measured standalone and in 18650 cells). In year two, we aim to perform some additional analytical characterization to quantify the degradation gas products in an effort to elucidate these breakdown mechanisms and reactions. Additional calorimetry experiments on 18650 cells show a destabilization in the onset temperature of thermal runaway from 225 to 215 °C using the HFE/ sulfonimide system, likely due to reaction of the HFE with the fully lithiated anode (also gives greater reaction kinetics). However, the total enthalpy of the thermal runaway of 18650 cells is reduced by ~10%.

We have also developed techniques to process highly porous terephthalate separator films using electrospun fibers. We have demonstrated that fibers can be deposited and processed into separator sheets 50-100 μm thick with permeabilities on the order of ~100 s/100 mL (Gurley). While these are as much as five-fold too thick to compete with commercial materials the permeability suggests a high degree of usable porosity in these films as battery separators. Work will continue to process these into larger area (>100 cm^2) and thinner sheets (≤25 μm). These prototype separators are thermally stable to temperatures >210 °C (DTA/TGA) and show good cell cycling and capacity performance in full 2032 coin cells.

Significance

The accomplishments of this program will contribute to the mission as well as road mapping efforts in transportation energy. This program will also have an even greater impact on the broader S&T community. For example, the electrolyte flammability testing that has been developed as part of this work could potentially be adopted by a number of test manuals (SAE J2464, Underwriters' Laboratory, US Advanced Battery Consortium, etc.) en route to becoming a certified test procedure that would influence how future batteries are evaluated. This type of testing could be rolled into follow-on work for others or cooperative research and development agreement programs with outside partners who are interested in evaluating other electrolyte systems. Moreover, in out years, a mature separator materials technology could be licensed to an industrial partner for manufacturing and scale-up.

In general, the results of this program will be used to make recommendations about materials choices in lithium-ion cells that have the potential of improving their overall safety. This work will be leveraged using our comprehensive understanding of safety and abuse response of cells, our ties to the DOE Vehicle Technologies (VT) Programs (FreedomCAR, US Automotive Battery Consortium, and Advanced Battery Research), and association with the general battery community (automotive industry, developers, etc.) to implement system improvements. Given our unique position of being an applied testing laboratory mixed with fundamental research interests makes us well suited to integrate these materials into actual systems and demonstrate their performance. Presenting results from this work to the community led to a great deal of visibility for this program. Our hope is that with good results through the duration of this program, we will be able to apply for follow on funding through the DOE VT office.

Bridging the Gap Between Atomistic Phenomena and Continuum Behavior in Electrochemical Energy Storage Processes

141615
Year 1 of 3
Principal Investigator: S. K. Griffiths

Project Purpose

One of the most significant impediments to advances in electrochemical energy storage lies in the gap between fundamental understanding of atomistic phenomena and the understanding of the impact of these phenomena on system performance at device scales. Atomistic models (density functional theory [DFT], molecular dynamics [MD], Monte Carlo) provide insight into such phenomena and a computational means to quantify these, but such models are too computationally intensive to address device-scale behavior. Similarly, device-scale insight for design and optimization can be obtained through continuum models that are sufficiently fast, but these models account for only the simplest atomistic phenomena. There is thus a large gap between our ability to develop fundamental understanding and our ability to use this understanding to make rapid advances in energy storage technologies. The goal of this project is to help bridge this gap through an innovative synthesis of atomistic and continuum approaches in which atomistic phenomena are captured through fast reduced-order integral methods that can be imbedded directly into continuum-like models describing device-scale behavior. Such a synthesis requires very significant advances in three principle areas, forming the basis of our three project goals: 1) to develop fast but rigorous integral methods describing the electric double-layer structure; 2) to incorporate this description of the double-layer structure into integral models of viscous, diffusive, and electrophoretic transport processes; and 3) to develop accurate reduced-order integral descriptions of surface electrochemical reactions that explicitly account for both the double-layer structure and ion transport. Success in these goals will represent a major advance in our ability to incorporate atomistic electrochemical phenomena into device-scale simulations, thereby enabling accelerated innovation in materials and devices for electrochemical energy storage.

Summary of Accomplishments

To develop the desired integral formulations capturing atomistic phenomena, we have approximated the densities appearing in DFT integrands using simple analytical functions that allow closed-form analytical evaluation of the integrals. To date we have explored three approximations to these density distributions: a local density approximation (LDA) such that densities are uniform over the DFT integration volume; a uniform density approximation (UDA) that all densities are uniform over discrete layers of molecular thickness; and a Dirac density approximation (DDA) representing density distributions as localized spikes, each enclosing a finite mass of each species. We also developed numerical schemes to solve the resulting equations for the equilibrium double-layer structure. We find that each approximation offers strengths and weaknesses. LDA, for example, yields species densities that vary continuously, as in a modified Poisson-Boltzmann equation, and this enables numerical solution of equilibrium states via extremely accurate shooting techniques; however, these solutions do not agree very well with DFT results (discrepancies exceeding 20%). UDA and DDA, on the other hand, yield only discrete density distributions that must be determined by solving a set of nonlinear algebraic equations, but the agreement with DFT is good. This good agreement was confirmed over a very wide range of bulk electrolyte ion concentrations and surface potentials up to 1 Volt, and execution times are much less than one second for most problems. In support of these efforts, we have also extended our DFT capabilities to address high ion concentrations and surface potentials and began developing an MD model (to be completed

8/10) along with a canonical problem set for benchmarking both our DFT results and those of the various integral methods. Here we have identified and explored several increasingly complex and accurate methods for computing the highly problematic long-range electrical interactions between charged species.

Significance

This project supports Sandia's energy and science missions through a new approach to modeling electrochemical energy storage that is fast, accurate, and fully capable of capturing macroscopic manifestations of atomistic phenomena. This approach will enable accelerated innovation in batteries and capacitors for both vehicle electrification and renewable stationary power generation. It also supports our nuclear weapons mission through improved models of the safety and reliability of weapon power supplies.

Development of Coherent Germanium Neutrino Technology (CoGeNT) for Reactor Safeguards

141616
Year 1 of 3
Principal Investigator: B. Cabrera-Palmer

Project Purpose

The purpose of the project is to demonstrate a new antineutrino detector that is much smaller and safer than existing designs, and therefore more likely to find widespread acceptance as a monitoring tool. This detector would be based on high-purity germanium (HPGe) detector technology, which has been widely used for gamma-ray spectroscopy (including by the nuclear power industry). Our objective is to improve the performance of a HPGe detector to be sensitive to an as-yet undetected antineutrino signature — the antineutrino coherent scattering (NCS) off germanium nuclei (we use the acronyms NCS since both neutrinos and antineutrinos interact equally with the germanium nuclei). This process is universally predicted and has a much higher probability of occurrence than other antineutrino interactions, such that a germanium detector of 10 kg would have similar sensitivity to 1 ton of the current scintillator-based detection technology. This would allow a significant reduction in the necessary scale for a complete detector.

The neutrino signature in germanium is not larger than 350 eV, quite below the typical energy threshold of ~1-2 eV of large-mass (~1 kg) germanium detectors. Although state-of-the-art small-mass x-ray detectors have achieved electronic noise thresholds as low as ~60–90 eV, more than 100 channels of electronic readout would be necessary to integrate enough of them. CANBERRA Industries have recently developed a new design for large-mass germanium detectors that has significantly reduced the theoretical noise limit to a level matching the small-mass detectors. Our group had previously acquired an 800 g-prototype from CANBERRA, and preliminary measurements show that it has an electronics noise threshold of ~300 eV. Our goal is to work on a new type of electronic readout and detector mounting that combined with a reprocessed HPGe crystal, would achieve a threshold of ~100–150 eV. This would provide a rate sufficient for the construction of a viable monitoring system.

Summary of Accomplishments

We learned that the measured noise cannot be attributed to the operation of the analog electronic components independent from their connection to the detector enclosure. This was understood by performing detailed SPICE simulations of the existing the pre-amplifier, the high-voltage circuitry, and the junction field effect transistor amplifier that eliminated those components as major sources of the observed noise behavior. This conclusion was confirmed by the noise performance reported by CANBERRA of their small-mass detectors with similar analog electronics. As a result, we isolated the source of unwanted noise contributions to the specific interfaces where the germanium crystal comes in contact with either the preamplifier front-end or the surrounding mounting systems.

To further our understanding of these sources and investigate possible improvements that can be made, we established collaboration with a group from Lawrence Berkeley National Laboratory (LBNL) that develops novel germanium detector systems for radiation detection. Specifically, they have recently been demonstrating a small-mass germanium detector with a noise threshold of ~120 eV that would be sufficient for NCS detection, if this performance could be maintained in a larger detector. The LBNL group is using a novel mounting and electronics system that minimizes any contact between the crystal and any outside materials. We constructed a specific mounting hardware that will allow us to directly integrate our crystal into the LBNL system. We estimated that a near-sea-level deployment, with shielding of manageable size, should not suffer from a significant increase in background from cosmic rays and solar neutrinos. To reach that conclusion, we benefited from the measurements with a similar detector deployed at near-sea-level site in a reactor tendon gallery and at a deep underground mine. Proper thermal-neutron shielding is crucial to control backgrounds associated with nuclei activation. Another lesson is that a large portion of the background can be eliminated through signal processing.

Significance

This project seeks to support Sandia's national security mission by creating a new technology to enable enhanced nuclear safeguards for the Assured Nuclear Future. By creating a new detector technology that will be able to directly monitor and verify the fissile operation of a nuclear power reactor non-intrusively and in real-time, we will be able to assist the international safeguards agencies in supporting the safe and secure expansion of nuclear energy. There is a growing interest in the global safeguards community for the development of antineutrino detection technologies for reactor monitoring. The Novel Technologies division of the International Atomic Energy Agency (IAEA) has already shown great interest in our previous work on antineutrino monitoring of nuclear reactors, and in a recent report ("Final Report: Focused Workshop on Antineutrino Detection for Safeguards Applications", IAEA, 28-October-2008), recognized this technique as a "highly promising technology for safeguards applications." Currently, our work with scintillator technology is supported by DOE, but they consider the coherent germanium technology to be too far from an applicable technology to support under their existing programs. Other agencies have shown interest in the possible advantages that could be provided by a working coherent neutrino detector, but they all await demonstration that the technology is sufficiently mature to warrant developing an applicable detector system.

While antineutrino monitoring of a nuclear reactor has already been demonstrated, the IAEA identifies three technical limitations that prevent immediate incorporation (in the safeguards regime):

- the toxicity and flammability of (liquid) scintillator materials;
- shielding against cosmic backgrounds; and
- the physical footprint of the detectors."

The new germanium detector technology that we propose to establish here directly addresses all of these technical limitations. Cryogenic germanium detectors are already well known and are frequently used at nuclear reactor facilities around the world. As such, the technology would have far greater accessibility with little or no safety concerns from the facility operators. In addition, the ability to shrink the active detector from 1 ton of scintillator material to on the order of 10 kg of germanium would allow for much more flexibility in finding locations suitable for detector installation.

The successful completion of this project would place Sandia in an advanced leadership position for safeguarding the global future of nuclear energy. Successful demonstration that this technology performs with the desired sensitivities will allow the mission-oriented sponsors to fund the further deployment and development that would be necessary to demonstrate this technology's true potential for reactor safeguards. With long-term sponsors such as the IAEA on the horizon, we foresee the potential for eventual collaboration with our industrial partners to transform this into a commercially viable product that would be deployed in all future nuclear reactors around the world. If successful, an important technical output of this project would be the development of a new large-mass germanium detector with unprecedented low noise. First-time observation of neutrino coherent scattering would represent a significant scientific breakthrough.

First-Principles Flocculation as the Key to Low Energy Algal Biofuels Processing

141617
Year 1 of 3
Principal Investigator: J. C. Hewson

Project Purpose

Algal biofuels have the potential to substantially contribute to energy diversity if certain hurdles can be overcome. A significant hurdle is the energy/cost associated with harvesting and dewatering algae. In theory, algae flocculation could drastically lower harvesting costs, but flocculating mechanisms that are reliable, effective, and efficient have yet to be identified. The propensity of algae to flocculate can be related to the properties of the algae surface and its interaction with the water around it. Of key importance is the tendency of algal surfaces to develop a negative charge and the ability of ions in the water to alter the resulting electric double layer. We propose a fundamentally scientific approach to understanding the algae-water interface, its dependence on water chemistry and the manner in which this affects algae flocculation. The objective is to identify conditions favorable to flocculation that take advantage of algal pool chemistry (salinity, pH, etc.) and low-tech flocculating agents (clays, bubbles, etc.). The project will employ an iterative sequence of theoretical predictions leading to hypotheses to be tested experimentally to develop a comprehensive understanding of the algae-water interface physics at the scale of the electric double layer formed on the algal surface and at the scale of potential inter-algae bridging particles. This understanding will be supplemented by fundamental experimental measurements of algae-algae interactions and by high-fidelity simulations of the agglomeration fluid dynamics. A combination of highly controlled experimental environments and those more typically experienced in scaled-up production systems will be studied to identify scaling challenges. The objective is a predictive model of the flocculation potential as a function of water chemistry, fluid mixing rates and low-cost additives that could be applied in the future planning of algal resource development.

Summary of Accomplishments

In the first year, substantial progress has been made in developing capabilities and protocols to improve the understanding of algae flocculation. Algae species of relevance have been identified; initial focus is on species known to grow well in brackish and saline waters. We have identified the importance of life-cycle variations in the surface chemistry of each species since algae surface structure evolves as desirable lipids accumulate; the study of life-cycle variations of the algal surface chemistry has been prioritized. Diagnostics to characterize the algal surface state have been fielded and employed to measure the state of inorganics (kaolin, a model clay flocculant). Models for surface chemistry have been employed to understand surface-charge variation with salt concentration for organic-acid functionalized surfaces characteristic of algae. To measure the sticking affinity of algae, we have employed optical tweezers to trap algae and measure interaction forces as they are brought together and separated. Challenges in these measurements associated with different optical properties of algae relative to yeast (prior work) have been addressed; previous calibrations method used for colloidal particles were found to cause intracellular damage and have been replaced by diffusion-based calibration methods. We are developing simulation capabilities to predict mesoscale floc evolution as a function of fluid shear. Lab-scale facilities and diagnostics for controlled environment measurements of floc population dynamics are nearing completion, and measurements will be initiated this fiscal year. We are implementing models to predict the population balance evolution, on schedule. We have changed an initial plan to focus on moment-methods more suitable for computational fluid dynamics predictions to initially focus on sectional models providing greater fidelity to floc-size effects. The primary reason for this change is to better understand which aspects of moment-based models are required to predict the transition from shear-driven agglomeration to a settling-dominated regime.

Significance

Energy security is a key Sandia mission supporting DOE objectives. Factors such as depletion of worldwide petroleum-based energy resources, coupled with increasing competition for global energy supply from emerging economies such as China and India have created an energy challenge in the US. A DOE energy security goal is energy diversity to increase energy options and reduce dependence on oil. Biofuels are a viable energy option if they can be produced economically and abundantly. Algae represent a novel domestic resource stream for biofuels with many potential benefits. This project addresses key technical hurdles in realizing algae as a resource for substantial energy production. Algal biofuels hold great promise because algae have high lipid contents and can be grown easily in areas otherwise unsuitable for crop production. However, algal biofuels face techno-economic hurdles. A significant hurdle to algal biofuels is the energy cost associated with harvesting and dewatering prior to lipid extraction from the algae. This project moves toward reliable and controllable low-energy flocculation approaches that could drastically lower costs and overcome this hurdle. The outcome of this project will be an improved understanding of algae flocculation and its dependence on the water chemistry, fluid flow patterns, inexpensive additives and algae life cycle. This understanding is developed through fundamental methods, both experimental and computational, and is related to application-scale environments. At the fundamental scale we will demonstrate the use of advanced methods (optical tweezers to measure forces, sophisticated surface complexation models, particle dynamics simulations, etc.) to predict algae flocculation. At the application scale, we will relate algae flocculability to easily measured quantities (pH, salinity, shear mixing rates, etc.). In addition, the improved understanding will be translated into predictive models at three scales. At the algae-water interface, we will develop models to predict the surface energies as a function of water chemistry based on measureable quantities. At the scale of the floc structure, we will enable prediction of relevant geometric quantities like the fractal dimension as a function of the ratio of the shear energy to the surface energy. Given inputs from these fine scales, we will predict the floc population evolution through agglomeration to settling. This improved understanding and the predictive tools associated with it could sharply reduce the energy costs and risks associated with algal biofuels investments. The primary anticipated outputs will be in the form of new knowledge communicated through publications and presentations. Successful approaches to economical and energy-efficient algae harvesting will be converted to intellectual property, if possible.

Novel Room Temperature Synthesis of Nuclear Fuel Nanoparticles by Gamma-Irradiation

141618
Year 1 of 3
Principal Investigator: T. M. Nenoff

Project Purpose

The purpose of this project is the investigation of a novel room temperature synthesis technique for advanced nuclear fuels. This process will use radiolysis to form nanoparticle (NP) nuclear transuranic fuel surrogates. This low-temperature synthesis virtually eliminates any volatility, which is particularly important for syntheses including highly volatile Am melting point, 994 °C). Metallic and oxide alloys of varying compositions can be produced.

Radiolytic formation of nuclear fuel NPs is a completely novel approach to thinking about fuel materials synthesis. This research uses gamma-irradiation for the radiolysis of solvating water to perform room temperature synthesis of metal alloy and oxide NPs. The radiolysis will be performed at Sandia Gamma Irradiation Facility (GIF) ^{60}Co source (3×10^6 rad/hr). This project will focus on the synthesis and characterization of surrogate fuels NPs and their formation to bulk fuels. We will study the NP formation (through the room temperature chemistry of radiolysis and its effect on metal(s) solutions), composition (through use of proper surrogates, such as depleted uranium [dU] and choice of lanthanide for americium), and sinterability to bulk (via high-resolution transmission electron microscopy [HRTEM] at Sandia/CA) of the surrogate fuels.

Production of bulk fuels from NPs is of equal importance to this project. Both metal and oxide NPs will be sintered to achieve consolidation at low temperatures. We will research new powder processing techniques to achieve high density (85 to 90%) bulk fuels. As a result, large quantities of fuels for research purposes will be produced for accelerated advanced nuclear fuel development.

Benefits include the following: 1) low-temperature synthesis conditions mean no volatility of fuel components; 2) production of NPs for sintering; 3) control NP particle size, 4) high reproducibility of the products as pure/homogenous phases; 5) an inexpensive method to make research quantities of fuel surrogates for science-based approaches for fuel cycle R&D needs.

Summary of Accomplishments

We accomplished our milestones for FY 2010 and have started on milestones for FY 2011. We have completed the designing and building of six new reaction vessels for use in the irradiation field at the GIF. Prior to experimentation, we completed all required ES&H RAD Worker I/II classes (handling dU), wrote and accepted operating procedures for dU NP synthesis, wrote and accepted the GIF experimental plan.

Experimentally, we have successfully synthesized dU metal NPs from a variety of starting reactants. These include $dUCl_4$ and $dUO_2(NO_3)_2$ in aqueous solutions. We have begun experiments with alloying dU and $Y(NO_3)_3$. We synthesized NPs and characterization is underway to determine if alloys were formed. All products were characterized by ultraviolet-visible spectroscopy (UV-Vis) for NP formation and composition. High-resolution transmission electron microscopy energy dispersive spectroscopy (HRTEM/EDS) was performed for

NP size and composition.

In an effort to manipulate the oxidation state of the final U metal, we began experiments to replace the water reaction solvent with ionic liquids (IL), such as ethyl-methyl-imidazolium acetate. Literature has shown its ability to sustain metal catalyst NPs and not degrade in radiation environments. To date, we have successfully irradiated the solvent in both short-time, high-dose-rate (300 rad/sec), and long-time, low-dose-rate (6.3 rad/sec) environments without degradation to the IL.

NP samples of the NPs formed at long time, low dose rate (dUO_2) were sent to Sandia/CA and run in heated stage transmission electron microscopy sintering experiments. A number of samples have been sent of varying NP sizes and reaction conditions.

In modeling, we have applied ab initio molecular dynamics to examine the hydration of U(IV) and U(III) species in water. Also, the model to simulate microstructural evolution during solid-state sintering was validated with experimental data.

Significance

This projects addresses the areas of nuclear fuels, and intrinsic and global security. In particular, it focuses on developing novel nuclear fuel systems via new fuel alloy/oxide phases for fuel cycle R&D needs. It also addresses intrinsic and global security by developing a method of introducing tags in fuel alloys for use in verification and safeguard systems (transparency and safe expansion of nuclear energy).

Programmable Nanomaterials for Reversible CO_2 Sequestration

141619
Year 1 of 3
Principal Investigator: B. C. Bunker

Project Purpose

The purpose of this project is to adapt nature's primary CO_2 sequestration processes into an artificial setting. The DOE has set targets for cheaply and reversibly removing one billion metric tons of CO_2 from the atmosphere per year to mitigate the contribution to global warming associated with the burning of fossil fuels. While technologies exist for scrubbing CO_2 from coal fired power plant effluents, these methods are not viable for atmospheric scrubbing because, 1) current sorbants either interact too weakly with CO_2 for efficient capture or too strongly to allow for cost-effective sorbant regeneration, and 2) the sheer volume and cost of sorbant materials required to process billions of tons of CO_2 are prohibitive. In nature, much of the CO_2 being produced is already being removed via: 1) partitioning of CO_2 into water (i.e., the oceans), and 2) biological processes. This project will explore duplicating some of Nature's reversible CO_2 sequestration processes by: 1) utilizing water as the capture agent; 2) utilizing enzymes such as carbonic anhydrase to promote the capture and release of CO_2 from water via the reversible conversion of relatively insoluble CO_2 gas into highly soluble carbonate ions; and 3) utilizing programmable polymers to reversibly switch the solution pH to mediate CO_2 solubility and/or enzyme activity.

Summary of Accomplishments

This project involves learning how to program water to capture and release CO_2 using thermally activated polymers and switchable enzymes. All processes under evaluation involve: 1) promoting capture by converting relatively insoluble CO_2 into highly soluble carbonate ions, and 2) promoting release by catalyzing the reverse reaction. Progress includes the following:

1. Assembly of Capture/Release Equipment — We have procured equipment and established a methodology that allows us to introduce and collect CO_2, quantitatively measure CO_2 concentrations in both gas and solution phases, measure carbonate concentrations in solution, and continuously monitor the extent and kinetics of both capture and release processes. Characterization capabilities include a CO_2 sensor, infrared spectroscopy to monitor both CO_2 and carbonate concentrations, and pH electrodes for following conversions using either pH drift or pH stat titrations.
2. Baseline Capture/Release Experiments — To test our methodology, we have conducted CO_2 capture/release experiments in which CO_2-to-carbonate conversions are induced by adding acid or base to water. We now know how much and how rapidly we can dissolve CO_2 gas into water, convert dissolved CO_2 into carbonates, and release CO_2 gas by decomposing the dissolved carbonates, all in the absence of switchable materials.
3. Theory and Modeling — We have deployed a series of models aimed at understanding the mechanisms by which CO_2 is converted into carbonates in water. As a first step, we have determined the hydration energy for dissolving CO_2 in water based on the competition between ionic, hydrophobic, and steric interactions.
4. Programmable Nanomaterials — We have procured native carbonic anhydrase, and we have developed protocols for genetically modifying this enzyme. We purchased the peptides needed to produce our first programmable polymer based on the protein elastin.

Significance

The ability to cheaply capture CO_2 from the atmosphere is a critical component of the Department of Energy's strategy to mitigate global warming while allowing the expanded utilization of North American reserves of coal, oil, heavy oils, tar sands, and even biofuels. Atmospheric capture would allow us to address this critical environmental issue without requiring the cooperation of other users of fossil fuels such as China.

Radionuclide Transport from Deep Boreholes

141668
Year 1 of 3
Principal Investigator: P. N. Swift

Project Purpose

The purpose of this project is to investigate new approaches for the permanent disposal of high-level radioactive waste in deep boreholes. Disposal in deep (>3 km) boreholes is increasingly seen as a high-safety, low-cost alternative to mined geologic disposal because of low potential for migration and the fact that boreholes can be constructed with existing technology in a reasonably short time-frame. Moreover, the ubiquity of suitable low-permeability crystalline rocks at depth would allow modular disposal of nuclear waste at multiple, regional sites in the US and abroad. However, fundamental technical obstacles remain. 1) The thermal-hydrologic-chemical-mechanical (THCM) controls over radionuclide transport up/along the borehole and through salinity-stratified groundwater must be better understood. 2) New wasteform/backfill additives are needed that will chemically stabilize I-129, the most significant long-lived radionuclide that is mobile under deep borehole conditions. 3) The thermomechanical controls over bentonite backfill and borehole seal materials performance must be predicted. We are conducting an integrated theoretical and experimental analysis of radionuclide transport from deep boreholes that will answer each of these technical questions and produce a science-based plan for borehole disposal. THCM modeling in progress is a “first of its kind” numerical examination of coupled hydro-geomechanical processes under salinity-stratified conditions. Backfill additive research has identified potential bismuth-iodide sequestering agents. Mechanical modeling of borehole seals performance will be verified and calibrated through a parallel experimental program, including investigation of the potential to use molten rock as a sealing agent. Our effort, if successful, will position Sandia to lead US and international efforts in innovative nuclear waste disposal concepts.

Summary of Accomplishments

The project team has presented or published preliminary results in multiple venues, including *Nuclear Engineering International*, The *Annual Meeting of the Geological Society of America*, the *Probabilistic Safety Assessment and Management* 2010 Conference, and multiple internal DOE and national laboratory meetings. Sandia and the Massachusetts Institute of Technology (MIT) co-hosted a well-attended workshop on deep borehole disposal in Washington, DC on March 15, 2010, engaging experts from the US and international community. A brief summary of that meeting has been published as a SAND report.

THCM far-field modeling efforts involved testing and evaluating a suite of codes including: Finite Element Heat and Mass, Java Agent Simulator 3D, ARIA multiphysics and ADAGIO. We set up a test problem for thermal-mechanical processes to consider thermal loading of a 2D system with anisotropic horizontal stress by spent fuel and vitrified waste. THCM near-field modeling efforts resulted in a 3D model for thermal conduction using an unstructured grid for multiple boreholes. We used the model to test thermal interference from multiple boreholes as a function of borehole spacing and thermal load type. We have constructed a 3D thermal-hydrologic model and completed preliminary simulations.

We have synthesized five different bismuth-based sorbents of iodine-129 and tested them for iodide retention at 25 and 60 °C in 0.05 molar sodium sulfate, sodium chloride, and sodium bicarbonate brines. We have identified a prototype bentonite-sand backfill/seal for subsequent testing of chemical transport retardation strategies. We performed simulations of downhole oxygen fugacity to quantify the intrinsic stability of candidate waste forms.

We have completed a preliminary cost analysis for a representative deep borehole disposal concept, and it concludes that although costs are highly uncertain, they can reasonably be expected to be comparable to or less than those projected for Yucca Mountain, which provides the basis for the only detailed estimate of total life cycle costs for a mined repository.

Significance

The ongoing work benefits DOE's national security mission by enhancing the energy security of the US through the development of a technically defensible strategy for storing nuclear waste generated by commercial reactors and DOE defense activities. Demonstrating the potential effectiveness of deep borehole disposal of nuclear waste should enhance the acceptability of domestic nuclear power generation, thereby contributing to national energy security.

Evidence of the national significance of this topic can be seen in the interest in deep borehole disposal shown by the Blue Ribbon Commission on America's Nuclear Future, Nuclear Waste Technical Review Board, the DOE Nuclear Energy Advisory Committee on Fuel Cycle Research and Development, the MIT 2010 Summary Report on The Future of the Nuclear Fuel Cycle, and broad interest in the national press. Sandia's leadership role in R&D related to deep borehole disposal is widely acknowledged.

Safeguards and Arms Control Authentication

141669
Year 1 of 2
Principal Investigator: P. B. Merkle

Project Purpose

International safeguards inspection and nuclear disarmament protocols require rapid and confident determinations that associated equipment and facilities are authentic and free from tampering. Each party must be able to detect counterfeit items or facility alterations that might enable treaty subversion. Periodic inspections ensure the integrity of large structures such as pipe networks, process vessels, and process gloveboxes, since undetected alterations (wall penetrations or hidden ports) may allow material diversion. Inspection to detect tampering or alteration of smaller safeguards monitoring equipment such as cabinets, housings, and communications conduit is necessary to ensure the authenticity of their data, create cost savings through joint use of inspection equipment, and deter material interception. Dismantlement gloveboxes, structural elements, and equipment enclosures must be inspected for subtle alterations to assure confidence in nuclear dismantlement operations. The sealed housings for security and process monitoring equipment must be quantitatively inspected to ensure against data compromise or interception. At present, technology for rapid sensing of physical tampering is not available; a broadly applicable method is challenging, since the materials and surfaces in question vary considerably in complexity, composition, and size. We propose to investigate and develop flash thermographic inspection technology to detect alterations in equipment and structures used for safeguards and arms control. We will research and develop field-applicable inspection methods and materials for coating surfaces to establish the authenticity of equipment and structures for disarmament protocols and international safeguards inspections. This research will provide a unique and widely applicable solution for NNSA, the Defense Threat Reduction Agency, and the International Atomic Energy Agency (IAEA) support program to address known shortfalls in facility and equipment authentication capabilities.

Summary of Accomplishments

The flash thermography system was selected and ordered upon availability of funding in November 2009. The first set of surface treatments were selected and acquired to establish baseline defect detection performance and field application suitability. These were a) clear adhesive plastic film, b) lightly pigmented adhesive plastic film, c) flat black water-soluble paint, and d) high emissivity black tape. We acquired or fabricated material samples for analysis, including ceramic, clay, wood, and concrete panels. We used expert tampering methods to create and repair large full-thickness penetrations in the ceramic, clay, and concrete tiles. We analyzed tiles with a clear plastic coating surface treatment in an initial study. In the initial evaluation, the flash thermography technique showed very promising results on tampered clay, ceramic, and aluminum samples. We studied subsurface cylindrical defects in aluminum using a flat black water-based paint on the front, untampered surface of the metal plate. Inhomogeneities in the applied coating were seen as speckle defects. This highlights the need to develop effective and robust methods for treating the surfaces of inspected objects in the field, since coating or appliqué defects can make inspection more difficult.

Significance

The benefit is a flexible and widely applicable field authentication tool to ensure that other arms control and safeguards capabilities are protected against compromise. This project will bring a novel sensing capability to the field prototype stage, to enable more robust physical authentication for nuclear disarmament operations and IAEA safeguards and other contingency inspections, especially in locations where established safeguards regimes are not in place.

Transportation Energy Pathways

141670
Year 1 of 3
Principal Investigator: T. H. West

Project Purpose

In the coming decades, personal transportation options and the required infrastructure must undergo a fundamental transformation to achieve the nation's economic, environmental, and national security needs. New fuel sources, stronger consideration of greenhouse gas emissions, and application of new technologies will contribute to this transformation to sustainable transportation solutions. Moreover, the heterogeneous distribution of potential resources and populations suggests that the US should consider regional transportation energy systems rather than monolithic national architectures. The complexities and unintended consequences of such a multipronged approach are not well understood. Systematic, dynamic, integrated analysis methodologies and tools are needed to understand the complex transformation from the current petroleum-based transportation system to one that incorporates alternative fuels and electric vehicles.

This project will develop an Energy Pathways Model (EPM) of regionally deployed transportation systems for a representative set of future transportation-energy sources, technologies, and demands. This project will build the modeling and analysis capability required to characterize options for robust, comprehensive and sustainable transportation energy solutions. The EPM will be unique in its comprehensiveness and its ability to analyze the time-evolution of technological development across multiple transportation energy systems. By considering the complex interrelationships of potential transportation energy systems, this capability will enable assessments of the synergies and potential of these systems, identification of technological gaps, and compatibility with the current and future vehicle fleet. This project will create a modular transportation energy pathways analysis methodology that can be continually expanded and improved to provide an enduring capability to answer the transportation energy questions of highest importance to the nation. The EPM will provide a foundational tool for Sandia's transportation energy strategy, will enable Sandia and its partners to assess technology gaps with the highest risks/rewards, and will identify key issues and constraints in transitioning to future transportation energy mixes.

Summary of Accomplishments

We have developed an overall energy pathways systems dynamics model framework that includes three major model components: energy supplies, energy carriers, and vehicles. Macro-level flows consist of cost and energy consumption across each of these major components. Each of these components is further broken down into key variables and flows.

We constructed a national level model that illustrates the role of improved internal combustion engine efficiencies, vehicle electrification, biofuels, and hydrogen vehicles in meeting aggressive national targets for the reduction of greenhouse gas emissions and petroleum use by 2050.

Milestone

1. Reference scenario defined
2. Analytical methodology defined: initial analytical methodology and model structure defined and iterated with outside experts and stakeholders.
3. Input data collection completed: collaboration with University of California (UC)-Davis initiated, graduate student and data collection goals and approach identified; principal data for model components collected.

4. Component model of vehicle electrification complete: national level systems dynamic model developed to demonstrate soundness of basic approach.
5. Year 1 results communicated: multiple discussions with outside stakeholders about model approach and initial results. Model vetted with external partners and UC Davis collaborators.

Significance

This project will create a unique, enduring capability to address the transportation energy questions of highest importance to the nation. The EPM will significantly advance the nation's capability to assess transportation energy transitions to new energy portfolios, evaluate infrastructure implications, and explore technology requirements. This capability will provide a foundational tool for the United States' transportation energy strategy.

Guiding Options for Optimal Biofuels

148066
Year 1 of 3
Principal Investigator: S. M. Paap

Project Purpose

It is widely recognized that current biomass-derived transportation fuels, especially corn-derived ethanol, suffer from a number of shortcomings, including incompatibilities with existing vehicles and infrastructure, resource-intensive production methods, and low energy densities. It is also increasingly well recognized that any sustainable biofuels solution will be highly region-dependent due to differing feedstock growth conditions and available infrastructures. A key piece missing in our understanding is how to integrate these sometimes-competing considerations in order to enable large-scale deployment of biofuels in a responsible manner.

The complex problem of selecting an optimal biomass-derived transportation fuel requires physically relevant yet computationally manageable models that adequately represent the main processes driving the overall system. These components are currently lacking. This project will help close this critical gap by developing simplified models representing the production and composition of biomass feedstocks as well as the conversion of these feedstocks to various fuels. These simplified models will then be incorporated in a multiscale and multidomain model framework that couples the selection and development of feedstocks and conversion processes to provide a basis for exploring the entire pathway from agricultural inputs to the end use of the fuel, while incorporating realistic region-specific constraints such as agricultural conditions, cost, and infrastructure requirements.

The proposed project looks beyond existing technologies and infrastructure in order to probe the fundamental constraints and trade-offs affecting the deployment of biomass-derived transportation fuels. The real innovation here lies in the multidisciplinary integration across temporal, spatial, and conceptual scales that will result in a unique modeling framework that leverages Sandia strengths in systems modeling and analysis in a way that informs better decision-making with sparse and/or uncertain data inputs. We seek to ultimately gain valuable insight into what a future biofuels solution could and should look like.

Summary of Accomplishments

Based on an extensive literature review, we have selected the biomass feedstocks, fuels, and conversion process pathways that will be the focus of investigation. We have constructed frameworks for models of biomass feedstock production and conversion to fuels, and specified the model inputs, outputs, and metrics. The feedstock production model takes as inputs weather data, crop-specific growth parameters, soil data, water availability, and crop management parameters. The model provides as output the yield (tons/ha/year) of dry plant matter, along with the composition in terms of cellulose, hemicelluloses, lignin, starch/simple sugars, ash, and water. The conversion model yields the fuel production (kg/ton of dry biomass) for the chosen fuel and conversion pathway. Both component models will track the following metrics: cost, energy and materials consumption, and net greenhouse gas emissions.

The key processes governing feedstock growth have been identified, based on a survey of the crop modeling literature. Based on widely applied modeling concepts and strategies, a simple model that predicts the accumulation and partitioning of dry biomass over the course of a growing season for a given crop has been established in the MATLAB computing environment. The current model yields potential biomass growth, assuming no limitations on water or nutrients and no adverse effects from pests, weeds, and disease. Additional components will be added to this model framework to enable regional analyses of the production of switchgrass, miscanthus, and short-rotation woody crops.

Based on discussions with colleagues at the Joint BioEnergy Institute (JBEI), several promising biochemical conversion pathways have been identified to produce ethanol as well as so-called “drop-in fuels” from the chosen feedstocks. Major processing units have been identified, and work has begun in modeling the performance of biomass pretreatment, hydrolysis of cellulose and hemicelluloses to sugars, fermentation of sugars to fuels, and product recovery based on key parameters.

Significance

Our efforts to model the conversion of biomass feedstocks to transportation fuels have led to a collaboration with the China Automotive Energy Research Center (CAERC) at Tsinghua University in Beijing, China. A visiting researcher from CAERC is currently participating in joint model development efforts during a two-month stay at Sandia. The joint project will continue beyond this visit, strengthening Sandia’s ties to an important partner and potentially offering opportunities for further collaboration. Our partnership with Tsinghua University in the area of biofuels modeling recently served as the analysis component of a successful proposal to establish a US-China Clean Energy Research Center (CERC) for Clean Vehicles, demonstrating the potential for leveraging our ties to Tsinghua University and CAERC to generate new work for Sandia.

We have also leveraged connections between Sandia and the Department of Energy’s Joint BioEnergy Institute (JBEI) to ensure that our work reflects state-of-the-art knowledge of advanced technologies being applied to the production of biofuels. Our unique access to expert opinion from subject matter experts at JBEI has allowed us to create a framework for the analysis of biofuels production that is general and flexible enough to readily incorporate advances in technology across the entire process. Beyond the current project, this modeling framework may be expanded to incorporate new conversion process pathways; it may also be incorporated into larger models and analyses in support of Sandia’s Energy Security mission.

High Performance Computing for Advanced National Electric Power Grid Modeling and Integration of Solar Generation Resources

149016
Year 1 of 1
Principal Investigator: J. S. Nelson

Project Purpose

Design and operation of the electric power grid (EPG) relies heavily on computational models. Despite being the most complex system ever created by humans, the computational techniques in use today so far have not scaled beyond the workstation level. This has been made possible by accepting a tradeoff between model fidelity and network size. High-fidelity, full-order models are used to study transient phenomena and control interactions; computational limitations dictate that only a small part of the network be represented explicitly. On the other hand, reduced-order dynamic and power flow models are used when analyses involving thousands of nodes are required. This approach works, in part, because the system is normally operated with narrow voltage and frequency tolerances, where system behavior is approximately linear or well understood. The level of complexity of the future EPG will dramatically increase due to large-scale deployment of variable renewable generation, nonlinear controls, active load and distributed generation resources, adaptive protection and control systems, price-responsive demand, and full integration of information networks. The additional complexity introduces a range of new forcing functions or system interactions, ranging from weather-driven generation variability to malicious cyber attacks that can propagate through the system and degrade reliability over wide regions. This will require the simulation of increasingly complex scenarios with higher-fidelity models and much larger number of nodes and network explicitly represented. Modeling of this future grid will require significant advances in the use of high performance computing for higher fidelity, coupled, multiscale tools. This project seeks to demonstrate Sandia's capability to apply HPC resources (e.g., Red Mesa) to the following:

- High-fidelity, large-scale modeling of power system dynamics
- Statistical assessment of grid security via Monte Carlo simulations of cyber attacks
- Development and validation of photovoltaic (PV) output variability models and solar resource forecasting

Summary of Accomplishments

We have developed first-of-a-kind, high-performance massively parallel simulation capabilities for the electric power grid infrastructure in the areas of solar resource forecasting, cyber security attacks, and power systems analysis of high-fidelity temporal and large network topologies. With an increase in variable (solar, wind), distributed renewable energy generation resources on the grid, higher fidelity simulation capabilities are needed to design, operate, and protect the electric power infrastructure. We have developed novel computational algorithms and data handling approaches to enable complex electric grid network performance simulations on the new DOE/Energy Efficiency and Renewable Energy Red Mesa supercomputer at Sandia. Satellite imagery from southern Nevada was analyzed at 15 minute intervals over a year. We developed and tested methods for image stabilization, cloud detection, and textural classification of clouds. Neural networks, using imagery and trained on ground-based measurements of irradiance, were tested and showed promise as a means for predicting irradiance variability. We used Monte Carlo methods to determine reliability impacts for cyber attacks (RICA). RICA approaches measure the impact of cyber attacks by determining unserved loads, many times for different load and grid conditions representative of an attack scenario. We implemented 20,000-bus model of the WECC

(Western Electricity Coordinating Council) on Red Mesa to study cyber attacks and validate the computing algorithms. We developed the power system model by adapting Sandia's scalable electric circuit simulator, Xyce, to include power engineering functions —generators, transformers, transmission lines, loads, substations, feeders, transformers, storage, PV, etc. To demonstrate the new power system simulation capability, we modeled the power grid of New Mexico, including roughly 500,000 residential loads, 200,000 commercial loads, 1000 industrial loads, and 129 generating units. We developed a Google-based visualization map application to display and analyze the simulation data.

Significance

This work aligns with renewable energy and national security mission space while taking advantage of our capabilities in high-performance computing. These models both significantly increase our ability to predict performance and security of the grid and of solar resources.

PV Self-Assembly

149212
Year 1 of 1
Principal Investigator: R. Kemp

Project Purpose

Due to strengths in microsystems technology, Sandia and DOE have significant interests in the manufacture of improved individual photovoltaic (PV) cells, as well as the assemblage of these PV cells into more efficient and effective arrays. The practical uses of these PV cells range from commercial implementation to military applications. The state-of-the-art method now used for placing PV cells on a substrate involves "pick and place" methodology, which is an effective process for current PV chips. However, with advancements in PV cell manufacture leading toward smaller and smaller PV cells, the pick and place technology will become problematic due to increased difficulty in handling these smaller chips, leading to significantly higher costs of placement for each cell as the size decreases. Therefore, fast and versatile assembly of massive numbers of these PV cells by methods other than machine movement is desired. Our objective in this project is to investigate using the chemical principles of "self-assembly" to order PV chips onto a Si-based substrate. These self-assembly principles are well known in other systems such as materials science, but have only been applied in a limited fashion to assembling PV cells. The practical limits of the application of self-assembly techniques to these PV chips are not known. During this initial study, we plan to investigate possible methods of high-throughput self-assembly to provide cost-effective arraying technology for current and next-generation PV cells.

Summary of Accomplishments

Our results have yielded many important and noteworthy findings to those working in PV research. Because "pick-and-place" technology will not be suitable either technologically or economically as PV chips get both thinner and smaller, alternative methods of placing PV cells on ordered arrays will become more important. In fact, alternatives will be required to meet the technology needs. Our approaches have involved using chemical properties frequently employed in molecular self-assembly processes and applying them to much larger objects — micron-sized PV cells. In our recent work, we demonstrated conclusively that gold-dithiol interactions, used prominently in materials science to produce self-assembled monolayers, can also be used to direct the attachment of 250-micron PV cells to substrates. This is very exciting as it demonstrates that objects much larger than molecules can be manipulated into specified locations. In this approach, we also demonstrated that Ag-nanoparticles and Au-mesh particles could also be attached with dithiol chemistry. Hydrophobic patterns were templated onto glass substrates using photolithography techniques. Using these substrates, we demonstrated conclusively that hydrophobic/hydrophilic interactions can be used to selectively direct 1 mm (and smaller) PV cells onto these patterned substrates over a path of several centimeters. Additionally, we also showed that surfactants can be used to alleviate clumping and clustering of the PV cells in solution. This advance will facilitate the future implementation of this self-assembly technology. Most importantly, the movement over a long distance (relative to the chemical scale) of PV cells to pre-designed positions on substrates has been demonstrated. Lastly, the chemical concepts addressed in this work are scalable to larger arrays.

Significance

The use of chemical forces to assist in the assembly and placement of micro-photovoltaic (PV) chips and surrogate objects (gold and silver nano-to-micro sized particles) onto substrates was one of the key technical developments achieved during this project. We used different combinations of chemistry (sol-gel) and techniques (superhydrophobic/hydrophilic patterning) to place chips onto patterned arrays on a substrate. In addition, we used other chemical methods (dithiols leading to self-assembled monolayers) to facially orient micro-PV chips in two-phase solvent systems. These methods directly impact core Sandia and DOE missions in microsystems technology as they can influence the manufacture of improved PV cells. These methods pertain specifically to the assembly of these PV cells into more efficient and effective arrays. Overall, results from this work have shown that the proposed concept of using chemically-assisted assembly of micron-sized objects is clearly achievable. The chemistry involved in these processes is relatively straightforward and can be scaled to large arrays. Furthermore, it is entirely conceivable that these methods can be engineered to be continuous (for example, roll-to-roll processing). Specifically, we have shown that by floating micro-PV chips (ranging in sizes from 250 microns to 1 mm) on water over a superhydrophobic-coated substrate with hydrophilic areas, and then removing the water, the chips are deposited onto the hydrophilic regions. We have also demonstrated that using dithiols in conjunction with micro-PV chips (gold-coated on one side), we are able to facially orient these chips at the boundary layer between a system consisting of water and an organic solvent. This technique allows for the positioning of one-sided, gold-coated chips to be facing upward. Although yet to be demonstrated, taken together, these two methods should allow for the placement and facial orientation of chips (gold-coated on one side) on a superhydrophobic/hydrophilic patterned substrate. These results are of significant interest to the microsystems PV Group and with further development, should allow them to go forward with confidence to manufacture more efficient smaller and thinner PV chips. This chemical-assembly technology should also be adaptable to other systems that require the placement in large arrays of micron-sized electronic components, mirrors, or other microelectromechanical system devices. We believe there are many significant aspects of our research that will resonate with the outside scientific community and the PV groups and microsystems researchers within Sandia. We likewise believe that industrial PV manufacturers will also be interested in the advances in this work, thus aiding the economic security of the US.

Ground Water and Snow Sensor Based on Directional Detection of Cosmogenic Neutrons

149563
Year 1 of 3
Principal Investigator: R. L. Cooper

Project Purpose

The impact of water in society is hard to overstate. Water security and management is only possible with advanced models of hydrologic processes. To build an accurate model, experimental observations of soil water, snowpack, and canopy water content are required. These observations serve as direct inputs into a wide array of applications: rainfall-runoff modeling, stream flow forecasting, ecoclimate, vegetation dynamics, hill slope stability, surface and groundwater interactions, drought monitoring and prediction, fire hazard assessment, and weather prediction. Understanding the climate water cycle requires an unprecedented focus on water measurements that is currently lacking.

The problem addressed in this project is a matter of scale in water content measurements. At one extreme, hydrologists and geologists can assay water content by direct, invasive probing. This method is accurate at length scales of a few centimeters, but it can be quite expensive to obtain time-dependent data for a large number of locations. At the other end of the spatial scale, there is satellite monitoring, which is sensitive at the level of a hundred kilometers square and can provide long-term monitoring. One concern about the satellite data is that it requires on-the-ground calibrations over an area with a diameter of up to several hundred meters. Measurements in this regime have been lacking.

This project addresses the creation of a field-deployable, directionally sensitive neutron detector that utilizes the ubiquitous shower of cosmic-ray neutrons to monitor the local water content. This approach would be a significant improvement over the current procedure of using a single ^{3}He thermal neutron absorption detector where the response is dominated by the water content in the immediate proximity of the sensor. The success of this R&D could lead to the adoption of a new type of sensor into a large-scale, nationwide network of cosmogenic neutron detectors used for water monitoring.

Summary of Accomplishments

- We designed an impulse model of dry and water saturated soil. An impulse response assumes mono-energetic and mono-directional neutron bombardment of the soil mixture. In this way, a completely general, and generic, model for the cosmic ray neutron spectrum can be assumed and convoluted with the individual responses. We are currently analyzing a well-known cosmic ray neutron spectrum model that was previously used in single-event upsets in integrated circuits experiments. We have learned how to model the cosmic ray neutron spectrum from first principles in simulation, in order to corroborate these models. We designed program extensions to MCNP (a well-known monolithic Monte Carlo code) and its various flavors. We have discovered that we can accurately simulate radioactive sources (e.g., Cs-137, Ba-133) to include all steps in its decay chain (beta decay spectra, internal conversion, gamma conversion, x-ray excitation, Auger excitation, etc.).
- We have demonstrated success in similar non-sensitive work, and we intend to write a paper about these helper programs. These results are vital for proper detector calibrations.
- We have discovered our effective detection area for the proposed detector to soil backscattered fast neutrons. We are analyzing the effect of water on these results. We have shown that the proposed detector alleviates oft-cited criticism of single detector counters — sensitivity to only the local area.

- We have designed, constructed, and tested the Mark 1 data acquisition system (DAQ) with plastic scintillators. The DAQ currently uses hardware logic boards to establish a viable trigger to record hardware-processed pulse information (pulse height and a pulse shape parameter and onset time). We are designing a more sophisticated DAQ to extract a higher level of detail.
- We have demonstrated the ability to measure background data from this simple system with plastic scintillator.
- We are designing a liquid scintillator system for accurate background data.

Significance

The primary mission of this project is detection of water in its various forms (rain, soil moisture and saturation, snowpack, forest canopy trapped water, etc.). In order to do so, we use the ubiquitous cosmic ray neutron spectrum as a probe whose behavior is highly susceptible to the hydrogen in water. Active monitoring of water easily presents itself as a defense of the water supply in the face of the very real threat of global climate change. There has been work under this mission. The COSMOS project is a NSF-sponsored program to place water-monitoring stations across the country to track water content. We believe we are designing a complementary detector that is superior in many ways to their proposed ^{3}He thermal neutron counters. We believe that our directional capabilities are a necessary (and possibly sufficient) approach to accurately monitoring a large swath of soil, forest, snowpack, etc.

Outside of defense, the knowledge of the water supply has direct impact on infrastructure, energy use and planning; especially those pursuits that are dependent upon the water supply. Successful conclusion of this work means that planners have access to non-invasive soil moisture measurements over a large swath of land. There is no current technology that can boast a large range (in this case ~100–1000 m) and is non-invasive. Satellites scan over too large an area; direct measurements are short-range and invasive. Hence, this work fills a glaring void in hydrology measurements.

We also maintain a strong overlap with fundamental science because we are measuring effects arising from the cosmic ray neutron spectrum. Because we are essentially measuring changes in the background neutron spectrum and correlating these changes with water content, we must understand the origins of the background spectrum precisely.

Measurement of the background can be extended to measurement of sources that do not resemble the background. In this vein, special nuclear materials detection is an obvious application. Designing a compact, low-power detector, rugged enough to be deployed outdoors is suggestive of a "backpack" SNM detector, for example.

Exploration and Development of Air Bearing Heat Exchanger Technology

149941
Year 1 of 1
Principal Investigator: J. P. Koplow

Project Purpose

Air-cooled heat exchanger technology has changed so little in the past half century that its role in determining the efficiency, reliability, and net carbon footprint of our energy infrastructure has largely been forgotten. Air conditioners, heat pumps, and refrigeration equipment comprise nearly 20% of the load on our nation's electrical grid. A breakthrough in air-cooled heat exchanger technology could reduce this figure by ~30%. The electricity demand spikes imposed by cooling loads are also very detrimental to grid reliability and operating margin. Advances in air-cooled heat exchanger should therefore be a central tenet of any grid-surety strategy. Fundamental advances in air cooling are also badly needed in the information technology sector. For example, CPU clock speeds have remained at ~3 GHz for the past several years simply because of limitations in CPU cooling technology.

As part of prior LDRD funding, we obtained breakthrough results in a proof-of-concept demonstration of the "Air Bearing Heat Exchanger" (SAND report 2010-0258). This work was unusual in that it represented a fundamentally new approach to a very old problem of great importance in the energy sector that appeared to have been studied exhaustively.

At this point, the top priority is the development of a comprehensive fluid dynamic system model. A complete understanding of device physics is required to determine device scaling laws, optimization, and performance trade space. Despite the breakthrough performance obtained with our version-one prototype device, a key point is that this device was designed without the benefit of any fluid dynamic modeling. Based on work conducted to date, we estimate that a factor of three improvement may be attainable in an optimized version of this new air-cooled heat exchanger architecture.

Summary of Accomplishments

The primary objective was technology maturation. Specific tasks include: 1) construction of the version-two prototype, which is predicted to reduce thermal resistance to ~0.1 C/W; 2) implementation of the hydrodynamic air bearing structure; 3) development of the computational fluid dynamics (CFD) analysis capability required for rational design/optimization of the heat-sink-impeller structure; 4) construction of a test bed dedicated to direct measurement of heat-sink-impeller thermal resistance (to facilitate rapid and accurate evaluation of candidate geometries); 5) internal heat flow analysis directed towards reducing the thermal resistance of the base plate and platen while maintaining heat spreading performance; and 6) internal mechanical stress analysis directed towards reducing the thickness of the base plate and platen without adversely effecting mechanical rigidity.

A significant amount of progress has been made in all of these areas, including version 2 prototype fabrication, hydrodynamic air bearing implementation, establishing the CFD analysis capability required for rational design/optimization of the heat-sink-impeller structure (internal heat flow analysis), construction of the heat-sink-impeller test bed for direct measurement of heat-sink-impeller thermal resistance, flow imaging, thermal imaging, and acoustic signature correlation (to facilitate rapid and accurate evaluation of candidate geometries and to elucidate all "missing physics" in the CFD model under development), mechanical stress analysis directed towards reducing the thickness of the base plate and platen without adversely effecting mechanical rigidity, centrifugal deformation analysis, and heat pipe mechanical deformation analysis. Work has commenced on a version-one heat pipe base plate, as has an investigation of how best to carry out de-rotated flow and thermal imaging measurements. All of the above work will be leveraged in FY 2011 activities.

Significance

The proposed work is very relevant to DOE's mission. As applied to cooling equipment such as air conditioners, heat pumps, and refrigeration equipment, for example, a breakthrough in air cooling technology could provide as much as a 6% reduction in total US electrical power consumption. Cooling loads are also the main culprit with regard to electricity demand load spikes. Peak electrical grid loading has a direct bearing on grid surety.

Neutron Imaging of Warheads for Future Treaty Monitoring

149943
Year 1 of 1
Principal Investigator: N. Mascarenhas

Project Purpose

Future strategic arms control treaties may include the need for warhead counting. Such inspections will likely be subject to certain constraints. One of these is that the measurement must not reveal classified warhead information. In addition, a highly desirable feature would be the ability to determine, within a single measurement, the warhead count of a missile. This may be exercised under various formulations such as: 1) explicitly counting each warhead, 2) confirming the declared number of warheads, i.e., by incorporating a priori assumptions, 3) confirming agreement between a measurement and a pre-defined template.

Fast neutron imaging appears to be especially attractive for this arms-control application. Unlike gamma rays, fast neutrons emitted by a warhead do not have the potential to reveal detailed information about the composition of the source, and they easily penetrate the warhead and surrounding material. This project describes an exercise that applies fast neutron imaging to the counting of missile warheads. The goals of this exercise are to demonstrate the application of fast neutron imaging to the mission of arms control and treaty verification. With that in mind, the specific challenge considered here is the counting or verifying of the number of special nuclear material (SNM) sources in a missile.

Summary of Accomplishments

We have developed a neutron surveillance camera (NSC) that directly images fast fission neutrons from SNM sources while simultaneously measuring energy spectra, a feature that potentially allows identification of the source material. We have made many significant advances in the design and implementation of such instruments leading to a dynamic platform that can be switched between high sensitivity mode of operation and high angular resolution mode rapidly. Simulation and modeling of the NSC concept has led to two related advancements in the cameras design. First, that the efficiency of the camera can be improved by decreasing the spacing between the front and rear detector planes. This results in a decrease of resolution by up to a factor of 50%. This also leads to the second result, where increased plane spacing improves the angular resolution of the camera by up to 50%, at a cost of lower efficiency.

We have optimized the camera using MCNP/PoliMi (Monte Carlo N-Particle Transport Code System). We conducted measurements of shielded and moving sources with a 12+12 cell NSC, as well as selected results with a high resolution mode 16+16 cell NSC to count multiple sources simultaneously. We have developed advanced imaging methods namely maximum likelihood estimation methods that enable us to count multiple sources simultaneously. The camera shows great promise for warhead counting and material monitoring applications.

Significance

The START treaty has recently been negotiated. Future warhead reductions the START treaty will require verification. This project helps develop leading-edge technology necessary for verification of warhead reductions and treaty monitoring. Additional benefits accrue in the areas of weapons assurance and weapons or nuclear security. This work directly supports the Sandia national security mission at DOE/NNSA and the Defense Threat Reduction Agency. We have engaged with DOE to conduct a warhead counting exercise.

Analysis of Advanced Biofuels

150114
Year 1 of 1
Principal Investigator: C. A. Taatjes

Project Purpose

The development of new liquid fuels that can readily be derived from cellulosic biomass is one key strategy for reducing the greenhouse-gas intensity of the transportation sector and for improving the nation's energy security. Furthermore, new clean, high-efficiency combustion strategies that rely on compression ignition may be facilitated by chemical characteristics of new fuels. This project analyzes the combustion characteristics of one particular candidate, isopentanol, for which potentially efficient biosynthetic pathways have been identified. Both engine performance and fundamental chemistry of this fuel will be investigated. The coupling of elementary chemistry and engine performance will help determine what molecular structure is related to desired combustion characteristics for advanced engines and begin to provide feedback to the development of fuel biosynthesis strategies.

Summary of Accomplishments

This study characterized some fundamental properties of a C5 alcohol, isopentanol, as a fuel for homogeneous-charge compression-ignition (HCCI) engines. Wide ranges of engine speed, intake temperature, intake pressure, and equivalence ratio were investigated. The elementary autoignition reactions of isopentanol were investigated by analyzing product formation from laser-photolytic Cl-initiated isopentanol oxidation. Carbon-carbon bond-scission reactions in the low-temperature oxidation chemistry were observed that may provide a basis for modeling the intermediate-temperature heat release observed in the engine experiments. Overall, the results indicate that isopentanol has a good potential as a HCCI fuel, either in neat form or in blends with gasoline.

Significance

The development of advanced clean, high-efficiency engines and the design of new biomass-derived fuels are both central parts of the nation's strategy for energy security and climate-change mitigation. We have begun to establish an understanding of the engine performance of isopentanol that is based on knowledge of its fundamental chemistry, demonstrating cooperation among engine, chemical kinetics, and biosynthesis research for biofuel development, an area of strong programmatic interest at DOE. This work introduces isopentanol as a new biofuel to the automotive and fuels industries, and shows that isopentanol performs well. This is a critical first step toward the potential implementation of this fuel.

Refereed Communications

Y. Yang, J.E. Dec, and N. Dronniou, "Characteristics of Isopentanol as a Fuel for HCCI Engines," 2010-01-2164, *SAE International* Paper.

Markings and Patterns for 3D Packages and Components

150120
Year 1 of 1
Principal Investigator: D. P. Adams

Project Purpose

The purpose of this project is to investigate the interactions of continuous wave (CW) laser light with various metallurgical materials in an air environment. In general, we intend to determine if laser-induced oxidation occurs and whether this process is reproducible. With CW laser light inducing oxidation at a metal surface, we explore the microstructure, phase and conformality of surface oxide layers. Additionally, we analyze the rate of oxidation and the roughness of laser-formed oxides. These characteristics are correlated with different laser parameters to examine the feasibility of tailoring surface color pixel-by-pixel.

Summary of Accomplishments

We have demonstrated that a variety of metals and metal alloys can be reproducibly colored in air using a continuous wave Nd:YAG (neodymium-doped yttrium aluminum garnet) laser. The characteristics of laser-grown oxide layers have been investigated. This includes the spectrum of generated colors, the growth rate of oxide layers, the composition of oxides and the evolution of surface roughness. Oxide layers are generally thin, approximately tens of nanometers. Evidence suggests that initial formation of oxide coatings presents a barrier to continued growth, likely limiting oxygen absorption or metal atom outdiffusion to a growing surface. As a result, laser power (as opposed to repeated scanning) is a more effective strategy to tailoring color.

Significance

The work is of general interest to the scientific community interested in laser light-solid interactions. We have revealed details regarding laser-induced, pyrolytic oxidation. In particular, we have demonstrated rates of oxide growth for several materials not previously investigated. We have correlated the colored appearance with the thickness and composition of the formed oxides. Additionally, we have revealed details regarding the surface roughening of laser-grown oxides formed by continuous wave laser irradiation in air.

Enhanced Performance Assessment Tools for Carbon System Management

150632
Year 1 of 1
Principal Investigator: Y. Wang

Project Purpose

Carbon capture and sequestration (CCS) is an option to mitigate impacts of atmospheric carbon emission. Numerous factors are important in determining the overall effectiveness of long-term geologic storage of carbon, including leakage rates, volume of storage available, and system costs. Recent efforts have been made to apply an existing probabilistic performance assessment (PA) methodology developed for deep nuclear waste geologic repositories to evaluate the effectiveness of subsurface carbon storage. However, to address the most pressing management, regulatory, and scientific concerns with subsurface carbon storage (CS), the existing PA methodology and tools must be enhanced and upgraded. For example, in the evaluation of a nuclear waste repository, a PA model is essentially a forward model that samples input parameters and runs multiple realizations to estimate future consequences and determine important parameters driving the system performance. In the CS evaluation, however, a PA model must be able to run both forward and inverse calculations to support optimization of CO_2 injection and real-time site monitoring as an integral part of the system design and operation. The monitoring data must be continually fused into the PA model through model inversion and parameter estimation. Model calculations will in turn guide the design of optimal monitoring and carbon-injection strategies (e.g., in terms of monitoring techniques, locations, and time intervals). Evaluation of carbon sequestration (subsurface carbon storage) systems tools need expansion to deal with uncertainty and optimization on high-performance computing (HPC) systems. This project will develop new structures to approach, link the appropriate software, and conduct a prototype analysis of such system tools.

Summary of Accomplishments

We explored the concept of an enhanced performance assessment system (EPAS) for carbon sequestration and storage. In spite of the time constraints, significant progress has been made on the project:

1. Following the general PA methodology, we performed a preliminary feature, event, and process (FEP) analysis for a hypothetical CS system. Through this FEP analysis, relevant scenarios for CO_2 release were defined.
2. We developed a prototype of EPAS by wrapping an existing multiphase, multicomponent reservoir simulator (TOUGH2) with an uncertainty quantification and optimization code (DAKOTA).
3. For demonstration, we successfully performed a probabilistic PA analysis for a hypothetical CS system based on an existing project in a brine-bearing sandstone. The work lays the foundation for the development of a new generation of PA tools for effective management of CS activities. We conducted both a deterministic case (single realization) and a multi-realization case. Runtime was approximately 4 hours per realization.

During this work, we had substantial interactions with both Lawrence Berkeley and Lawrence Livermore National Laboratories. Several publications are being prepared.

Significance

The proposed work supports energy security and climate change/adaptation by furthering the capability to effectively manage proposed carbon capture and sequestration activities (both research and development as well as operational), and it will greatly enhance technical capability to address this national problem.

Investigation of the Condensing Supercritical CO_2 Brayton Cycle

150635
Year 1 of 1
Principal Investigator: S. A. Wright

Project Purpose

This project evaluated the potential improvement that "condensing" supercritical carbon dioxide (S-CO_2) power cycles can have on the efficiency of light water reactors (LWR). The analytical portion of the project identified that a S-CO_2 "condensing" re-compression power cycle with multiple stages of reheat can increase LWR power conversion efficiency from 33-34% to 37-39%. The experimental portion of the project used Sandia's S-CO_2 research loop to show that the as designed radial compressor could "pump" liquid CO_2 and that the gas-coolers could "condense" CO_2 even though both these S-CO_2 components were designed to operate on vapor phase S-CO_2 near the critical point. There is potentially very high value to this research as it opens the possibility of increasing LWR power cycle efficiency, above the 33-34% range, while lowering the capital cost of the power plant because of the small size of the S-CO_2 power system. In addition, it provides a way to incrementally build advanced LWRs that are optimally designed to couple to S-CO_2 power conversion systems to increase the power cycle efficiency to nearly 40%.

Summary of Accomplishments

The research program consisted of two major tasks. This first task performed a series of modeling efforts to evaluated potential performance improvements that can be obtained in both LWRs and liquid metal reactors by using a condensing supercritical CO_2 power cycle. The second set of tasks operated the existing Sandia S-CO_2 research test loop to verify the compressors ability to "pump" liquid CO_2 and the gas-cooler's ability to "condense" CO_2.

Three types of experiments were performed. The first performed a series of tests to show that the radial compressor could effectively compress liquid CO_2 even though it was designed to operate near the critical point. The second series of tests operated the S-CO_2 test loop in the two-phase saturated vapor/liquid. The third effort modified the S-CO_2 research loop by adding a small heater (50 kW) to increase the temperature of the CO_2 after compression. With the addition of the heater it was then possible (in one experiment) to provide a saturated vapor or two-phase mixture to the tube and shell heat exchanger and condense the fluid in the gas cooler. These experiments therefore demonstrated that condensation occurred in the gas cooler and that this fluid could be pumped by the S-CO_2 compressor.

The results of the research effort have therefore demonstrated that the small-scale proof-of-concept design of the Sandia re-compression Brayton cycle is capable of both condensing the CO_2 in the gas cooler and pumping the fluid in the S-CO_2 main compressor. Overall the analysis and the experimental test results effectively demonstrate that the proposed designs of operating S-CO_2 power plants can operate in the condensation mode. When used with a re-compression power cycle with multiple-stages of reheat, they can be uses in LWR power plants to increase the power cycle efficiency.

Significance

Advanced power conversion systems that optimally couple to the thermal output characteristics of next-generation advanced reactors have the potential to provide higher efficiency nuclear electricity at lower costs. Improvements in plant efficiency can increase plant electrical output directly and have the same impact as direct reductions in plant construction and operating costs. There can be additional cost savings, if the power conversion system capital costs can also be reduced in comparison to current systems.

Supercritical Brayton cycles and other advanced supercritical cycles are promising approaches to achieving higher efficiency and more cost effective power conversion. These cycles have the potential to achieve higher efficiencies across the range of advanced reactor outlet temperatures and due to the high power densities and liquid like fluid densities everywhere in the system are extremely compact.

The research presented here shows S-CO_2 power cycles can be applied to LWRs to increase the power cycle efficiency, while lowering the capital cost of the power plant because of the small size of the S-CO_2 power system. In addition it provides a way to add an advanced S-CO_2 power system to existing LWRs to increase the power cycle efficiency, but also a way to incrementally build advanced LWRs that are optimally designed to couple to S-CO_2 power conversion systems to increase the power cycle efficiency to nearly 40%.

Optimizing Infrastructure Investments in a Competitive Environment

151411
Year 1 of 3
Principal Investigator: R. L. Chen

Project Purpose

In many complex systems, individuals or institutions compete for the use of a finite amount of infrastructure capacity. As examples, generation firms compete for transmission capacity and commuters interact in a de facto competition for highway capacity. In such complex systems, the optimization of infrastructure investments must take into consideration the impact of investment decisions on individuals or institutions competing for the use of these resources. However, many existing models assume a centralized resource planning approach where investment decisions are made in a coordinated fashion to maximize some measure of social welfare (e.g., minimizing overall system cost). Such coordinated system models are unrealistic in many cases where competition plays a crucial role. In a deregulated electric power industry, for example, generation investment decisions are made by individual institutions with little centralized coordination. In such cases, institutions make their decisions on the basis of expected future prices and returns on investments. Consequently, it is critical that decision-makers consider the complex interactions amongst competitors when making infrastructure investments. This research will develop new models and optimization methods to effectively analyze Stackelberg games (leader-follower games) for infrastructure planning, specifically taking into consideration competition among the infrastructure users (followers). These models and optimization methods will allow decision-makers to predict the responses of competing individuals and institutions to infrastructure investment decisions, analyze infrastructure investment risk, and perform sensitivity analyses to objectively trade-off multiple system criteria.

Summary of Accomplishments

We developed/implemented a new interior point algorithm for dense linear programs (LPs whose constraint matrix contain mostly non-zero terms) and drafted a paper on “Including Wind In Power System Siting and Capacity Expansion Models” (to be submitted to *IEEE Transactions on Power Systems*).

Significance

The proposed research will facilitate the design of the electric power grid to support high penetration of renewables. Additionally, these models and optimization methods will enable new predictive capabilities for analyzing the impact of competition and adversity in hierarchical infrastructure planning problems. Military decision-makers can use these capabilities to enhance situational awareness and perform vulnerability assessment.

The optimization methods will also be applicable to energy infrastructure models developed for the Sandia Water Energy Nexus and the National Energy Modeling System. For example, the quadratic programming algorithm based on the sphere method is computationally efficient and may improve scalability of risk-constrained models, such as those under development for the Sandia Water Energy Nexus.

HOMELAND SECURITY AND DEFENSE INVESTMENT AREA

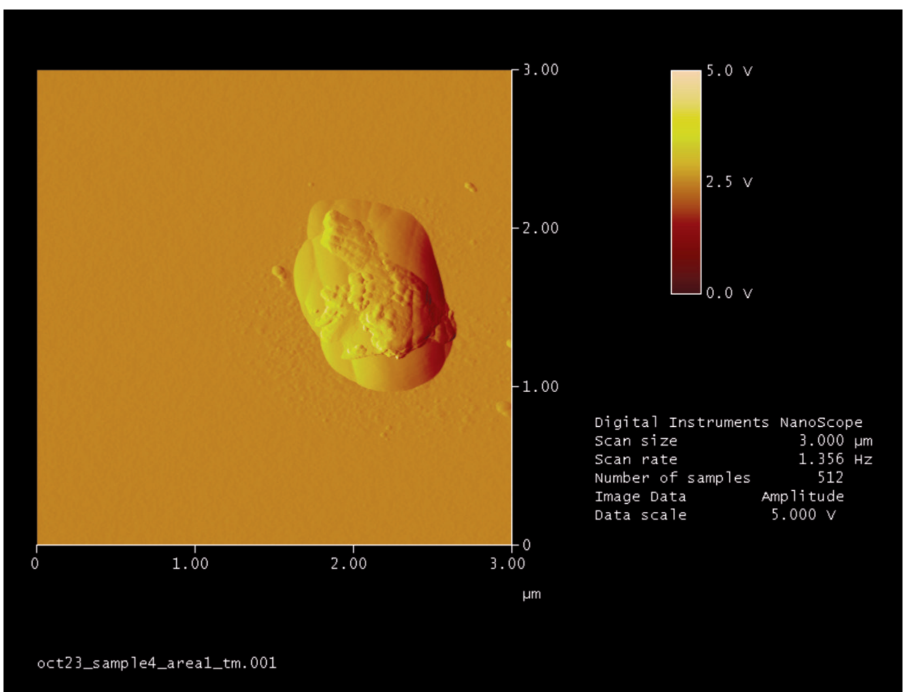
Projects in this investment area focus on the physical and computational tools and the underlying science necessary to protect our nation — its citizens, military personnel and diverse types of infrastructure — from a multiplicity of threats. From detecting the entry of biological, chemical, and nuclear threats, to lighter, more-effective armor for warfighters, to computational tools for intelligence analysts such as filters for the trafficking of messages along the internet and other networks, the reach of this IA extends broadly into a diversity of science and engineering areas.

Non-Toxic, Non-Corrosive Approach for Decontamination of Anthrax Spores

Project 130761

Because bacterial spores are extremely difficult to kill by comparison to fully metabolic bacterial cells, current decontamination methods against spores of threat organisms such as Bacillus anthracis (anthrax) require the use of highly toxic and/or highly corrosive chemical solutions, such as chlorine dioxide. These corrosive chemicals not only damage materials, but also require complicated, expensive deployment systems.

This project has developed a far less corrosive and less-expensive method for killing bacterial spores (such as anthrax) in contaminated areas. A novel nontoxic germination solution activates spores, causing them to germinate into vegetative (fully metabolic) bacterial cells. Subsequent to germination, these cells can be far more easily killed than their spores, with relatively nontoxic chemicals such as hydrogen peroxide, alcohols, quaternary ammonium compounds, or other simple treatments such as ultraviolet light. Initial tests have resulted in ~20 million bacterial spores killed on coupons mounted in various locations in a test chamber.

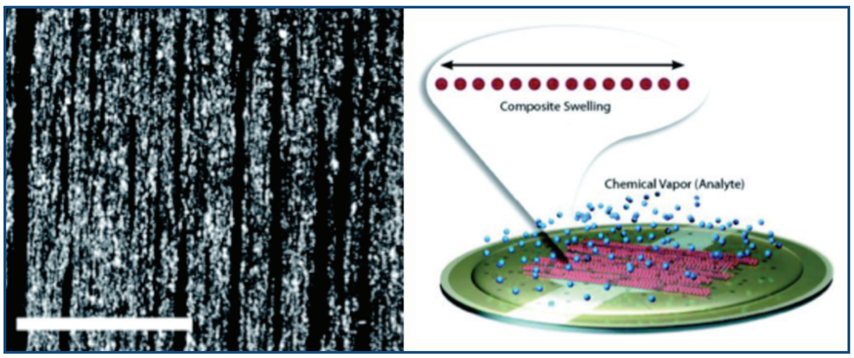


Micrograph of a germinating spore.

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives

Project 149568

Readily made from common household automotive items such as hair bleach and battery acid, homemade explosives (HMEs) present an emerging threat to both US military forces and civilians. In the Middle East, where the supply of munitions from previous conflicts has more-or-less dried up, terrorists are progressively turning their attention toward improvised explosive devices (IEDs) with an energetic-material component derived from commonly available household agents, most notably hair bleach, fingernail polish, and automotive battery acids. Exemplary is triacetone triperoxide, a dangerously unstable homemade explosive that was used as an explosive initiator by British shoe-bomber Richard Reid, and whose synthesis requires the reaction of hydrogen peroxide with acetone in a sulfuric acid medium. There is no currently field-deployed technology to detect such HMEs, and therefore, this early career project's research with portable sensors — polymer-based devices known as field-structured chemiresistors (FSCRs) — is directly aligned with Sandia's national security mission in threat detection. This FSCR research examines several schemes for field-detection of the presence H_2O_2 (hydrogen peroxide), which could alert security personnel to the potential presence of an HME.



Polymeric matrix (micrograph, left) and schematic drawing during swelling upon binding analyte (right), that could serve as chemiresistor detectors of homemade explosives. Upon binding a relevant analyte the polymer swells with a separation of its components and an increase in its resistivity.

HOMELAND SECURITY AND DEFENSE INVESTMENT AREA

Two-Pulse Rapid Remote Surface Contamination Measurement

117814
Year 3 of 3
Principal Investigator: T. J. Kulp

Project Purpose

The response to a broad class of homeland security threats requires rapid remote analysis of chemical and biological surface residues. Examples include the assessment of biological agent contamination during decontamination, detection of explosive residues on improvised explosive devices, and the sensing of viscous chemical agents. It is desirable to perform this remotely (few meters to tens of meters) to cover large spatial areas rapidly (saving cost) and to protect personnel.

This project sought to develop and demonstrate a new two-pulse optical method to enable remote surface contamination detection. While the need for standoff detection suggests a solution based on optical sensing, those techniques often fail to distinguish trace, nonvolatile materials from the surface in which they are embedded. This stems from masking of the target species signal by the background signal clutter created by the matrix. An example is the infrared (IR) detection of chemical agents in the field. Systems such as Fourier transform infrared spectrometers (FTIRs), and LIDARs (light detection and ranging) exist to measure plumes of airborne agents via IR absorption. However, when agents settle on the ground, their absorption signature is converted to a reflectance signature that is dominated by the reflectance spectrum of the ground. Thus, contaminated areas become difficult to identify. The proposed method will mitigate these problems by using a measurement based on two laser pulses. The first separates a fragment of the molecule to be detected from the matrix and activates it to become fluorescent. The second stimulates fluorescence from the fragment in a wavelength range where the surface matrix exhibits very little background.

Summary of Accomplishments

During the course of this project we successfully demonstrated a two-pulse standoff surface-detection method that employs a laser photoablation step (LA, meaning that atoms and molecules are “ablated” from the surface), followed by a laser-induced fluorescence (LIF) step. Its performance in detecting organophosphonate (OP) nerve agent simulants was evaluated under conditions relevant to its use for homeland security and defense applications. When applied to OP sensing, the LA pulse releases phosphorous monoxide (PO), which is subsequently detected by LIF. Through experimentation, we discovered that the PO forms by recombination of P+O, both of which are created during ablation. This differs from past gas-phase studies, where PO was observed to be removed as a molecular fragment, and has implications regarding the manner in which the measurement would be implemented as a portable instrument.

Lab study allowed us prove the generality of the method in detecting a range of OP compounds at high sensitivity (μg/cm^2 with a single pair of laser pulses) as they are deposited on several real-world surfaces (e.g., concrete). Its ablative nature was shown to have benefit in releasing surrogate that has seeped into porous surfaces (such as those in concrete). This is in contrast to measurements made by Raman spectroscopy, which is the primary competitor to this method and is restricted to probing only surrogate at the surface. Moreover, through comparison under identical conditions, we established that LA-LIF is >1000× more sensitive (and thus, rapid) than Raman.

Our study also revealed that common phosphate-containing soaps are interferents for the method. To mitigate this, we proposed Raman spectroscopy as a tool to be used to confirm LA-LIF "hits." To support this, we demonstrated that Raman can distinguish phosphate soap from OP surrogate. Moreover, we demonstrated that an LA-LIF instrument can also conduct Raman measurements at little added cost.

Significance

The results of this project justify further development of LA-LIF as a rapid search tool for low volatility chemical agent (LVA) surface residues. They also provide information of interest to those advancing remote surface contamination detection. The former is substantiated by comparison to performance metrics that guide users of the technology. Both are confirmed by external recognition that the project has achieved, such as invitations to present results at national conferences organized by both scientific and user organizations. Participation in this project has also yielded general experience in the problems associated with surface-contamination detection. This prepares the team for work involving other sensing methods or for the study of basic phenomena, such as the chemistry involved in the fate/transport of LVAs on surfaces. For example, the team has been awarded FY 2011 LDRD project funding to study explosives detection on surfaces by Raman.

Two performance metrics were selected to gauge the utility of an LA-LIF instrument. The first originates from discussions with DHS. The second targets an application in which LA-LIF would substitute for a conventional surface-swipe/lab analysis clearance process. That is a "stretch" goal, as clearance implies detection at levels low enough to be safe for human occupation. Our lab results show that an LA-LIF instrument exceeds the sensitivity needed for the DHS goal by a factor of 14. They also show a large improvement (1000× under similar conditions) over the competing Raman method. For the 10-s swipe replacement measurement they suggest that LA-LIF would fall short of the sensitivity needed for clearance by a factor of 60. However, because this measurement could be made in-situ (without requiring lab analysis) and the a factor of 60 level is still quite sensitive, it is also likely to have application as a swipe surrogate.

Several interactions with outside agencies occurred during this work. Program managers (at DHS and the Defense Threat Reduction Agency [DTRA]) were periodically apprised of the project's progress. Another strategy is the teaming with scientists at Edgewood Chemical Biological Center, who can work with live agents and could serve as important partners in testing technologies at that level.

Automatic Recognition of Malicious Intent (ARMI)

117816
Year 3 of 3
Principal Investigator: M. W. Koch

Project Purpose

A major goal of many next-generation physical protection systems is to extend defenses far beyond the usual outer-perimeter fence boundaries surrounding protected facilities. Extended defenses greatly shift the outcome of an intrusion in favor of protective forces by providing additional awareness and time, allowing for preparation to achieve a more effective protective posture. On the other hand, extending existing defenses beyond traditional boundaries incurs penalties in operational performance by comparison to existing technologies in terms of nuisance and false alarms. Both of these penalties can be used by adversaries to mask their presence and render the system ineffective. The evolution of these distributed systems also creates unanticipated consequences such as information overload for system operators.

This project addresses both negative impacts created by extended defenses. To mitigate the nuisance and false alarms introduced when deploying in unengineered terrain, this project will identify and create seismic, acoustic, and imaging algorithms that can be deployed for better target discrimination. To address information overload the project research will examine algorithms that can help automate actions to make the system operator more effective by reducing the time to make a response decision. In NAR (nuisance alarm ratio) reduction the team is focusing on autonomous identification of human behaviors through imaging in complex terrain. Algorithms that can autonomously identify activities beyond merely detection and declaring activities by means of active interrogation techniques encompass next steps in next-generation security systems. These algorithms with post-stimuli responses can provide enhanced knowledge beyond traditional detection. They seek to extract activities in larger data sets that may be not readily observable by an operator due to the high volume of alarms, and in effect, can make the operator more situationally aware.

Summary of Accomplishments

- Development of automatic recognition of malicious indicators for DOE and DoD sites with extended defense system using a stimulus
- Autonomous operations increasing operator sensitivity and overall effectiveness
- Remote identification of malicious indicators allows operator to increase the interval available to respond and increases opportunities to establish intent through passive and active technologies
- Developed behavior matrix for pre-stimulus and post-stimulus behaviors and their relationship to malicious indicators
- System analysis of ARMI concept and system-level progression
- Developed an ARMI test bed consisting of a radar, infrared (IR) imager and stimulus
- Data collection of different malicious and nonmalicious scenarios using ARMI testbed
- Reasoning algorithm development and testing
- Presented results at the Carnahan Security Conference in October 2010

Significance

The successful development of the proposed ARMI capabilities will strengthen Sandia's capabilities in physical security. Benefits to DOE, DoD and DHS are anticipated in physical and border security, extended defense systems, and insider identification and detection. ARMI is expected to be a major component of next-generation physical security systems.

Active Coded-Aperture Neutron Imaging

117818
Year 3 of 3
Principal Investigator: P. Marleau

Project Purpose

There is an urgent national security need for systems that can detect special nuclear material (SNM) that is at a great stand-off distance and/or is obscured by shielding. Because of their penetrating power, energetic neutrons and gamma rays offer the possibility of detecting shielded or distant SNM. Of these, fast neutrons offer the greatest advantage due to their very low occurrence in natural background. We are investigating a wholly new approach to fast-neutron imaging — an active coded-aperture system that uses a coding mask made of neutron detectors. Low-energy neutron sources have been imaged at short range with passive coded-aperture neutron imaging systems. However, only fast neutrons are likely to travel long distances without scattering, and the penetrating nature of fast neutrons limits the ability of passive coded-apertures to modulate them effectively. Thus, the only previously demonstrated method for long-range neutron imaging is double-scatter imaging, but that method has limited detection efficiency. Active coded-aperture neutron imaging should be more efficient for improved detection speed, range, and sensitivity. This efficiency advantage is achieved by simultaneously imaging using both double-scatter and coded-aperture methods. In coded-aperture imaging, neutrons originating from different locations are very efficiently detected at the image plane as the superposition of mask patterns. In double-scatter imaging, the incident angle and energy of any neutron that is detected in two or more different detectors can be determined. By simultaneously imaging using both coincident and anti-coincident detection events, this new, dual design allows for high-efficiency imaging of sources of energetic neutrons and should lead to an instrument capable of locating SNM at greater distances than any existing instrument or technique. The project directly addresses a major national need in homeland security. In addition, it assures Sandia leadership in a highly competitive technical domain.

Summary of Accomplishments

- We developed detailed Monte Carlo models that include full detector response.
- We developed powerful C++ based analysis tools and image reconstruction algorithms including maximum likelihood techniques and point source hypothesis tests.
- We demonstrated the feasibility and benefit of coded-aperture imaging including dual-mode gamma/neutron and dual-mode double/single scatter in simulations and experiments.
- We successfully designed, built, and tested a homeland security use case demonstration imager.
- We successfully designed, built, and tested a time encoded neutron imager based on our experience with spatially modulated coded apertures.

Significance

Both government and private sectors are seeking better tools to search for radioactive threats. This new concept for a high-efficiency imaging of fast neutrons could yield dramatic improvements over existing tools. This project addresses the protection of the US public on US soil against weapons of mass disruption.

A *C. Elegans*-Based Foam for Rapid On-Site Detection of Residual Live Virus

130755
Year 2 of 3
Principal Investigator: C. Branda

Project Purpose

In the response to and recovery from a critical homeland security event involving deliberate or accidental release of biological agents, initial decontamination efforts are necessarily followed by tests for the presence of residual live virus or bacteria. Such "clearance sampling" should be rapid and accurate, to inform decision-makers as they take appropriate action to ensure the safety of the public and of operational personnel. However, the current protocol for clearance sampling is extremely time-intensive and costly, and requires significant amounts of laboratory space and capacity ("Method Detection Limits and Non-Detects in the World of Microbiology," *National Risk Management Research Laboratory, EPA, 2006*). Large numbers of samples may be required to achieve a high degree of statistical certainty, depending upon the physical dimensions of the contaminated area. The samples must then be transported to the lab for measurement of biological activity. Detection of residual live virus is particularly problematic and time-consuming because it requires evaluation of replication potential within a eukaryotic host such as chicken embryos. We intend to revolutionize clearance sampling, by leveraging Sandia's expertise in the biological and material sciences in order to create a *Caenorhabditis elegans* (*C. elegans*)-based foam that can be applied directly to the entire contaminated area for quick and accurate detection of any and all residual live virus by means of a fluorescent signal. This novel technology for rapid, on-site detection of live virus would greatly interest the DHS, DoD, and the Environmental Protection Agency, and hold broad commercial potential, especially with regard to the transportation industry.

Summary of Accomplishments

In year two, we have made significant progress towards three critical project milestones: 1) isolation of *C. elegans* with increased susceptibility to viral infection, 2) production of molecular sensors of viral infection, and 3) construction of a mechanism to amplify a fluorescent signal indicative of viral infection. Towards production of *C. elegans* strains with increased susceptibility to viral infection, we have 1) identified strains with cuticle defects that are more susceptible to viral infection than wild-type strains, 2) developed a protocol utilizing chemical (chitinase/collagenase) and pressure (10 kpsi) treatments to facilitate viral infection of *C. elegans*, 3) generated *C. elegans* strains expressing exogenous viral receptors enabling infections not normally possible due to a lack of appropriate cellular receptors, and 4) generated recombinant viruses expressing the red fluorescent protein, mCherry, enabling visualization of viral infection in both intact *C. elegans* and mammalian and *C. elegans* cell lines.

We have attempted to generate molecular sensors of both Rift Valley Fever Virus (RVFV, an RNA virus), and Vaccinia Virus (VacV, a DNA poxvirus), as described in our original proposal. We have generated and tested several different sensors of RVFV infection, but, in all cases, unacceptably high background expression from the sensor has been observed, with only modest increases in fluorescence observed following infection with RVFV (MP12 strain). By contrast, we have had much more promising results in production of a molecular sensor for VacV infection. We are currently generating and testing different molecular sensors for VacV infection. For one type of sensor, we have used a VacV-specific promoter to drive mCherry expression only in cells infected with VacV.

Towards construction of a mechanism to amplify a fluorescent signal indicative of viral infection, we are developing a cell permeable Cre recombinase-based system for activating fluorescence production in cells neighboring a virally infected cell.

Significance

The critical need for improved methods of clearance sampling (faster, cheaper, yielding higher statistical certainty) applicable to all types of biological agents has been emphasized by both the DHS and the EPA. Our technology for clearance sampling is substantially faster and cheaper than state-of-the-art culture-based techniques, and addresses multiple mission elements by facilitating response and recovery efforts following biological attacks on US interests here and abroad.

Deployable Pathogen Diagnostic System

130756
Year 2 of 2
Principal Investigator: A. Hatch

Project Purpose

No field-deployable devices for monitoring pathogen infection exist, even though the need is widely recognized. For example, according to the NIH website, "there is a need for rapid, highly sensitive, specific, easy to use, adaptable, and cost-effective medical diagnostics for…laboratories, and point-of-care use to diagnose individuals exposed to and/or infected with priority pathogens or their toxins…so appropriate therapeutic intervention or containment can be executed."

While Sandia has considerable experience developing deployable field-monitoring systems, the criteria are much different for medical diagnostic systems designed to monitor pathogen infection/exposure while conforming to FDA requirements. We have demonstrated that our unique microfluidic diagnostic platform meets key performance criteria (rapid, specific, sensitive) but the platform has not progressed beyond a bench-immobilized system that only highly trained technical staff can utilize. We have also been constrained from demonstrating diagnostics for priority pathogens since the current format cannot be deployed in a biosafety cabinet to satisfy BSL-2 containment on-site, nor can it be deployed at collaborating institutions that also include BSL-3/4 containment needs. We propose a systems engineering approach to manufacture and refine a robust and deployable prototype system that facilitates collaborative research and development for diagnostics of priority pathogen infection. First-generation prototypes will be built during year 1 and then deployed in BSL-2 labs at Sandia and BSL-3 facilities at the University of Texas Medical Branch (UTMB) for evaluation and refinement during year 2, yielding an easy to use, field-deployable device ready for field assessment by the end of year 2. Development will also be guided by a commercial partner, Bio-Rad Laboratories, Inc., to satisfy commercialization criteria and conformance to FDA regulatory requirements. Realizing a functional prototype is key to further develop and promote the platform for priority pathogen diagnostics, obtain funding for continued development, and eventually widespread deployment.

Summary of Accomplishments

We demonstrated state-of-the-art integration and control over key microfluidic components in a portable system. Components include pumping, valving, high-voltage distribution, a laser/PMT (photomultiplier tube) detector, and a motorized stage. The high-voltage distribution board pushed the envelope in complexity and density of electrical interfaces to replaceable microfluidics via holes to meet the desired goals of easy use. The analysis cartridge is designed to simply be dropped in place (with design guides and registry) on top of spring loaded electrical contact pins. We designed, built, verified and programmed operations with several new microcontroller boards and a central processing unit (CPU). The CPU board will also communicate with a personal digital assistant or any HTML-enabled device with options for wireless communication. We implemented a powerful, user-friendly graphical user interface with a color touch-screen display. The device was also programmed to allow users to toggle controls on the touch-screen to record complicated scripts for automating lab-on-a-chip processes.

We demonstrated an easy-to-use disposable microfluidic analysis cartridge overcoming significant challenges prohibiting routine use of microfluidics in diagnostic applications. We uniquely demonstrate a clear and viable option for meeting ease-of-use goals with minimal training by an operator while keeping costs of the cartridge affordable. A key enabling advance is snap-together cartridge technology that utilizes parts that could be injection molded along with a standard printed circuit board. Clever design approaches allowed us to demonstrate complex fluid and high-voltage routing through the cartridge. For example, samples such as blood, can be loaded by the user to a single port and the device subsequently controls sample and reagent distribution through the chip.

We demonstrated the usefulness of portable system technology by deploying the integrated device at our collaborating institution that has infectious disease expertise. Novel assays were performed using this system with a demonstration that rickettsial pathogens can be detected using this device.

Significance

This work is crucial for continued development of solutions to biological weapons and infectious disease concerns in Sandia's Homeland Security and Defense (HS&D) strategic management unit. Bringing prior investments in platform development to fruition requires deployability to ultimately contain and mitigate outbreaks/attacks. The system will also bolster capabilities at Sandia to demonstrate meaningful test results and studies of infectious disease with priority pathogens by satisfying BSL-2 or greater containment criteria. The high-throughput analysis capabilities of this system are attractive to a number of external agencies in the areas of infectious disease and biothreats. Notably, the National Biodefense Analysis and Countermeasures Center is interested in evaluating a deployable system to meet their Homeland Security mandate in the area of forensic analysis of potential biotoxin samples. Lovelace Respiratory Research Institute is interested in the platform technology to bolster their research efforts in basic research on biological mechanisms of actions of toxins including inhalation animal models. This system will also be leveraged in the area of radiation biodosimetry and upcoming program opportunities.

Development of an Explosive Materials Threat Assessment Tool

130759
Year 2 of 2
Principal Investigator: F. A. Bouchier

Project Purpose

A bewildering array of explosive materials can be used to carry out a wide variety of illicit acts. One recent study conducted at Sandia identified approximately 300 explosive materials that might be considered realistic threats. Since the best approach to explosive detection often depends upon the type of explosive, decision-makers tasked with protecting facilities or airplanes against threats require information on the types of materials that are most likely to be used. There is at present no good source for such information. The purpose of this project is to develop a computer-based assessment tool that would allow decision-makers to obtain such information by answering a series of questions about the nature of the threat being considered and the specific facility or object they are tasked with safeguarding. Different threats that could be assessed would include large vehicle bombs, mail/package bombs, airplane bombs, and small bombs planted by a perpetrator.

The output of the tool would be a prioritized list of explosive materials — each given a numerical score — that would be most likely to be used to carry out the threat based upon considerations such as the mass of the explosive needed, the availability of the explosive or the materials required to make it, the explosive power of the material, the availability of knowledge to construct a functional explosive device, security equipment and procedures already in place at the facility in question, cost of the explosive or starting materials, etc. If not known, the explosive mass required to carry out a threat would be calculated using blast-modeling capabilities incorporated into the tool.

Summary of Accomplishments

We have developed the first well-documented process for ranking explosive threat materials in a systematic manner based upon material characteristics. The ranking procedure utilizes the widely used Analytic Hierarchy Process. All previous rankings of threat materials are based upon expert opinion and/or compilations of recipes from the terrorist literature. Our ranking system is likely to be of greater predictive value concerning the explosive materials that might be used in future terrorist incidents. We have already seen wide interest in our ranking system within the Department of Homeland Security.

We have developed a computer-based tool to apply our explosive material ranking system at specific facilities. An end-user inputs specific information regarding the facility, such as physical layout and information on the security system already in place. This tool thus allows a facility-specific ranked list of explosive threat materials to be produced — the first tool that has this capability. We have worked with prospective end-users to produce a more user-friendly tool.

We have compiled a database of TNT-equivalence for approximately 100 types of explosive materials. Since the concept of TNT-equivalence is not well defined for some homemade explosives (HME), we list several measures of equivalence and indicate which equivalence measure we believe is most valid. Experiments have also been performed measuring the blast properties of several HMEs.

Two reports have been written on how the final output of the tool varies with changes in inputs. A report written in 2009 examined variability in probability of detection values for explosives detection techniques already in place at a facility being studied. A classified report written in 2010 investigated how our explosive material rankings are influenced by changes in various inputs.

Significance

The Explosive Materials Threat Assessment Tool (EMTAT) project has already had demonstrated significance and, in certain areas, a path forward for future work has been identified.

Most notably, we have begun to vet our methodology for ranking explosive threat materials with the explosives protection community and have received much interest and some positive feedback. We have provided several briefings to Department of Homeland Security (DHS) personnel, most recently in mid-September 2010 to two personnel from the DHS Science and Technology Directorate. We have also given briefings to the Department of Defense (Army Asymmetric Warfare Group) and the Nuclear Regulatory Commission. Because DHS is currently deciding how to rank homemade explosive threat materials, DHS expressed particular interest in the EMTAT ranking methodology and we expect to have further interactions on this topic with both DHS and the other weapons labs through the Department of Homeland Security National Explosives Engineering Sciences Security (NEXESS) Center. Indeed, since the NEXESS Center is currently funded to work in the area of HME research, including threat assessment, funding is available to make presentations on the EMTAT ranking methodology, obtain feedback, and possibly to improve the ranking scheme. While it is too early to say whether the EMTAT ranking methodology will be widely accepted in the explosives protection community, the methodology is sufficiently well-documented that it can serve as a basis for discussions going forward, and it seems likely that at least some aspects of the methodology may come to be a part of whatever ranking system is ultimately widely used.

Our interactions with Pantex and Sandia security personnel in explaining and utilizing the computer-based tool have been productive and the tool appears to have been well received. It is too early to determine whether the tool will be widely used but future interactions with end-users in applying the tool are certainly possible, particularly with the security personnel at Sandia because studying classified scenarios on-site at Sandia is straightforward. If nothing else, the tool can provide an excellent reality check on the types of explosives with which security personnel at particular sites concern themselves, perhaps influencing decisions on the deployment of explosives detection equipment and the training of security personnel to recognize certain types of HME.

This project's work on the blast properties of homemade explosives — both the compilation of the TNT equivalence table and the experimental measurements of detonation velocities and other blast properties of HMEs — are also likely to find future use by those interested in HME properties.

Intrinsic Security Principles

130760
Year 2 of 2
Principal Investigator: C. J. Silva

Project Purpose

Current security design practices are based on a collection of best practices developed over many years in many different domains by many different practitioners. Despite their disparate origins, many have come to operate on the security principle of timely detection—i.e., a security system must detect an attack and delay the adversary to provide enough time to effectively respond with means to interrupt and neutralize the attack. These principles have provided the cornerstone of security system design for more than 40 years. These traditional security methods tend to be reactive in nature – systems built around known threats with a focus on winning the fight because detection is often limited to the first attack (first bullet fired, an alarm at the perimeter intrusion detection and assessment system, etc.). Since the threat space has changed dramatically, it is no longer cost effective to build and maintain these systems. It is the belief of this team that by changing the security focus from a 'reactive' to 'proactive' approach, it will have a fundamental change not only in system effectiveness but can provide a significant cost advantage. This is partly because being proactive begins with a different initial objective of prevention, by addressing unknown threats and focuses on avoiding the fight. This is the fundamental idea behind intrinsic security (IS).

While many agree with the general concept of IS, a common understanding of how it is applied to a real world problem and how the previously identified principles are integrated is lacking. Determining how the existing IS principles are interrelated will further fundamental understanding of IS and ultimately support our programs in the development of new, robust, and more cost effective security design and analysis methods based on fundamental IS principles that can form the basis for all security solutions, regardless of the domain or application.

Summary of Accomplishments

Key Accomplishments:

- Reviewed Intrinsic Security (IS) principles
  - Identified additional principle: Management of Information (e.g., create uncertainty for adversaries)
  - Strong temporal influences for each principle
  - Principles are interrelated, but cannot be combined
- Principles found to apply across domains since IS principles derived from broadly diverse domains
  - Instantiations of Intrinsic Security vary widely between domains
  - Vulnerabilities often found in seams and gaps

Significance

Using an intrinsic security methodology leads to designs that improve security performance, robustness, and/or efficiency across domains. This study advances Goal 1 of the DOE Strategic Plan, by utilizing core intrinsic security principles to inform development of a new generation of weapons surety practices. The use of such principles in the development of security design and analysis methodologies for critical infrastructure also advances the DHS Strategic Goal for protection.

- Helps remove security impediments to enable new and more cost-effective security designs across traditionally separate domains.
- Extends Sandia's long history of providing systems solutions to systems problems within nuclear weapons, homeland security and defense, and energy and nonproliferation realms. International Programs Center has included IS principles in security guidance for next-generation reactor designs in Japan. IS has also been referenced in US Department of Energy Fuel Cycle Technologies Program — in the context of used-fuel storage security.

Non-Toxic, Non-Corrosive Approach for Decontamination of Anthrax Spores

130761
Year 2 of 2
Principal Investigator: M. D. Tucker

Project Purpose

Bacterial spores (e.g., *Bacillus anthracis* [anthrax]) are one of the most resistant forms of life and are several orders of magnitude more difficult to kill than their associated vegetative cells. Consequently, remediation of facilities (e.g., the Hart Building) or other spaces (e.g., the interior of aircraft) contaminated with anthrax spores requires the use of highly toxic and corrosive chemicals such as chlorine dioxide gas, vaporous hydrogen peroxide (i.e., a 35% concentration of liquid hydrogen peroxide deployed in vapor form), or high-strength bleach. Even the much less corrosive, Sandia-developed DF-200 formulation utilizes an oxidative chemistry that will not be suitable for certain applications such as the interior of aircraft and extremely sensitive equipment.

The objective of this project is to develop a new approach for killing anthrax spores using very mild chemicals. We have developed and optimized a chemical formulation that triggers the germination process in bacterial spores and causes those spores to rapidly and completely change to much less-resistant vegetative cells. These cells can then be exposed to mild chemicals (e.g., low concentrations of hydrogen peroxide, quaternary ammonium compounds, alcohols, aldehydes, etc.) or natural elements (e.g., heat, humidity, ultraviolet light, etc.) for complete kill. We have utilized this approach to demonstrate, at the proof-of-concept level, practical decontamination methods to kill spores in interior spaces and on sensitive equipment (e.g., computers, electronic equipment, etc.) in enclosed chambers. In pilot-scale tests, the germination and kill formulations were introduced sequentially as a fog/mist into an enclosed test chamber. This process resulted in high levels of kill of bacterial spores (greater than 10^6 spores per square centimeter) that were located on coupons throughout the test chamber. This approach may result in a faster, cheaper, safer, and non-corrosive decontamination method that will allow our nation to quickly and efficiently recover from the release of a biothreat agent.

Summary of Accomplishments

The objective of this project has been to develop a new approach for killing anthrax spores using very mild chemicals. During the course of the project, Sandia developed a proprietary mixture of nontoxic chemicals that triggers the germination process in bacterial spores and causes those spores to rapidly and completely change to much less-resistant vegetative cells. We used this proprietary mixture of chemicals to rapidly germinate highly resistant bacterial spores to vegetative cells that were then exposed to mild chemicals (i.e., low concentrations of hydrogen peroxide or alcohols) for complete kill. This method was then demonstrated in vitro and at the pilot-scale level in a large test chamber at Sandia. In the pilot-scale tests, the germination solution and kill solution were applied sequentially through an aerosol generation device that creates very fine, charged droplets (i.e., the droplet sizes are approximately 3–10 µm in diameter). This aerosol deployment method could potentially be used in place of current “fumigation” methods (e.g., chlorine dioxide gas or vapor-phase hydrogen peroxide, as described above) for facility decontamination or as a method to decontaminate sensitive equipment in an enclosed chamber, and would potentially result in a faster, cheaper, and much less destructive decontamination method. The nontoxic, noncorrosive approach developed as part of this project will require no safety controls beyond what is required to minimize exposure to the biothreat agent itself. It will also not require the use of specialized, expensive equipment and could allow our nation to quickly and efficiently recover from the release of a highly persistent biothreat agent such as *Bacillus anthracis* spores.

Significance

A key need in homeland security and in military applications is to develop the capability to rapidly recover from an attack that utilizes chemical and biological warfare agents. Decontamination of contaminated equipment, personnel, and facilities is a key element of that capability. Work conducted under this project has demonstrated proof-of-concept for the nontoxic, noncorrosive approach for decontamination of anthrax in critical facilities (e.g., major transportation facilities) or critical assets (e.g., the interior of aircraft). Experience since the October 2001 anthrax incidents has shown that most chemicals used for anthrax decontamination causes damage to facilities and/or sensitive equipment. In many cases, sensitive materials must be removed from the facility or asset prior to decontamination to prevent damage. This method could be used to decontaminate facilities with little or no effects on the facility itself or on the sensitive materials found inside of that facility. A method that would enable sensitive materials to be left in place could greatly increase the speed at which the facility or asset could be decontaminated and returned to normal operations. In addition, a method that minimizes safety issues could also speed up the facility or asset remediation process.

Risk-Based Security Cost-Benefit Analysis Tool

130762
Year 2 of 2
Principal Investigator: G. D. Wyss

Project Purpose

Traditional risk-based cost-benefit approaches are difficult to apply to security assessment problems. Problems include reliance on linear utility theory, aggregation of disparate consequences, difficulties predicting attack likelihood, and lack of scalability to large "systems of systems." In particular, many existing methods for risk-based security cost-benefit analysis are severely limited because they require the analyst to estimate the likelihood of each attack. For large attacks, these likelihoods are highly subjective, extremely uncertain, and rapidly changing as geopolitical and even interpersonal events unfold. Because of these limitations, security budgets are often allocated by "gut instinct," and resulting security systems are often very sensitive to changes in threat assumptions and human factor uncertainties.

The purpose of this project is to overcome these problems by developing a scalable risk-based security cost-benefit analysis tool that enables objective security investment prioritization at all levels across an enterprise. To accomplish this, we developed an enhanced definition of security risk that replaces "scenario likelihood" with "scenario difficulty for adversary success" in order to reflect established adversary planning behaviors. In so doing, our methodology extends the basic underpinnings of risk theory to overcome the above obstacles. The purpose of the resulting tool is to address stated needs from DoD, DOE and DHS by enabling risk-based security resource allocation both locally and across facilities, leading to more robust and cost-effective security across disparate targets and infrastructure systems. It also advances Sandia's core nuclear weapon security mission by enabling security cost-benefit tradeoffs during weapon life extension programs.

Summary of Accomplishments

We recast the definition of risk to replace "scenario likelihood" with "scenario difficulty for adversary success" in order to reflect established adversary planning behaviors. We discovered a strong basis for this theory in observed attack planning behaviors, and strong parallels to game theory. We developed and demonstrated a multivariable semi-quantitative metric for scenario difficulty for adversary success, and tested this metric on several real-world attack scenarios (both actual attacks and "red team" demonstrations). We developed and demonstrated methods to aggregate this metric over its several dimensions. This success enabled ranking of attack scenarios by risk while eliminating the need to directly estimate or elicit the highly uncertain and rapidly changing likelihood of attack for each scenario.

We aggregated the difficulty metric with quantitative consequences to form an attractive attack frontier that is a graphical representation of the characteristics of the highest risk attack scenarios. This ensures that the most risk-significant attack scenarios are assigned the highest priority for mitigation. We demonstrated that risk-based cost-benefit security investment prioritization is straightforward using both qualitative and quantitative optimization approaches for scenarios and targets that result in similar consequences. Indeed, numerical optimization using common genetic optimizers is straightforward and was demonstrated using Sandia's Technology Management Optimization software. We also demonstrated a robust qualitative approach to security investment prioritization that can be applied for scenarios and targets that result in highly disparate consequences. Numerical optimization of these investments was demonstrated, but more research would be required to make this method robust. In all cases, both the qualitative and quantitative investment prioritization methods were found to be completely scalable and equally applicable at scales ranging from a single target within a single facility up to an entire enterprise that is composed of several sites that contain multiple facilities and a large number of targets.

Significance

In programmatic terms, a risk-based security cost-benefit tool advances DOE Strategic Theme 2, Nuclear Security (Goal 2.1), and the DHS Strategic Goal related to protection, which seeks to "safeguard our people . . . from acts of terrorism." The resulting tool addresses stated needs from DoD, DOE and DHS by enabling decision-makers to perform risk-based security resource allocation both locally and across facilities, leading to cost-effective security across disparate targets and infrastructure systems.

In practical terms, the tools and methods developed in this project enable risk-based security resource allocation both locally and across facilities, and can lead to cost-effective security across disparate targets, facilities, and infrastructure systems, and can enable security cost-benefit tradeoffs during for weapon life extension programs, thereby advancing Sandia's core nuclear weapon security mission. Portions of the method have already been used to evaluate proposed requirements in the B61 Life Extension Project and are being used in a similar capacity in discussions related to other possible life extension projects. The method has been briefed to representatives from various security programs within DOE (including health, safety and security) and NNSA, as well as the Department of Defense Office of Nuclear Matters, and was received enthusiastically. In addition, concepts from this project were used for NNSA to help them respond to congressional language that tasked them to justify recent and planned security investments. Finally, the Nuclear Regulatory Commission Office of Nuclear Security and Incident Response has been presented with and is considering using methods developed for this project as a starting point for developing its "risk-informed regulation" process for security for its licensees. Thus, the methods developed in this project are showing significance even before completion of the project.

But the most significant impact of the work from this project may be nontechnical. The methods developed for this project enable security analysts to engage in more productive investment prioritization deliberations. Instead of using hard cutoff criteria as to whether a particular extreme scenario "counts" within the "design basis threat" for a facility (which often leads to controversy), the difficulty-based risk ranking allows all scenarios to be considered in the investment prioritization process. The method helps ensure that the most risk-significant attack scenarios are assigned the highest priority for mitigation, and that the insights from even more extreme attack scenarios are captured and appropriately considered in the security investment prioritization process.

Target Detection and Tracking in Cluttered Environments using Rapidly Deployable VPED Sensor Networks

130763
Year 2 of 2
Principal Investigator: M. W. Koch

Project Purpose

The ability to robustly detect, localize, and track multiple human targets in uncontrolled, cluttered environments (e.g., forested areas) is a difficult and unsolved problem in Virtual Presence Extended Defense Systems (VPEDS). The difficulty is due to both the wide range of operational environmental conditions that cause excessive nuisance alarms and the inability to rapidly deploy these systems without time consuming calibration and testing. The two main difficulties to overcome are environmental conditions and the challenge of rapid deployment. These two difficulties contain subsets of obstacles that require the development of new algorithms. These new algorithms must be realizable in a deployed unit in varying environmental conditions that range from deserts to rain forests with an operational constraint on power. In order to address the challenge of rapid deployment, the algorithm approach must address issues such as rapid real-time installation and configuration of the system with a constraint on limited infrastructure. While these two categories appear independent they share key enabling elements that will be addressed in this research. The related enabling functional elements are self-calibration and near-real-time vulnerability assessment of coverage area during installation. Each of the listed functional elements will require the development of data aggregation algorithms that can infer detection volumes based on signal propagation and an associative algorithm that can in near real time assess and provide a vulnerability map.

Summary of Accomplishments

- Developed sensor probability of detection function (SPDF) concept and learning algorithms for isotropic and anisotropic response functions
- Designed, developed, and tested algorithms to take SPDFs and create detection map
- Developed and tested algorithms to automatically find vulnerabilities and suggest additional sensor placements
- Created, tested, and demonstrated a TRL 5-6 real-time system for learning a detection map for a network of unattended ground sensors
- Developed and tested algorithms to find low probability of detection paths
- Performed simulation and real-time validation tests
- Presented work at the Computer Vision and Pattern Recognition, MSS Battlespace Acoustic and Magnetic Sensors, Automatic Target Recognizer Working Group (USAF), and Society of Photographic Instrumentation Engineers conferences

Significance

Areas that would benefit include the DOE Mission in national security for facility and nuclear security. These areas would benefit from the algorithms and systems mitigating uncertainty of security system sensing patterns and from the rapid identification and elimination of area vulnerabilities that an adversary can exploit.

Uncooperative Biometric Identification at a Distance

130764
Year 2 of 3
Principal Investigator: K. R. Dixon

Project Purpose

One of the greatest challenges facing the security of public facilities and infrastructure is the rapid identification and verification of persons of interest. The problem becomes especially acute when considering that some subjects have a motivation to be deceptive or otherwise uncooperative toward identification. Some domains require a high degree of accuracy, such as granting access to a secured building or sensitive area for Force Protection or Virtual Presence and Extended Defense applications. Other domains require high throughput and recognition at a distance, such as the Department of Homeland Security's Transportation Safety Administration airport screening, Immigration and Customs Enforcement's passport control, and monitoring persons around high-value facilities such as the Capitol and White House. The proposed project aims to create a high-accuracy, high-throughput biometric identification system that works with both cooperative and uncooperative subjects at multi-meter distances.

The human iris is one of the most promising avenues for biometric identification for several reasons. First, the iris is believed to be one of the most stable, unique biometric measurements throughout the course of an adult's life; the iris does not change as a subject ages and is extremely difficult to alter. The project will explore new research and development, combining Sandia's expertise in adaptive optics with state-of-the-art research at Carnegie Mellon University in iris identification and facial-pose correction algorithms. The integrated system will provide a high-accuracy, high-throughput, multi-meter distance iris recognition of both cooperative and uncooperative subjects. We will work closely with Sandia's Force Protection groups to validate the performance of the proposed system with human-subjects data and verify its capabilities in mission-relevant scenarios.

Summary of Accomplishments

In FY 2010, we have demonstrated long-range identification of subjects in an outdoor environment out to 20 meters. We are continuing to improve the performance of the system, particularly illumination and tracking, currently.

Significance

The project ties to the DOE mission of the development and deployment of technologies to replace costly and manpower-intensive physical protection strategies, and can be used to secure sensitive facilities with a standoff biometric identification of potential threats. The proposed research addresses an acute need of the Department of Homeland Security to create a high-volume biometric identification system to protect public infrastructure and ensure continued public confidence.

Vulnerability of Multi-Network Infrastructure to Cascading Failure: Design of Robustness to Novel or Orchestrated Perturbations

130766
Year 2 of 3
Principal Investigator: R. J. Glass Jr.

Project Purpose

The US critical infrastructure is a network of dynamically interacting systems designed for the flow of information, energy, and materials. Under certain circumstances, disturbances from a targeted attack or natural disasters, can cause cascading failures within and between infrastructures that result in significant service losses and long recovery times. Reliable interdependency models that can capture such multi-network cascading do not exist. This project will extend Sandia's infrastructure modeling capabilities through the following research activities: 1) addressing interdependencies among networks, 2) incorporating adaptive behavioral models into the network models, and 3) providing mechanisms for evaluating vulnerability to targeted attack and unforeseen disruptions.

We will apply these capabilities to evaluate the robustness of existing infrastructure systems, and to identify changes in design and operation that will decrease the chance of large-scale disruption. This capability has direct application within the National Infrastructure Simulation and Analysis Center (NISAC) and to DHS, as well as, potentially, any other complex adaptive system-of-systems (CASoS) that can be modeled as networks such as emergency service providers or DoD logistics and net-centric operations. With modifications, the results of this project may also apply to analysis of physical and cyber security systems and lay the foundation for developing advanced security solutions that include autonomous triage and augmented cognition for infrastructure control systems. The propensity of infrastructure networks to fail catastrophically depends on: 1) the "physics" of the individual infrastructure systems; 2) system assurance mechanisms tailored to historical operations and perturbations; 3) the connections or interdependencies between infrastructures; and 4) the types of perturbations that a network has or has not been designed to withstand. Current practice in infrastructure analysis is almost entirely concerned with single infrastructures, with models of the interconnection of multiple infrastructures constituting the frontier of such research.

Summary of Accomplishments

We chose primary and stretch use-cases as, respectively, critical infrastructure at the national scale and military facilities. Multi-network interdependency modeling capability has been conceptualized, developed, implemented and is currently under continual refinement as we move toward application in context of primary and stretch use-cases. The CASoS is modeled as a network of interacting nodes, where each node represents an entity in the network. Each entity maintains a set of resources that are critical to its operations and interacts with other entities in the network by exchanging resources. Key characteristics for generic entities include the inventory that it maintains of its input resources, the number of connections it maintains to sources of inputs and users of outputs, and its policy for searching for alternative sources and users. Entity internal and interactional behavior can adapt to maximize some objective or reinforcement from the environment. This conceptualization allows general treatment of simple physical components as well as complicated institutions, making it suitable for a variety of CASoS that require entities of varying levels of sophistication. Detailed study of the operating regimes of individual entities and of interacting populations of entities is nearly completed. We are focusing on identifying the parameters that control the robustness and stability of entities, and that determine the critical time constants of their response. Interaction studies are focusing on how alternative stylized designs for constructing exchanges influence the efficiency and stability of coordination among entities. Initial configurations for the use cases have been developed. By the end of FY 2010, we will be able to use our general understanding of the robustness and stability of interacting entities to identify vulnerabilities in these specific use cases.

Significance

This project will demonstrate a capability to model human dependencies, interdependent complex adaptive systems of systems such as US infrastructures, security systems, and net-centric warfare concepts. The project will also develop methods evaluating the human in task functions in order to optimize responses. Systems utilizing this technology will be resilient to both random and targeted disturbances, and recovery to full operational capacity will be easier, cheaper, and faster.

Advanced Plastic Scintillators for Neutron Detection

141674
Year 1 of 1
Principal Investigator: A. Vance

Project Purpose

New materials could benefit the homeland security and defense mission to detect fissionable material, and organic scintillators represent an area of opportunity for significant advances. The goal of this project is the creation of a new class of plastic scintillators with pulse shape discrimination (PSD) capabilities. Current neutron detection devices feature neutron counters such as ^{3}He tubes, liquid scintillators or lithium-loaded fibers. PSD is helpful for neutron detection because it permits the detection of neutrons in the presence of background gamma radiation and is a requirement for successful neutron spectrometers. It would be advantageous for the production of robust neutron detectors to use solid scintillators instead of liquids or ^{3}He tubes; however, existing solid scintillators have distinct limitations.

Solid organic scintillators capable of neutron detection fall into two classes: single crystals and plastics. Single crystals, such as trans-stilbene (tSB), offer the advantage of exhibiting PSD for gamma-neutron differentiation; however, they are costly, fragile, and difficult to grow in sizes greater than two inches in diameter. Plastic scintillators are available in a variety of formulations and sizes; however, they do not exhibit PSD. While plastic scintillator materials have remained essentially unchanged over decades, significant advances have been made in the field of polymer science that should enable a new class of scintillator materials to emerge. As a proof of concept, we propose to prepare block copolymers based on a functionalized tSB. The goal will be to show that a single polymeric material containing nanoscale stilbene-rich domains could exhibit PSD. The polymeric scintillators proposed in this project would be transformational in the field of radiation detection and would lead to a new class of robust, easily manufactured neutron detection materials. Proof of concept at this project stage would provide the possibility to build our capabilities in the area of neutron detection materials.

Summary of Accomplishments

The project goal of demonstrating a PSD-capable plastic was not realized; however, the new plastics that were prepared and tested functioned as scintillators. In addition, as a result of this project, the test setup for evaluation of plastic scintillators for gamma/neutron detection was restarted. This project demonstrated that increased tSB loading of the copolymers provided an improved scintillation response to gamma radiation.

Significance

This class of materials may be of interest to several agencies, including DOE, DoD, and DHS, because they are single-component plastic scintillators that do not require the addition of dopants or wavelength shifters to produce a measureable light yield. It may be possible to tailor copolymers to specific applications. Additional studies could be pursued to further explore copolymers as plastic scintillators for applications that do not require PSD.

Characterizing Pathogens Based on Host Response

141676
Year 1 of 2
Principal Investigator: S. Branda

Project Purpose

Biological weapons of mass destruction and emerging infectious diseases pose serious and growing threats to our national security. Effective response to an outbreak critically depends upon rapid and accurate characterization of the causative pathogen. Current detection systems focus on notorious pathogens (e.g., anthrax) but are blind to unanticipated pathogens (natural or engineered). This is because they rely upon pre-selected, highly-specific affinity reagents (antibodies, PCR primers) that recognize physical/chemical features of the pathogen; change or absence of those features can wholly thwart detection. Current systems also provide no information as to the viability and virulence of detected pathogens.

We are developing a system for rapid detection of pathogens and assessment of their virulence capacity, based on characteristic responses that they elicit in immune cells. This system relies upon: 1) exquisitely precise culture and infection of immune cells, to ensure reproducible responses; and 2) capture of responses that are robust and complex enough to support identification of pathogen-specific response signatures. To meet these outcomes, we are developing a "digital" microfluidics (DMF) platform that offers unprecedented control over the microenvironment experienced by the cell, as well as capture of the global transcriptional response (transcriptome) of individual cells. In tandem, we are developing a new information-handling architecture that, via coordination and integration of existing data analysis tools, accelerates and automates identification of pathogen-specific response signatures. Our system will provide response signatures of greater discriminatory power, enabling accurate inference of the pathogen's identity and virulence capacity, based on analysis of its impact on the host cell's transcriptome.

Summary of Accomplishments

We proposed to use microarrays for transcriptional profiling; however, via the RapTOR Grand Challenge LDRD project, we gained access to next generation sequencing, the best tool for transcriptional profiling (referred to as "RNA-Seq"). We are among the first to use RNA-Seq to study host-pathogen interactions, so our work is finding a large and interested audience. We also chose to work with primary cells, rather than immortalized cell lines, because the results are more biologically relevant. To our knowledge, we are the first at Sandia to isolate, culture, and infect primary cells in-house. Both of these changes consumed time and resources, but we are still meeting our milestones and staying within budget. For our *Francisella tularensis* infections, we have one RNA-Seq in hand and a second arriving soon; for our Rift Valley fever virus infections, we are completing pilot studies and should have two RNA-Seq datasets within 4 months.

- We now have a microdroplets platform for infectivity assays. We are able to move both host cells and pathogens on chip, and are currently standardizing an infection protocol as well as methods for monitoring the infection process (e.g., pathogen internalization).
- We found that transition from microdroplets (infectivity assays) to picodroplets (transcriptome amplification) is too slow when generating the picodroplets in series; therefore, we developed a method for parallelized picodroplet formation, and are currently fine-tuning the method for greater uniformity in picodroplet size.
- We have generated an in-house pipeline for standard analysis of RNA-Seq datasets; we are currently developing informatics tools for more-sophisticated analysis and interpretation.

In summary, we are making excellent progress toward achieving our goals; some of our plans and milestones have been modified, but we are very much on target for successful completion of the project.

Significance

This project unites two concepts that individually attract avid interest from biodefense and biomedical researchers: 1) cell-based sensors for pathogen detection; and 2) inference of pathogen features from host response patterns. Given our core strengths in host-pathogen biology, materials science, microsystems integration, and advanced computational analysis, Sandia is ideally suited to advance these concepts.

Successful development of our system will benefit a variety of ongoing efforts at Sandia; for instance, our new capability in microfluidics-enabled transcriptome analysis via RNA-Seq will benefit biodefense research (e.g., host-pathogen studies, biomarker discovery, diagnostics development) as well as bioenergy research (e.g., algal physiology studies). Indeed, in developing our system, we are making significant contributions to basic science, particularly with regard to understanding transcriptional regulation of pathogen-recognition signaling pathways. These results will be published in high-impact peer-reviewed scientific journals, and will seed new proposal submissions to funding agencies such as DHS, the Defense Threat Reduction Agency (DTRA), and NIH. Our accomplishments are already drawing recognition from the biodefense research community: our work will be featured in invited oral presentations at two key biodefense conferences (Detection Technologies 2010, Arlington, VA, and the 2010 Chemical and Biological Defense Science and Technology conference, Orlando, FL). We have also featured the project in briefs for visitors from DTRA, DHS, and the National Biodefense Analysis and Countermeasures Center (NBACC); all have responded positively. We plan to follow up on these contacts, particularly with regard to partnering with scientists at NBACC to further develop our pathogen characterization system in follow-on work; we are currently searching for interested sponsors for this effort.

Detection of Nuclear Radiation by RF Susceptibility

141677
Year 1 of 1
Principal Investigator: R. J. Anderson

Project Purpose

Agencies charged with detecting and identifying nuclear radiation constantly seek new, more effective detection schemes. This is especially true of semiconductor-based techniques, which all rely on transport of free carriers, created by nuclear radiation, across the bulk of the sensor element. This requires a bias voltage that can cause sensor polarization and that limits the geometry to monolithic blocks of homogeneous material, excluding schemes that utilize multiple materials, such as converters for neutron detection. An alternative view is that energy deposition changes the electric susceptibility of the material, the free carriers forming a loss mechanism (shunt resistance) in a now partially conducting medium. We propose detecting nuclear radiation by measuring the susceptibility change of a semiconductor in the radio-frequency (RF) regime, not by measuring transient charge transport in the quasi-DC regime as now practiced.

The scheme is similar to the earliest nuclear magnetic resonance (NMR) experiments. There, changes in the magnetic susceptibility of a sample in the inductor of a high-Q RF circuit induce a measurable loss of energy stored in the circuit. The same effect attends creation of a loss current (free carriers) in the dielectric (semiconductor) between the plates of the capacitor.

We propose a proof-of-principle experiment using an RF bridge with a sensor composed of a semiconductor (single crystal diamond) filling the capacitor gap of a high-Q tank circuit. High power is not needed, since the AC voltage at the sensor increases by a factor Q over that of the traveling wave. Because semiconductor fills the capacitor, this approach is superior to distributed circuit element (microwave) schemes that have a lower filling factor. Bridge measurements of transient Q-spoiling caused by irradiation with a known alpha source will allow an accurate measure of the sensitivity and linearity, since free-carrier generation in diamond is well calibrated.

Summary of Accomplishments

We have suggested that the detection of nuclear radiation using semiconductors could be improved by probing the electric susceptibility of the sensor in the RF part of the spectrum, rather than by measuring the charge transport in the conventional fashion. To attempt a proof-of-principle demonstration, we have designed, fabricated, and analyzed a narrow-band resonant RF circuit that incorporates as a capacitor a high-quality diamond crystal. We demonstrated that the diamond crystal functions as a high-quality detector of 5.5-MeV alpha particles emitted by ^{241}Am, and that the RF circuit satisfies the design requirements for bandwidth and sensitivity. The final test of the fully assembled probe system as a detector of nuclear radiation was inconclusive. The oscillator chosen to test the system was unexpectedly noisy, and caused amplitude bursts of size and duration similar to those predicted from absorption of radiation, at a repetition rate much greater than the radiation source. The principle is neither proven nor discredited, but rather awaits a more suitable test with an oscillator of sufficiently high quality.

Significance

The use of nuclear radiation detectors is pervasive within Sandia and by many other agencies. All of these users would benefit from successful development of the functionality described here.

This project seeks to take initial steps in demonstrating a novel approach to radiation detection by measuring a radiation-induced change in RF susceptibility in a semiconductor material. With compelling evidence that this concept works as predicted, successful proposals for follow-on funding would be sought to further develop this technology. Ultimately, the aim of this research is to replace the current generation of detectors based on liquids and large single crystals with smaller, cheaper, more robust detectors. Variations of this technique, such as replacing the RF bridge with a marginal oscillator, are anticipated to allow for detection of multiple types of radiation, and several such compact detectors could be combined into one device to simultaneous detect and discriminate between neutron and gamma radiation, for example.

Successful demonstration of the methodology described here would open the possibility for alternative semiconductor sensor structures that, by relaxing materials constraints, would provide cheaper, robust, compact, low-power consumption detectors that could be used to mitigate radiological/nuclear threats.

Graded Engagement of Small Aircraft and UAVs for Physical Protection

141678
Year 1 of 3
Principal Investigator: J. F. Jones

Project Purpose

Sites critical to national security are vulnerable to threats posed by small, low flying aircraft such as small fixed wing airplanes, helicopters, and unmanned aerial vehicles. To counter this threat, a system is needed that is able to detect the aircraft, discourage it from proceeding toward the sensitive area, and, if necessary, prevent it from carrying out a nefarious task.

Some capabilities exist for the detection, tracking, warning, and destruction of small aircraft. Systems for detecting and tracking potentially hostile aircraft have been an active area of research and development beginning prior to World War II. Massachusetts Institute of Technology's Lincoln Laboratories has recently demonstrated a distributed radar and electro-optical sensor system with central data collection, fusion, and decision processing for the small aircraft threat. Some engagement options for warning (e.g., radio broadcast, laser dazzler) and lethal force (e.g., missile intercept) currently exist, but few less than lethal deterrence and disablement options exist. In addition, capabilities, conducts of operations, and system architectures for employing a graded engagement approach against the small aircraft threat do not exist.

For a graded engagement approach to be realized, several technological gaps must be addressed. Technologies that can project effective discouragement or deterrence toward a variety of manned and unmanned aircraft must be identified and matured. Capabilities that can neutralize the aircraft with minimal collateral damage to the surroundings must be identified and matured. A system architecture that is capable of integrating detection, assessment, response, and real-time effects assessment to guide the graded engagement, with appropriate human authorization, must evolve. If these areas can be addressed, a revolutionary new capability for the protection of facilities against threats posed by small aircraft intrusion could be realized.

Summary of Accomplishments

We documented needs and objectives of a system: Our research scope is defined as capabilities for the detection, assessment, and engagement of small aircraft; however, the entire problem is broader and we documented the scope of the problem in a system functional diagram.

We defined a set of features including infrastructure, geography, population density, etc., that describe a target area and searched the Defense Critical Asset database to locate a set of locations that possess a range of variability in the desired feature set. We defined the threat performance envelopes for manned aircraft. The performance envelopes stem from a single-engine aircraft (Cessna 172/182) and commercial medium helicopter (Bell 412) because they are the most commonly available in their class. We will focus our initial scenario on a recent incident in the national capitol region because it provides a source of data to validate our models.

We determined performance characteristics of candidate detection systems. Candidate detection systems are Federal Aviation Administration radar, military radar, and electro-optical surveillance. Lincoln Labs conducted extensive research on these systems for the Enhanced Regional Situational Awareness (ERSA) system. Unclassified ERSA performance descriptions are in open literature, and we will use those performance metrics for our analysis.

We determined performance characteristics of candidate deterrence technologies. Our investigation focused on deterrence (intended to be less than lethal) aircraft engagement technologies because it was not obvious at the outset of this research that applicable technologies exist. We conducted an extensive literature survey on nonlethal weapon technologies from open and proprietary sources. We found several interesting technologies and documented our results to date with their expected performance. In addition, we investigated some advanced concepts being pursued for other applications. Currently, we are investigating neutralization technologies including anti-aircraft guns and missiles.

To date, we have published our initial findings at two conferences.

Significance

This research could lead to the development of a revolutionary new capability for protection of facilities against threats posed by small aircraft intrusion into areas containing nuclear material and possibly for the protection of a wide range of other critical infrastructures. This work addresses an important need of DoD, DOE, and DHS.

Rapid Radiation Biodosimetry to Mitigate Exposure Scenarios

141680
Year 1 of 3
Principal Investigator: G. J. Sommer

Project Purpose

Radiological and nuclear incidents continue to threaten the homeland security landscape. Sandia systems analyses addressing high-consequence terrorist threats, including radiation dispersal device (RDD) and improvised nuclear device (IND) scenarios, highlight the need for rapid triage and assessment of priority victims and the "worried well" following a radiological event. Responsive therapeutic administration requires dosimetry tools that detect doses of 1-8 Gy (1 Gray [Gy] = 1 Joule of radiation absorbed per kg tissue) within 24 hours post-exposure for avoidance of long-term health effects and improved survival rates. For mass-exposure scenarios, these tools need to be available at the point-of-incident and operate at a rate of 1 assay every 10 minutes. However, state-of-the-art biodosimetry (chromosome-aberration cytogenetics) often requires 72 hours to one week with highly trained personnel at a limited number of laboratories, which is a logistical problem for homeland security and defense (HSD) scenarios.

Current early-response measures (i.e., time-to-onset of vomiting and external emission dosimetry) provide only broad qualitative dose approximations, lacking the sensitivity required for proper therapeutic response. The Armed Forces Radiobiology Research Institute (AFRRI) has identified changing protein levels in serum within minutes to days following exposure to even low levels (< 1 mGy) of radiation through exhaustive animal model testing. When combined with white blood cell differential counts, these biomarkers provide precise statistical dose assessment. However, traditional methods for detecting these protein level fluctuations and cell counts do not satisfy logistical needs of HSD scenarios. We propose to address this unmet need by: 1) developing a point-of-care platform based on microfluidic technology for parallel hematology and proteomic screening of small-volume whole blood samples, and 2) through animal model sampling and validation in collaboration with AFRRI, demonstrating that the platform satisfies the need for a rapid, deployable biodosimeter enabling timely and effective therapeutic response even for large population exposure incidents.

Summary of Accomplishments

We have developed two novel assays based on centrifugal "lab-on-a-disk" technology to accomplish the objectives for this project. Microfluidic channels are formed within CD-sized polymer disks.

The hematology assay involves separating cells across layered density media on the device, based on the cells' sizes and densities. For this project, we are targeting absolute lymphocycte and absolute neutrophil counts, although we can easily include monocyte, platelet, and RBC counts in the system. We have demonstrated quantification with 0.1% (% solid) accuracy using this method to count fluorescent particles. Preliminary results demonstrate assay efficacy with whole blood.

The immunoassay method is based on mixing of antibody-coated beads with the sample and a detector antibody suspension, followed by sedimentation of the beads from the sample. Preliminary data shows detection of several panel biomarkers, including C reactive protein (CRP), the cytokines interleukin-6 (IL-6) and Flt3-ligand, and others, with a limit of detection of ~100 pM and approximately three order of magnitude dynamic range.

Both assays are novel. Challenges involving plasma extraction, reagent mixing, and valving have been addressed, enabling automated processing of whole blood samples. This approach allows us to achieve parallel white blood cell counts and protein detection from whole blood samples, an accomplishment not yet achieved in the microfluidics community. Preliminary designs and fabrication of an integrated, portable platform for automated testing demonstrate point-of-care assay capabilities.

Two patent applications have been submitted covering each technique. We are preparing manuscripts describing each assay for submission to *Lab on a Chip*. This work will be presented at both the International Conference on Miniaturized Systems for Chemistry and Life Sciences and the Defense Threat Reduction Agency Chemical and Biological Defense Science and Technology Conference.

Animal model sampling will begin FY 2011 with a planned assay development study at AFRRI using both our platform and gold standard techniques to process mouse whole blood samples.

Significance

The proposed work will significantly enhance Sandia's capabilities to support current national needs in the response to nuclear or radiological terrorist events. Current DOE- and DHS-funded research at Sandia in these response areas emphasizes threat definition, prevention, and early crisis management. New medical response capabilities for such events would permit a more comprehensive systems approach to these threats and will assist Sandia's very strong programs addressing radiological dispersal device scenarios.

This work directly addresses the need for a point-of-care biodosimetry platform capable of combined hematology and proteomic screening. While extensive research has been focused on development of modular microfluidic devices for either protein detection *or* hematology, no other system is capable of achieving both measurements from the same sample. We foresee broad application areas beyond radiation biodosimetry spanning the healthcare and research communities for such a device. For example, combined white blood cell counts and protein marker quantification are commonly used in diagnosis and treatment of cancer and heart disease. Hematology is also a proven diagnostic tool in viral or bacterial disease outbreaks, but is not often used in remote areas due to lack of access to conventional hematology analyzers. Transferring these assays from centralized labs to a point-of-care device provides numerous benefits, including reduced healthcare costs and diagnosis delays, the ability to perform the tests in the field, such as for military scenarios or for global health/ emerging threat outbreak situations, and testing in high biosafety level facilities in which precious samples are available in low quantities and exposure risk to select agents must be minimized.

Use of Metal Organic Fluors for Spectral Discrimination of Neutrons and Gammas

141681
Year 1 of 1
Principal Investigator: F. P. Doty

Project Purpose

This project investigated enhanced organic scintillators that enable a new spectral shape discrimination (SSD) signature for n/gamma discrimination. SSD has the potential to simultaneously increase signal levels, relax timing requirements, and eliminate the need for hazardous liquid scintillators. The new scintillators are enhanced with metal organic fluors that reduce the radiative lifetime of triplet excited states through spin orbit coupling, enabling increased intensity of delayed (submicrosecond) triplet radiative decay. Wavelength discrimination works like pulse-shape discrimination (PSD), except that the delayed triplet light is much higher intensity and longer wavelength.

Summary of Accomplishments

This approach substantially increased scintillation yield and provided separable triplet and singlet emission spectra that can be used to discriminate particles by either SSD or PSD. All project objectives were met or exceeded. We incorporated triplet fluors into solid organic scintillators, and determined the relative luminosities and time constants for singlet and triplet emissions as functions of composition and particle type. In addition to demonstrating the approach with the proposed scintillating plastic and cubic metal organic frameworks (MOF) hosts, we compounded and tested several compositions of an oil-based liquid. The generality of this approach is an important aspect of the intellectual property being claimed in an international patent application now in preparation.

Key Accomplishments

1. Developed independent control of delayed luminescence wavelength, timing, and intensity in organic scintillators. This enables new particle discrimination materials to be engineered for spectral and timing-based discrimination of neutrons and gammas.
2. Demonstrated new spectral shape discrimination (SSD) signature in 20 host materials. These include the plastic scintillator, polyvinylcarbazole, oil-based compositions, and several types of cubic nanoporous framework materials. The generality of the approach is due to the use of non-interacting singlet and triplet derived luminescent states.
3. Derived an SSD figure of merit statistically equivalent to the PSD metric.
4. Presented initial MOF results at the 2010 Symposium on Radiation Measurements and Applications (proceedings manuscript to be published in *Nuclear Instruments and Methods*).
5. US and international patents applications.
6. During the research it became clear that the approach can also be used to engineer improved PSD in low-cost plastic materials, for direct replacement of liquid scintillators in existing systems. A proposal to develop such materials was submitted to DOE, and was selected as a 1-year exploratory research project in FY 2011.

Significance

The new materials will enable enhanced detection of special nuclear materials, supporting Sandia's missions in homeland security and defense, nonproliferation, and nuclear weapons. Anticipated benefits include the following: 1) increased sensitivity for fission neutrons, 2) simplified pulse processing and timing requirements, and 3) elimination of hazardous material.

Benefits from this R&D:

- Immediate benefit: defense systems and assessments — (DOE advanced materials) materials/methods for nonproliferation
- Near-term benefit: Energy, Resources, and Nonproliferation — (Defense Threat Reduction Agency [DTRA] basic research, FY 2012 and broad agency announcement [BAA], FY 2011)
- Future benefit: homeland security and defense — (Domestic Nuclear Detection Office academic research initiative) supporting systems for border security

Follow-on:

- DOE Plastic Scintillators for FY 2011 exploratory research
- DTRA BAA Final selections announced ~January 2011, Starts ~May
- DOE Anticipated 3-year life-cycle proposal for 2012–2015
- S&T advance: New signature for particle discrimination
- International Patent application in process for SSD method and method of introducing extrinsic signature for PSD/SSD compositions
- Strategic partners: Building on our existing relationship with Saint Gobain for commercialization of new scintillator materials.

Web Sensor

141682
Year 1 of 2
Principal Investigator: R. Colbaugh

Project Purpose

There is a strong need in many areas of national security to monitor world situations and trends and detect anomalous events. The Worldwide Web provides a powerful means of obtaining information, but continual tracking and searching is laborious and detecting subtle changes is challenging. This project will create an easily configurable and launchable tool to allow individuals and workgroups to specify domains and event classes to monitor. The tool will then commence ongoing monitoring of key websites (news, blogs, etc.) as well as web crawling to locate additional sites; source "authoritativeness" will be assessed automatically to determine whether sites are reliable sources of information in domains of interest. User feedback to refine the search will be solicited based on information identified as potentially useful.

The web-monitoring tool will be server-based with a web interface to allow work group interaction and view construction. The tool will combine three analytic methodologies: 1) content analysis (e.g., to identify matches to desired information using a variety of techniques); 2) hyperlink topology analysis (e.g., to detect web "communities" relevant to a given domain and assess their authority); 3) temporal analysis (e.g., evolution of topics of interest and web communities). Machine learning-based anomaly detection algorithms will enable the key product: informing users of key changes in the world situation. Bayesian techniques will allow tracking of uncertainties in both key site selection and anomaly detection, and will help prioritize user interactions limiting user burden and maximizing value of information gained. Key technical challenges include combining three distinct, complementary web analysis methodologies, and incorporating sophisticated anomaly detection into a system that allows user groups to collaboratively maintain situational awareness. Constructing an analyst configurable and modifiable system represents an additional challenge. Overcoming these challenges will result in significant differentiating technical capabilities.

Summary of Accomplishments

R&D accomplishments can be organized into three areas:

<u>Data collection:</u> We have completed development of CACTUS (Computational Analysis of Cyber-Terror against the United States), our web data collection tool. CACTUS provides standard capabilities, including sophisticated crawling and collection of web data, fast indexing tools, and wrapping/extraction of metadata, link graphs, and temporal information. Additionally, CACTUS provides four advanced features: 1) crawling/collection from social media sites 2) encoding/archiving data as time series of semantic graphs; 3) guided data collection within our predictability framework; and 4) assessment of website authoritativeness.

<u>Computational analysis:</u> The main objectives for computational analysis include the following: discovering and characterizing web data sources, situational awareness and warning analysis for national security domains such as extremism and nuclear facility security, and analyst-guided drill-down analysis of situations and events of interest. New capabilities developed to date include the following:

1. sentiment analysis tool for social media that outperforms existing methods and that has been successfully implemented in an extremism study;
2. "influentials" detection tool for discovering and characterizing influential blogs which represents the first scientifically grounded capability for identifying influentials;

3. early warning tool for social diffusion events (protests, emerging threats) that provides the first such early warning capability to be demonstrated on real world protest events;
4. predictive analysis tool for social dynamics that enables identification of web data features possessing predictive power; and
5. emerging topics discovery tool for blogs that enables early detection of new topics at webscale.

Case studies: Web sensor performance is being evaluated and demonstrated through two case studies, namely, alerting for threats to nuclear installations and early warning analysis for extremist radicalization. Results from the latter case study have permitted us to attract external funding for a web-based analysis project with DoD.

Significance

The primary anticipated outcome of the project is a genuinely differentiating capability for collecting and analyzing web data for national security applications. The web sensor has the potential to significantly impact DOE and national security missions. The project directly impacts DOE's NNSA mission (through the main case study) and infrastructure security activities (by developing threat discovery and warning capabilities that are applicable to such systems). Additionally, we expect the web sensor to be directly relevant to programs at DHS (e.g., via the extremism/radicalization case study) and DoD (in, among others, influence operations, counterterrorism, and cyber security). We anticipate that web sensor capabilities will be applicable to other areas as well (e.g., human health with the Department of Veterans Affairs). In some instances the new capabilities will exceed state of the art by an order of magnitude (e.g., sentiment analysis), and in others, the new tools will provide capabilities that do not currently exist (e.g., reliable early warning for real world events using web data). Expected outputs include new intellectual property, typically reflected in journal and conference publications and presentations, and software prototypes for all automated analysis methods. Effort will be made to impact relevant scientific domains beyond informatics, such as social science and national security fields. This work impacts Sandia's DOE/DHS/national-security missions by detecting threats that currently cannot be detected, or are detected too slowly to avoid significant cost in life and economic disruption. Sandia mission areas strongly benefitting from application of the proposed tool include, information management and risk-based human decision-making and complex systems modeling, analysis, test and assurance, information and intelligence technologies, and intrinsic security.

Refereed Communications

R. Colbaugh, K. Glass, and R. Laviolette, "Deep Information from Limited Observations of Robust yet Fragile Systems," *Physica A*, vol. 388, pp. 3283-3287, October 2009.

R. Colbaugh and K. Glass, "Some Intelligence Analysis Problems and Their Graph Formulations," *Journal of Intelligence Community Research and Development*, vol. 315, 2010.

R. Colbaugh and K. Glass, "Modeling and Analysis of Social Network Diffusion: The Stochastic Hybrid Systems Approach," to be published in the *Journal of Mathematical Sociology*.

Modeling a Chemical Defense Strategy

148373
Year 1 of 3
Principal Investigator: T. M. Hoette

Project Purpose

Despite the long history of use of chemical weapons and repeated indications that terrorist groups possess both the ability and intent to employ chemical agents, surprisingly little attention has been focused on developing defensive concepts, much less a comprehensive strategy for civilian chemical defense. The objective of this project will be to develop a comprehensive model of chemical terrorism events to enable the clear delineation of which phases of the attack cycle provide optimal opportunities for intervention, what strategies offer the most promise of preventing or mitigating these attacks, and where significant gaps exist in our capabilities to prevent, detect, or respond to a potential attack.

The main product of this project is a top-down systems model of civilian chemical defense developed through the methodologies of complex adaptive systems of systems (CASoS) engineering. Given the wide diversity in defense architecture components and the need for flexibility in the face of an ever-evolving threat, we argue that an effective defense structure will, and indeed must, exhibit the hallmark features of a CASoS: emergent behavior, self-organization, and adaptability. Two specific components of the defense expected to significantly drive CASoS behavior, medical response and chemical agent dissemination, will be enhanced and reincorporated in order to observe impact of new injects and help verify the model. Given the short timelines typical in acute chemical attacks, the efficacy of medical intervention is crucially interdependent with other response actions. An examination of the means available to an adversary to effectively disseminate chemical agents in an attack is required to better quantify credible attack sizes, an aspect of the threat that strongly influences the scale of the overall defense system.

Summary of Accomplishments

We have developed a preliminary systems model framework through the use of diagramming tools from Systems Dynamics. This top-level framework, which continues to develop as the system is explored further, has also led to work on subsequent milestones. Causal loop diagrams and stock and flow diagrams (built in VenSim [Ventana Systems, Inc.]) are being used to investigate the structure of the system by describing the organization of the system variables and identifying cause-and-effect interactions among these variables. We have also constructed an interaction matrix to illustrate the variable interfaces. Model boundary diagrams have been developed to define what variables are endogenous and exogenous to the system, as well as those that should be excluded from the model entirely.

We have also made significant strides toward identifying tools associated with CASoS methods that will support our efforts in the first-year milestones. Modeling of the behavior of the stakeholders in the system (e.g., adversary deterrence, social acceptance of security measures, etc.) will be based on human factor engineering. Subject matter experts within Sandia on human factors and adversary deterrence have been engaged in the project. Game trees, which are analogous to decision trees for single-entity processes, are a tool of game theory that will enable us to describe the interdependence of adversarial decision-making (e.g., if the US introduces policy X, the adversary will adopt strategy Y). Network thinking is a toolset from graph theory that provides a measure of "clustering" and "distribution" in the system, which ultimately reveals the transmission of ideas through the system. Efforts toward improving the systems model framework (milestone #1) and identifying and describing interactions within the system (milestones #2 and #3) are ongoing and will include the use of the broad collection of tools and methods described here.

Significance

Chemical terrorism continues to be viewed as a significant risk at the highest levels of government. Sandia is a national security lab with appreciable investments in chemical detection, remediation, and threat assessment. Ultimately, Sandia aims to provide full systems solutions to complex national security problems. This project is aimed at developing a model to explore systems solutions for chemical defense. This project will specifically benefit programs funded by DOE, as well as programs funded by DHS/CSAC (Chemical Security Analysis Center) and DHS/S&T.

The goal of this work is to further our nation's defensive efforts in several areas (detection, protection, and response) and to develop fully integrated solutions to chemical security problems. The model we are developing will be used to understand the cross-cutting impact of these types of defenses (i.e., how does detection impact response). The chemical defense model has already seen a positive response from stakeholders developing these defense measures. A briefing to CSAC on this project led to a new project sponsored by CSAC.

Development of Chemi-Responsive Sensors for Detection of Common Homemade Explosives

149568
Year 1 of 3
Principal Investigator: C. M. Brotherton

Project Purpose

One of the newest terrorist threats to both the public and the military is referred to as homemade explosives (HMEs). HMEs can be synthesized using commonly available chemicals, and one of the most dangerous new threats involves HMEs made with peroxides. Peroxide-based HMEs are particularly dangerous because there are few viable detection methods to identify them. This project will focus on developing a new sensor capable of detecting peroxide-based HMEs. The sensor technology of interest is a polymeric chemi-response sensor first developed at Sandia. The sensor consists of aligned conductive particles embedded in a polymer monolith. Upon exposure of the monolith to the analyte, the polymer swells causing the embedded particles to separate thus providing a change in conductivity. Previous work using this technology focused on detecting contamination of organic solvents in water. This project will expand the capability of these sensors by developing new polymeric materials that are sensitive to peroxides. This will be achieved by investigating different embedded particle types, sizes and configurations and by studying and understanding the kinetic response of the polymeric materials to analytes in the gaseous phase. At the conclusion of this project, we expect that a sensor design will be identified that will be able to sense peroxides in the gas phase.

Summary of Accomplishments

Since its inception, work for this project has focused on ensuring that the appropriate environmental safety and health procedures and documentation are in place, reviewing relevant literature regarding previous developments in the field of sensing using chemi-resistive sensors, purchasing the necessary equipment and designing/building a sensor evaluation system. The evaluation system consists of a gas handling system that has the ability to expose chemi-resistive sensors to environments with varying concentrations of gas-phase solvents. The solvents of particular interest are peroxide-based and additional care is required to reduce the interaction of the evaluation system with the highly reactive peroxide materials. Additionally, we improved the sensitivity of the chemi-resistive sensors to common organic vapors by reducing the polydispersity of the embedded particles. The sensor response to peroxide-based materials is expected to be lower than common organic solvents and sensors with increased sensitivity will improve the likelihood of success. We also began characterizing the sensor response to water vapor. We expect that water vapor will be the most commonly encountered interfering substance, in potentially high concentration; therefore, understanding the sensor response to this interference is necessary to determine the efficacy of the sensor in real-world environments.

Significance

The development of biaxially aligned magnetic particle/polymer composites as sensor elements aligns with DOE goals for scientific discovery and innovation. Improved sensor technologies and new approaches to the identification of terrorist materials will benefit DHS and DoD.

The improved chemi-resistive sensor sensitivity increases the chances of success in detecting peroxide-based HMEs, and may potentially enable the use of chemi-resistive sensors in other sensing applications. Completion of the sensor evaluation system increases the capabilities of the contraband detection group at Sandia.

Enabling R&D for Accurate Simulation of Non-Ideal Explosives

149656
Year 1 of 1
Principal Investigator: R. G. Schmitt

Project Purpose

Homemade explosives (HME) and improvised explosive devices (IEDs) are an increasing domestic threat and are commonly used in foreign conflicts dominated by sectarian disputes and/or non-state terrorists. Protection or countermeasures against these weapons could be significantly improved with a better technical understanding of their behavior. Termed "nonideal" explosives (NX) because their behaviors are not well represented by classical one-dimensional steady detonation theory, relatively little fundamental research has been performed to characterize them and predictive numerical modeling is largely absent. An improved level of understanding relies on tightly coupled pursuit of experiment, theory, and numerical modeling. In particular, numerical modeling is essential for the discovery of reaction mechanisms and simulating the coupled, nonlinear evolution of composition, temperature, and pressure of the reactive flow behind a shock front in a highly heterogeneous continuum, particularly at extreme conditions that are not readily accessible by current experiment measurements.

While predictive simulation of nonideal explosives will require accurate treatments of diverse phenomena across the multiple scales of atomistics, mesoscale, and the engineering continuum scale, a staged approach should begin by focusing on two tasks: 1) extend the chemistry treatment in conventional hydrocode simulation of reactive flow to include a thermodynamically consistent equilibrium based description of reaction products, and 2) extend classical molecular dynamics capabilities for discovery and characterization of reaction pathways in NX explosives. These two near-term tasks are significant research endeavors. Hence, for this brief study, we propose to implement the TIGER thermochemical equilibrium code into the CTH shock physics code as a primary equation of state. We will work to improve the performance and robustness of the TIGER code. The multiscale shock technique will be implemented into Sandia's molecular dynamics code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). This work will result in tools for the development and analysis community that can be exploited to further the science and analysis of NX explosive behavior.

Summary of Accomplishments

The TIGER thermochemical equilibrium code was implemented into CTH as a primary equation of state. This implementation is compatible with all existing reactive flow models in CTH. We also made improvements to the equilibrium solver within TIGER to make it more robust and efficient. We have also implemented new commands to the TIGER code to allow multiple atomic populations to be specified and to allow for implementation into the parallel architecture of CTH. TIGER is incorporated into the current version of CTH and goes through the routine testing and benchmarking with the code. This assures us that new capability remains functional as the code changes. We added the TIGER output information on chemical species, temperature, and pressure to the CTH database for analysis and plotting, with significant effort invested in the task of modifying the equilibrium solver. We reorganized the routine for clarity and unraveled some of the assumptions concerning the species database ordering. By manipulating the species ordering, we were able to improve the efficiency of the solver. We began to address robustness and efficiency by implementing a backup capability for TIGER and alternate algorithms for generating trial solutions that initiate the iterative equilibrium solver. An additional molecular dynamics method called the Multiscale Shock Technique (MSST) was implemented in LAMMPS. The method's incorporation was a collaboration with Stanford University. In order to test the underlying assumptions of the MSST method, as well as the validity of the LAMMPS implementation, we ran MSST simulations for pentaerythritol tetranitrate with the same ReaxFF potential and initial crystal configuration as used in the previous direct simulations. MSST simulations compared favorably to those prescribed in our direct simulations.

Significance

The proposed research supports the R&D thrust on explosive threats. The desired predictive simulation capabilities would provide tools that could benefit DHS and DOE by enhancing threat assessments and substantially accelerating development of effective and economic countermeasures against HME and IED weapons. This project addresses the first stage of developing the needed predictive simulation capability for non-ideal explosives. The computational tools produced during this project are now in a position to be exploited to further the science and analysis of NX behavior. The TIGER thermochemical equilibrium code implementation can be used to study the effects of changing composition of explosive materials. This computational capability is positioned for the performance of advanced multiscale analysis with advanced mixing. The MSST molecular dynamics technique is a significant new capability added to LAMMPS and will provide a much broader analysis capability in terms of time. This will help to develop the needed thermochemical understanding necessary to accurately simulate NX.

Target Materials for Dual Neutron/Gamma Generators

149660
Year 1 of 1
Principal Investigator: A. J. Antolak

Project Purpose

Detecting and characterizing shielded special nuclear materials (SNM), especially highly enriched uranium, is a challenging problem. Conventional passive methods rely on spectroscopy of low-energy gamma rays from natural decay, but this approach fails when thick shielding is present. Active interrogation, using high-energy neutron and photon sources to stimulate high-energy fission neutron and gamma-ray signals, provides an unambiguous signature of fissile material. While compact neutron generators are well studied and mono-energetic gamma generators are emerging, dual-particle generators producing both neutrons and gammas have not been fully proven. A dual-particle generator allows the optimal source to be used in each situation. Reliable, robust generators that are easy to operate in the field are necessary to truly make active detection technologies accessible. While, in most cases, the accelerator technology is mature, the associated power supplies, ion sources, and production targets are areas in which significant improvements are presently needed. This project focused on the development of target materials for use in next-generation dual-particle neutron/gamma generators that utilize low-energy nuclear reactions to produce high-energy radiation for active interrogation. The idea of using nuclear reactions to produce mono-energetic gammas and neutrons is not widespread; most of the work has been conducted at Sandia. The neutron/gamma production targets for these nuclear reactions must be easy to fabricate, withstand the harsh radiation environment inside the generator, and also have good thermal, electrical, and mechanical properties. Although there may be other reactions of interest, one nuclear reaction that shows promise for this technique is $^{7}Li\ (d,\ n\gamma)^{8}Be$, producing 12–17 MeV gammas (near the peak of the photofission cross section at 14 MeV) at a deuterium energy of 360 keV and 13.3 MeV neutrons over a broader deuteron energy range (capable of penetrating thick shielding similar to 14 MeV D-T neutrons, but without the need for tritium).

Summary of Accomplishments

There are four major components to this work: research possible nuclear reactions, identify and prepare candidate target material samples, conduct irradiation testing, and perform post-microscopic examination to analyze the samples. The research investigated the performance, robustness, and lifetime of lithium-containing materials to be used as neutron/gamma production targets in dual-particle generators. We assessed the viability of selected materials through a program of electron (e-beam)- and deuteron-beam (i-beam) irradiation experiments followed by microscopic analysis to assess their operational performance limits in the environment of a dual-particle generator. Through combined electron and deuterium ion beam irradiation experiments, we demonstrated that both LiF and Li_2O could be used as solid-type targets for these systems. While both target materials exhibited physical and chemical changes during the high intensity e-beam and i-beam exposures, these changes did not deplete lithium from the exposed areas, so the performance and lifetime of these target materials are expected to be suitable for their use a dual-particle neutron/gamma interrogation source.

Significance

There is an immediate need to search and identify SNM at fixed ports-of-entry, on cargo ships and vessels at sea, and at man- or vehicle-portable locations. Active neutron and gamma interrogation are not currently deployed for the detection of fissile material. The development of reliable interrogation sources that can penetrate a variety of shielding configurations can make this technology accessible to a variety of homeland security applications. Passive detection of SNM is not successful, so active interrogation is needed. A dual-particle neutron/gamma generator assists in the Sandia, DOE, and DHS missions of stopping the proliferation of nuclear material, particularly SNM, and radioactive material that can be used as radiological dispersal or exposure devices. The replacement of radioisotopic interrogation sources with neutron or gamma generators would reduce the quantity of material in circulation throughout the world.

Persistent Surveillance using a Tethered Aerostat

150121
Year 1 of 1
Principal Investigator: M. W. Koch

Project Purpose

Using a tethered aerostat for persistent surveillance (TAPS), we can develop an affordable, adaptable, and favorable geometry tactical system for use at critical facilities, bases, borders, and disaster areas. The successful deployment of unmanned aerial vehicles (UAVs) has shown the importance of using pilotless aircraft in surveillance and situational awareness. UAVs allow their operators to see over obstacles at large stand-off distances. Unfortunately, their high purchase plus operating costs have put UAVs out of range for all but a small number of agencies. UAVs also require specialized infrastructure for launch and recovery operations and have severe weight and power restrictions with limited communication bandwidths for their payloads. Conversely, a tethered aerostat can be launched and recovered from a flat bed truck or trailer and the tether can provide power and high communications bandwidth for the payload. Global Near Space Services has developed a self-contained, highly mobile, remote area and scalable aerostat system. Their patented hybrid envelope and airfoil shape can handle wind conditions up to 80 mph and provide up to 30 days of continuous operations.

We plan to determine the feasibility of Sandia technologies such as networked unattended ground sensors (UGS), automatic target recognition (ATR) algorithms, and radar technologies such as ground moving target indications (GMTI) and/or synthetic aperture radar (SAR) with coherent change detection (CCD) as payloads on a tethered aerostat to provide persistent surveillance. One concept will be UGS cueing an electro-optical imager to provide confirmatory and assessment capabilities, and to extend current ATR algorithms for detection, tracking, and classification. The second concept will be GMTI or SAR with CCD on a tethered aerostat using a Sandia mini-SAR. The addition of radar sensing modalities to a TAPS platform enables day/night, all-weather detection of moving objects at ranges much farther than conventional video systems could provide.

Summary of Accomplishments

- Identified key performance characteristics for electro-optical color and infrared cameras, SAR and GMTI radar
- Cost comparisons between aerostat vs. UAV and aerostat vs. perimeter fence
- Identified research challenges for the different sensing modalities
- Designed, developed, and tested an algorithm tracker to process color video from an aerostat that has enabled severe perspective and affine transforms over thousands of frames
- Connected solution spaces to operational parameters
- Initiated a cooperative research and development agreement with Global Near Space Services (GNSS)

Significance

This work would be relevant to any federal agency that needs persistent surveillance for defense, protection, situational awareness, or intelligence. Application areas include forward operating bases, critical facilities, border surveillance, maritime patrol, and disaster area monitoring. Solutions areas include wide-area imaging and enhancement, surveillance, assessment, tracking (following and searching), and sensor fusion. Examples include Department of Homeland Security (DHS) (such as Coast Guard, Border Patrol, and Federal Emergency Management Agency [FEMA]), Department of Energy (DOE) (site security), US Northern Command (NORTHCOM), Global Strike Command, Air Combat Command (ACC), Air Force Space Command (AFSPC), and US Navy.

Multidimensional Security Analysis

150125
Year 1 of 1
Principal Investigator: J. Clem

Project Purpose

The state of a system's security is dependent on many considerations including the positive and negative forces of various domains in which the system exists: human, cyber, physical, etc. A gap in our understanding of the multifarious nature of threats to modern systems (including critical protection and infrastructure systems) is reflected in the lack of a robust approach for assessing, designing, and optimizing them to ensure their mission in the face of sophisticated adversaries capable of hybrid attacks (attacks that span multiple domains). In order to develop techniques to counter the threats related to multidimensional security, we must first understand and describe the collision space for the multiple security domains in a system, identify key issues related to the multidimensional security space, and opportunities to maintain required performance despite uncertainty respective of the adversary. At the time this project was proposed, there had been inadequate investigation of how vulnerabilities in our critical systems arise from the issue of multidimensional security. The objective of this project was to investigate, define, and document the nature of multidimensional security, identify an approach to support systems engineering analysis of multidimensional security issues, and develop a small-scale test bed to support visualization of the multidimensional security problem. One noted national security expert remarked that, to his knowledge, "nobody else is looking at this problem." Today's approach to provisioning security, remains one based in individual domain stovepipes, and lacks a holistic or integrated approach.

Summary of Accomplishments

First, the project team collected the technical perspectives of security domain experts and obtained buy-in for the technical approach to the R&D. These perspectives were vital to understanding the individual domain perspectives and associated security issues representative of systems that would be assessed using a new approach. Second, we identified the challenge of multidimensional security as both a wicked and a fragmented problem. We contextualized the problem against a representative challenge of designing a physical protection system. Third, the team explored the issue of the collision space between different security dimensions in a system, and arrived at a definition and model of what the "security seams" are. We learned that the security seams themselves are multifarious in nature. They exist between security domain stovepipes, within individual security domains, between organizations, and between multiple missions supported by a system. The seams change over time and many consequential changes in them are opaque to stakeholders. Fourth, the team identified recommended, domain-agnostic approaches for analyzing and modeling multidimensional security at a systems level. We determined that functional-level analysis permits the security engineers to work at a level of abstraction that avoids trappings within the individual security domains by examining the security functions across the entire system, i.e., a holistic rather than piecemeal approach. Finally, we identified an initial set of questions that the recommended approaches should attempt to answer.

Significance

The research performed in this project supports the national security community with a sorely needed first step for combating sophisticated adversaries targeting our critical infrastructure and strategic military and economic assets and resources. Benefits of the work include the identification of an approach to analyze the trade space for multiple dimensions of security; helping experts overcome security seams created by engineering stovepipes, addressing problems holistically, rather than domain-by-domain. The recommended approaches of functional-level analysis, and modeling and simulation support an evolution or even revolution in how we cope with the wicked problem of multiple domain security. The approaches will support cost-efficient analysis for resource allocation; testing of current and new system designs, components and operational configurations; evaluation of security-significant interactions between domains that are not currently being evaluated; adversarial analysis (e.g., red teaming); investigation of the impacts of security-related assumptions and dependencies; and enhanced communication between stakeholders by providing a framework for common system-level analysis.

This work supports critical infrastructure, physical security, force protection, defense systems security, and international security capabilities for DOE, DHS, and other federal agencies of the US government. The team used a systems engineering approach resulting in research that is broadly applicable to a large set of system stakeholders, and one that will support improved collaboration between them. The knowledge derived from the exploration of the issues surrounding multidimensional security supports next steps to perform functional-level integrated analysis for multiple security domains, build example models, and perform simulations of multidimensional security environments.

Measurement and Optimization of Infrastructure Resilience

150276
Year 1 of 1
Principal Investigator: E. D. Vugrin

Project Purpose

Critical infrastructure resilience (CIR) has become a priority for federal homeland security authorities. To make CIR an actionable concept, several challenges must be overcome. Most fundamentally, very little of the necessary groundwork has been done that would enable a systematic framework for the quantitative measurement of infrastructure resilience.

In prior work, we proposed a generally applicable definition of resilience for infrastructure and economic systems. We assert that costs associated with impacts to system performance, as well as the cost of recovery after disturbances, must be incorporated in the mathematical system description used for resilience analysis. In this context, costs are not necessarily measured in economic terms; rather, the term "costs" is used to represent the more general consequences resulting from decreased system performance (e.g., lives lost due to unavailable antibiotics) and the resources and efforts expended in recovery efforts (e.g., importing antibiotics from foreign suppliers instead of domestic producers). Existing resilience measurement methodologies do not consider the cost of recovery processes, so new mathematical methods must be developed that comprehensively measure resilience costs.

We propose the development of new mathematical techniques for measuring resilience costs that will indirectly provide a measure of system resilience. We will focus on identifying, developing, and applying control and optimization techniques for resilience quantification. The goal of this effort will be to develop rigorous, methods that incorporate impacts to the system, as well as the cost of recovery to disturbances. These methods will be generally applicable to most critical infrastructure systems; thus, enabling the consideration of cross-infrastructure dependencies.

These techniques will enable a more comprehensive accounting of resilience-determining factors. Recovery resources tend to be limited, and this project aims to provide guidance on how to efficiently utilize those resources. Enhanced resilience evaluation will ultimately result in more stable and secure infrastructure systems.

Summary of Accomplishments

The primary objective of the project was to determine how to solve the following problem:
In the context of a disruptive event affecting a discrete, (non)linear network, what is the optimal recovery sequence that minimizes resilience costs given that recovery resources are limited, multiple recovery modes are available, and multiple asset restoration sequences are available.

Key results related to the development of mathematical approaches for solving this problem include the following:

- The development of a bi-level optimization that describes the problem in mathematical terms
- The application of a solution technique, leveraged from the literature on multimodal resource constrained project scheduling problems
- Application of these approaches to a set of models that are used in critical infrastructure analysis

Additional, more-general results include:

- The adaptation of a complex, existing infrastructure model to develop a resilience analysis capability
- Application of this capability to a national rail network model and a dynamic supply chain model of army munitions
- A case study involving a scenario in which four bridges have been damaged by flooding. Using our mathematical formulation, we identified the optimal sequence and mode of bridge restoration. When compared with conventional recovery strategies, application of our approach resulted in a 20% reduction in total recovery time. Costs to the railroad from rerouting, loads not moved, etc., could be decreased by 43% with only a 10% increase in repair costs.

Significance

The capability to quantitatively evaluate infrastructure resilience will advance the nation's ability to design and improve infrastructure with the objective of minimizing the impacts of disruptions from hazards. Increasing the resilience of national infrastructures will increase stability and national security by ensuring that the critical systems maintain functionality during disruptions. We envision this capability will enable rigorous quantification for infrastructure resilience assessments and the subsequent design of systems-level solutions that increase the reliability of a wide variety of infrastructures that would be of interest to DHS, DOE and DoD.

Southbound Borders Inspection

150970
Year 1 of 1
Principal Investigator: J. C. Reinhardt

Project Purpose

The escalating violence in Mexico, particularly in cities and areas near the US border, have taken the lives of thousands of law enforcement, military forces, cartel leadership, smugglers, foot soldiers, and innocent citizens from both nations. This level of disruptive violence threatens the long-term security of both Mexico and the United States, especially southwest border s``tates. Efforts to reduce the flow of illicit southbound movement of the weapons, drugs, and other contraband that fuel the cartel activities are important tools in stemming the violence and other crimes. The expansion and enhancement of existing outbound inspection activities in the US has been proposed as a method to improve the ability to interdict smuggled weapons and cash, and therefore improve law enforcement's control on this unstable situation.

The cost and benefit trade-offs of various methods of performing outbound inspections have not been systematically examined. Moreover, a systematic comparison of outbound inspection to other approaches (i.e., policy measures, investigations, etc.) has not been completed, but is necessary in order to make sound policy decisions that could have positive impact on this issue. Recent US Senate language has indicated a desire to potentially witness performance of such analyses from DHS or other agencies. Central to these trade-off decisions are estimates of effectiveness of inspections in detecting contraband, economic impacts of the proposed measures on both sides of the border, and perceived impact on criminal activities and organizations. Sandia and other institutions have developed economic models, technology models, and logistical models that can be applied to examine those aspects of performance. However, there is no systematic and rigorous method for assessing impacts to the organizations responsible for crime. This project is focused on developing such a methodology to complement other Sandia tools in analyzing trade-offs in border management approaches.

Summary of Accomplishments

Much interest has been expressed by policy-makers in actions that the US could take to help in thwarting the violence and organized crime in Mexico. One proposed method has been to perform southbound inspections to stem the flow of guns and money into Mexico from the US. Performing a full analysis on the impact and feasibility of this concept would require that analysts be able to estimate the impact on the crime and violence within Mexico. This project elaborated a methodology, including potential metrics, estimating the potential impact and options to be explored for performing that analysis. We found that even perfect measures to stop the movement of guns south may have much less impact than currently thought. We also found that stemming the flow of bulk cash and funds from supporters in the US presents a unique set of challenges in practice and analysis. Metrics and methodologies for assessing impact and success of countermeasures have been proposed and defined. A comprehensive report, detailing the findings of the effort, as well as next steps in the analyses has been produced and submitted.

Significance

Sandia, has, as one of its core missions, homeland security. DOE and DHS have worked closely to leverage national laboratory capabilities towards homeland security issues, such as border management and security. This project will directly extend previous work and support borders related homeland security activities through creating an enhancement to modeling and assessment capabilities.

NUCLEAR WEAPONS INVESTMENT AREA

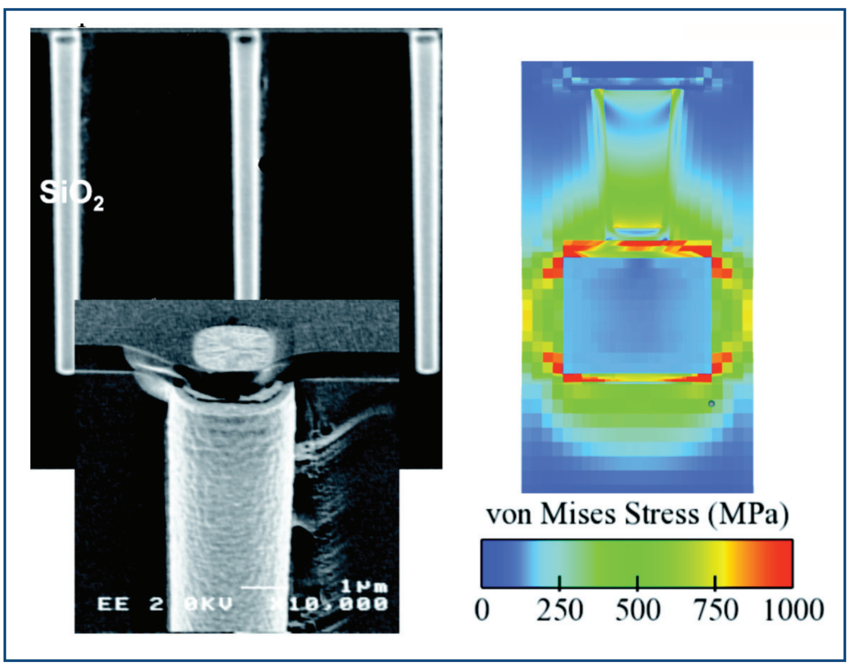
From fundamental studies into novel material combinations underlying better sensors and actuators, to more immediately employable sensors for monitoring the environment of weapon components, to improved nuclear weapons communications architectures, the projects in this investment area all aim to provide better, more-reliable methods of stockpile stewardship, with potential impacts to related mission areas (such as advanced battery construction and the role of the hydrogen economy in non-fossil-fuel energy generation).

3D Integration Technology for Highly Secure, Mixed Signal, Reconfigurable Systems

Project 117847

Design of novel system solutions for nuclear weapons components must meet numerous requirements deriving from factors such as harsh environments, smaller component volumes with reduced power budgets, and increased security. These constraints demand novel architectures compatible with existing fabrication technologies that are also reconfigurable as novel surety solutions emerge. Three-dimensional integration of electronic elements is a desirable solution, enabling combinations of separate analog, digital, and other technology functions in a single low-volume package, which can also significantly improve system security.

Utilizing high-fidelity modeling to guide design and processing requirements, this project has devised a low-temperature three-dimensional wafer and chip-stacking capability to provide 3D integrated solutions. In addition to reducing volume and power requirements for electronic subsystems, this approach leverages optimized independently developed application specific integrated circuitry while reducing pin count. It also enables multiply redundant subsystems, thus facilitating an adaptive design for meeting security and reliability requirements. Success with bonding dissimilar materials at low temperatures will also benefit other national security applications.



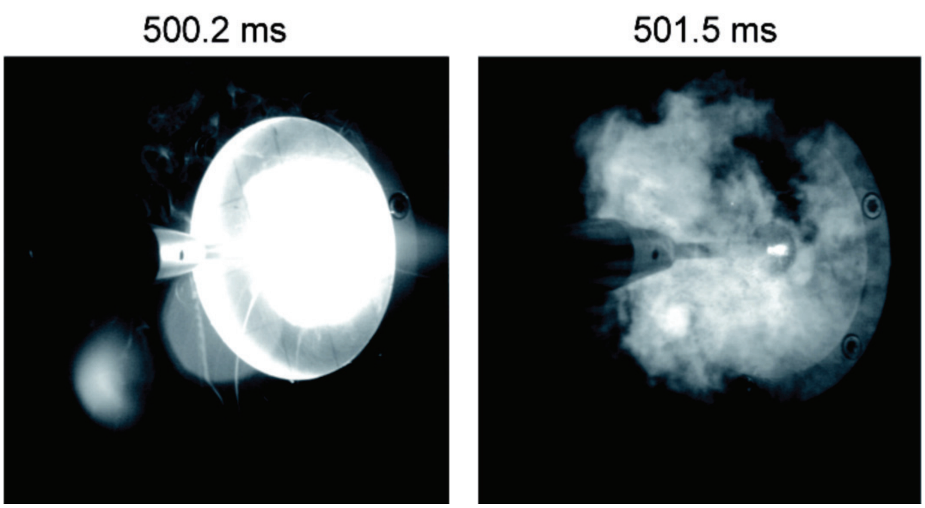
Left: Electron micrographs of front-end-of-line through-Si-Vias (FEOL-TSVs) created at Sandia's Microfabrication facility. Right: High-fidelity modeling of fabrication-induced von Mises stress distribution in a vertical and horizontal interconnect (2 million mesh elements).

Field and Charge Penetration by Lightning Burnthrough

Project 130793

Many crucial Sandia-engineered electrical systems are threatened by lightning strikes possibly breaching protective metallic enclosures and insulation, thereby interrupting proper function. The design of shielding for safety-critical components depends upon a better understanding of the processes by which such lightning burnthrough occurs, ensuring that critical electrical systems are protected from failure.

This project is seeking to develop a quantitative understanding of the physics that limits voltage and current penetration in lightning burnthrough. One component of this research employs the Sandia lightning simulator, which permits the study of the various phases of electrical discharge associated with a lightning strike. High-speed photography and other detailed instrumentation of these experiments permits diagnostics of the various event phases with submicrosecond resolution. Additionally, the project is developing and applying models for the various physical penetration mechanisms. Ultimately, this research will provide a quantitative basis on which to make safety assessments and may permit the development of new methods of protection against lightning strikes.



Monitoring lightning effects over microsecond time scales.

NUCLEAR WEAPONS INVESTMENT AREA

Determination and Optimization of Spatial Samples for Distributed Measurements

117843
Year 3 of 3
Principal Investigator: H. D. Tran

Project Purpose

When measuring or inspecting products for acceptance, inspection criteria typically require a single value; however, this single value is not representative of the way that the measurement is taken. For example, a form specification on a machined part, such as circularity or roundness, gives a single value for maximum acceptable deviation of a part's radius. The inspection of this radius, however, will typically require multiple measurements. There are no accepted standards for determining how many measurements to take or where to take them, nor for assessing confidence in the evaluation of acceptance based on these measurements. We propose developing a standard method for determining the number of measurements, together with the spatial distribution of measurements and the associated risks for false acceptance (accepting a part that does not conform to specifications) and false rejection (rejecting a part that is, in fact, conforming). We propose, in this project, to develop this method initially for dimensional inspection; however, the fundamental method developed should easily be extensible to other measurement domains that have spatial distribution, such as temperature distribution.

The project focuses on applying orthogonal transforms, such as the discrete wavelet transform to computer model-based geometry, to determine optimal sampling locations. We will then apply the inverse transform to reconstruct measured geometry, and compare with model geometry for acceptance. We will then assign computer confidence bounds.

The developed method provides a mathematical basis for assigning measurement uncertainty and risk for complex measurements. In addition, we developed an algorithm for adaptive sampling and tested it for 1D (lines, line segments, or arc) geometry. The objective is to have this general method adopted as an internationally recognized standard practice. The general method crosses many disciplines, and therefore, supports broad manufacturing initiatives that impact nuclear weapons (NW) product realization.

Summary of Accomplishments

We demonstrated a wavelet-based method to construct confidence bands, to assess form errors, and to determine a sampling strategy for CMM (capability maturity model) measurements in coordinate metrology. The confidence band for the measurement data is computed via specifying its baseline and the half-width of the confidence band; the former can be constructed via the wavelet shrinkage method, and the latter can be obtained via simulation based on the Lipschitz regularity. For the form error assessment, we predict the surface of the geometric feature (a dense set of measurements) using a small number of observed samples, and find the maximum inscribing and minimum circumscribing geometry that bounds all points on the predicted surface. For the sampling strategy, a wavelet-based random curve-interpolating algorithm is considered. We discuss the optimal choice of new sampling positions under our model. The proposed method has been validated with synthetic and real data.

We have also demonstrated the feasibility of programming an adaptive sampling subroutine on existing CMM software. While this demonstration is limited to one-dimensional geometry, such as lines, with suitable change of coordinates, it also yields arcs or curves. Using experimentally obtained data, the proposed adaptive sampling algorithm correctly increases sampling density where the measured line segment has greater curvature than where the measured line segment is straighter. The logic in the adaptive sampling algorithm is readily implementable on commercial CMM software. We believe that implementing the algorithm described above would be a useful addition to existing CMM line segment measurement methods, which are all based on uniform density sampling. The MATLAB algorithm for adaptive sampling that has been developed can be used for quantitative offline evaluation of scanned point data. The offline evaluation could suggest where higher densities are needed when formulating measurement inspection plans during the pilot manufacturing phase.

Significance

The research results include a wavelet-based method to estimate confidence bounds in measurements. This confidence bound method can be used in a standard practice for inspection. The use of improved confidence bounds can be incorporated in risk-based assessments and decision-making for product acceptance. The research results also include the demonstration of a simple algorithm for adaptive sampling that can be implemented in existing commercial CMM software. This can help guide engineering and development in deciding where greater resources are needed in the transition from development to manufacturing.

These methods will provide manufacturers with greater confidence that their product meets specifications, and eliminate superfluous inspections. This benefits both the economical and reliable manufacture of stockpile components, and also advances DOE's goal in advancing scientific knowledge. This also ties into federal support for manufacturing.

Intrinsically Secure Communications Through Adaptive Beam Forming

117844
Year 3 of 3
Principal Investigator: M. Forman

Project Purpose

We seek to develop intrinsically secure communications for storage containers that utilize novel physical-layer enhancements to provide security through channel physics. We propose the creation of an intrinsically secure wireless link that utilizes channel complexity and reciprocity to create shared cryptographic keys. The system will be capable of generating keys via channel reciprocity, complexity, and entropy; modifying channel sampling and key-generation functions cognitively based on channel measurements; and communicating over a private link using a symmetric cryptographic algorithm.

In detail, two nodes will generate symmetric keys by exchanging a series of wireless signals. Through channel reciprocity, signals exchanged by two nodes simultaneously will experience identical fading. This identical fading is shared information between the two nodes and is used to create symbols in a symmetric key. It is difficult for an eavesdropper to intercept the key and computationally prohibitive to deduce the key. The use of a symmetric-key algorithm eliminates the need for a key-management system. The completed product will be an intrinsically secure wireless link, implemented initially in software and later with bench-top test equipment.

Summary of Accomplishments

We created a full-duplex system for the generation of private keys for cryptographic communications using channel impulse-response estimation at 60 GHz. The full-duplex system is composed of two transceivers implemented with commercial millimeter-wave VubIQ transceivers, laboratory equipment, and software implemented in MATLAB. We have presented this work in two publications and two conference demonstrations. We have also submitted a patent application.

Significance

The proposed intrinsically secure link supports core DOE missions by developing novel hardware through the application of cutting-edge science.

Advanced Cathode and Electrolyte for Thermal Batteries

117845
Year 3 of 3
Principal Investigator: D. Ingersoll

Project Purpose

We propose, in this project, to develop a high-voltage cathode and electrolyte for thermal batteries, the main power supply used in all nuclear weapons and many smart conventional weapons. The materials used in today's weapon systems were developed 20–30 years ago and generate only 2 V per cell, as compared to the > 3 V per cell proposed here (a >150% increase). The new materials developed will allow modernization of thermal batteries resulting in lower production cost/time and improved performance through increased reliability and decreased size and weight. Furthermore, the reduced size/weight have the added potential for increasing weapon system mission range and payload.

To meet this goal, questions of both an applied and fundamental nature will be addressed, such as the thermodynamic stability of the novel materials at high temperature and in the presence of high concentrations of ligands, reversibility of the redox process and its functional dependence on temperature, the electrochemical stability of the electrolyte, and the nature of the charge transfer process. These issues will be investigated using a suite of synthetic, electrochemical, spectroscopic, and in-situ spectroelectrochemical methods. Included in the proposed work is the development of new methods of characterization, such as in-situ neutron diffraction, which can then be applied to other energy storage needs.

The fundamental and high-risk nature of this work is at odds with the demands associated with the cost/time constraints and low-risk approach typically associated with specific programmatic system objectives. Furthermore, this activity has the potential for impacting all future weapon system power supplies.

Summary of Accomplishments

We have determined that our original cathode candidates, the class of transition metal phosphates that have gained widespread acceptance for lithium-ion batteries used in consumer products, are unsuited to the thermal battery (TB) environment. The combination of high temperature and electrolyte composition found in the TB, particularly the high chloride content, leads to their decomposition. However, we have identified other high-voltage alternatives, including TiS_2 and CF_x. In our quest for alternative cathodes and electrolytes, we have also discovered a new class of room-temperature, transition metal ionic liquids (MetILs). Although none of the MetILs so far studied are suited for TB use, as a class, they exhibit properties that make them of particular interest for other electrical energy storage needs.

We have also developed a better understanding of lithium-ion mobility in the mixed metal oxide solid-ion conductors that we studied as alternatives to the chloride-based systems. We have also developed a synthetic approach to tailor the relative concentration of mobile species. Using this approach, it may be possible to tailor the lithium-ion conductivity for select needs. We have also developed a new means for monitoring all aspects of battery behavior in a practical device, and this was done using in-situ neutron diffraction coupled with multivariate data analysis. The highly penetrating nature of the neutron source allowed probing of an intact cell, and its high sensitivity to lithium allowed us to focus on the more important aspects of the lithium-based battery chemistry. Finally, we have used molecular simulations and computational chemistry methods to examine structural details and molecular mechanisms of the phosphates. Idealized structures and compositions can be examined using either classical force field or electronic structure tools, with the ultimate goal of using them to guide cathode synthesis and material development.

Significance

Batteries occupy an intriguing position as critical elements in weapon systems, and in serving as a foundational technology on which our modern electronic society is based. And in an age when access to energy has concurrent national-security, global-security, economic and environmental implications, development of advanced battery technologies for electrical energy storage is of critical importance.

In our search for a higher voltage cathode and new electrolyte, we discovered a new class of room temperature transition metal ionic liquids and a method for their single-step synthesis. This, to our knowledge, is a previously unpublished accomplishment. (We have since published the first report in what will be a series.) The low cost and widespread availability of precursors, and the general applicability of this approach to a number of inexpensive transition elements, creates the possibility for developing a low cost battery technology for stationary storage and in meeting the long term DOE- Advanced Research Projects Agency energy cost goals of < $100/kWh. Although our primary candidate cathode material was not stable in the thermal battery, we developed the knowledge base and expertise necessary to synthesize the parent compound and doped analogs. We have since used this capability to synthesize other compounds that can be used in other advanced battery chemistries, particularly those based on sodium-ion, that are free of the geopolitical constraints of other battery chemistries like lithium-ion. Examples of some of these other materials include the sodium titanates and manganates.

In order to develop batteries having optimum performance including long life, the structure-activity relationships of the materials undergoing repeated charge and discharge must be understood, which necessarily implies the availability of suitable diagnostics. Because of the interactions between all of the species in the battery, these characterizations are most meaningfully carried out in the intact cell under normal conditions of operation. We have developed a means to probe the fundamental materials properties in a fully operational cell, and the mathematical means to extract useful information from the resultant data. These techniques can now be used to interrogate power sources for all applications.

The traditional approach to new materials development for advanced batteries generally consists of an iterative build-and-test approach that is both time-consuming and costly. Being able to make predictive statements about new materials and material behavior could revolutionize battery development. Toward that end, our modeling activity focused on making predictive statements about select materials properties. We have successfully used both classical force field and electronic structure tools to evaluate key battery performance parameters to guide cathode synthesis and battery testing, focusing in this case on the structure and lithium transport in Li_xFePO_4 and other related olivine phosphate materials. Finally, we have identified two other potential cathode materials for thermal batteries. Although they do not have the higher voltages we expected for the iron phosphate, they are higher than the cathode material currently used in thermal batteries. Further development of these materials can lead to improved performance of thermal batteries for weapon applications.

Refereed Communications

M.D. Nyman, T.M. Alam, S.K. McIntyre, G.C. Bleier, and D. Ingersoll, “An Alternative Approach to Increasing Li-Mobility in Li-La-Nb/Ta Garnet Electrolytes,” to be published in *Chemistry of Materials*.

M.A. Rodriguez, M.H. Van Benthem, D. Ingersoll, and S. Vogel, “In-Situ Analysis of $LiFePO_4$ Batteries: Signal Extraction by Multivariate Analysis,” *Advance in X-ray Analysis*, vol. 53, 2010.

MEMS-Enabled Integrated Optical Circuits for Nuclear Weapons Applications

117846
Year 3 of 3
Principal Investigator: G. N. Nielson

Project Purpose

Microelectromechanical system (MEMS)-enabled integrated optical circuits have the potential to significantly impact a number of nuclear weapon components (such as discriminators and encryption systems), particularly as steps are taken towards further optical control of weapons. To date, only very preliminary work in MEMS-enabled integrated optical circuits has been done. This project is intended to expand that initial work, raise the technical readiness level (TRL) level of current devices, and explore the potential benefit to nuclear weapon components. The primary challenges are, first, creating a fabrication process that compatibly incorporates optical waveguides, MEMS, and germanium photodiodes, and second, applying appropriate design principles to achieve the optical and mechanical performance desired. It is anticipated that the MEMS-enabled integrated circuits will provide a unique set of performance characteristics. Chips can be fabricated requiring only optical inputs and outputs with the optical input signals controlling the resulting optical outputs. No additional electrical power or signal inputs are required. The chips will handle high optical power levels (up to at least a few watts — free space optical MEMS can handle, at best, hundreds of milliwatts). The optical isolation between optical paths is incredibly high, thus crosstalk is virtually nonexistent and, with the light confined in waveguides, there is no stray light going in unintended directions. Logic can be implemented in the optical circuit to provide a number of results, including enforcing sequence without requiring a clocking mechanism or external application specific integrated circuit.

Summary of Accomplishments

The key accomplishments within this project are in creating a fabrication process that incorporates MEMS, waveguides, and photodiodes, and in creating photodiodes for allowing on-chip optical control of MEMS devices.

We have demonstrated a fabrication process that allows functional MEMS devices to be combined with low-loss optical waveguides. This was a much more significant challenge than initially anticipated. The different material and temperature requirements for the MEMS and the waveguides required new methods of waveguide fabrication and, given that the silicon waveguides were clad with silicon oxide, there needed to be a completely new method of “release” of the MEMS device, where silicon oxide is typically the sacrificial material. We have demonstrated, after a number of iterations, functional MEMS devices that actuate functional optical waveguides on chip. This development paves the way for creation of MEMS-controlled optical devices such as switches and attenuators. We have successfully demonstrated the creation of InGaAs photodiodes and used indium solder bumps to flip-chip bond the photodiodes to a silicon chip with waveguides and emitters with metallization on chip for direct control of the MEMS device with light. These devices functioned well. We were able to demonstrate up to 16 devices in series operated from one single optical input to the chip, allowing a pathway to the relatively high voltages required for the electrostatically operated MEMS devices.

Significance

This project will advance the state of the art in integrated optical circuits and will lead to new capabilities in optical circuit technology. The expected performance characteristics are well suited to the needs of nuclear weapon systems, providing significant benefit to Sandia’s nuclear weapons mission. Other applications that may benefit include quantum computing, telecommunications, parallel computing, and secure data transmission. This work utilizes the Microsystems and Engineering Sciences Applications (MESA) complex.

3D Integration Technology for Highly Secure, Mixed Signal, Reconfigurable Systems

117847
Year 3 of 3
Principal Investigator: S. L. Shinde

Project Purpose

This project is aimed at addressing Sandia's future needs (near and long-term) for multifunctional, miniaturized systems via development of key technologies required for 3D Integration. 3D integration enables diverse architectures to be fabricated, while increasing the density of vertical interconnects by orders of magnitude. The current 2D approaches for assembly of complex systems are substantially vulnerable from a security standpoint. 3D integration enables combination of separate analog, digital, and other technology functions in a single low-volume solution utilizing vertical die stacking. Furthermore, combining these stacked elements will disable probing or visual inspection of the circuitry, significantly improving system security.

In this project we are continuing to develop the core capabilities in Sandia's Microsystems and Engineering Sciences Applications (MESA) complex (silicon fabrication [Fab], and the microfabrication facility [MicroFab]) to enable 3D integration of wafers produced at Sandia as well as wafers obtained from trusted vendors (e.g., IBM). Considering the compatibility of the conceived process modules with the existing tool-set in MESA, we have identified the main capabilities required, as follows: 1) wafer-to-wafer and die-to-wafer bonding, with an alignment accuracy of ±1 micron, of wafers/die with vertical interconnects at low temperatures (<100 °C); 2) front end of line (FEOL) compatible through-Si-via (TSV) processing to enable very high density vertical interconnects; 3) wafer thinning of bonded wafer and die stacks down to ~50 micron thickness to reveal the TSVs and backside metallization to make contacts with them; and 4) high-fidelity modeling of 3D structures to calculate stresses in all features as a function of processing during production as well as operating conditions to identify potential reliability risks, while also providing ground rules for designing structures with optimized stress levels. Each technology area represents a substantial development activity in terms of materials compatibility and complexity of process development.

Summary of Accomplishments

The project focused on developing technologies relevant to 3D integration in following areas: 1) front end of line through-Si-via (FEOL-TSV); 2) chemo-mechanical polishing (CMP) to create surfaces that can be activated and bonded; 3) surface activation and bonding technologies to enable low-temperature bonding of both the metal and oxide surfaces; and 4) very high fidelity modeling of 3D structures.
Accomplishments in each area include the following:

1. FEOL-TSVs: We demonstrated a fully complementary metal oxide semiconductor (CMOS)7 compatible FEOL-TSV process, and produced TSVs that are 2 μm in diameter and 45 μm deep on a 20 μm pitch. TSV dimensions and pitch allow for millions of vertical interconnects between stacked layers. A novel process was developed for filling these vias with tungsten. We are currently testing the CMOS7 compatibility of the developed process using standard gate oxide integrity monitor test vehicles.

2. CMP development involved qualifying a tool, debugging the process, and then developing CMP process modules for oxide, and oxide-metal composite surfaces. To this point, we have demonstrated oxide, nitride, and oxide-Ni CMP processes. Surface roughness is highly dependent on the quality of low-temperature oxide, however the CMP process is quite reproducible.

3. The surface activated bonding process development was quite successful. We have demonstrated <180 °C bonding of Au-Au, In-Au (both wafer level and die to die), with alignment accuracy better than 2 µm and <100 °C bonding of oxide to oxide surfaces. We have also shown bonding of Si to InP, Sapphire, and $LiNbO_3$.

4. High-fidelity modeling demonstrated construction of geometrical structures from Fab design data, and their hierarchical meshing with enough fidelity to mesh features that were a few nm in size. Modeling has shown stress variations in the fabricated structures as a function of Fab processing steps, thus providing a powerful tool to provide real- time feedback on thermomechanical stresses to designers.

Significance

Sandia's system needs are evolving to include requirements not addressed by today's microelectronics technologies. Some issues with utilizing existing technologies are characterized as follows:

- Changing needs for increased system functionality in same or reduced volumes
- System architectural options limited by difficulties in integrating dissimilar technologies
- Single chip solutions limited by incompatible operating parameters and functions
- Increasing interconnect densities and traditional board stacking technologies for packaged devices that drive development and manufacturing complexity, schedule, and cost up, and reliability down
- Potential security vulnerabilities associated with the interconnection technology

Considerable technical advantage is obtained by combining separate analog, digital, and other technology functions in a single low-volume solution utilizing vertical die stacking. One avenue of this extremely promising technology utilizes surface activated bonding and is the basis for this research. The technology would enable stacking of very thin (<50 µm) individual functional layers from different technologies (e.g., digital, analog, radio frequency [RF], microelectromechanical system [MEMS], etc.). Stacking addresses the described problems by drastically increasing the number of potential inter-chip interconnections (>200,000 vertical interconnects in a 5x5 mm^2 area) while reducing interconnection complexity and cost, and improving reliability. Furthermore, combining these stacked elements precludes probing or visual inspection of the circuitry, significantly improving system security.

The TSV technology enables millions of vertical interconnects in a 3D architecture providing parallelism. The low-temperature, surface-activated bonding creates a path for bonding wafers or die with different functionalities and also different coefficient of thermal expansion. Both these technologies in combination have relevance to imaging, high performance computing, MEMS and photonics integration with electronics etc. The very high fidelity modeling methodology developed in this project will allow designers to have realtime feedback regarding how their design elements affect the stresses created in the structure as a function of process steps, and hence would allow their design for longer-term reliability.

From an applications perspective, 3D integration will enable a variety of new system architectural and security options utilizing cross-cutting technologies. It is an enabler for significantly higher gate-count designs while retaining Sandia's CMOS7 radiation tolerance and provides a path for new and innovative solutions to existing surety problems. It also provides a foundation for building trusted anchor hardware solutions that meet severe environmental requirements, while providing the performance and computing resources needed for securing the nation's high-consequence infrastructure elements. It will open the door for innovative new architectures for cryptography, communications, high-performance computing, and data processing in severe environments.

Creating a Smart Fast-Neutron Calibration Source

117849
Year 3 of 3
Principal Investigator: D. S. Walsh

Project Purpose

During certain surveillance activities, measurement of neutron generator (NG) performance characteristics is constrained by small or awkward physical spaces. In these instances, the in-situ calibration of solid state neutron monitors (SSNMs) used to test NG performance is degraded from the best achievable because the standard reference neutron detector, the lead probe, cannot be directly used to calibrate the SSNM. Instead of comparing the output performance from the lead probe and an SSNM under simultaneous exposure to neutrons and developing an inter-calibration coefficient for the SSNM based upon the calibrated lead probe, indirect processes must be used. The SSNM calibration in these cases includes calculations of correction factors using secondary transfer standards, numerical simulations of radiation transport, and engineering analysis; each of these approximations introduces uncertainties that degrade the final calibration precision of the SSNM.

To address this challenge, we propose developing a special fast neutron reference source that can self-report its neutron yield and neutron rate using sensors embedded within a sealed neutron tube. This neutron generator will integrate a small semiconductor diode within the vacuum boundary of the neutron tube to directly measure alpha particles ejected from the hydride target during the D + T fusion reaction. Measurement of the alpha particles associated with DT fusion will provide a "first principles" quantitative gauge of neutrons produced during operation. This reference neutron source will see application throughout the nuclear weapons complex, in all cases where a Controlatron neutron generator or lead probe is used. In stockpile surveillance and joint test assembly activities, this instrument will provide a new calibration capability allowing more precise calibration of monitors used to assess neutron generator functional performance. In neutron tube and neutron generator production activities, the Smart Fast Neutron Reference Source will directly address Lean Six Sigma production goals by providing a self-consistent calibration capability within war reserve functional test equipment.

Summary of Accomplishments

We have successfully modeled two different associated particle detector configurations for use in measuring the neutron output from a controlatron neutron generator. The second technique, which we call the APD-target configuration, shows good potential for use in a controlatron neutron generator. Experiments have shown that we achieve large signals with virtually no noise. This could significantly decrease the inaccuracies in neutron measurements that arise from estimating the neutron attenuation caused by real tester applications. The technique may also have potential application for other Sandia neutron generators but only if those generators employ x-ray suppression designs. In that case, we can envision neutron generators that are able to accurately (due to large signals with virtually no background) measure their own neutron output over their lifetime. This could reduce measurement inaccuracies associated with tester design changes over a neutron generator's lifetime.

We have demonstrated that plastic fiber scintillators have good potential applications in fast neutron counting systems if the problems of the photomultiplier tubes (PMTs) and associated electronics can be solved. One solution is to reduce the count rate per channel by increasing the number of channels but further work is needed to select the best PMT for this task. Advanced signal analysis, although not explicitly dealt with in this report, may allow processing of pulses that are piled up, allowing higher count rates. Such an approach is already being taken by many vendors of signal acquisition systems. This spin-off approach from this project is actually expected to provide near-term impact on Sandia neutron generator measurements. In those scenarios where generators emit x-rays together with neutrons, the plastic fiber scintillator is especially attractive because of its ability to easily discriminate neutrons from x-rays.

Significance

An improvement in the accuracy of calibration of neutron generators results in a potentially large benefit in their late-life evaluations and lifetime predictions. The calibration process at this time makes use of a lead probe in combination with a controlatron generator, against which other neutron generators may be compared. Because of the necessary separation between the lead probe and generators, the measurement is affected by changes in materials, such as those comprising test stands, which might be in the vicinity. Coupled with the inherent statistical uncertainty of the measurement caused by high noise and low signal levels, this results in a measurement uncertainty that translates into an uncertain evaluation of the health of the generator. This effect is particularly large for generators nearing end-of-life.

We have explored how associated particle detectors and plastic fiber scintillation counters might be applied to this problem. One approach we studied is to monitor the controlatron output with a closely coupled associated particle detector such as a silicon diode. If the detector were inside the controlatron structure, then it would be completely insensitive to the test measurement environment. The other approach we examined is to couple an extremely fast-counting scintillation detector-based system as close to the tube as possible. This approach may be particularly suitable for the lower output generators or generators with high x-ray-to-neutron output ratios.

The direct impact to Sandia's national security mission is in more accurate planning and managing of the nuclear weapons stockpile based upon more accurate measurement and estimate of neutron generator performance. It is also likely that similar technology to that studied in this work could be spun off for security applications in which neutron generators are used to detect contraband materials.

Microresonators for Advanced RF Systems

117851
Year 3 of 3
Principal Investigator: C. Nordquist

Project Purpose

As radio-frequency (RF) systems are transformed to reduce the number of piece parts and improve reliability, reliable high-Q miniature resonators become a need that commercial suppliers cannot meet. These resonators must have high Q for reduced phase noise, be integrated with radio-frequency integrated circuits (RFICs) for reduced parasitics, and be more reliable than other components in the system. Commercial devices such as surface acoustic wave, bulk acoustic wave, or ceramic resonators are large and bulky and do not integrate well into a chip-and-wire environment. Additionally, they are designed for high-volume applications, so that specific designs for low-volume applications incur high non-recurring expenses and unit costs. To address these needs, we have explored acoustic aluminum nitride (AlN) resonators for realizing high-Q resonators for highly integrated RF systems.

AlN technology has the potential for Q>1500, in an acoustic device that can be integrated using chip-and-wire approaches. This technology allows batch microfabrication of different designs of microresonators meeting a variety of functionalities on a single wafer. While some demonstrations have been completed in this technology, the temperature stability and failure mechanisms of these devices must be understood and addressed. Additionally, the devices must be packaged to allow intimate integration with other technologies such as GaAs or Si RFICs.

This project has increased fundamental knowledge in microresonator technology and has put foundations in place towards a mature microresonator technology for future RF systems. The project has explored reliability and drift mechanisms of these devices, wafer-scale packaging of microresonators, and temperature stabilization of these devices. This project has advanced the readiness level and state-of-the-art in microresonator devices, lowering the barrier to future system insertion.

Summary of Accomplishments

This project advanced Sandia's microresonator knowledge and maturity in several areas. These areas include co-integration with other materials, wafer-level-packaging, temperature stabilization, understanding failure mechanisms, and filter design.

In the area of integration, we demonstrated one of the first process flows utilizing the Microsystems and Engineering Sciences Applications (MESA) capabilities in both the silicon fabrication (SiFab) and microfabrication (MicroFab) facilities. Microresonators were fabricated in the SiFab using silicon-based materials, followed by integration of low-loss metal layers, bonding layers, and wafer-level-packaging in the MicroFab. This allowed the integration of microresonator technology with high-Q planar inductors and gold-based eutectic bonding materials. In the area of wafer-level-packaging, we demonstrated miniature (1.3 mm x 1.3 mm x 0.2 mm) packages realized by bonding of a lid wafer onto a microresonator substrate. We determined the scaling rules of lateral feedthroughs and measured insertion loss less than 0.2 dB at 2 GHz. We evaluated the quality of the package seal with built-in test structures including resonators and pirani gauges, and showed good correlation among three different types of devices. In the area of temperature stabilization, we demonstrated improvement in the temperature coefficient of frequency for microresonator devices by adding a compensating silicon dioxide layer to the device. The predicted optimum thickness of the compensating layer was validated by experiments in which the temperature dependence of frequency reduced from –21 ppm/K to +2 ppm/K. In the area of failure mechanisms, we evaluated the power handling and linearity of the microresonator devices for both in-band and out-of-band signals. We demonstrated that the in-band power handling is improved with the use of a passivation layer and specific anchoring designs. In terms of filters, we explored microresonator-based filters comprised of individual microresonator devices. We learned about the modeling and synthesis of these types of filters, and fabricated and measured demonstration filters.

Significance

This project has significant impact on the S&T community and Sandia's national security mission areas. The project has achieved many advances that are significant to the S&T community. First, the method for stabilizing the center frequency of these microresonators can be applied to many different types of piezoelectric resonant devices, and offers a route towards device stabilization. Additionally, to our knowledge, this project achieved the first application of gold-germanium eutectic to wafer-level-bonding, adding to the community's knowledge base for wafer level packaging. The correlation of the pirani gauge and microresonator pressure results is significant in terms of comparing different pressure evaluation techniques for miniature package volumes. The demonstration of microresonators integrated with high-Q inductors provides additional capabilities and drives the application of this technology into new directions. The study of the power handling and power-dependent failure mechanisms is the first of its kind on these types of devices. The filter synthesis work is essential to the community, and adds to application of this miniature filter technology.

The project also developed essential understanding and capabilities benefitting Sandia's national security mission. The wafer-scale-packaging approach developed on this project will improve microresonator device performance, improve the reproducibility and yield of the technology, and reduce the packaging cycle time of the technology. These advantages will improve Sandia's position for delivering moderate quantities of devices based on this technology as critical enablers for future systems. Additionally, the advantages of this packaging capability can be extended to other critical microtechnologies. The integration of low-loss metals and high-Q inductors increases the application space of the technology by allowing its extension to higher bandwidths and frequencies, and allows alternate coupling approaches for filter synthesis. The temperature stabilization work will increase the utility of the technologies to encompass applications with more stringent frequency stability demands over broader temperature ranges. The understanding of the power handling will allow better scaling decisions for covering increased power and linearity demands. The development of filter design techniques will allow custom filter designs for specific national security applications, with the technology also offering the benefit of multiple frequency and bandwidth filters on a single die.

Novel Foam Encapsulation Materials and Processes

117853
Year 3 of 3
Principal Investigator: L. A. Mondy

Project Purpose

Foam encapsulation provides protection from shock, vibration, and thermal influences for a wide variety of electro-mechanical weapon components. Processing of encapsulants in complex electro-mechanical components has been a challenge in previous weapons systems, and there are advocates of eliminating foam encapsulation entirely. That may not be an option for current and future components because foam is a strong but lightweight material that provides a good compromise between the conflicting design needs of structural stability and electronic function. An attractive alternative is to design novel foam materials that eliminate the difficulties encountered in the past such as insufficient filling, density gradients, and potentially high residual stresses, while bearing in mind the desirability of ease of removal. Current processes produce epoxy foam in situ using a physical blowing agent that is heated to its boiling point, which can lead to the above challenges. We will develop a new process using novel chemical reactions, both for chemical foaming and alternative cure approaches. We will explore the possibility of creating the foam outside the part and then injecting it. The injection pressures will be higher than in-situ foaming to better fill tight spaces, but will be low enough to avoid wire sweep. Fundamental studies will provide better knowledge about foam stability and how to optimize formulations for new materials. Development of processing models will provide guidance for future weapons systems early in the design process to optimize the hardware for encapsulation including the placement and size of gates and vents, component spacing, and operating parameters. We have brought together a multidisciplinary team of experts in polymer chemistry, foam processing, foam engineering and multiphase modeling that are both creative and pragmatic and have a history of successfully developing new processes and chemistries.

Summary of Accomplishments

We developed novel chemically blown epoxy foams that are more resistant to foam collapse than current physically blown epoxy foams. In initial testing in a geometry relevant to component encapsulation, these foams showed more uniform and finer bubble size structure and fewer large voids than REF308, a currently used epoxy foam of the same density. In addition, we demonstrated that these foams could be pressure filled into a mold after the foaming reaction had occurred, without degradation of the microstructure, but that this was unnecessary for low-density foams because they were stable enough to resist drainage that this filling process was designed to minimize. Solid properties of the foam compared well to properties of encapsulation foams currently in the stockpile. In addition, we performed a series of tests of foam stability to determine the effects of continuous phase viscosity, surfactant or particle stabilizers, and pre-gelation with an isocyanate-polyol reaction. Also, we studied foam rheology and used infrared spectroscopy to elucidate foam stability and chemical reactions. Information gained was used not only to fine tune the novel foam chemistry, but also to develop an engineering model to predict chemically blown foam rise in a mold. The numerical model was preliminarily tested against data on chemically blown PMDI-4 (polymeric methylene diisocyanate) PU (polyurethane) foam.

Significance

During this project, new tools to create and characterize foams were developed, leading to a better understanding of the processes that define rigid encapsulation foams. This understanding will be useful in the event that problematic issues arise during production, because we will be able to identify specific processes as likely causes rather than pursuing a blind trial-and-error approach to solving the problem. Furthermore, the numerical model methodology can be extended to other foams and then used to help design the encapsulation process with fewer build-test cycles.

These new materials will better insulate nuclear weapon components from shock and vibration; therefore, they will help create nuclear weapons that are safer, more reliable, more easily transportable, and more resistant to aging. Because processing of these new materials will be more easily controlled than current foams, this work will improve yield and reduce cost.

Refereed Communications

J.M. Kropka and M. Celina, "Viscoelasticity of Liquid Organic Foam: Relaxations, Temporal Dependence, and Bubble Loading Effects on Flow Behavior," *Journal of Chemical Physics*, vol. 133, pp. 024904-8, July 2010.

R.R. Rao, L.A. Mondy, D.R. Noble, H.K. Moffat, D.B. Adolf, and P. K. Notz, "A Level Set Method to Study Foam Self-Expansion: A Validation Study," to be published in the *International Journal of Numerical Methods in Fluids*.

M. Celina, J.M. Kropka, L.A. Mondy, R.R. Rao, and J.H. Aubert, "Improved Foam Materials Through Characterization of Foam Stability," *PMSE Preprints*, vol. 101, p. 873, 2009.

Embeddable Optical Current Monitors for High-Current Signal Confirmation

130791
Year 2 of 2
Principal Investigator: M. Cich

Project Purpose

Monitoring of high-current pulsed signals is of great interest for a number of nuclear weapons (NW) applications including signal confirmation in joint-test assemblies (JTAs) as well as built-in-test and state-of-health monitoring for advanced firing sets. Also, nuclear weapon design requires the ability to generate, transmit and control high-current pulses. Measurement of these current pulses is required during development, production and subsequent surveillance. Current-voltage transformers (CVTs) are now typically used to measure current signals but consume considerable power and are subject to electromagnetic interference (EMI). CVTs are also difficult to implement and integrate with cable systems for testing and limits application. Recent work on magneto-optical current sensors have shown great promise in performance as well as gaining advantages of EMI-immunity and low power consumption. Our team has recently developed optical current sensors using bismuth doped iron garnets in a two-pass reflective geometry, demonstrating sensing of current pulses with 150-ns rise times and peak currents ranging from 500 A to 3 kA, limited by the range of the capacitor-discharge unit used for testing. In order to develop sensors that are more fully integrated into the test cable and improve sensor performance, we propose to fundamentally investigate several key areas: 1) the B-field distribution around conventional and novel cable geometries to understand optimum sensor implantation; 2) the local domain properties of these magneto-optical films under external and local magnetic field bias; 3) fabrication of magnetic films for local domain control; and 4) controlled high-speed testing of these sensors.

Summary of Accomplishments

We have built and demonstrated an all-optical current sensor using bismuth iron garnet. The sensor has a dynamic range of ~1200× and an upper measurement limit of 60 G. The active volume used for sensing is roughly 1 x 1 x 0.25 mm^3. There is some frequency limitation to the performance of this sensor that reduces sensitivity to frequencies above 3 kHz. The origin of this limitation is still under investigation, but is not expected to be fundamental given previous results with these materials. This sensor underwent vibration and shock testing, and the sensor hardware is available for application testing.

Significance

This embeddable optical current monitoring technology would benefit several NW applications such as built-in JTA end-event confirmation, built-in-test and state-of-health monitoring in advanced firesets and benefit nuclear design through development production and subsequent surveillance.

Faraday Micro-Shields and Novel Electromagnetic Isolation Structures

130792
Year 2 of 2
Principal Investigator: K. A. Peterson

Project Purpose

Electromagnetic isolation (EMI) for advanced radio-frequency (RF) modules is challenging current capabilities. Such modules are presently dependent on via-fence enclosures and metal lids that are showing strains with 150-dB requirements. These, like metal cans, clamshells, and gaskets are bulky and add no value to the module. Naturally, there is a premium on inherent shielding and shielding that will permit miniaturization with high performance as radars and many electronics move toward multichip modules. New techniques promise improved isolation with good production at low cost using low-loss materials. Polymer encapsulation will be evaluated to protect circuitry and strengthen solder and wire-bonded attachments. Conductive coatings will then be applied directly to the encapsulant, providing effective electric-magnetic radiation shielding. Additional techniques use novel board-level approaches for sidewall metallization and for low-loss materials adjacent to RF lines. This new approach to electromagnetic isolation will serve multiple future stockpile needs for microwave modules, as well as to stop interband and interoperability issues in many other electronic systems.

Summary of Accomplishments

Accomplishments include the design, refinement, fabrication, and testing of a test board for measurement of performance and isolation. This is a test board that can be used both as an RF generator and as a receiver. The materials study pointed to new materials. Performance tests indicate that the dielectric affects the frequency and loss, but the addition of the shield has a minimal further effect. A new technique for providing maximum isolation in the board itself has been demonstrated. The technique, previously thought to be impossible, provides solid walls of metal in place of via fences. This technique has also been used to isolate input/output pins and to fabricate lids for baseline measurements. Additional test vehicles were designed to examine the effects with actual radio-frequency integrated circuits and effects of heating — expected for high-power devices. This demonstrated a benefit from the use of alternate materials that better survived the thermal environment. In addition, a new technique for measurement of leakage was employed.

Significance

There is a clear benefit to an electric-magnetic isolation approach that is readily usable for future programs dependant on custom and commercial components. This technology will be available to multiple Sandia program areas (including safeguards). The generation of intellectual property has resulted from each phase of this project. The ability to design and fabricate high-isolation components in several future programs will result in manufacturable hardware.

Field and Charge Penetration By Lightning Burnthrough

130793
Year 2 of 3
Principal Investigator: L. K. Warne

Project Purpose

The continuing current component of the lightning environment is capable of breaching many shields. However the breach takes the form of a small hole (typically on the order of a centimeter), which is surrounded by a hot plasma. Because lightning is made up of large amplitude return strokes separated by these continuing current intervals, there has always been a concern that such a breach will leave vulnerable interior cables or other components proximal to the hole. One valuable measurement set was made in the early 1990s on a cable behind a burn-through hole subjected to a return stroke, which yielded relatively low levels of induced voltage and current. But it is not known whether the setup in this measurement captured extreme levels, or what physical principles were at work to prevent more extreme levels from being observed.

We propose in this project to examine, both theoretically and experimentally, the physical principles at work in the transfer of field and charge through the hole. The goal is to provide a rigorous basis for levels of induced voltages and currents. Such an understanding will allow a more realistic assessment of this threat (perhaps in some cases even allowing it to be dismissed). An understanding of this penetration is lacking. It is thought to involve several effects having to do with the state of the gas surrounding the hole and the geometry of the hole and cable arrangement. The approach taken here will include both the construction of a theoretical model for each effect and an experimental investigation of its importance. Work in the past has concentrated on assessing barrier damage from the lightning continuing current. From Sandia's perspective this is only the first stage of the problem, because we have a unique interest in subsequent large amplitude coupling to cables.

Summary of Accomplishments

We carried out experiments with several return strokes by means of a new technique to address the issue of how large the burn-through hole might become under the action of multiple return strokes associated with severe lightning. We initiated the flash with a thin starter wire and used the two return strokes of the lightning simulator in a manner to maximize damage, including worst case lightning charge transfer and the capability to produce worst-case action. Although larger hole sizes were achieved, coupled voltage levels were limited to under 100 V.

Work was done in FY 2010 to understand the two main physical processes involved: 1) the role of the discharge plasma in shielding (or conducting) to the interior collector; and 2) the conditions under which discharges form to the interior collector.

Investigations into the plasma extent and conductivity have focused on electrical discharge current distributions. We developed and applied three new measurement techniques (split anode for continuing current, as well as a symmetric ring probe and a non-perturbing groove probe for return stroke currents). We compared results to model predictions for discharge expansion indicating that centimeter diameters are achieved.

Finally, we conducted the first experimental examination of the conditions required for discharges to the collector. Interior voltages in excess of 20 kV were recorded. The cathode positions required to achieve these interior discharges were more severe than those predicted by last year's static threshold calculations. We are currently examining whether this is caused by the dynamics of the discharge or other reasons. Controlled experiments have been carried out using a lower-level pulser and are being compared to breakdown threshold calculations. So far, these appear to be in reasonable agreement. A short paper has been prepared on indirect coupling and discharge thresholds.

Significance

Opinions about the significance of the vulnerability posed by lightning burn-through have varied widely. The understanding, as well as models, of the energy transfer process to be developed in this project will provide a quantitative basis on which to make assessments about this penetration, which is relevant for many existing systems.

MEMS-Based Non-Volatile Memory Technology

130794
Year 2 of 3
Principal Investigator: M. Baker

Project Purpose

Electrical non-volatile memory (NVM) technologies are currently used for several purposes in nuclear weapons systems. Each application has different requirements for the number of bits stored, the speed and power required to read and write, duration of storage without power, erasing/rewriting without a trace of previous storage (lack of remnance), and radiation hardness. The perfect NVM technology does not exist, so compromises are made in system design and operation.

We propose to create a microelectromechanical system (MEMS)-based NVM that would enable new system designs by overcoming some of the weaknesses in current memory technologies. Data would be represented by the position of a buckled beam, e.g., up or down for 1 or 0, respectively. Electrodes above and below would electrostatically actuate each beam and capacitively sense the position. We believe that this scheme has inherent advantages in radiation hardness, duration of storage, and completely erasing previous data. Further, this technique should be highly reliable because it involves no rubbing or contacting surfaces.

Successful development of a mechanical NVM device requires the development and integration of several key elements including the fabrication of very thin beams and gaps with highly controlled residual stress, the design of an integrated circuit for capacitive sensing and actuation, the packaged integration of the MEMS die with the integrated circuit, and the material science studies required to demonstrate lifetime and reliability of the mechanical beam element. Of these technical challenges, the beam fabrication is the largest, and pushes the state of the art in thin-film mechanical MEMS. Understanding the evolution of stress during the fabrication process, and controlling this stress in a polysilicon beam is an active area of research, and is a high-risk aspect of this project.

Summary of Accomplishments

Project milestones can be divided into three general categories: design and fabrication, materials reliability, and packaging and integration. In the area of design and fabrication, we have successfully demonstrated a single-bit memory element in the out-of-plane fabrication process that has been electrically actuated between its two buckled states and capacitively sensed to determine beam position using an off-chip capacitive sensing circuit. In the process of developing this memory element, we have gained an understanding of the factors that control residual stress in the beam and have been able to demonstrate a consistent stress level on two different fabrication runs. This understanding of stress allows us to determine the appropriate beam thickness, gap and length to achieve the desired buckling amplitude.

In the area of packaging and device integration, we have developed a process for flip-chip bonding the MEMS die to an application specific integrated circuit (ASIC) that uses indium bumps on the MEMS bond pads to form a liquid phase bond to gold metallization on the ASIC. While ASIC die do not typically have gold metallization, the gold can be formed on aluminum bond pads using a gold bump wire bond tool. We have demonstrated 100% yield on a 252 bond-pad array

While we did successfully demonstrate a single-bit memory element, it was not without complications. When actuating between buckled states the memory beam is pulled into contact with the actuation electrode. This occurs due to the nonlinear relationship between electrostatic force and gap, and results regardless of the initial gap or beam stiffness. While the buckled amplitude of the beam may initially be less than the gap, once the beam makes contact with the electrode the forces of surface adhesion dominate and the beam remains stuck to the electrode. Our current research efforts are focused on addressing this problem.

Significance

This project ties to Sandia's national security mission in the area of nuclear weapons technology development. The advantages provided by this new memory technology would enable new system architectures that would have advantages over existing solutions.

We expect this project to result in a significant increase in the understanding of residual stress and creep in polysilicon, with this knowledge published in scientific journals and of general interest to the research community. In addition, this project has already and will continue to push the state of the art in MEMS processing in the Microsystems and Engineering Sciences Applications microfabrication facilities. The final output is expected to be a new nonvolatile memory technology with some initial level of demonstrated performance.

Novel Dielectrics with Engineered Thermal Weak Link

130797
Year 2 of 3
Principal Investigator: S. M. Dirk

Project Purpose

In this project, we propose to engineer a dielectric system that has a known, predictable failure mechanism built into the polymer backbone that will fail predictably and irreversibly in a designed manner and at a designed temperature. This dielectric system will fail by its permanent transformation to a conducting polymer at a specified temperature. When the polymer transforms into a conducting polymer it will have the same conductivity of an amorphous metal, significantly altering the capacitor's ability to store the necessary charge. In addition, it is projected that under normal environment operation, the proposed polymer will provide a significant current leakage path, in effect, creating a robust/intrinsic bleed path (in-situ bleeder-resistor) for removing stored charge when power is removed.

Summary of Accomplishments

During FY 2010, we succeeded in electrically characterizing our first switchable polymer dielectric system throughout the thermal transformation process (from a dielectric to a conducting polymer). We determined that, after the thermal transformation, the capacitance values typically dropped more than 80% while the dissipation factor increased ~75 times, clearly demonstrating irreversible capacitor failure and showing the ability of these systems to serve as weak-link dielectrics. We synthesized and characterized two new analog polymer systems to understand how different chemical substituents would affect the thermal transformation process and the electrical properties. By incorporating different halogen substituents onto the polymers, we were able to increase the dielectric constant by 11% and 25%, respectively. Our best polymer system has a dielectric constant of 5.2, that is 1.6-times higher than Mylar (3.25), and better than most commercial dielectrics. We further demonstrated that the two new systems also successfully function as weak-link polymer dielectrics by electrically characterizing their conversion from a dielectric to a conducting polymer at high (> 200 °C) temperatures. Accelerated aging studies are currently underway to determine the activation energy and the lifetime of these systems. Initial results indicate these materials are incredibly stable (no capacitors failed after being stored at 175 °C for 1 month).

We also began to synthesize and evaluate alternate polymer systems with simpler synthesis and potentially improved properties. We evaluated several new xanthate precursor polymers and determined that while these materials are easily synthetically accessible, have good electrical properties at room temperature, and conjugate to form conducting polymers at high temperatures, they do not perform well as dielectrics at elevated temperatures because the polymers have low glass transition (T_g) temperatures. We have designed several alternate high T_g xanthate polymer systems to improve the thermal characteristics, which should allow these materials to function as weak-link dielectrics.

Significance

This work represents the following significant accomplishments. 1) It illustrates the first utilization of the thermo-switchable properties of precursor poly(p-phenylene vinylenes) for an application. 2) The application has important safety ramifications for capacitors in general because the capacitors will irreversibly shut down in the event of a fire or overheating. 3) We show that under normal operating conditions these polymers have better dielectric properties than commercially available Mylar and other non-fluorinated polymer dielectrics. 4) Through the synthesis of several new precursor polymers, the thermoconversion temperatures of these materials are shown to be directly related to the stability of the leaving groups, which allows the failure temperature to be preset. 5) The ability to lower the thermoconversion temperature is an important finding for the general processing of semiconducting polymer-based electronics because it increases the number of materials that can be coprocessed in a device without degradation of the constituent materials.

Refereed Communications

R.S. Johnson, K.N. Cicotte, P.J. Mahoney, B.A. Tuttle, and S.M. Dirk, "Thermally Induced Failure of Polymer Dielectrics," *Advanced Materials*, vol. 22, pp. 1750-1753, 2010.

Signal Processing Techniques for Communication Security

130798
Year 2 of 3
Principal Investigator: R. J. Punnoose

Project Purpose

Wireless communication can enable new logistics and tracking applications for the storage and transport of sensitive materials. This will provide accurate real-time inventory, prevent theft, and decrease the cost of protecting this material. Also, environmental conditions can be monitored during storage and transport. Since radio communication occurs over an open, broadcast medium, security is an issue. The goal of this project is to use time-reversal electromagnetics to provide inherent wireless communication security at the physical layer by focusing the communication signal at the receiver. This technique has potential to provide low probability of intercept/low probability of detection characteristics to radio communication, independent of any spread-spectrum modulation. This proposal aims to develop a differentiating technology to increase the reliability and security of radio communication.

The focusing ability of an antenna depends on its size and is limited by the Rayleigh diffraction limit. Recently, experimental proof-of-concept research showed that it is possible to focus beyond the diffraction limit in a spatially cluttered environment using time-reversal techniques. Time-reversal techniques have the following properties: 1) background clutter is beneficially used to create a large virtual aperture; 2) increased focusing ability; 3) no need for knowledge of receiver position; and 4) no need for line-of-sight. For practical application, it is imperative to determine the relationship between focusing ability, the number of antennas and their spacing, and the degree of clutter. For security applications, it is also desirable to simultaneously detect and suppress potential threats. The objective of this work is to characterize the impact of the factors listed above on the ability to focus signals on a target, selectively detect and reject hostile signals using time reversal techniques, and simultaneously focus and null the signal at desired/undesired locations.

Summary of Accomplishments

In FY 2009, several techniques were investigated for creating channel models of cluttered environments. The time-reversal technique is dependent on the physical environment and thus requires detailed transient electromagnetic simulation. The finite difference time domain (FDTD) method is most suited for providing an adequate simulation environment. Commercial FDTD tools were examined for suitability and were found to be lacking in the ability to create arbitrary clutter objects. We implemented an FDTD simulation environment where arbitrary objects can be placed. To reduce computational complexity, a 2D simulation model was used.

In FY 2010, the work was expanded to characterize the effect of antenna parameters such as number and bandwidth upon time-reversal focusing ability. We made some initial progress towards an FY 2011 goal of performing focusing at a target location and nulling at an eavesdropper location simultaneously.

Significance

This work supports DOE's defense strategic goals by enhancing the security of sensitive material transported in containers. In addition, this technique can be useful for tagging and tracking, which have asymmetric communication needs. Time-reversal processing can be applied at the tag reader to focus the energy at the tag, which has very little processing power. This technique can therefore be of use in the intelligence, surveillance, and reconnaissance area.

Solid State Neutron Sources

130799
Year 2 of 3
Principal Investigator: J. M. Elizondo-Decanini

Project Purpose

This project's goal is to create a solid-state based neutron source using non-conventional materials, structures, geometries, and topologies.

Summary of Accomplishments

The following was accomplished during FY 2010:

1. Demonstrated initial neutron output using a large resistor–capacitor (RC) constant counter
2. Demonstrated operation using geometries as described in the original proposal.
3. Demonstrated source and target construction independent from each other.
4. Demonstrated integration into a single operational geometry.
5. Demonstrated ion sources in the regime as stated in the original proposal.
6. Demonstrated ion source consecutive operations with hundreds of pulses.

Significance

We have advanced the state of the art in neutron generators and created a number of designs that will transform the way neutron sources are built. There is one design that allows the use of neutron generators for medical applications in such fashion that a patient can take the device home and receive a low repetitive dose in a portable, inexpensive device.

We submitted four invention disclosures connected with this work.

Understanding and Predicting Metallic Whisker Growth and its Effect on Reliability

130800
Year 2 of 3
Principal Investigator: D. F. Susan

Project Purpose

Tin (Sn) whiskers are conductive Sn filaments that grow from Sn-plated surfaces, such as surface finishes on electronic packages. The phenomenon of Sn whiskering has become a major concern in recent years due to requirements for lead (Pb)-free soldering and surface finishes in commercial electronics. At Sandia, Sn whiskers are a reliability concern due to increased use of commercial off-the-shelf (COTS) parts, possible future requirements for Pb-free solder joints and surface finishes in high-reliability microelectronics, and the transition of Sandia's electronics supply chain to Pb-free processes. In general, pure Sn finishes are more prone to whisker growth than their Sn-Pb counterparts and high profile failures (short circuits) due to whisker formation in space applications have been documented. Despite the long history of Sn whisker research and the recently renewed interest in this topic, a generally accepted explanation of the whisker growth mechanism has never been developed. We proposed that, through a combination of carefully designed experiments and computational modeling, an understanding be developed of the underlying mechanisms that control the nucleation and growth of Sn whiskers. The experimental part of this work will include the effects of critical variables such as Sn microstructure, grain orientation, temperature, and stress on the propensity for Sn whisker formation. Concurrently, computational modeling, which is based on molecular dynamics techniques for describing stress-driven mass transport processes, will be developed to predict transport mechanisms feeding whisker development. The modeling will utilize realistic atomistic simulations based in part on the detailed characterization obtained in the experimental portion of this work.

Summary of Accomplishments

This year, we communicated our results to the Sn whisker community through several technical conference presentations and publications. In particular, two Sandia presentations were given at the Fourth Annual International Sn Whisker Symposium.

Summary of this year's technical accomplishments is as follows.

We have developed an extensive catalog of Sn-plated samples, many of which show Sn whisker growth. The most prolific whisker-forming samples are generally thin Sn layers (~ 1 micron) deposited under constant-current or constant-voltage conditions (no pulse plating). Thicker samples were deposited (> 4 microns) and these Sn layers showed much less whisker growth than the thin Sn layers plated previously.

We now understand the crystallography of tin whiskers. Through advanced electron backscatter diffraction and crystallographic pole figure analysis, we have statistically determined the crystallographic growth directions of about 60 whiskers. The relationship between the whisker growth direction and the original Sn grain orientation can also be obtained with these methods.

Other significant advances were made on tin whisker characterization this year. 1) The whisker kink process has been studied and two types of kinks have been documented. In Type I kinks, the spatial orientation of the original leg remains unchanged. Those whiskers continue to grow. In Type II kinks, the original leg changes orientation and whisker growth slows down or stops. Type II kinks appear to be related to grain boundary movement at the base of the whisker. This is based on changes in morphology and diameter of the whiskers associated with kinking. 2) Physical growth angle data has been compiled on over 140 whiskers. Statistical analysis of growth angles has never before been reported and allows for more accurate measurement of whisker lengths. The data indicate several favored growth angles and the angles are being correlated to the crystallography of the whiskers and the original Sn plate texture.

Significance

This year, we communicated our results to the Sn whisker community through several technical conference presentations and publications. This puts Sandia at the forefront of Sn whisker research. Sandia researchers are now participating in high-level consortia such as the PERM (Pb-free Electronics Risk Mitigation). This is a group of high reliability aerospace and microelectronics manufacturers concerned about Pb-free implementation. In particular, Sandia researchers have been an integral part of the Sn whisker subgroups within the PERM.

The careful analyses of both crystallographic whisker orientation as well as physical growth angles are unique capabilities at Sandia. No other research group is analyzing whiskers at this level of rigor and statistical breadth. This work is leading to a complete understanding of whisker crystallography. Our results will be published in technical journals this year.

This work exercises Sandia's unique materials characterization capabilities in a challenging way and is maintaining our expertise in this area. Sn whiskering is of increasing concern for nuclear weapons, satellites, and homeland security applications. As such, it is a very relevant research field for Sandia, considering our emphasis on high reliability microelectronics, the shift toward COTS parts, possible future Pb-free requirements, and the shift of the supplier base to Pb-free processes. Furthermore, it will be possible to apply the techniques and modeling tools developed in this work to other, yet unforeseen materials problems involving thin films, diffusion, and residual stress.

Vapor Phase Lubrication for Advanced Surety Components

130801
Year 2 of 3
Principal Investigator: M. T. Dugger

Project Purpose

Materials selected for manufacturability, strength, etc. frequently exhibit poor friction and wear properties, necessitating lubricants. Conventional solid lubricants oxidize, and depositing lubricants uniformly on surfaces of complex shape without damage is difficult with current methods, and will become even more problematic as the dimensions of small mechanical assemblies decrease. The elimination of hazardous solvents has created a critical need for new stainless steel bearing lubricants as well.

The goal of this project is to develop a completely new paradigm for surety component lubrication known as Vapor Phase Lubrication (VPL) that will provide a low-friction film of molecular dimensions that is self-healing, and that forms automatically during sliding on small parts of complex shape. The underlying scientific discovery has already been demonstrated by an invention disclosure. VPL is based on a reaction between gas-phase molecules and the surface that forms a lubricant film only at contact locations. This approach has shown a 10,000-fold increase in operating life of silicon micromachines without failure, and recent experiments indicate that VPL is also effective on stainless steel. The use of VPL in weapon components requires understanding the reaction mechanisms, optimizing vapor chemistry for different substrates, developing vapor delivery strategies compatible with weapon components, investigating aging of the resulting film, and determining the compatibility of the vapor with other component materials. Significant development, with relatively high risk, is required both to mature VPL for the range of weapon operating temperatures required and also to create vapor delivery approaches.

Summary of Accomplishments

Doping of the vapor phase lubrication environment with oxygen was conducted to test the radical initiation hypothesis of polymer formation. Wear-less sliding was still achieved with this environment. This important result also suggests that packaging components in inert gas may not be necessary, thus significantly simplifying device packaging requirements.

We designed, synthesized, and evaluated polymer systems based on polyphenylene vinylene (PPV) precursors with xanthate leaving groups as vehicles to deliver alcohols. Thermal gravimetric analysis of the ethanol xanthate polymer showed a loss of 55% (theoretical 47%) when heated to 175 °C indicating the delivery of carbon disulfide and ethanol. Gas chromatography/mass spectrometry analysis confirmed the delivery of both ethanol and carbon disulfide. Thermogravimetric analysis of the pentanol xanthate polymer confirmed the delivery of carbon disulfide and pentanol.

Mechanical assembly prototypes tested in pentanol vapor exhibited reduced and more consistent minimum operating voltage (MOV), compared to when the same device was run in N_2. The MOV is a measure of the total friction in the mechanism, with lower MOV corresponding to lower friction. This is the first demonstration of vapor lubrication of a metallic strong-link. Operation in pentanol vapor was also found to result in more consistent electrical contact resistance, with differences from dry N_2 values within the measurement uncertainty.

We fabricated microelectromechanical system cantilever beams with glass sacrificial layers to improve sensitivity of the beams to capillary adhesion, and we verified sensitivity to adsorbed water. All beams were released in a 50% P/Psat pentanol, placing an upper bound of 1.5 μJ/m² on the apparent adhesion energy. This compares to ~20 mJ/m² for water, and is comparable to the best hydrophobic self-assembled monolayer films.

Significance

If successfully matured, VPL has the potential to free designers from accommodating lubricant thickness in dimensional tolerances, avoid the extra processes and inspection steps needed to apply lubricants to small parts of complex shape, and result in a simpler, more reliable product at reduced cost. The result will be improved yield and reduced variability, thereby improving our ability to quantify margins and uncertainty in mechanism performance. Application of vapor phase lubrication to complex devices would be applicable to commercial mechanisms. Progress thus far includes the development of an approach for delivering the vapor inside a hermetic volume and demonstration of major performance improvements in conventional mechanisms as well as microsystems, as compared to baseline lubrication approaches.

Refereed Communications

A.L. Barnette, D.B. Asay, J.A. Ohlhausen, M.T. Dugger, and S.H. Kim, "Tribochemical Polymerization of Adsorbed n-Pentanol on SiO_2 during Rubbing: When Does It Occur and Is It Responsible for Effective Vapor Phase Lubrication?" *Langmuir*, vol. 26, pp. 16299-16304, August 2010.

S.H. Kim, M.T. Dugger, A. Erdemir, A.L. Barnette, E. Hsiao, M.J. Marino, and O. Eryilmaz, "MEMS Lubrication With Alcohol Vapour," *Tribology — Materials, Surfaces and Interfaces*, vol. 4, pp. 109-114, September 2010.

Antennas with Integrated Metamaterial High-Impedance Surfaces on Flexible Substrates

141684
Year 1 of 1
Principal Investigator: M. Forman

Project Purpose

This project addresses the nuclear weapons surety systems product area that calls for novel physics-based solutions, enabling secure, robust communications for advanced surety applications.

Container communications systems, whether used as part of an intrusion detection system or remote inventory system, require the use of unobtrusive antennas. Typically used in inventory systems, these electrically small antennas are conformal, contain integrated circuitry, and are applied directly to the surface of an object. However, the metallic surface of a container enforces boundary conditions on an incident electromagnetic wave that renders an applied antenna nonfunctional. The traditional solution is to utilize an antenna topology with an integrated ground plane; however, it is difficult to fabricate such an antenna on a flexible substrate that is also electrically small.

We propose the creation of an electrically small antenna with an integrated high-impedance metamaterial surface fabricated on a multilayer flexible substrate. This topology allows traditional, electrically small conformal antennas to be applied directly to metallic surfaces. The enabling technology is a high-impedance Sievenpiper metamaterial, which over a narrow band, presents a high-impedance to an electromagnetic wave.

Summary of Accomplishments

We discovered a novel geometry for a reduced volume antenna that can be deployed on conductive surfaces with similar performance to an antenna several times larger. The reduction of volume is realized by integrating a familiar geometry with a supporting resonant high-impedance surface. An invention disclosure has been submitted.

Significance

By utilizing the novel properties of metamaterials, this proposed work provides a path forward for secure, robust communications for advanced surety applications. With application to multiple mission needs, an investment in this technology will provide a critical capability for future systems. Beyond laboratory applications, this work will develop a capability that can attract future collaboration with industry in the field of electromagnetics and communications.

Feasibility Study of a Secure ASIC Hybrid for Surety Systems

141685
Year 1 of 1
Principal Investigator: J. Farrow

Project Purpose

This project investigates the feasibility of creating a hybrid application-specific integrated circuit/ field programmable gate array (ASIC/FPGA) chip architecture that combines the flexibility of an FPGA with the rad-hard robustness, high gate density and surety/security of an ASIC. A hybrid ASIC/FPGA chip will contain both a fixed ASIC implementation and an adjacent, but closely coupled reconfigurable fabric. The reconfigurable portion of the chip will add great flexibility and adaptability, allowing a common system function to fit into an array of applications or environments with modifications to the reconfigurable region. Weapon systems could greatly benefit from the flexibility of a hybrid ASIC/FPGA, allowing for system upgrades and interface changes without having to replace a complete major component. To successfully implement the planned common adaptable system architecture (CASA), it is desirable to create a hybrid chip that combines the benefits of both ASICs and FPGAs. In this study, the hybrid will be specifically targeting surety applications; however it would provide great benefits in other systems in the weapon. A reconfigurable fabric would allow hardware updates long after the ASIC is fabricated, as well as the ability to implement different real time encryption/decryption algorithms techniques. Since a hybrid ASIC/FPGA design can be shared across multiple platforms or used multiple times in a system, development and non-recurring engineering costs can be significantly reduced.

Summary of Accomplishments

Throughout this year we have discovered a great deal of information. We found that some of our initial assumptions required further clarification. For example, when we first proposed this project, we thought that reconfigurable fabric would represent only an approximately 10-fold disadvantage in terms of extra area utilization, compared to traditional ASIC fabric (that is, if a design was placed in reconfigurable fabric the area used would be 10 times larger than if the same design was implemented in an ASIC). However, the reality was that the cost of using reconfigurable fabric was an extra area utilization of approximately 40-fold or greater. Given that the intent of the study was to define issues such as these and to study the technology and the downsides to its implementation, this was valuable data.

We investigated two technologies, the 350-nm and the 90-nm commercial cores. We identified and documented the strong points and weak points of each technology. We also documented the several different case studies that we researched, showing the wide variety of different digital designs that could benefit from reconfigurable technology. In the feasibility study we reviewed the Microelectronics Development Laboratory's capability and determined that we have the ability to develop reconfigurable fabric.

Significance

Having access to a rad-hard hybrid ASIC/FPGA will offer great benefits to designers striving to meet the demands of lower budgets and quicker design cycles. This also gives system engineers greater flexibility when updating legacy architectures because components with a hybrid ASIC/FPGA could be modified or upgraded without replacing the whole major component. Surety can benefit from the use of reconfigurable logic to implement different encryption scheme, without ASIC refabrication.

Fully Integrated Switchable Filter Banks for Advanced Radar Applications

141688
Year 1 of 2
Principal Investigator: E. R. Crespin

Project Purpose

The purpose of this project is to demonstrate switchable filter banks for radar applications. Switchable filter banks represent a critical technology gap for realizing the next generation of advanced radar systems. Current radar designs use a number of wideband filters to supply the necessary frequency selectivity; but this is inefficient (power, cost, size, and component count). Radar designs using radio-frequency integrated circuit (RFIC) technology still require many wideband filters that drive up component count despite the push towards higher levels of integration. Ideally, a radar designer requires a bank of narrowband filters with the ability to switch filters depending on the various radar modes of operation. Microfabricated resonators offer a smaller, more highly integrated filter technology than what is available using traditional bulk or surface acoustic wave techniques. Microresonators can realize arrays of filters from 20 MHz to several GHz on a single chip and can be fully integrated directly over Sandia's complementary metal oxide semiconductor (CMOS)7 technology without altering the CMOS7 fabrication. CMOS7 technology is already being pursued in advanced radar development efforts. This integration ability is fundamental to providing a switchable array of narrowband filters as microresonators that can be fabricated along with the CMOS7 process and integrated with the circuitry for higher reliability and lower component count.

With this research, we will learn to design multipole, low-impedance filters with low loss using microresonator technology, and CMOS switch designs will be fabricated in the CMOS7 process. The chip and wire integration will also take place, paving the way for full on-wafer integration in year two, when new materials integration techniques will be tested. This development will improve the performance and reliability of our current advanced radar development efforts.

Summary of Accomplishments

During the first year of the project, both the CMOS radio-frequency switches and aluminum nitride filters were developed in parallel. In the second year, these will be integrated realizing a fully integrated switchable filter bank. CMOS switches were designed and fabricated on a CMOS7 multiproject wafer. Eight different switches were developed, implementing three different multiplexing functions. Two different switch topologies were used in the designs; the first used only negative-channel metal-oxide semiconductor (NMOS) transistors while the second was implemented with complementary transmission gates (TGATE). Switch characterization revealed that three of the eight transistors were functional: the single pole, double throw using only NMOS and without matching, the single pole, three terminal NMOS, and the single-pole four-throw TGATE. The single pole NMOS switch without any impedance matching elements worked best and had the lowest insertion loss (2.6 dB at 2.5 GHz). We learned that inductors in the CMOS7 process are not straightforward and the electronics thus requires more modeling of substrate and device parasitics. This contributed to the overall mismatch and nonfunctionality.

The first AlN fabrication run was used to develop an initial prototype filter at 2.5 GHz and to fine-tune our models by designing arrays of resonators where area, electrode width, and wavelength were varied. Their center frequencies were ~10% higher than predicted by simulation, most likely due to differences between the material properties used in simulations and actual values. Finally, we measured the response of a 2.5-GHz filter comprised of two resonators. This is the first time S-Band resonators and filters have been demonstrated at Sandia.

The chip and wire integration performed as expected with ~15 dB of insertion loss, ~10 dB from the filters and the ~5 dB from switches on either end of the filter bank. This demonstrates functionality of the switches and filters together, paving the way for the full on-wafer integration in year two.

Significance

The benefit to Sandia's mission, and to nuclear weapons, of integrating RF switches and filter banks is increased reliability, in part by decreased component count. Also, the improved frequency selectivity of the switchable narrowband filtering greatly relaxes the dynamic range and power requirements for each stage that follows the filtering, improving both sensitivity and jam resistance. The size, power, component count and performance improvements will impact a wide range of national security related RF systems.

Mesoscale Highly Elastic Structures (MESHES) for Surety Mechanisms

141689
Year 1 of 3
Principal Investigator: B. H. Jared

Project Purpose

The purpose of this project is to investigate a new approach to mesoscale elastic elements that meet advanced requirements for surety mechanisms. Current coil-wound wire springs have high variability due to material and process variations forcing mechanism parts to be significantly overdesigned, antithetical to design goals requiring reduced mass and improved response time. Mesoscale highly elastic structures (MESHES) will be demonstrated that yield repeatable spring response with lower component uncertainties. Required research includes investigations of material science and direct machining processes at the mesoscale, and the ability to accurately predict performance of complex, 3D, highly elastic structures including material response and surface effects from the fabrication processes. Important research will include the material properties of small features where assumptions of homogeneity break down. This breakdown is especially important for highly elastic members, but will apply to small features in weapons components and to small mechanisms in general. Process research will quantify the surface effects of several machining processes and evaluate their modification of material behavior in mesoscale structures. Design development will integrate material and process understanding into an integrated design capability, including strategies for creating spring-like response from fundamentally different structures. The resulting structures will exhibit significantly higher repeatability than wire-wound springs, and will significantly open the design space to new materials, new geometry, and added capabilities. Also possible will be multi-strut features that reinforce critical component features. The results will be applicable to all surety mechanisms and will also have application to small mechanisms in general.

Summary of Accomplishments

Progress against FY 2010 milestones continues on schedule in each of the project areas. Design efforts have identified baseline spring geometries based on two different extension spring designs. We have generated single start, equivalent MESHES springs, providing insights into various design trade-offs and demonstrating the suitability of MESHES geometries to small springs. Continued work has highlighted opportunities for MESHES geometries that were not identified during the initial proposal stage. The benefits include increased force to volume ratios, more robust end geometries, better control of resonance modes and the introduction of damping. Material efforts have focused on 304L stainless steel due to its existing presence in the stockpile, its use in other complementary research efforts and its commercial availability as hypodermic needle tubing that is useful for MESHES geometries. Material processing efforts have resulted in the formation of micro-mod stainless with grain sizes on the order of 2.5 µm through the use of snap annealing, pickling (i.e., acid etching) and compression forging. The resultant increase in yield strength compared against annealed 304L is on the order of 50%. Direct machining has been investigated through cutting tests on annealed 304L stainless using a nanosecond pulsed laser, a femtosecond pulsed laser and micro-wire-EDM (electric discharge machining). Tests examined process parameters such as laser power, scan velocity, wire diameter and number of passes. Femtosecond pulsed laser and micro-EDM processes provided superior cutting with heat-affected zones on the order of 1-2 µm and improved surface quality. A post-process step (i.e., electro-polishing) has also been examined to remove surface damage and subsequently improve structural fatigue life. Prototype springs have been fabricated yielding important understandings for femtosecond laser and electro-polishing processes as actual spring rates have been measured and compared against model predictions.

Significance

Sandia's key mission, to maintain nuclear surety in the face of evolving threats, requires continued development of sophisticated surety strategies. Many strategies require decreases in mechanism mass/volume to add capability within the limited space or to increase event rate capability. Small elastic structures with high certainty are key to reliable mechanism performance in adverse environments. This effort will benefit arming, fusing and firing development, one of Sandia's core missions.

Selective Stress-Based Microcantilever Sensors for Enhanced Surveillance

141691
Year 1 of 3
Principal Investigator: M. D. Allendorf

Project Purpose

Assessment of component aging and degradation in weapon systems remains a considerable challenge for the Integrated Stockpile Evaluation program. Analysis of weapon atmospheres can provide degradation signatures and indicate the presence of corrosive vapors. However, a critical need exists for compatible in-situ sensors to detect moisture and other gases over stockpile lifetimes. Lack of such sensors inhibits development of both "self-aware weapons" and fully instrumented weapon test platforms that could provide in-situ data to validate high-fidelity models for gases within weapons. We will develop a platform for on-demand weapon atmosphere surveillance based on static microcantilevers (SMC) coated with nanoporous metal organic frameworks (MOFs) to provide selectivity. SMC detect analytes via adsorbate-induced stress and are low-power, highly compact devices that can be manufactured using complementary metal oxide semiconductor (CMOS) technologies. MOFs have ultrahigh surface areas (up to 6000 m^2/g), are extremely radiation resistant, and have a hybrid inorganic-organic structure providing much more flexibility to tailor pores for selective adsorption than do other nanoporous materials. A prototype MOF-coated SMC we created has a 20 ppm H_2O detection limit (60 °C frost point). We will create MOF-based recognition chemistries for H_2O, CH_4, O_2, and other critical gases using validated modeling tools to guide synthesis. We will also test a stress-based hydrogen detection capability using a NiPd coating. We will use MOFs exhibiting large adsorbate-induced structural deformations, to maximize sensitivity by creating large interfacial stresses. We will fabricate novel cantilever designs incorporating reference cantilevers and integrated temperature measurement for in-situ self-calibration. We will develop sensors operating in either dosimeter or real-time mode. Finally, using simulated weapon atmospheres, we will quantify long-term device performance (drift, calibration, noise, and cross sensitivity). The project leverages the Center for Integrated Nanotechnologies' microcantilever discovery platform, the Microsystems and Engineering Sciences Applications facility, and an ongoing collaboration with Georgia Technical University (Georgia Tech) School of Mechanical Engineering to develop SMC devices, fabrication methods, and data collection.

Summary of Accomplishments

1. We completed assembly and testing of a novel layer-by-layer pseudo-epitaxial growth method to deposit nanoporous framework materials (NFM) films on device surfaces using a sequential repeating immersion paradigm, meeting our first project milestone. This reduces the growth period from almost two weeks to two days for 40-cycle growth. An enhanced version of this method, which uses a quartz crystal microbalance, is now on line and allows us to monitor the growth process in real time.

2. Using atomistic modeling techniques, we screened a broad range of NFM for potential use in detecting CH_4 and O_2. We also identified NFM that can selectively adsorb a range of organic analyte molecules, a number of which are of interest to this project. Compounds such as naphthalene and benezene derivatives are significantly adsorbed by the target NFM at low pressure, consistent with the high isosteric heats of adsorption (12–49 kcal/mol) computed for these analytes.

3. An extensive investigation of device performance was completed by our team partner at Georgia Tech to determine the optimal materials and design for an NFM-coated microcantilever sensor. The current microcantilever sensor array design was modified to improve its structural robustness and reduce the number of fabrication steps.

4. We developed an NFM coating for humidity sensing that absorbs as much as 40 wt% H_2O. NFM films

grown surface acoustic wave (SAW) devices were used to rapidly screen NFM coatings. The coating works remarkably well to concentrate moisture, inducing measurable frequency shifts relative to an uncoated reference SAW. The response is largely reversible, with a repeatable profile over multiple two-day-long instrument cycles, and humidity levels as low as 50 ppbv (–95 °C frost point) were detected. These results demonstrate that NFM-functionalized microcantilevers are capable of ultrasensitive chemical detection.

Significance

A state-of-health predictive capability is a critical aspect of the Integrated Stockpile Evaluation (ISE) embedded-evaluation contribution to Common-Adaptable-System-Architecture stockpile transformation objectives. A second key application is deployment in the emerging ISE component surveillance program. DoD has analogous needs: a prognostic health monitoring system is required in all new major systems. A third application is for DHS-related real-time chemical detection schemes.

Refereed Communications

J.A. Greathouse, N.W. Ockwig, L.J. Criscenti, T.R. Guilinger, P. Pohl, and M.D. Allendorf, “Computational Screening of Metal-Organic Frameworks for Large-Molecule Chemical Sensing,” *Physical Chemistry Chemical Physics*, vol. 12, pp. 12621-12629, October 2010.

The Role of Hydrogen Isotopes in Deformation and Fracture of Aluminum Alloys

141692
Year 1 of 3
Principal Investigator: C. W. San Marchi

Project Purpose

Tritium reservoirs for Gas Transfer Systems (GTS) are composed of high-energy-rate forged austenitic stainless steel. The forging process is designed to control strength, grain size, dislocation microstructure, and forging flow lines. Commercial forging operations do not attempt to meet all of these requirements, making it difficult to source forgings from the commercial sector. Aluminum alloys represent a potential solution that has several important advantages: structural aluminum alloys can be strengthened by precipitation and have very low solubility and permeability of hydrogen. Aluminum is also often considered to be "immune" to high-pressure gaseous hydrogen; however, the critical scientific understanding to support this view has not been adequately demonstrated in the literature. Hydrogen transport within the metal must precede hydrogen-assisted fracture and this limiting condition appears impossible to quantify in conventional tests. This project seeks to clarify the surface kinetics of hydrogen uptake and transport in aluminum alloys during exposure to gaseous hydrogen, and to determine the structural compatibility of aluminum in high-pressure gaseous hydrogen. We plan to employ advanced characterization techniques (such as low-energy ion scattering and thermal desorption spectroscopy, that are not widely available but ideal for this investigation), to enhance our understanding of the thermodynamics and kinetics of both hydrogen on the surfaces of aluminum alloys and hydrogen transport in the bulk. Knowledge of these physics will be coupled with testing in the high-pressure hydrogen laboratory with the aim of establishing methods for determining conservative engineering properties appropriate for the design of aluminum vessels for the containment of high-pressure gaseous hydrogen and hydrogen isotopes. In addition to offering an improved option for GTS designs, aluminum is a desirable candidate for hydrogen fuel applications; therefore, this work will impact the growth of the hydrogen energy sector, contribute to improved energy security and possibly foster new programs.

Summary of Accomplishments

We have shown that 3 keV Ne^+ ions are convenient for removing oxygen and distinguishing the adsorption of hydrogen and deuterium on aluminum surfaces using Sandia's angle-resolved ion energy spectrometer (ARIES). In addition, the crystallography of the surface is confirmed, showing that the ion beam does not damage the surface. In short, the work thus far demonstrates the likelihood of success for the surface science objectives, as there appears to be no fundamental physical limitations to characterizing hydrogen isotopes on aluminum surfaces. In addition, Auger electron spectroscopy has been incorporated into ARIES, allowing us to qualitatively determine impurity content on specimen surfaces; this will significantly improve the interpretation of our experiments. We have found that the change in overall hydrogen inventory in aluminum alloys subjected to high-pressure gaseous hydrogen is below our current detection limit; however, deuterium can be detected in the alloy after exposure to high-pressure gaseous deuterium. It is unclear if this deuterium represents additional hydrogen isotope inventory in the metal, or whether this represents isotopic exchange between the deuterium and intrinsic hydrogen. The importance of understanding the sources of hydrogen and its transport in aluminum alloys relates to: 1) the amount of tritium that may ultimately reside in the aluminum (as this affects tritium/helium embrittlement of the metal); and 2) the metal as a source of hydrogen (as this affects the purity of the tritium in the containment structure). Initial mechanical testing suggests essentially no effect of hydrogen on the fracture toughness of aluminum alloy 7475 in gaseous hydrogen at a pressure of 138 MPa. To our knowledge, these are the first tests of aluminum at such a high pressure. Additional testing is planned to enhance hydrogen transport in aluminum (based on input from the other tasks) during the execution of the test.

Significance

To enhance reliability and expand design space, new structural materials must be identified for tritium compatibility in nuclear weapons (NW) applications: aluminum is the obvious candidate for improving manufacturability and long-term reliability for tritium service. Aluminum is also an important structural material in the context of establishing energy security; aluminum represents a desirable alternative to the expensive materials currently in use, thus lowering barriers to market penetration for hydrogen-energy technologies.

Austenitic stainless steels for containment of tritium require costly manufacturing processes and lifetimes can be limited by tritium permeation into the pressure boundary; consequently, advanced GTS concepts require enabling new materials options for the design of tritium reservoirs. Structural aluminum alloys represent the leading candidates to reduce cost of GTS reservoirs, as well as to increase long-term reliability and expand design options. The mechanical properties of aluminum alloys in gaseous hydrogen will be assessed, and the fundamental principles of hydrogen uptake and transport will be elucidated for quantifying long-term structural integrity and lifetimes for aluminum containment vessels. This information informs the necessary (but subsequent) work on tritium/helium embrittlement to be pursued in collaboration with Savannah River National Laboratory. In addition, this program will engage two early career scientists with the opportunity to address interesting scientific questions and contribute directly to innovative engineering developments within NW and fostering a healthy, innovative science and technology environment.

From an energy perspective, the effects of hydrogen on aluminum alloys and the appropriate methods of evaluating aluminum alloys for high-pressure gaseous hydrogen are of fundamental importance to implementing safe and reliable components for hydrogen fuel applications. Aluminum alloys are commonly used in dry gaseous hydrogen environments; however, a mechanistic understanding of interactions between hydrogen and metal surfaces as well as hydrogen and defects in bulk aluminum are largely missing. This work seeks to provide foundational understanding to address the engineering needs of hydrogen fuel applications; in other words, we seek to provide tools for science-based engineering to mitigate hydrogen-assisted fracture and fatigue in aluminum alloys.

Trusted Computing Solution for an Un-Trusted Computing Environment

141700
Year 1 of 3
Principal Investigator: W. R. Johnson

Project Purpose

The nuclear weapons (NW) community necessarily relies on COTS (commercial off the shelf) computing platforms (including hardware and software) to process, store, and share mission-critical, product-related information. Rootkits are an emerging class of malware (malicious software) that target COTS computing platforms at lower layers in the hardware/software stack, and as a result, have proven to be relatively immune to the defenses of antivirus software. Various techniques have been employed at the hardware level in an attempt to defend against this class of malware with very limited success. The concept of a hardware/software trust anchor (developed at Sandia) leverages the best features of these attempts, and early development has shown a great deal of promise in its ability to solve this extremely difficult problem. However, the hardware element of the trust anchor platform has unique and stringent requirements that severely limit the viability of commercial solutions (due to their performance driven design). We are proposing the development of a reusable trusted computing platform designed with security in mind in order to meet the needs of a trust anchor solution, thereby providing the means to protect critical NW networks. The capabilities of this trusted computing solution are synergistic with the needs of many other NW product areas such as surety and state-of-health, and therefore have direct application in these areas as well.

Summary of Accomplishments

We started this effort in FY 2010 with an independent assessment of the Score processor to identify the general classes of potential threats, weaknesses, or exploitable features that might be present in the current Score architecture and/or implementation. The results of this exercise were completed and documented in March of 2010.

Each of the general classes of threat requires further exploration to determine the following critical pieces of information.

1. Is there, in fact, any weakness in the current architecture?
2. Is the weakness exposed in such a way that it is actually exploitable?
3. What are the consequences of exploitation?
4. What are the potential architectural or implementation mitigation strategies?

We are currently heavily leveraging our Orchestra modeling and simulation capabilities to perform this exploration of the identified threat space and to answer the questions stated above for each threat category. Simulation has proven to be instrumental in this effort as it provides a level of control and visibility that is not possible in other simulation tools or in direct hardware prototype environments. At this stage, we are on track to fully explore a handful of the identified threat spaces by the end of FY 2010.

Significance

Due to the nation's reliance on commercial computing platforms and the increasing frequency of network-based attacks, cyber security is becoming a vital part in preserving national security. The vast majority of Sandia's critical information is stored, processed, and managed using COTS software and hardware solutions. If this project is ultimately successful, the proposed solution would address these vulnerabilities for general COTS computing platforms.

Investigation of Materials Compatibility Issues Associated with the Feasibility of Liquid Metal Use in Harsh Environments

142545
Year 1 of 1
Principal Investigator: P. C. Galambos

Project Purpose

This project was undertaken to investigate the feasibility of liquid metal (LM) use in environment-sensing devices (ESDs), such as accelerometers, from the perspective of materials compatibility. The LM ESD consists of an LM droplet that closes a switch when it has navigated a predefined flow path under a specified series of environmental conditions. While such a feasibility investigation cannot identify all possible materials compatibility problems that could arise when actually fabricating and testing an LM ESD, it can address what are considered the highest risk materials compatibility issues.

We assessed feasibility based on material compatibility issues raised during the project review process by Sandia experts in materials science and high-reliability systems applications. These issues were the following: 1) low temperature limit (–55 °C); 2) adsorption of LM potentially leading to electrical shorts and variation of LM droplet motion; 3) oxidation or vaporization followed by dissipation of LM; 4) voltage breakdown.

The investigation involved literature search, selected experiments, and fabrication of a materials compatibility LM containment microsystem. A hermetically sealed containment microsystem is needed to prevent oxidation or escape of LM vapor. The liquid metals investigated were mercury and a mercury/thallium eutectic alloy, because these were identified through literature search as remaining liquid at low temperatures. Experiments using a quartz crystal microbalance were conducted to address the LM adsorption issue by identifying a set of materials (electrodes and insulators) that do not adsorb or react with LM. The motivation for this project was to address material compatibility concerns prior to actually building an LM ESD, in order to avoid the problem of the inability to identify a set of materials that is compatible with the harsh conditions and challenging specifications of interest for Sandia missions.

Summary of Accomplishments

A literature search revealed one LM (Hg-Tl eutectic, 8.5 % Tl) that remains liquid at the low temperature limit; Hg remains liquid to –38.8 °C, low enough for some applications. Property variation (density, resistivity, surface tension, viscosity) with temperature was deemed acceptable as long as ESD system design takes these variations into account. Quartz crystal microgravimetry experiments identified candidate insulating materials (glass, SiO_2, Si_3N_4) and electrode materials (Ni and Cu) that do not adsorb Hg (and probably not Hg-Tl eutectic) for the temperatures of interest (up to 50 to 80 °C). These materials can be used in a hermetically sealed (oxygen free) LM containment package to create an ESD microsystem that eliminates the possibility of LM oxidation or dissipation. The containment package components were fabricated, but have not yet been assembled. The containment package consists of an SOI (silicon-on-insulator) chip with SiO_2 surfaces containing etched flow channels, a glass cover chip containing electrodes (Au for first prototype, but later Ni or Cu), and copper tubes for LM filling ports. The glass cover can be attached to the SOI wafer with a non-LM-adsorbing glass frit or by anodic or compression bonding. Literature search revealed possible electrode spacing, gas pressure (e.g., Paschen curve), and design parameter variations that eliminate the possibility of voltage breakdown for standoff voltages up to 1 kV.

In summary, none of the materials compatibility issues raised appear to preclude the concept of a liquid metal ESD. Careful design and selection of materials is required, and preliminary design specifications and materials sets have been identified. Further investigation is needed to confirm material compatibility for the specific ESD designs and material sets that will be developed in the follow-on project aimed at creating a functional LM ESD that meets the challenging Sandia mission requirements.

Significance

Liquid metal drops have potential use as a non-wearing contact switch, environment sensing device with applications to various DOE and DoD systems that fit within the Sandia mission space. This project was a study of materials compatibility between candidate liquid metals and typical semiconductor materials such as silicon and glass. Because we were successful at showing materials compatibility, we can proceed to develop a device, microsystem, and model that enables a liquid metal ESD. We will still need to conduct confirmatory experiments on materials compatibility in the areas of LM adsorption, sealing of the containment package, low temperature operation, and the effect of surface roughness on the device developed in the follow-on project.

The interaction of different materials with surfaces is of interest to the S&T community. The movement of the LM droplet in the ESD is largely controlled by the interaction of surface forces with the inertia of the drop subject to acceleration. This droplet motion is what makes an LM ESD switch function. The high surface energy and density of the LM droplet enables us to potentially shrink the size of an LM ESD down to the 100-micron scale. This in turn enables incorporation of an LM ESD subsystem directly into larger micro-meso scale sensing and control systems. The extent to which we can shrink the LM ESD switch enhances the utility of such a system.

This project and the follow-on project provide the opportunity to understand the scientific phenomena, specifically the effect of surface properties on local surface energy, forces and liquid/solid interactions that control droplet motion sensitivity to acceleration (g-level). Control of surface roughness in terms of asperity size and distribution as well as surface charging is required to shrink the size of an LM ESD. A physics-based model that predicts surface interactions and the incorporation of this surface interaction model into a system dynamics model that predicts droplet motion should result in novel scientific knowledge and publications and should enable the novel applications of interest to Sandia S&T and mission areas. The phenomena of interest span multiple scales (nano-to-meso-to-macro).

The materials compatibility project just completed and described herein was the first step down the path just described. It identified the liquid metals (Hg and Hg-Tl eutectic), insulating solid surfaces (silicon dioxide, silicon nitride, various glasses), electrode materials (nickel and copper), and configurations (micro-to-meso flow channels) that will be investigated further in the follow-on project that focuses on scientific understanding and modeling of the controlling physics, and science-based development of a liquid metal ESD Microsystem.

Localized Temperature Stable Dielectrics for Low-Temperature Co-Fired Ceramic

148900
Year 1 of 3
Principal Investigator: S. X. Dai

Project Purpose

The purpose of this project is to examine a concept of introducing a localized temperature-stable region in a global temperature-dependent material system, more specifically, in low-temperature cofired ceramic (LTCC) systems. LTCC is a multilayer 3D packaging, interconnection and integration technology. In the past 10–15 years the biggest growth of LTCC technology occurred in wireless communications ranging from radio-frequency (RF) to microwave (MW) frequencies. The three key material parameters most important to this application space include dielectric constant e, quality factor Q (inverse of dielectric loss), and temperature coefficient of resonant frequency T_f. For RF/MW circuits incorporating resonator functions it is highly desirable to have a zero or near-zero T_f to fully utilize the communication bandwidth and achieve temperature stability. All current commercial LTCC systems have a Tf, coefficient of resonant frequency, in the range –50 ~ –80 ppm/°C. Instead of developing an entirely new zero-T_f LTCC system, our approach is to establish a localized zero-T_f structure in most widely used LTCC systems to take advantage of existing LTCC technologies and infrastructure. We will explore a method to achieve 0 ppm/°C T_f by: 1) developing novel compensating materials that have opposite T_f to that of the LTCC base dielectric, and 2) incorporating the compensating material locally to LTCC structures where the resonant functions reside. The key materials science challenges include synthesis of T_f compensating materials and tailoring of their compatibility, both physical and chemical, to the existing LTCC system. Our objective is to examine the concept of localized temperature stability for advanced radio and microwave frequency (RF/MW) applications by addressing related materials science and engineering issues. If successful, it would enable more widespread use of LTCC materials for a broad range of applications at Sandia and in the commercial world.

Summary of Accomplishments

During the initial phaseof this project, we concentrated on screening of candidates for synthesis of T_f compensating materials and establishment of a T_f characterization capability. The following is a summary of accomplishment measured against goals/milestones.

Technology benchmark.
We have completed the initial literature survey. Assessment of impact of zero-T_f on targeted applications is still an ongoing effort.

T_f characterization capability
We acquired an Agilent E4991A Impedance/Materials Analyzer for measurement of T_c (temperature coefficient of capacitance) and an E5062A network analyzer for measurement of T_f. We have also designed and fabricated both microstrip and stripline ring resonators using DuPont 951 LTCC and successfully measured T_f over –50 to ~ +80 °C in manual mode. Construction of a LabView program for automated data acquisition is underway.

T_f compensating materials development

1. Executed an agreement with DuPont, Inc. to use their LTCC glass to form T_f compensating materials.

2. Sourced and characterized Al_2O_3, TiO_2, $SrTiO_3$, $CaTiO_3$, Viox 1449 and DuPont 951 glasses as ingredients of T_f compensating materials.

3. Formulated base LTCC compositions: a) 50wt% Al_2O_3 + 50 wt% DuPont glass, and b) 50wt% Al_2O_3 + 50 wt% Viox 1449 glass, to evaluate the effect of Al_2O_3 particle size on densification of the glass-ceramic dielectric. We experienced some difficulties in densification of these compositions and formed a plan to address the sintering issues.

Looking forward, we anticipate focusing intensely on the synthesis and cofireability of T_f compensating materials.

Significance

One unique aspect of the proposed research stems from the locality of temperature stability. To our knowledge this approach is novel and has not been attempted previously. If successful, the approach could become a universal zero-T_f technology that could be readily implemented into other LTCC systems. Furthermore, the concept could be extended to other integrating packaging technologies like printed circuit boards and high-temperature cofired ceramics.

From a DOE mission perspective, we expect this research to address challenges in the science and technology aspect with potential impact on national security. If successful, the new materials developed in this project will find application in radio-frequency (RF) cavity resonators and filters for DOE and DoD. These materials will also enable development of passive components operating in the MHz regime, with application to reference devices, and may provide means of constructing antennas for specialized radar and ultrahigh-frequency applications. In all such applications, the new materials would enable elimination of temperature-compensating circuits, reducing complexity and cost of components, while likely improving reliability.

IR Energy Harvesting: Traveling Wave Surface Plasmon-Enhanced IR Rectenna

150119
Year 1 of 1
Principal Investigator: P. Davids

Project Purpose

Thermal sources can be used to power low-energy sensing and monitoring circuitry in nuclear weapons systems and satellite platforms. Currently, radioiotopic thermo-electric generators (RTGs) based on thermoelectric devices perform these functions and are limited by thermoelectric conversion efficiencies of 1–3%. We will examine in detail a new infrared (IR) technology for highly efficient direct conversion of thermal IR radiation into electricity. This novel technology is based on a new IR "rectenna" concept that consists of a large area IR antenna and a new rectifying element. The enhanced IR rectenna can be highly efficient, potentially converting >85% of in-band thermal radiation. The potential efficiency gain is a four- to six-fold improvement over existing RTGs with smaller form factors. Furthermore, the IR rectenna can be used in conjunction with existing RTG devices or as an RTG replacement. It is based on radiative heat transfer and therefore is not in thermal contact with the heat source, allowing greater design freedom. The design is inherently thin, volume efficient, and lightweight.

Summary of Accomplishments

In this project, we have examined the feasibility of direct rectification of thermal light by a novel IR rectenna both experimentally and theoretically. The theoretical coupling efficiency of our novel rectenna structure has been examined using an advanced mode matching technique and compared to numerical rigorous electromagnetic calculations. The power coupling efficiency can be quite high, greater than 90% of the theoretical maximum efficiency. This can be further enhanced by engineering the multiple scattering in the cavity.

We have designed, fabricated, and are in the process of testing a prototype proof-of-concept device that will demonstrate direct rectification of infrared light. Our test structure utilized a coherent CO_2 laser as the infrared source and grating couplers to efficiently couple the IR radiation into the device andhas been verified by Fourier transform infrared spectroscopy. Integrated metal-insulator-metal (MIM) diode rectifiers have been fabricated and their current-voltage characteristics measured in the test chip configuration.

We have developed detailed models of the quantum mechanics of the tunneling process in the MIM diodes and developed semiclassical and compact models to fit experimentally determined IV characteristics.

Significance

While the stated goals are very challenging, they enable revolutionary possibilities in energy harvesting for nuclear weapons and other applications. If successful, this project will demonstrate Sandia's ability to advance the current state of the art in nanoscience and photonic microsystems while developing technology solutions with the potential to impact a broad range of future systems for internal and external application.

Refereed Communications

R.D. Kekatpure and P.S. Davids, "Channeling Light into Quantum Scale Gaps," to be published in *Physical Review B*.

GRAND CHALLENGES INVESTMENT AREA

Grand challenge project are designed to address scientific challenges and urgent national security issues that are broad in scope and potentially game-changing in their impact. As such, these projects require the assembly of often large, always interdisciplinary teams of scientists and engineers, and are commonly funded at an annual level of from $1M–$5M. Examples come from areas such as quantum computing, sensor architectures for moment-to-moment surveillance of the environment, nanoscience applications in high-power laser technologies, molecular immunology studies at single-cell resolution, and computational approaches to the discovery of clandestine terrorist networks.

Reimagining Liquid Transportation Fuels: Sunshine to Petrol

Project 131303

Domestically produced carbon-neutral transportation fuel: meeting this challenge would be a huge advance toward mitigating the problem of global climate change and ensuring the availability of energy. A direct solution is to recycle the carbon dioxide that results from burning gas, oil, and other fossil fuels by converting it back into hydrocarbons like ethanol, gasoline, and diesel. Unfortunately, this is thermodynamically costly, requiring an uphill "push" from some other source of energy.

In this project, solar thermal energy is being applied to supply the required uphill push. Concentrated sunlight provides thermal energy to heat redox active metal oxides to high temperatures where they give up oxygen. The resulting reduced metal oxide is then capable of converting chemically stable and unreactive carbon dioxide (CO_2) to carbon monoxide (CO). This step regenerates the starting oxide and provides the CO for fuel-producing syngas chemistry. Monoliths of the active metal oxides have been developed for the unique CR5 reactor in which the cyclic reaction occurs, a device designed and fabricated as part of this project's R&D.

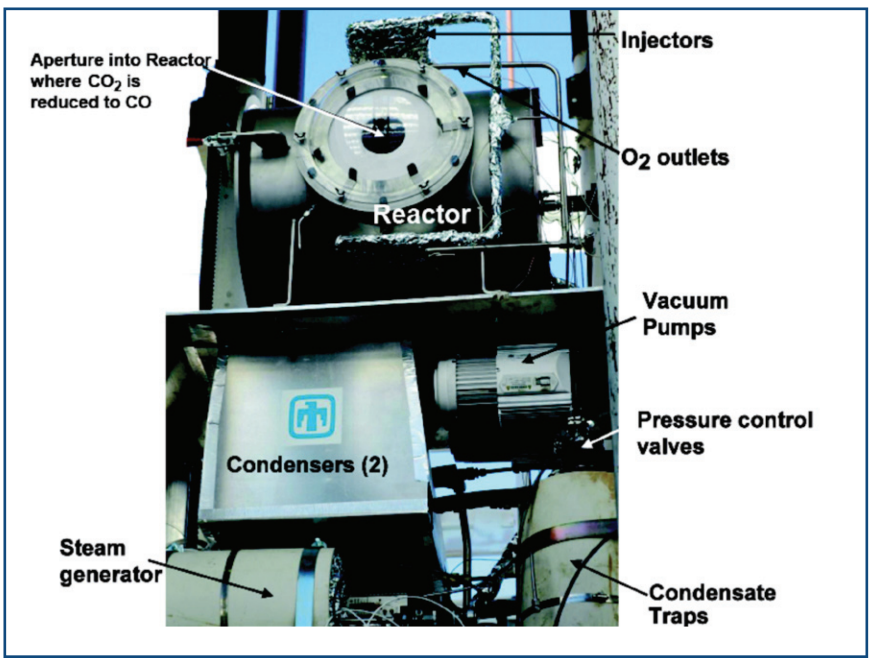


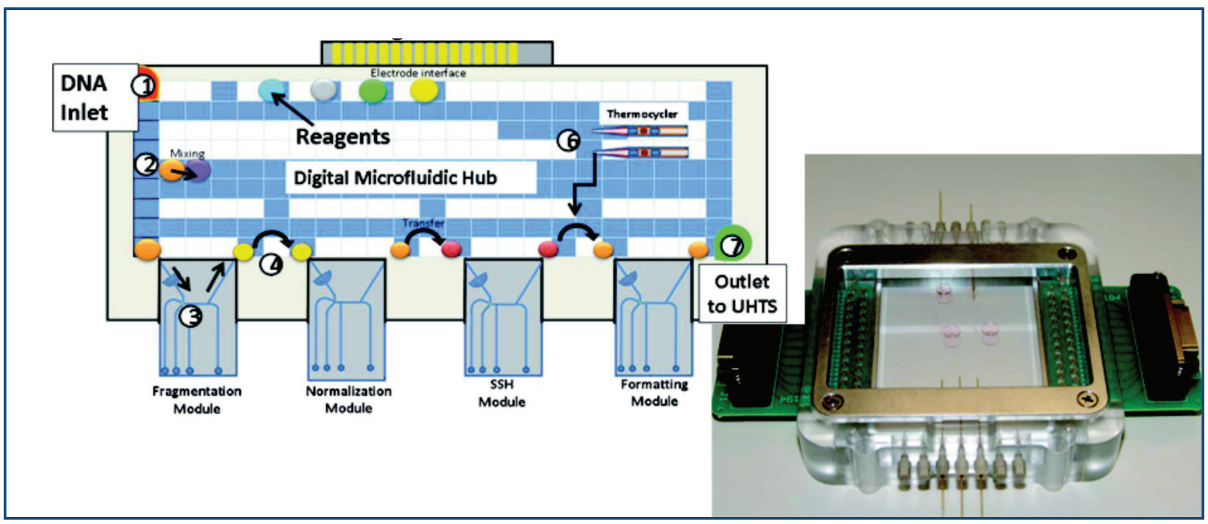
Photo of the CR5 reactor and ancillary structures designed and engineered in this project.

RapTOR: Rapid Threat Organism Recognition

Project 142042

Amid concern about bioterrorism threats to national security, there is, in addition to the need for rapid diagnostics for known biothreat agents, another requirement to detect unknown biological threats, that is, pathogenic microorganisms not previously encountered and possibly genetically engineered to increase threat/avoid detection. The technique of ultrahigh-throughput DNA sequencing (UHTS) is capable of characterizing such unknown organisms at the genetic (DNA sequence) level, but only if a suitable sample of the pathogenic organism's DNA is available. This is usually not the case because the nucleic acid (DNA or RNA) of the pathogen will exist against a background of the far greater quantity of the infected individual's DNA.

The RapTOR project is designing an automated molecular biology microfluidics platform that will selectively suppress and subtract the far more numerous human DNA sequences, while amplifying pathogen sequences. "Normalization" is a hybridization-based process resulting in the preferential destruction of numerically abundant sequences thus increasing the relative abundance of rare sequences. RapTOR uses hydroxyapatite capillary-based chromatography (HAC) to achieve normalization, thereby increasing the ratio of pathogen sequences to host sequences such that sequencing can accomplish identification of a threat organism.



Left: Drawing representing the four modules of a microfluidic system that prepares a mix of human/pathogen DNA for ultrahigh-throughput DNA sequencing. Right: Prototype device.

GRAND CHALLENGES INVESTMENT AREA

Network Discovery, Characterization and Prediction

119351
Year 3 of 3
Principal Investigator: W. P. Kegelmeyer

Project Purpose

Many of the most pressing threats to our national security are enabled by networks of proliferators, terrorists, hackers, financiers, and recruiters. We may preempt individual attacks, but if the network survives, the threat remains. Under this Grand Challenge project we are discovering the means to identify and analyze these networks, creating the unique capability to answer previously unanswerable questions.

This project combines analyst-focused elicitation and design, novel and scalable analysis techniques, network prediction, uncertainty assessment, and advanced visualization, all implemented in a scalable informatics software framework. We are building upon high-quality capabilities already at Sandia in technical analysis, information visualization, high-performance graph analysis, and prediction. The project encompasses seven directorates combining application expertise, mathematics, high performance computing, knowledge management, and human factors. We are repeatedly bundling the fruits of our research into prototypes for analyst use and feedback.

The challenges associated with discovering, characterizing and predicting adversarial networks are enormous, and require a broad range of research and development. In response, we are pursuing the following approaches:

- Developing advanced methods and abstractions for fusing heterogeneous data from cyber events, intelligence reports, communication links, and more.
- Researching novel network analysis methods and implementing them at scale.
- Inventing new techniques for predicting network behavior.
- Creating scalable exploration and analysis tools that allow an analyst to interact with orders of magnitude more information than before.
- Performing fundamental research in the characterization of uncertainty in the intelligence domain.

This fundamental, high-risk research has resulted in specific Sandia capabilities, as well as broad and deep expertise in informatics. More and more of our Laboratory missions require knowledge processing; the capabilities resulting from this project are providing a foundation for those undertakings.

Summary of Accomplishments

- Developed (and proved) new, fundamental, and practically useful understandings of network properties, including, for example, methods for hypothesis testing of graph properties that can help explain to an analyst the rationales for the communities detected in a social network.
- Developed novel applications of tensor decompositions to problems in cyber and text. Demonstrated these decompositions through, for instance, analysis of internet protocol traffic payload and metadata to find and present related concepts as they develop over time; and, through analysis of email traffic, to discover and understand non-obvious relationships between senders, receivers, time, and topic, such as the effective leadership hierarchy.

- Integrated linear algebra, computational linguistics, high performance computing and data warehouse architecture design to build a capability for translation-free massive-scale multilingual document clustering in analyst time.
- Developed and demonstrated scalable applications of statistical methods for anomaly detection, providing the ability to detect, for example, an illicit exfiltration event involving only 0.016% of the collected network traffic.
- Developed, provided a theoretical basis for, and demonstrated via prototype the ability to predict when fervent on-line conversation will spill over into real-world consequences.
- Designed and conducted original human studies research resulting in new insights into, and new methods for, the design and evaluation of analytic tools for analysts.
- Developed and implemented libraries for parallel multilinear algebra for large-scale tensor decompositions, and for parallel statistical characterization, allowing the use of applications at scale.
- Established TITAN (Titan Informatics Toolkit) as an enduring R&D computational framework for scalable graph and text informatics, and demonstrated its capacity for integrating informatics into useful tools via the construction of three surprisingly popular prototypes, each focused on a different analyst-suggested network analysis problem.

Significance

There have been significant applied impacts in several national security mission areas, especially cyber security and nonproliferation analysis. These have been demonstrated by project-developed analytic capabilities that have already attracted significant external funding.

Informatics projects at Sandia have been, up to now, small and largely disjoint. This Grand Challenge project coalesced that work, leveraging it to connect with new research in areas where Sandia can establish a leadership position and make a difference to the nation’s “big data” challenges; it provides a unifying programmatic focus that defines a sustainable science and technology research area. The project’s work is relevant to a range of Sandia programs. For example, capabilities demonstrated in our first prototype have already provided new insights into cyber security problems. Complex data challenges exist in remote sensing, energy systems, stockpile stewardship, and numerous other national-scale problems. Further, there are large data problems encountered by decision-makers in energy, critical infrastructures, transportation, and national defense. The project has developed capabilities that can be leveraged across multiple problem areas. In sum, the Network Grand Challenge project has created a unique capability to answer previously unanswerable questions. In the future, we see that capability being applied beyond the field intelligence element; our advances are likely to be pertinent anywhere the data is so complex or so voluminous as to defy its effective use.

Refereed Communications

R. Colbaugh, J. Gosler, and K. Glass, “Some Intelligence Analysis Problems and Their Graph Formulations” *Journal of Intelligence Community Research and Development*, vol. 315, 2010.

Quantum Information Science and Technology

119352
Year 3 of 3
Principal Investigator: M. S. Carroll

Project Purpose

Quantum computing can potentially realize efficient solutions to problems that are inefficiently solved on classical computers. Specific problems of interest to Sandia and DOE include materials science, searching, and optimization problems. However, quantum information science breakthroughs are required to realize fundamental devices, that is physical quantum bits (qubits) and logical qubits (error-corrected qubits). The vision for this Grand Challenge project is to develop the quantum equivalent of a scalable classical transistor that may eventually realize the full potential of quantum computation. To achieve this vision, the focused goal for this project is to demonstrate a qubit gate in silicon and generate the computer engineering design for a self-sustaining error-corrected logical qubit.

The experiment that demonstrates a silicon spin qubit would represent a seminal breakthrough in the quantum computing community, and we anticipate that it would generate enormous enthusiasm for increased research effort in the field. Several Si electrostatically gated quantum dot (QD) groups around the world have duplicated all the separate critical steps used in the GaAs qubit experiments, although not all simultaneously. Because all the precursor experiments appear to be demonstrated in Si quantum dots there is a tantalizing perception that the spin qubit in silicon may soon be realized. This motivates both direct work on the Si qubit, as well as forward looking research on next-step topics like experiments and theory supporting the area of logical qubit design, to evaluate whether these forms of silicon qubits are really viable to scale to a logical qubit.

Summary of Accomplishments

Silicon physical qubit:

- Developed fabrication processes for reduced defects
- Measured double quantum dot in many-electron regime
- First charge sensing measurement of single dot in metal-oxide-semiconductor system
- Improved detectors for single ion implantation
- Improved ion beam line
- Publications in *Physical Review B and Applied Physics Letters*

Modeling:

- Guided design and gate bias voltages to achieve few electron quantum dot and donor spectroscopy results
- Developed cluster expansion method for modeling of spin diffusion
- Developed model for exchange interaction in double QD systems for evaluating sensitivity in controlled phase (CPHASE)
- Publications in *Institute of Electrical and Electronics Engineers Nanotechnology* and *Physical Review Letters*

Classical electronics:

- Developed models for complementary metal oxide semiconductor (CMOS) electrical behavior at low-temperature (e.g., at 4 K)
- Developed thermal models for low-temperature CMOS
- Designed and tested CMOS read-out circuits
- Refined small signal analysis to estimate tolerances for Z and CPHASE gates

Logical qubit architecture

- Developed architecture design for a Si double quantum dot (DQD)
- Developed optimal scheduler for DQD logical qubit operations
- Analyzed architecture performance (i.e., error threshold)

Significance

Sandia is engaged in basic quantum information sciences research in support of its nuclear weapon and national security missions. This research is motivated by advanced computing architectures and the fact that future engineered systems will require increased understanding of quantum effects. In 2009 the Office of Science Technology and Policy (OSTP) published a national strategy document in Quantum Information Processing. From the OSTP website: "In January 2009, the United States National Science and Technology Council <http://www.ostp.gov/cs/nstc> issued A Federal Vision for Quantum Information Science <http://www.eas.caltech.edu/qis2009/documents/FederalVisionQIS.pdf>. The report proposes that: "The United States . . . create a scientific foundation for controlling, manipulating, and exploiting the behavior of quantum matter, and for identifying the physical, mathematical, and computational capabilities and limitations of quantum information processing systems in order to build a knowledge base for this 21st century technology."

Metamaterial Science and Technology

131302
Year 2 of 3
Principal Investigator: M. B. Sinclair

Project Purpose

Metamaterials form a new class of artificial electromagnetic materials that have the potential to enable a wide range of revolutionary new optical devices and profoundly impact National Security applications. For example, theoretical designs for electromagnetic structures capable of rendering objects invisible at chosen frequencies have recently been proposed and validated using radio-frequency (RF) metamaterials. However, progress toward practical implementation of metamaterials, particularly at infrared and visible frequencies, has been hampered by high absorption losses of the metallic structures used in most metamaterials. The goal of this project is to create useful infrared metamaterials through a comprehensive approach using new geometries, material sets, and state-of-the-art nanofabrication techniques. Achievement of this goal will also represent a first step toward increasing the operational bandwidth of metamaterials and providing tunability. This effort leverages Sandia's extensive capabilities in nanomaterials, nanophotonics, electromagnetic theory and modeling, high performance computing, materials science, electromagnetic characterization, and micro-/nanofabrication. This project will develop useful infrared metamaterials: low-loss, 3-dimensional infrared metamaterials that manipulate electromagnetic waves in a volumetric manner. The ability to control the 3D paths of optical rays using metamaterials relaxes the constraints of normal optics and will enable novel devices such as super-light, -thin and -fast lenses and concentrators. Thus, metamaterials will provide the capability to arbitrarily engineer key optical material properties to enable new optical designs and devices that can dramatically lower the size, weight, and power (SWaP) in nonproliferation and defense applications. The technologies developed in this project are expected to impact a broad range of Sandia missions. Furthermore, these technologies might also enable spin-off projects in RF metamaterials for high-impact national security applications. The exploding international research in this technologically disruptive area also mandates a leadership position in this field.

Summary of Accomplishments

During the past year, we have made significant progress in all aspects of our project. We have performed rigorous and quantitative analysis of metamaterial architectures based upon metals, polaritonic materials, and dielectric resonators. The results of these analyses quantitatively show the following: 1) the ohmic losses of metallic metamaterials are too large for metamaterial applications such as lenses that require good transparency; 2) polaritonic materials can be utilized to improve metamaterial performance, most notably by acting as negative permittivity host materials in dielectric resonator-based metamaterials; 3) dielectric resonator-based metamaterials represent the best route to low-loss metamaterials; and 4) independent tuning of the permittivity and permeability of dielectric resonators can be achieved using a variety of strategies. We have established a metamaterial design environment that integrates analytic models, group theory, optimization, full-wave simulation, and parameter retrieval. We have developed a "subcell" simulation tool that reduces the computational burden for metamaterial structures such as split ring resonators (SRRs) by a factor of 1000, thereby enabling the direct numerical simulation of entire metamaterial devices such as prisms or lenses. We have synthesized a new low-loss infrared polymer called polynorbornene that combines the attributes of low infrared loss, photopatternability, and chemical cross linking for mechanical strength. We have identified the best high dielectric constant materials to utilize for dielectric resonator-based metamaterials, and have characterized their infrared optical properties. We have developed a novel fabrication process called membrane projection lithography (MPL) for the production of SRR-based metamaterials. MPL enables a 1000-fold reduction in the unit cell dimensions and enables the production of fully 3D, bulk metamaterials in the thermal infrared. We have constructed two complementary characterization tools that allow us to experimentally determine the amplitude and phase of the transmission and reflection coefficients of metamaterial samples.

Significance

The proposed research is directed toward the development of low-loss infrared metamaterials that can be used for a wide variety of applications. These new materials will provide the capability to arbitrarily engineer key optical material properties, to enable new optical devices with dramatically lower the size, weight, and power requirements. Such devices have the potential to impact a broad spectrum of national security, nonproliferation and defense missions.

Refereed Communications

D.B. Burckel, J. Wendt, I. Brener, G.T. Eyck, M. Sinclair, R. Ellis, and J. Ginn III, “Fabrication of Micron-Scale Cubic Unit Cell 3D Metamaterial Layers,” to be published in *Advanced Materials*.

J. Wendt, R. Ellis, B. Burckel, I. Brener, G.T. Eyck, and M. Sinclair, “Fabrication Techniques for 3D Metamaterials in the Infrared,” to be published in the *Journal of Vacuum Science and Technology*.

D.B. Burckel, J. Wendt, G.T. Eyck, R. Ellis, I. Brener, and M Sinclair, “Fabrication of 3D Metamaterial Resonators Using Self-Aligned Membrane Projection Lithography,"” *Advanced Materials*, vol. 22, p. 3171, 2010.

Reimagining Liquid Transportation Fuels: Sunshine to Petrol

131303
Year 2 of 3
Principal Investigator: J. E. Miller

Project Purpose

We seek to address two of the most daunting problems facing humankind in the Twenty-first century: energy security and climate change. Our vision for achieving this is captured in one deceptively simple chemical equation:

Solar Energy + xCO_2 + $(x+1)H_2O \rightarrow C_xH2_{x+2}$(liquid fuel) + $(1.5x+.5)O_2$

Practical implementation of this equation may seem far-fetched, since it effectively describes the use of solar energy to reverse combustion. However, it is also representative of the photosynthetic processes responsible for much of life on earth and, as such, summarizes the biomass approach to fuels production. Regrettably, photosynthesis and, consequently, the biofuels approach, have a very low sunlight-to-hydrocarbon conversion efficiency and suffer from a number of other serious shortcomings. Thus, an alternative approach, one that is not limited by photosynthesis and more directly leads to a liquid fuel, is extremely desirable. The development of a process that efficiently, cost-effectively, and sustainably reenergizes thermodynamically spent feedstocks to create reactive fuel intermediates would be an important achievement and is a key challenge that must be surmounted to help solve the intertwined problems of accelerating energy demand and climate change. We propose that the direct thermochemical conversion of CO_2 and H_2O to CO and H_2 — universal building blocks for synthetic fuels — can serve as the basis for this revolutionary process. To realize this concept, we must address and solve the complex chemical, materials science, and engineering problems associated with thermochemical heat engines and the crucial metal-oxide working-materials deployed therein.

Summary of Accomplishments

Accomplishments for the principal focus areas are as follows:

<u>Materials</u>:

- Transitioned phase and density functional theory modeling into ceria-based systems. Applied techniques to problems of materials interactions and compatibility, as well as to reaction mechanisms.
- Grew ultrathin films of iron oxide on yttria-stabilized zirconia (YSZ); using low-energy electron microscopy, observed real-time transformations including structuring, phase change, and mixing and de-mixing.
- Characterized solubility of Fe in YSZ as function of loading, oxidation state, and temperature. Solubilized Fe is highly mobile and accessible for redox chemistry.
- Measured global rate parameters for peak H_2 and CO production for numerous ferrite and ceria materials. Demonstrated that the full rate expression is dependent on sample geometry and preparation and identified likely mechanisms.
- Demonstrated high activity for monolithic ceria materials. Characterized reaction via various in-situ probes including high-temperature x-ray diffraction and ambient-pressure x-ray photoelectron spectroscopy.

<u>Reactors</u>:

- Demonstrated key features of the counter-rotating-ring receiver/reactor/recuperator (CR5) including continuous production and separate recovery of CO and O_2.

- Transitioned CR5 to next generation ceria materials including fabrication of new rings. Laboratory evaluations indicate these should perform sufficiently to meet the project goals.
- Characterized potential for volatilization of reactive materials.
- Improved computational model for energy recuperation and improved geometric fidelity of reactor model to allow for assessment of more-realistic flow conditions.
- Predicted the distribution of solar flux for operating conditions expected during CR5 testing.
- Modified reactant rings to reduce thermal stresses based on computational assessments.

Systems:
- Improved fidelity of the CR5 reduced-order model.
- Developed Fischer Tropsch (FT) reactor model to replace the methanol reactor. FT shows potential for efficiency gains.
- Performed analysis of mixed (CO_2 and H_2) splitting. Mixed pathway is significantly more energy- and cost-efficient than previous architectures.

Significance
Energy security and climate change will be defining issues during this century. The availability and price of transportation fuels is coupled to economic and national security as are the effects of climate change. Development of a carbon-neutral technology to domestically produce fuels and reduce our reliance on imported oil supports DOE's strategic Energy and Environment goals.

Refereed Communications
J.E. Miller, R.B. Diver, N.P. Siegel, E.N. Coker, A. Ambrosini, D.E. Dedrick, M.D. Allendorf, A.H. McDaniel, G.L. Kellogg, R.E. Hogan, K.S. Chen, and E.B. Stechel, "Sunshine to Petrol: A Metal Oxide Based Thermochemical Route to Solar Fuels," *Energy Technology 2010*, pp. 27-38, February 2010.

B. Meredig and C. Wolverton, "First-Principles Thermodynamic Framework for the Evaluation of Thermochemical H_2O- or CO_2-Splitting Materials," *Physical Review B*, vol. 80, p. 245119, December 2009.

E.N. Coker, A. Ambrosini, M.A. Rodriguez, T.J. Garino, and J.E. Miller, "Production of Hydrogen and Carbon Monoxide from Water and Carbon Dioxide Through Metal Oxide Thermochemical Cycles," to be published in the proceedings of the *Material Challenges in Alternative & Renewable Energy Conference*, 2010.

A. Ambrosini, E.N. Coker, M.A. Rodriguez, S. Livers, L.R. Evans, J.E. Miller, and E.B. Stechel, "Synthesis and Characterization of Ferrite Materials for Thermochemical CO_2 Splitting using Concentrated Solar Energy," to be published in the proceedings of *Advances in CO_2 Conversion and Utilization,* 2010.

Featureless Tagging Tracking and Locating

131305
Year 2 of 3
Principal Investigator: R. C. Ormesher

Project Purpose

Tagging, Tracking, and Locating (TTL) is integral to several national security and defense missions. Existing TTL systems enable these missions within certain constraints. However, they do not provide the entire set of capabilities required for TTL missions, namely a TTL system that provides broad-area coverage with desired operational characteristics. Broad-area coverage means the ability to cover large geographical regions, continuously, twenty-four hours per day, seven days per week. Additionally necessary is a TTL system that supports tags with extended lifetimes, which can be detected and located in difficult conditions. An on-demand system with wide-area coverage and a high level of accuracy is also necessary. We propose to make several scientific and technical advancements that provide a framework enabling these desirable TTL system capabilities. We will create and develop new signaling waveforms, detection and geolocation algorithms, and a novel tag architecture resulting in such an innovative TTL capability. We will achieve technical advances in microelectromechanical system (MEMS) acoustic microresonator delay elements and antenna technologies, resulting in a tag device that can be small with low power consumption. Overall, these new capabilities will allow the US to better manage and mitigate national security threats.

Summary of Accomplishments

Our goal is to develop the key technologies and algorithms that enable new TTL capabilities, and to demonstrate some of those elements in an integrated fashion. A proof of concept tag supporting our proposed conduct of operations is in its final fabrication stage, with most subsystems successfully tested in the laboratory. The tag is possible thanks to technologies emerging from the project's three research thrusts: advanced signal processing, MEMS microresonators, and advanced antennas. Signal processing advances include two new phase-based processing techniques that enable near-coherent integration of otherwise unstable frequency sources. We have fabricated MEMS sources and demonstrated them at frequencies well above those previously demonstrated. A dual-frequency antenna has shown significant promise. In partnership with the University of Illinois, we developed a dual-frequency slot antenna, together with closed-form models for designing tag antennas in a variety of operating environments. Key advances have also been made in the system operation concept. During the past year, we have also made significant progress toward achieving the miniaturized delay goals. We scaled up the operating frequency, and created a frequency-diverse delay, filter, and oscillator technology for use in many other national security applications. We also increased operating bandwidth, which improves location accuracy, and reduced insertion loss, which reduces system power consumption. We continue to advance tag topology, thereby reducing power consumption. The tag prototype is significantly smaller than existing designs. Initial lab trials have demonstrated successful operation of tag subsystems in preparation for a final demonstration.

Significance

A December 2004 Defense Science Board study, *Transition to and from Hostilities* directs US technology development. The report states that "current US intelligence, surveillance, and reconnaissance (ISR) capabilities are inadequate for many tasks that emerge in asymmetric warfare" and that a "Manhattan Project of scale and intensity" is needed to develop these capabilities. Advancements in any of the three proposed technology pillars will assist in addressing these national security issues.

RapTOR: Rapid Threat Organism Recognition

142042
Year 1 of 3
Principal Investigator: T. Lane

Project Purpose

Of the two types of catastrophic weapons of mass destruction (WMD) attacks, biological and nuclear, experts consider a biological attack to be most probable, with an event likely to occur by 2013 (Commission on the Prevention of Weapons of Mass Destruction Proliferation and Terrorism, 12/2/2008). This reports states that rapid advances in biotechnology make technical surprise utilizing genetically engineered bioweapons a formidable and growing threat to national security. Unfortunately, our nation is currently blind to such "unknown" biological agents; its biodefense and public health infrastructure is primarily designed to counteract previously characterized (known) pathogens. Unknown pathogens are identified using methods that can take weeks to produce actionable information. That delay can be costly, in terms of casualties and economic damage, and can mean the difference between a manageable public health incident and a full-blown epidemic.

The present-day technological revolution of ultrahigh-throughput sequencing (UHTS) represents a paradigm shift in nucleic acid–based detection and analysis. However UHTS alone is incapable of obtaining sufficient genetic information from an unknown pathogen in the context of the overwhelming genetic background of the host. To solve this problem, the Rapid Threat Organism Recognition Grand Challenge (RapTOR) will radically increase the information content of a DNA sample and enable the effective use of UHTS. To accomplish this, RapTOR will carry out complex, multistep nucleic acid manipulations in a rapid, reproducible, and automated manner, and will adapt its process appropriately to the information generated. We will develop an integrated system for Automated Molecular Biology (AMB) that will accept nucleic acids from clinical samples, selectively amplify those derived from pathogens or those that are indicative of host response, and prepare them for analysis by UHTS. Additionally, we will build an information processing pipeline for efficient handling and annotation of short nucleic acid sequence reads, determining functional and phylogenetic identities to provide actionable information to decision-makers.

Summary of Accomplishments

The RapTOR team has made good progress and has been successful, to date, in meeting project milestones.

We have developed a first-generation, capillary-based hydroxyapatite chromatography nucleic acid normalization device for the removal of double stranded DNA and have demonstrated its effectiveness on nucleic acid mixtures. We have created a first-generation digital microfluidic hub for the movement of materials and have used this device to demonstrate droplet-based reagent mixing, reactions, and DNA detection. We have developed microfluidic devices for the concentration of DNA and have demonstrated on-chip melting and re-annealing reactions.

We have carried out *Francisella holarctica* infections of mouse bone-marrow-derived macrophages (BMDMs) and produced samples that were analyzed by UHTS. Similarly, we have also purified and sequenced nucleic acids from blood samples from healthy human donors. The data from both the experimental infection and the blood samples were used by the data analysis team to develop and test their data processing tools. We have developed methods for the removal of unwanted nucleic acid sequences (such as those from ribosomes) from complex mixtures of nucleic acid. This work constitute excellent progress towards the goal of detecting trace pathogen signatures.

We have successfully established specifications for data formats, software, and database components, and work to build applications for core bioinformatics functions is well underway. Data from DNA sequencing of human blood samples and mouse BMDMs infected with *Francisella holarctica* was subjected to de novo assembly to develop and train informatics tools for the detection of trace pathogens in complex samples.

Significance

Leaders at DoD, NIH, DHS, and other national security agencies are increasingly concerned about the impact of the exposure of civilian populations and military forces to enhanced, emerging, or advanced biothreats. RapTOR will develop and demonstrate the systematic strategy, the decision support framework, the scientific foundations, and the technical means to quickly characterize an unknown agent and to take actions necessary to mitigate its impact on public health and national security.

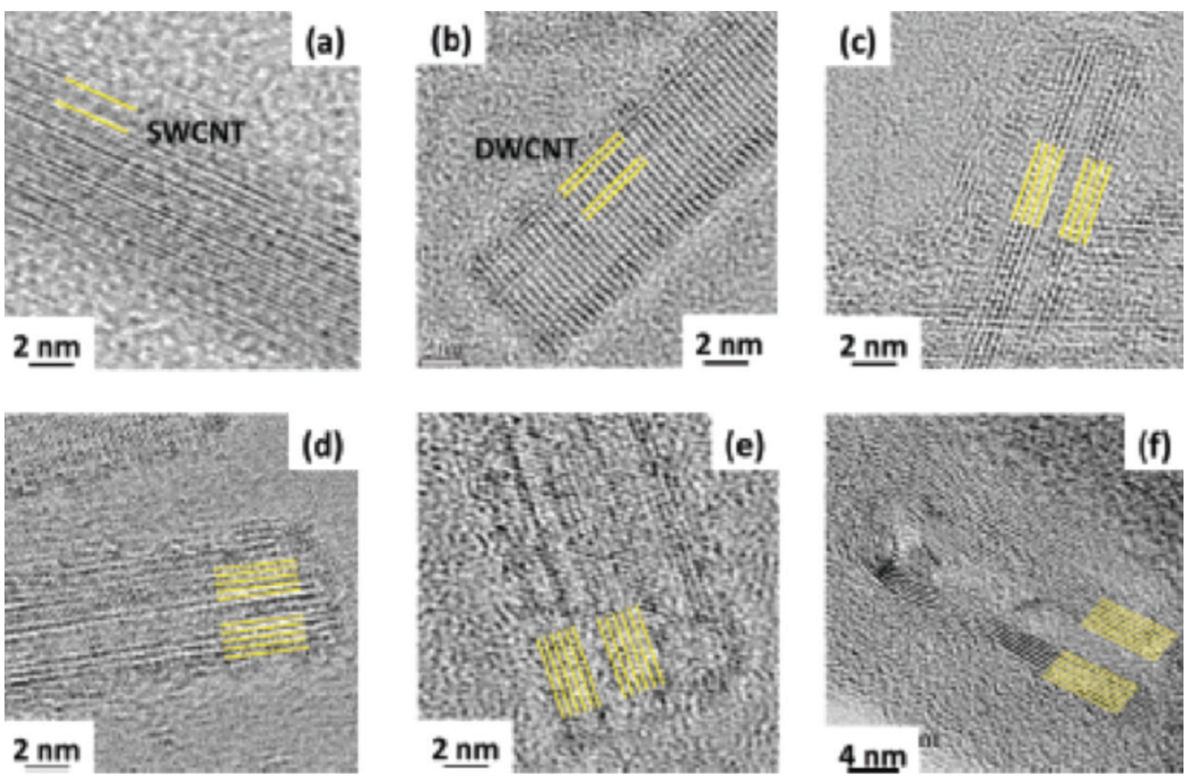
SENIORS' COUNCIL INVESTMENT AREA

This investment area supports a diversity of research projects under the national security umbrella, which are deemed worthy of funding under the auspices of the Seniors' Council, a cadre of Sandia senior scientists. Other than the fact that they tend to be of exceptionally high risk, there is no per se restriction on the topical area of the research proposal, so projects generally fall into several different scientific areas, whose only link is the common thread of the Laboratories' national security mission.

Development Toward a Nano-Thermal Interface Material

Project 145282

Heat dissipation is an ongoing critical issue for high-power electronic devices, such as radar, solid-state lighting, and a variety of detectors, and is becoming even more of an problem with each new smaller generation of microprocessors. Traditional solutions rely on thermally conducting metal particles embedded in polymer- or epoxy-based materials, and problematically, only incremental gains in thermal conductivity can be gained through optimization of this design. By contrast, this project is seeking an entirely novel solution to enhanced heat dissipation, namely using carbon nanotubes oriented in the heat-flux direction, from the thermal source to the thermal spreader, to provide unidirectional, high-thermal-conduction pathways for heat transfer.



High-resolution transmission electron microscopy images from carbon nanotube (CNT) bundles harvested from samples grown at (a) 530, (b) 550, (c) 570, (d) 590, (e) 610, and (f) 630°C. The lines are added as a guide to aid observation of the CNT wall structures.

SENIORS' COUNCIL INVESTMENT AREA

Unintended Consequences of Climate Mitigation

135039
Year 2 of 2
Principal Investigator: P. V. Brady

Project Purpose

The objective of this work was to identify and, to the extent possible, quantify, the unintended consequences of sulfate aerosol injection into the atmosphere to mitigate climate change. Traditional strategies for mitigating climate change envision carbon taxes, or cap and trade protocols, to force greater conservation ("demand reduction"), and/or increased reliance on renewables and nuclear power. Newer approaches emphasize geo-engineering solutions such as: terrestrial biomass storage (e.g., locking up carbon by growing trees, or converting biomass into inert soil carbon), carbon capture followed by sequestration, ocean fertilization, and albedo modification. The most-effective form of albedo modification entails pumping SO_2 into the atmosphere to form sunlight-reflecting aerosols. All strategies have the potential to trigger other global, often climate-affecting, processes. For example, reforestation produces methane, an even more potent greenhouse gas than CO_2. Introducing SO_2 into the atmosphere could diminish the earth's ozone layer. Ocean fertilization might rob nearby fisheries of nutrients, or lead to oxygen-free "dead zones." Meanwhile, engineering the climate by simply decreasing the burning of fossil fuels would incur stark decreases in global GDP (gross domestic product) — part of the reason for looking at geo-engineering efforts in the first place.

While climate mitigation schemes have received ample attention in the technical literature, the unintended consequences have received only marginal consideration. The fear of unintended consequences looms large, and the uncertainty is especially significant in the collateral damage of side effects of sulfate aerosol injection, the most likely geoengineering approach to be deployed. We therefore propose to: identify the most important side effects and quantitatively assess their likelihood, magnitude, and impact.

Summary of Accomplishments

1. We concluded that sulfate aerosol injection is the most probable geoengineering approach that will be employed in the foreseeable future.
2. We identified the primary unintended consequences of sulfate aerosol injection to be reductions in rainfall, slowing of atmospheric ozone rebound, and differential changes in weather patterns. At the same time, there would be an increase in plant productivity. Atmospheric sulfate injection would not mitigate ocean acidification.
3. We outlined how the economic value of each process could be modeled and provided a preliminary assessment of economic impact.

Significance

The key R&D accomplishment was the development of a way to address the multidimensional problem of climate change with a limited number of technically achievable actions. We identified the most likely solution to climate change (geoengineering). We determined how it would probably be applied (sulfate aerosol injection). We identified the research gaps that must be filled to guide its implementation (must quantify the unintended consequences first), and we began filling those gaps. Climate change has the potential to prompt multiple new national security challenges by, for example, undermining existing water supplies, disrupting agricultural production, and prompting unexpected migrations. By a better understanding of the economic factors and uncertainties that underlie and potentially limit mitigation of climate change, this work will better allow the nation to respond to these national security challenges.

Designer Catalysts for Next-Generation Fuel Synthesis

137804
Year 2 of 2
Principal Investigator: S. Thoma

Project Purpose

We have developed syntheses for single-layer transition metal sulfide (SLTMS) catalysts, specifically molybdenum and molybdenum-d-block metal sulfides. Our syntheses are a "bottom-up" approach, in which we produce SLTMS via assembly of smaller species as opposed to typical SLMTS synthesis that rely on delamination of macroscopic multilayer species to produce the single-layer form. Further, optical characterization suggests that we can synthesize mixed valence SLTMS by this method, which is also not possible from "top-down" synthetic methods. These synthetic methods are capable of producing supported or unsupported catalysts over a wide range of sizes and enables variation of the metal-to-metal and the metal-to-sulfur ratios.

Summary of Accomplishments

We have shown that non-stoichiometric molybdenum and molybdeunum-cobalt, molybdenum-iron, and molybdenum-nickel sulfides can be synthesized at room temperature. The synthesized materials consist of nanometer-scale primary particles that may aggregate into macroscale assemblies. However, the aggregates and the primary particles have very similar optical absorption spectra suggesting that primary particles are loosely associated as opposed to forming larger condensed species via, for example, Ostwald ripening. Further work including nuclear magnetic resonance spectroscopy or extended x-ray absorption fine structure spectroscopy would be required to fully determine the structure of the primary particles, but analyses herein suggest less-than-two-nanometer single-layer metal sulfides. Furthermore, the structure appears to be a distorted octahedral one, similar to the catalyst rhenium sulfide, and, as such, is this first reported direct synthesis of this structure in a non-rhenium system.

The primary particles and subsequent aggregates will likely not display catalytic activity similar to bulk transition metal sulfides as the metal-metal and metal-sulfur bonds are different from the bulk; i.e., the "rim-edge" model might not apply. These materials do, however, represent a "bottom-up" approach to transition metal sulfide synthesis that may be used as building blocks toward macrosized structures or may be catalytically active in other ways. It is also very likely that other metal sulfides and bimetal sulfide combinations could be prepared by these methods, but cannot be synthesized by traditional synthesis techniques. The scale-up and catalytic testing of these materials is the subject of another project and will be reported elsewhere.

Significance

This project ties to the DOE Strategic Plan by using scientific discovery and innovation to create energy security. We have discovered some fundamental science that, if developed, could greatly enhance the following:

- Reclamation of low-value crude/petroleum-processing-by-products
- Direct coal liquefaction
- Hydrogen generation by H_2O and H_2S splitting (photo-oxidation)
- Biofuel production: energy-efficient alcohol synthesis from bio-feedstocks via greater catalytic alkali promotion selectivity

Reduced-Order Models for Thermal Analysis

137807
Year 2 of 2
Principal Investigator: D. K. Gartling

Project Purpose

High-fidelity computational models of large, complex systems are now used routinely to verify design and performance. However, there are applications where the high-fidelity model is too large to be used repetitively in a design mode. One such application is the design of a control system that oversees the functioning of the complex, high-fidelity system model. Examples include control systems for manufacturing processes such as brazing and annealing furnaces, as well as control systems for the thermal management of optical systems. In these cases a reduced-order model (ROM) is needed that represents the overall behavior of the system with relatively few degrees of freedom. Such models are routinely used in solid mechanics where modal analysis has reached a high state of refinement. The same techniques have not been applied or developed for thermal problems, although the theory is very similar for standard conduction problems. One major difficulty with the development of ROMs for thermal analysis is the need to include the very nonlinear effects of enclosure radiation in many applications. This proposal is directed toward the development and testing of numerical algorithms that would allow ROMs to be generated for general conduction/radiation problems.

Summary of Accomplishments

Two main approaches to ROMs were considered. The first was modal analysis, which has been successfully used in solid mechanics. This method requires the solution of a generalized eigenvalue problem for the first few modes of the linearized, large, high-fidelity finite element model of the conduction/radiation problem. As it was not possible to determine an appropriate linearization for the radiation part of the problem, we did not pursue this approach. The second, more promising approach to ROM utilized Proper Orthogonal Decomposition (POD) of the combined conduction/radiation model. Again, this method requires the solution of an eigenvalue problem associated with the covariance matrix generated from solutions of the high-fidelity model. POD has none of the restrictions regarding linearization but does require that a fully coupled conduction/radiation solution be available. A significant part of this study involved the implementation and testing of fully coupled solution methods for conduction and radiation problems that are useful in parallel computing environments. This development was nontrivial because the assembly of the nonstandard matrix problem associated with both conduction and radiation equations involves full matrices and significant amounts of off-processor data generation and communication. Significant improvements in solution convergence and time-dependent solution behavior are realized by fully coupled methods. This algorithmic development would provide thermal analysis with a unique capability. Although we determined that this approach was promising and took initial steps in this direction, the project terminated before more-significant progress could be made on the POD approach to ROM.

Significance

Fully coupled solution methods for conduction and radiation problems, if implemented in production software, would give thermal analysts a significant improvement in solution efficiency for large thermal models. A viable approach to ROMs has been outlined and should be pursued. There are large benefits to a number of ongoing modeling and simulation projects that could be realized from both coupled solution methods and the development of a POD methodology.

The Theory of Diversity and Redundancy in Information System Security

139352
Year 2 of 2
Principal Investigator: M. D. Torgerson

Project Purpose

Because complete verification of computer software and hardware is usually infeasible, new approaches are needed to address the present and future dangers of malicious intrusion into information systems. Both accidental flaws and deliberate subversions can create vulnerabilities for attackers to exploit. This project has investigated new aspects and combinations of diversity and redundancy to bolster security.

In this context, diversity is the practice of applying differing implementation techniques to do the same task in different settings. Redundancy uses multiple implementations of the same functionality to arrive at a decision. Various aspects of the notion of combining diversity and redundancy have been explored by the computer security community; examples include replicated hardware, threshold cryptography, Byzantine fault tolerant protocols, and multiple operating systems. Depending on the technique, the research has seen varying degrees of success.

To mitigate the effect of an unknown implementation error (as opposed to random physical failures), one may replicate diverse implementations, all passing the required functional tests but not sharing the same implementation induced vulnerabilities. The output may be combined and/or voted upon to produce a final "answer." If done sensibly, this may dramatically reduce the probability of a damaging attack. Of course, the reduction will depend strongly on the degree of diversity achieved.

We feel that there is a spectrum based on the complexity of the underlying system for which replication and diversity may be appropriately applied. For simple systems and information flow models, these ideas are intuitively viable and have been shown to be useful in certain circumstances. On the other end of the spectrum, they are computationally untenable and impossible to synchronize. Our research was an attempt to delineate this spectrum and develop the theory behind measuring diversity in order to create a "diversity distance" between implementations.

Summary of Accomplishments

Our explorations in this study did cover a range of efforts from theory to practice. We developed benefit metrics given certain reasonable, but general, assumptions. We studied methods of generating diversity. We studied to some degree the voting issue. And finally we put these notions together for experimentation on a bench network of computers. We found and still believe that the underlying premise of combining diversity and redundancy has potential for adding real security benefit. However, we discovered a number of pitfalls in the full realization. The first is that it is difficult to carry over the general benefit metrics we developed and have them apply seamlessly to a specific, real system. Further, we can show that it may not be possible to develop a "diversity distance." We also discovered that real-world implementation of these ideas is more challenging than first thought. In particular, implementing reasonable and operational voting schemes is challenging. We were not able to make headway in quantifying how vulnerabilities in the voting scheme may combine with the benefits in the diversity and redundancy and what the overall result might be.

Significance

Threats against information and information systems are well known and adversely affect DOE as well as the nation at large. Providing a new paradigm to secure information systems is a worthy goal. This work examined a potentially game-changing security technology. Our small-scale feasibility study has shown that in combining diversity and redundancy, it may be that the technology and that each of the elements individually are sound. However, we have also shown that putting the pieces together in a real system is fraught with difficulties. From a feasibility standpoint, we have shown that the idea has merit, but some caution must be taken when laying out future research projects to ensure that the research plan is reasonable given any time and budget constraints.

Uncertainty Quantification for Large-Scale Ocean Circulation Predictions

139867
Year 2 of 2
Principal Investigator: C. Safta

Project Purpose

Uncertainty quantification in climate models is challenged by the sparsity of the available climate data due to the high computational cost of the model runs. Another feature that prevents classical uncertainty analyses from being easily applicable is the bifurcative behavior in the climate data with respect to certain parameters. A typical example is the Meridional Overturning Circulation in the Atlantic Ocean. The maximum overturning stream function exhibits discontinuity across a curve in the space of two uncertain parameters, namely climate sensitivity and CO_2 forcing. We develop a methodology that performs uncertainty quantification in the presence of limited data that have discontinuous character. Our approach is two-fold. First we detected the discontinuity location with a Bayesian inference, thus obtaining a probabilistic representation of the discontinuity curve location in the presence of arbitrarily distributed input parameter values. Furthermore, we developed a spectral approach that relies on Polynomial Chaos (PC) expansions on each side of the discontinuity curve leading to an averaged-PC representation of the forward model that allows efficient uncertainty quantification and propagation. The methodology is tested on synthetic examples of discontinuous data with adjustable sharpness and structure.

Summary of Accomplishments

Recent advances in computational capabilities have boosted algorithmic development efforts in uncertainty quantification of complex physical models. In order to properly characterize uncertainties in the model outputs, one can use a Monte Carlo sampling approach. This methodology remains inefficient due to its slow convergence rate, i.e., one typically needs a large number of forward model simulations in order to accurately characterize output uncertainties. In this regard, spectral expansions provide a more-efficient approach that allows efficient uncertainty quantification employing compact representation of the output with respect to the spectral basis functions of random variables. In this work we employed PC expansions to represent input parameters and output observables with respect to standard polynomial bases of input arguments that are standard random variables. We focused on a nonintrusive approach, where the forward model was used as a black box and was only evaluated at sampled input parameter configurations in order to obtain a spectral representation. The PC expansions represent the input-output relationship using a set of deterministic PC modes. The basis orthogonality allows Fourier-like projection formulae for these modes. However, this orthogonal projection requires the forward model runs to be taken at specific, predetermined parameter values. Often, the forward model runs are too expensive, or are given a priori, hence this restriction becomes a handicap. For this reason we also employed Bayesian inference as an alternative approach to determine the PC modes. This approach, though generically less precise than the orthogonal projection, allowed us to obtain a compact PC representation and associated posterior uncertainties without restricting the input parameter locations at which the forward model is evaluated. In cases where extra forward model runs are possible, we suggest using a hybrid approach that balances between the accuracy of the quadrature projection approach and the flexibility of the Bayesian inference.

Significance

This project should increase the application of uncertainty quantification techniques to global climate models, thereby improving the understanding of the limitations on the predictions. The methodologies developed are general and can be applied to a variety of systems with discontinuous behavior.

Refereed Communications

K. Sargsyan, C. Safta, B. Debusschere, and H.N. Najm, "Uncertainty Quantification in the Presence of Limited Climate Model Data with Discontinuities," in proceedings of the *IEEE International Conference on Data Mining,* December 2009.

Uncertainty Quantification of US Southwest Climate From IPCC Projections

140641
Year 2 of 2
Principal Investigator: M. B. Boslough

Project Purpose

The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (2007) made extensive use of coordinated simulations by 18 international modeling groups using a variety of coupled general circulation models with different numerics, algorithms, resolutions, physics models, and parameterizations. These simulations span the 20th century and provide forecasts for various carbon emissions scenarios in the 21st century. All the output from this panoply of models is made available to researchers on an archive maintained by the Program for Climate Model Diagnosis and Intercomparison at Lawrence Livermore National Laboratory.

There is significant variability among these models, which contributes to uncertainty in the degree of future global climate change. The results of these models were aggregated into best estimates and uncertainties by the IPCC, whose Summary for Policy-makers focused primarily on global averages such as radiative forcing, sea level rise, and mean global surface temperature as the most important metrics for quantifying climate change. We believe such global aggregations are inadequate because climate is like many nonlinear dynamic physical systems for which temporal and spatial fluctuations can be proportionately much greater on local and regional scales. Climate change is likely to continue manifesting itself in the most sensitive regions before serious global consequences are experienced.

We propose a project that focuses on metrics associated with regional climate change. The first region we have chosen to address in this study is the US Southwest, because it is important to the US economy and national security, it is the region we live in and are familiar with, and it is particularly vulnerable to climate disruptions. Proposed regional metrics for climate change span sustainability measures of water, energy, health, agriculture, and biodiversity, and include risks associated with extreme weather events and irreversible cascading chains of events associated with “tipping points.”

Summary of Accomplishments

We have collected and reviewed literature in the field of uncertainty quantification and climate. We have downloaded and examined archived data from ensemble climate change simulations. We have analyzed and plotted data and have begun developing a statistical framework for intercomparison of data sets. We have identified the US Southwest and the North Slope of Alaska as two regions of interest for our project. We have learned that the North Slope of Alaska is three times as sensitive to initial conditions as is the US Southwest. We have built a collaboration between Sandia and the University of New Mexico. We have identified the need for dynamically visualizing spatially varying data to allow users and analysts to see spatial trends and how those trends may change over time. The benefit lies in the additional insight and understanding that can be gained compared with looking at static maps and/or line graphs over time. We also addressed an additional regional climate change uncertainty quantification problem by analyzing sea surface temperature records from the Sargasso Sea, discovering a significant temperature increase between 1955 and 2008. This temperature increase had been ignored in a widely cited report that had argued that Sargasso Sea surface temperature records were evidence against anthropogenic climate change.

Significance

The US cannot afford to be surprised by regional climate change either within or outside our national boundaries. In regions of the Earth — such as the African Sahel — climate change has already led to agricultural collapse and chaos. Other regions — such as the Arctic — are changing very rapidly in a way that will have enormous impact on society and national security. Economic and national security considerations require the range of possible change be assessed within US territory. The results of this project include the recognition that the uncertainty in climate forecasts is large, and that regional forecasts are more uncertain than global average forecasts. When uncertainty quantification is included in risk assessments, the risk tends to be far greater than when uncertainty is ignored.

Quantitative Laboratory Measurements of Biogeochemical Processes Controlling Biogenic Calcite Carbon Sequestration

140764
Year 2 of 2
Principal Investigator: T. Lane

Project Purpose

This project is designed to address shortcomings in our understanding of biogenic calcite deposition and dissolution, and to provide climate modelers with improvements in the accuracy and uncertainty of key parameters. We will focus on producing data from organisms responsible for major biogenic carbon fluxes. A specific group of marine algae referred to as the *Coccolithophores* are considered to be the most productive calcifying organism on earth. A focus of the project will be to measure, under thermodynamic conditions found in the deep ocean, the rates of chemical reactions involved in the geochemical processing of coccoliths (calcite plates) produced by *Emiliania huxleyi* (EHUX), using material grown in temperature and pH ranges relevant to modern ocean surface conditions.

We propose a multidisciplinary study linking the underlying coccolithophore physiology of biogenic calcite deposition (coccolith formation) with the rate of biogenic calcite dissolution under oceanographically relevant physiochemical parameters. In this way we will relate the environmentally induced changes in coccilithophore physiology, regulation of the calcification process, and coccolith structure to the environmentally modulated dissolution characteristics of the resulting biogenic calcite. We will culture EHUX under different conditions of pCO_2 and seawater chemistry. We will measure the resulting calcification rates and characterize the morphology of the coccoliths by scanning electron microscopy. We will harvest coccoliths from culture grown under various conditions and determine their rate of dissociation under different conditions of pressure and seawater chemistry. We will use an artificial seawater formulation so that we can rigorously control the concentration of the relevant constituents. At the same time, we will carry out a digital transcriptomic analysis of culture to correlate specific growth conditions to physiological state and regulation of the calcification process. Digital transcriptomics will be carried out by ultrahigh-throughput sequencing of mRNA.

Summary of Accomplishments

We developed and demonstrated a flow-through system for the measurement of calcite dissolution under high pressure and low temperature. This system was designed to mimic the conditions that are present at oceanic depths where biogenic calcite dissolution occurs. This system will allow for the rapid testing of various parameters such as pH, calcium concentration, pressure and temperature on the rate of calcite and aragonite dissolution.

In addition we carried out a digital transcriptomic analysis of gene expression in EHUX under conditions of low (100 ppm), atmospheric (380 ppm), and high (750 ppm) CO_2. Three biological replicates were grown at each of these three conditions. Total RNA was purified from each of the 9 samples and subjected to digital transcriptomic analysis by next generation DNA sequencing. We obtained approximately 15 million reads (51 bases, paired end) per sample. Read mapping and transcript abundance determination are currently being completed.

Significance

This project is designed to address the goals of the US Carbon Cycle Science Plan to quantify and understand the uptake of CO_2 in the ocean. This research will help attain the plan outcomes of attributing observed changes in the ocean carbon sink to variations in circulation, biology and chemistry and incorporating improved oceanic flux estimates into climate models.

Development, Sensitivity Analysis, and Uncertainty Quantification of High-Fidelity Arctic Sea-Ice Models

141507
Year 2 of 2
Principal Investigator: P. B. Bochev

Project Purpose

The disproportional impact of the accelerating climate change on the Arctic, combined with the strategic and geopolitical importance of this region, call for high-fidelity, predictive sea-ice simulations that support science-based policy-making.

To address this need we propose to develop new high-resolution sea-ice models and study the sensitivity and the uncertainty in the predictions with respect to variations in the input and model parameters. This task requires sea-ice models that: 1) include motion and deformation in the plane of the ice and changes in ice thickness due to radiative fluxes from the sun, atmosphere, and ocean; and 2) can handle common physical features of the ice such as cracks and ridges.

To this end, we propose to use an elastic-decohesive constitutive relation and a Material-Point Method (MPM). The former incorporates explicit cracking and has better fidelity than the standard viscous-plastic model, while MPM offers benefits over standard Eulerian methods for sea-ice by simplifying the ice thickness transport through the use of Lagrangian material points and by providing a natural way to handle the interaction of the sea-ice with a coastline using two different particle regions. A predictive sea-ice model involves a large number of material and environmental parameters that are inherently uncertain. We will study the sensitivity of the new sea-ice model with respect to these parameters in order to assess their relative importance for the propagation of uncertainties. This will allow us to reduce the dimension of the parameter space in the uncertainty quantification process.

Summary of Accomplishments

We developed a new sea-ice model for basin-scale calculations of the Arctic Ocean that combines a new anisotropic constitutive model with a particle-in-cell numerical solution of the ice dynamics governing equations. We compared the sensitivity of this model to the sensitivity of the state-of-the-art Los Alamos sea ice model (CICE) code in a single year simulation of the Arctic basin. Although, the ice thickness distribution and velocity at the final time differ substantially between the codes, the code responses to perturbations in a set of ten dynamic and thermodynamic parameters is quite similar.

Of the ten parameters of interest, the maximum salinity and the ridging parameters do not have significant influence on any of the response functions evaluated in this study and can be neglected. The thickness and volume show a strong positive response to fresh ice conductivity in the first part of the year, but, as expected, the albedo parameters become more significant than conductivity between May and June. The velocity-related functions show strong negative responses to the ice-ocean drag coefficient. It is likely that only rheological parameters and ice-atmosphere drag parameters would have produced as significant an effect. Overall, the data show that volume and thickness are strongly dependent on albedo and other thermodynamic parameters, ice area and extent are strongly dependent on dynamic parameters in the winter months and on thermodynamic parameters in the summer months, and the ice velocity is strongly dependent on only one of the dynamic parameters.

The ocean and atmospheric data in this study were prescribed. Running the calculations with a fully coupled atmosphere and ocean model would produce different results due to feedback effects between the ice and atmosphere, and ice and ocean. However, the simple initialization was very useful for providing an identical initial state for both codes that allowed a direct comparison over time.

Significance

Climate change is a significant national security threat. Improving regional sea-ice models and understanding their uncertainty will enable more accurate climate predictions. Sandia has the opportunity to assume a leadership role in providing science-based decision support and mitigation tools that go beyond simulation, in an effort to fully evaluate the global threat of climate change.

Our study provided a first-of-its kind comparative sensitivity analysis of two fundamentally different numerical approaches for solution of the sea-ice model. Our analysis provides useful information on what the actual dimension of the problem space is and will be very useful for development of reliable, computationally efficient and scalable uncertainty quantification methodology for future high-fidelity Arctic sea ice model predictions in terms of best estimates and uncertainty ranges. For example, our study shows that the maximum salinity does not have notable influence on any of the ten response functions. Therefore, this parameter can be neglected in uncertainty quantification. The study confirms comparable sensitivities between CICE and the particle-in-cell MPM sea-ice model. Because CICE and MPM use fundamentally different numerical approaches (Eulerian vs. Lagrangian), such a finding increases our confidence in the physics built into the models. Furthermore, by ranking and comparing the three most significant parameters for both codes, we were able to glean useful information about the impact of various model components on the sensitivity. For example, the most significant parameter for total ice area often differs between MPM and CICE. Some of the differences between the responses for the two codes are likely due to the use of an ocean mixed-layer model in CICE. This algorithm allows for changes in sea surface temperature due to thermodynamic fluxes through the ice, which may have a strong influence on where ice grows and melts, thereby changing the ice area and extent.

Minority Carrier Recombination in III-Nitride Heterostructure Bipolar Transistors

143418
Year 1 of 1
Principal Investigator: J. Wierer

Project Purpose

III-Nitride minority carrier lifetimes are not well known, and typically only average lifetime data is measured with no separation of the individual recombination mechanisms (Shockley-Hall-Reed, bimolecular, and Auger). This has hindered the understanding of basic recombination mechanisms in III-Nitride materials. This knowledge gap is clearly evident in how the recombination mechanisms contribute to the internal quantum efficiency in III-Nitride LEDs, where there is a drop in efficiency with increased current density that is attributed to either carrier leakage or Auger recombination. Either theory cannot be conclusively proven with LED measurements. Heterojunction bipolar transistors (HBTs) on the other hand are an excellent way to investigate minority carrier recombination currents in semiconductor materials. Using HBTs, we can experimentally separate carrier leakage currents from Auger recombination providing an answer to the drop in efficiency in III-nitride LEDs. In this project, we will learn how to grow and process III-nitride HBT devices. Once we have achieved working HBT devices we will answer conclusively the mechanism behind the efficiency drop in III-nitride LEDs. This effort will lay a solid foundation for future III-nitride HBT work and improving III-Nitride HBT device and materials performance at Sandia.

Summary of Accomplishments

We demonstrated working III-nitride HBTs with collector over base current gains of 5, and breakdown voltage in common-emitter configuration with no base current of greater than 40 V. We found that lower indium composition (0.03 compared to 0.08) InGaN layers improved performance. Experiments were also performed using HBTs as a tool to identify the mechanism behind the efficiency droop in LEDs. The formalism to perform this experiment appears correct, but unfortunately the HBTs developed here did not have the performance necessary to make a conclusive argument on the cause of the efficiency droop.

Significance

We were successful at making a working III-nitride HBT, which have uses in various electronic systems such as high-voltage, high-temperature, and high-radiation operation. Additionally, III-Nitride HBTs provide differences at the system level compared to high electron mobility transistors, allowing more circuit design flexibility. Ultimately, understanding the mechanism of efficiency drop at higher current densities in III-Nitride devices will be a key to developing more-economical home and commercial solid-state lighting, whose potential to decrease US and global energy consumption has been well documented, and which is a key component in DOE's Energy Security strategic thrust.

Paradigms for Skill Assessments

145281
Year 1 of 1
Principal Investigator: E. Akhadov

Project Purpose

The purpose of this project was to determine if we could use a commercial off-the-shelf (COTS) electro-encephalography device that is currently being marketed as a computer interface device to gamers to replicate a visual recognition study that was published in the peer-reviewed cognitive neuroscience literature in 2001.

Summary of Accomplishments

We demonstrated that, with only minor software modifications, the COTS headset we tested (the Emotiv EPOC) is capable of sufficiently high-resolution sensing to both replicate the study we chose from the literature[1], and was sufficient to be used in what is called an "oddball" task, which elicits a large, positive waveform 300 milliseconds after the presentation of a critical stimulus.

Significance

This research demonstrates the utility of COTS EEG headsets for sensing certain cognitive states, which can aid in many different augmented-cognition types of applications. This has significant impact from an operational perspective, in that these headsets are significantly less expensive than laboratory-grade electroencephalography electrodes and they require significantly less time to apply to the head. In terms of the former, these headsets cost between $300 and $600 each, whereas a laboratory-grade system can cost in the tens of thousands of dollars. In terms of the latter, it takes approximately 2 minutes per electrode to apply a lab-grade EEG (which can have as many as 256 electrodes) whereas it takes approximately two to three minutes to apply the entire EPOC headset and achieve sufficient scalp connectivity.

Reference

1. J. W. Tanaka and T. Curran, "A Neural Basis for Expert Object Recognition," *Psychological Science*, 12, pp 43–47 (2001).

Development Toward a Nano-Thermal Interface Material

145282
Year 1 of 1
Principal Investigator: M. P. Siegal

Project Purpose

Revolutionary thermal-interface-material (TIM) advances are required to remedy thermal management problems associated with high-power electronics (e.g., radar, solid-state lighting, detectors) and next-generation microprocessors. Present TIMs consist of polymer- or epoxy-based materials containing large fractions of thermally conducting metal particles. Critical issues for conventional TIM performance range from degradation of the epoxy/device (heat source) interface to the optimal loading, geometry, and size of the thermally conducting particle additives used in the epoxy composite. However, only incremental gains in thermal conductivity can be obtained by optimizing this type of TIM. Instead, a revolutionary TIM design is needed to achieve large thermal-conductivity gains while maintaining adequate adhesion between the electronic device heat source and a Cu heat sink while minimizing thermal losses at the TIM/heat-source interface.

Instead, we propose a revolutionary architecture with the potential to improve thermal conductivity by greater than 100-fold, while simultaneously eliminating or reducing the adhesion issues associated with conventional TIMs by using carbon-nanotubes (CNTs) oriented in the heat flux direction between the heat source and thermal spreader to provide unidirectional, high-thermal-conduction pathways for heat transfer. For this geometry, heat resistance of the composite is modeled as parallel resistors. Increasing the CNTs/area decreases the effective TIM thermal resistance. In this design, no adhesives make thermal contact to the CNTs. Instead, adhesives will be used only on the outer perimeter of the TIM, away from the part of the device being used for thermal conduction. Since no epoxy is involved in the thermal contact regions, the thermal contact resistances for our proposed CNT-based TIM will be much lower than that for the surface layers for the metal-loaded adhesive-based TIMs. The contact resistance results from the direct mechanical contact of the CNTs to the backside of the heat source and will be controlled by an applied pressure built into the design.

Summary of Accomplishments

There were several key accomplishments for this project.

1. Extremely high-crystalline quality CNTs were grown on Si(100) substrates. We demonstrated independent control of CNT inner core diameters (from 1–3 nm) and the number of concentric walls in a CNT (from 1 to 8). The inner core diameter appears to result from the highest temperature experienced by the sample during the chemical vapor deposition (CVD) growth process, typically during the oxidation reduction anneal of the metal catalyst. This anneal sets the size of the catalyst islands. The number of walls relates linearly with the actual CVD growth temperature.
2. Anodized-aluminum-oxide (AAO) templates were formed on both Si(100) and Al substrates with high densities of small nanopores.
3. Ni catalysts were successfully electroplated into the AAO nanopores.
4. Au nanowire arrays were grown in AAO templates to produce structures with known thermal properties to test the thermal measurement fixture.
5. Two methods of measuring thermal conductivity for nanowire arrays were explored. The laser flash technique, while simple to operate, does not appear to be useful for thin samples. Instead, future work will focus on more direct measurements of thermal conductivity.

Significance

Since high-quality CNTs have thermal conductivities of ~ 30 W/cm•K, TIM improvements to values > 1 W/cm•K are conceivable. This will enable high-power devices to be more-efficiently cooled for superior operation, such as micro firesets, radar, direct optical ignition, thin disk laser, and waste heat recovery. It is important to note that we have not reached this goal, which is well beyond the scope of this project, however, significant progress was made on several of the many necessary critical steps, all of which were milestones for this project. Defense/commercial systems have conflicting needs for high performance and reduced size/weight. Heat rejection technology is a dominant limitation. Replacing metal/epoxy with lightweight carbon nanotubes can improve thermal performance by multiple orders of magnitude. This is important for Sandia's space strategic thrust and Military Technologies and Applications' delivery systems to improve overall performance. Other initiatives can benefit from directed flow of excess heat for integrated energy systems and energy harvesting.

Refereed Communications

M.P. Siegal, D.L. Overmyer, P.P. Provencio, and D.R. Tallant, "Linear Behavior of Carbon Nanotube Diameters with Growth Temperature," *Journal of Physical Chemistry C*, vol. 114, pp. 14864-14867, September 2010.

Physically Unclonable Function (PUF) Based Software Authentication and Component Binding

145283
Year 1 of 1
Principal Investigator: J. Hamlet

Project Purpose

The National Cyber Leap Year Summit 2009 Co-Chairs' Report establishes the need to "identify and develop standards for device identification," including "a way to describe a system or device top-to-bottom starting at integrated-circuit (IC) levels," and also asserts the following: "Today, hardware blindly executes any software, including malware. Tomorrow, the game change we propose is that even if the computer is penetrated by malware, this malware will not be executed." Recent work at Sandia has demonstrated the applicability of Physical Unclonable Functions (PUFs) to fingerprinting ICs and an infrastructure for detecting subversion by wholesale component substitution. That effort provides a mechanism for extending the trust afforded to individual IC components into the deployment portion of the life cycle. Although this technique permits easy recognition of each component within a system, the component configuration of the system as a whole cannot be easily verified. To enhance the security of systems we must extend the realm of trust beyond individual devices to encompass the system of components as well as any software that may execute on the system. The software authentication and component binding problems may have related solutions that leverage PUF technology. This project will examine solutions for the following:

1. "Component binding" within a system of components in which each component is attempting to discover if the system is composed of the same components as was previously configured, or if there may have been unknown or unauthorized changes among the interacting components
2. Enabling a trusted IC (or collection of ICs) to authenticate the software executing within them
3. Protection of field programmable gate array (FPGA) bitstreams

Summary of Accomplishments

We designed approaches for binding integrated circuits to each other, allowing for mutual authentication of the integrated circuits; for binding integrated circuits to software, defined in the broad sense as any sequence of instructions responded to by an integrated circuit, to include executable binaries, firmware, and FPGA bitstreams, allowing the hardware to authenticate the software prior to running it and to prevent software from executing on any hardware it had not been enrolled with. In addition, we designed approaches for binding the various factors in multifactor authentication schemes to avoid key storage problems and to increase the work factor required to extract keys and for binding integrated circuits to physical items, such as a system's packaging, to allow the integrated circuit to vouch for the integrity of the physical item.

Significance

The proposed research investigates advances in difficult cyber-security problems recognized by the national cyber-security community. The success of this research will provide mechanisms for expanding trust of individual ICs to collections of components and to software. It could establish a fundamental security capability and could be incorporated into trust anchors and high-consequence system designs that are of interest to DOE and to other agencies.

System Metrics for Comparative Analysis of Cyber Security Systems

145284
Year 1 of 1
Principal Investigator: P. J. Robertson

Project Purpose

This work examines a new approach to metrics for the resilience of cyber security systems. Our basic approach involves combining vectors of resilience metrics that have meaning in the various portions of the system life cycle (design, implementation, test, deployment, maintenance, etc.). Using combinations of these vectors of metrics over the life cycle, the viability of various protection measures against a sophisticated adversary can be assessed. We will analyze the adequacy of these metrics to differentiate resilience in certain well-studied cyber systems (such as various versions of "smart cards" etc.). The objective is to use these metrics to guide the system engineering of improved cyber security systems by providing an "objective function" that can be cost-effectively analyzed and optimized over various system design tradeoffs.

Summary of Accomplishments

We have developed a new approach to developing a set of metrics for cyber security systems that looks promising, but needs refinement and improvement by further application and adaptation to analysis of real systems. By developing the concept of "vulnerability tolerance" (similar in some ways to "fault tolerance"), an effective and game changing way of dealing with penetrations may emerge. We believe that metrics that identify which portions of the life cycle rely on secret-keeping, augmented with metrics for the exposure of components to the adversary during each phase of the life cycle will enable more robust analysis of these systems, and will enable comparison of resilience of different protection schemes against these kinds of failures.

Significance

Our national cyber infrastructure exists in a high-exposure environment and is vulnerable to multiple adversaries as evidenced by daily cyber attacks reported in the public literature. The points within our systems at which we maintain "operational secrets" in order to perform authentication or confidentiality services are the weakest, most-brittle points when exposed to a capable adversary. By developing metrics that pay close attention to how these secrets are treated in different systems, meaningful comparison of system resilience to cyber security attacks can be enabled.

Understanding the Physics of a Possible Non-Abelian Fractional Quantum Hall Effect State

145835
Year 1 of 1
Principal Investigator: W. Pan

Project Purpose

The fractional quantum Hall effect (FQHE) state at ν=5/2 is exotic. Unlike conventional FQHE states, for example, at ν=1/3 and 1/5, this 5/2 state may belong to the so-called non-Abelian quantum Hall states. In this new state of quantum matter, when a quasiparticle makes a full circle around another, the quantum state vector changes its direction in Hilbert space and the order of exchange of particles is relevant. Quasiparticles which behave in this way are said to obey non-Abelian statistics, and have never been definitely observed. It is now widely believed that the non-Abelian topological phases may hold the key for future highly fault-resistant topological quantum computation.

It has been a daunting challenge to measure and examine these exotic non-Abelian statistics. So far, there is no concrete evidence showing that the quasiparticles of the 5/2 state do obey non-Abelian statistics. Several device structures have been proposed in tackling this challenge. Among them, edge tunneling in a confined geometry is a promising one for detecting both the (non-integer) charge of the quasiparticle and the possible non-Abelian statistics. For a correlated electron state (in our case, the 5/2 state), charge excitations within the confined region (for example, edge tunneling) provide an experimentally accessible avenue for measuring quasiparticle properties. These kinds of experiments have been carried out by very few groups, and their data were, at best, not definitive. More data with less ambiguity are needed to determine unequivocally the nature of the 5/2 state. To the best of our knowledge, this ambiguity may be due to a lack of knowledge of the degree of coupling between the bulk state and the edge state at ν=5/2. If there is a coupling, what is its quantitative strength? So far, neither of these two questions has been answered nor even studied.

Summary of Accomplishments

We discovered that the nonlocal transport over macroscopic distances of several mm can exist at the Landau level filling factor ν=5/2 in narrow Hall bar samples fabricated in high quality GaAs/AlGaAs quantum wells. It clearly demonstrates edge-state conduction around ν=5/2. This result will help to build a possible qubit device structure using the ν=5/2 state.

We observed the conductance fluctuations in narrow channels around ν=5/2. This behavior is probably due to the breakdown of dissipation-less transport in narrow channels because of resonant reflection through magnetically bound states. We expect that detailed analysis will allow us to obtain the information about this behavior, such as the quasiparticle change of the ν=5/2 state, a necessary step towards confirming the exotic non-Abelian statistics at ν=5/2. We designed a photo-mask for narrow Hall bar samples. Multiple device structures with different dimensions are included in the design. This is necessary since different quantum Hall samples may need devices of different dimensions. We refined device fabrication procedures so that the sample quality can be maximally maintained after fabrication. We developed a recipe for chemical etching of the Hall bar so that the sample quality can be sustained after fabrication. This recipe also helps to create a sharp edge of the Hall bar and is very important for observing dissipation-less edge transport at ν = 5/2, a very fragile quantum Hall state. We set up a cryogenic system, a dilution refrigerator, for ultralow-temperature measurements. The lowest temperature reached in this system is 10 mK. This is the lowest temperature ever achieved at Sandia. With the operation of this system, we now are able to conduct a detailed, systematic study of edge-bulk transport in the 5/2 fractional quantum Hall regime.

Significance

Silicon (Si) is the foundation of our modern information society. The silicon microelectronics industry is built upon Si metal oxide semiconductor field-effect transistors. For example, in an Intel Dual-Core Itanium 2 processor, more than one billion transistors are integrated on a single chip. In order to extend this trend of ever increasing the number of transistors, the size of each transistor must be shrunk accordingly. However, this increasing miniaturization has its limits: 1) as the channel size continues to decrease, the conduction channel size will approach the wave packet size of an electron and some unpredictable effects will dominate the transport properties; and 2) the shrinkage of channel size requires that the gate insulator thickness be reduced accordingly. At this stage, it is expected that Moore's law is likely to run into a silicon wall by 2015. New physics must be identified and established for next-generation information processing and storage. Intensive research has been carried out in demonstrating the feasibility of quantum computation. Compared to a conventional computer, a quantum computer is much faster. Furthermore, a quantum computer can solve problems that are intractable for conventional computers, and quantum key distribution, using similar physical phenomena, enables secure communication between two sites. However, many fundamental issues remain unresolved. The goal of quantum information physics, to exercise precise control over quantum systems, is plagued by the strong coupling between electrons and their local environments (e.g., nuclear spins in host materials, sample impurities). This greatly reduces electron coherence times and requires complex error-correction schemes to manipulate quantum information before it is lost. There is a pressing need to identify new paradigms that will potentially enable revolutionary advances in the field of quantum computation, and to address their fundamental physics. The highly fault-resistant approach proposed here is just such a new paradigm.

So far, the most promising approach to construct a qubit structure in the quantum Hall topological quantum computation scheme is to utilize the edge state of the so-called 5/2 fractional quantum Hall effect state. Before this great challenge can ever be achieved, however, one has to gain a deep understating of the 5/2 edge state — whether it is stable against disorder; whether it is stable against rising temperatures; whether it can travel over a macroscopic distance. The results we obtained in this project show that indeed, the dissipation-less edge state at $\nu=5/2$ can extend over a distance of mm length. This result is significant as it supports the possibility of using the 5/2 edge state for constructing a qubit structure. Overall, the project may lead to possible demonstration of the unusual, non-Abelian quantum statistic properties, which might eventually enable us to implement robust quantum computation. The proposed research utilizes the capabilities in Sandia's core investment areas and aligns well with an existing Grand Challenge project on quantum computation in silicon and with the goals of DOE and other federal agencies.

Modeling Attacker-Defender Interactions in Information Networks

145998
Year 1 of 1
Principal Investigator: M. J. Collins

Project Purpose

The simplest conceptual model of cyber security implicitly views attackers and defenders as acting in isolation from one another: an attacker seeks to penetrate a system that has been protected to a given level, while a defender attempts to thwart particular attacks. Such a model also views all non-malicious parties as having the same goal of preventing all attacks. Our fundamental observations are that attackers and defenders are always part of the same overall system, and that different defenders have their own individual interests: defenders may be willing to accept some risk of successful attack if the cost of defense is too high. The purpose of this project is to model multiple offensive and defensive entities as interacting parts of this one system, and to use such models as the basis for a systems-engineering approach to problems in cyber security.

Our primary tool with which to model adversarial objectives is game theory. Game theory is an essentially economic theory: its models are formulated in terms of tradeoffs involving the finite resources available to the defender and the attacker, and in terms of the value of the assets being protected or attacked. The optimal tradeoff for one player depends upon what other players do, so interaction among players is integral to this approach.

Summary of Accomplishments

We have used the game-theoretic perspective to create novel models of attacker and defender behavior in computer networks that capture some of the richness of multiparty interactions, and we have analyzed successful strategies in these models. Although game theory has been applied in this area before, we have introduced some novel aspects of player behavior in our work, including the following:

- A model of how players attempt to avoid the costs of defense and force others to assume these costs
- A model of how players interact when the cost of defending one node can be shared by other nodes
- A model of the incentives for a defender to choose less expensive, but less effective, defensive actions

Significance

We have demonstrated the applicability of economic models to ongoing multiplayer interactions in network security. These preliminary results can be used to build a framework for agent-based modeling which can serve as a foundation for further, more-detailed investigation in this area, which will be of interest to DOE and DHS.

Laser Wafering — Accelerating Moore's Law for Silicon Solar

147486
Year 1 of 1
Principal Investigator: T. A. Friedmann

Project Purpose

The current technology for wafering in the solar industry cuts Si wafers by a wire saw process, resulting in 50% "kerf" loss when machining silicon from a boule or brick into a wafer. We want to develop a kerf-free laser wafering technology that promises to eliminate such wasteful wire saw processes and achieve up to a ten-fold decrease in the g/Wp (grams/peak watt) polysilicon usage from the starting polysilicon material. Compared to today's technology, this will also reduce costs (~20%), embodied energy, and greenhouse gas emissions (~50%). We will use femtosecond laser illumination sharply focused by a solid immersion lens to produce subsurface damage in silicon such that wafers can be mechanically cleaved from a boule or brick. For this concept to succeed, we will need to develop optics, lasers, and cleaving processing technologies capable of producing wafers with thicknesses < 50 µm with high throughput (< 10 sec/wafer). Wafer thickness scaling is the "Moore's Law" of silicon solar. Our concept will allow solar manufacturers to skip entire generations of scaling and achieve grid parity with commercial electricity rates. Yet, this idea is largely untested and a simple demonstration is needed to provide credibility for a larger-scale research and development program.

Summary of Accomplishments

We designed and fabricated novel optics systems including silicon immersion lenses for focusing laser light into silicon to shape the damage zone that should promote lateral cracking behavior. We have used a nanosecond laser to produce damage in silicon and characterized this damage using Raman mapping to reveal the laser damage profile and associated stress fields.

Significance

We have obtained important data that provide initial validation of this approach and that should form the basis of further funding through internal, DOE, or industrial partners. Ultimately, this capability, aligning with the DOE energy security strategic thrust, could reduce the cost/watt expense of crystalline silicon photovoltaics, such that grid parity would be in reach. This would allow diversification of our energy needs and reduced reliance on imports, reduced greenhouse gas emissions through displacement of fossil fuels, and development of a highly competitive US-based photovoltaic manufacturing industry.

Molecular-Scale Measurements of Electric Fields at Electrochemical Interfaces

147940
Year 1 of 1
Principal Investigator: R. L. Farrow

Project Purpose

Most electrochemical devices consist of an anode and cathode separated by an electrolyte. Voltage drops occur in thin layers, called electric double layers (EDLs), at the interfaces between the electrodes and electrolyte. These high electric fields profoundly affect electrochemical processes such as charge transfer. The purpose of this project is to investigate electrochemical interfaces using a novel approach to measure the electric field with nanometer spatial resolution. The optical mapping of fields will take advantage of field-sensitive (electrochromic) dyes similar to those currently coming into use for membrane-potential measurements in biological systems. One type of field-sensitive dye exhibits a shift in its fluorescence spectrum in response to local field strength. A second class of electrochromic dyes exhibits a strong dependence of the second-order susceptibility on electric field, allowing the local field to be measured via changes in optical second-harmonic generation (SHG). We will initially use simple flat interfaces to make direct comparisons of our measurements with theoretical models. Later experiments will use self-assembled monolayers (SAMs) to create interfaces by linking molecules of interest to conducting, but optically transparent, indium tin oxide surfaces via silanol or thiol linkages. Electrochromic dye molecules will be embedded at predetermined heights within or upon the SAM by altering the length of the dye tether. Single-molecule fluorescence detection derives spatial precision from the location of individual dye molecules, and SHG is inherently interface-specific because the signal is only generated from regions with non-centrosymmetric response. Development of these field-mapping capabilities has the potential to impact fundamental understanding in areas ranging from ultracapacitors, batteries and photoelectrochemical systems to biological charge distribution.

Summary of Accomplishments

The properties of the fluorescence probe molecules are an important consideration. Dyes should ideally be small to provide high spatial resolution and possess high sensitivity to electric fields. We tested several candidate dyes including Prodan (6-propionyl-2-dimethyl-amino-naphthalene) derivatives and determined that near-UV excited dyes (~400 nm) emitted fluorescence susceptible to interference by stray fluorescence from glass substrates. Consequently we implemented a longer laser wavelength (470 nm) and selected an electrochromic dye that efficiently absorbed this wavelength, with resulting increased sensitivity. We developed methods for linking dyes to both conductive oxide and metal surfaces. Dye functionalization with a silane group facilitated attachment to conductive oxides (indium tin oxide), while thiol chemistry was used to attach to gold films. For the latter, we measured upper-state dye lifetimes for dye attached to gold and compared them to lifetimes of dyes in solution. We learned that lifetimes of gold-attached dyes were shorter (<1 ns) than those in solution (several ns) as a result of quenching. However, the quenching effect was not so severe as to prevent detection of single monolayers of dyes.

To conduct the experiments, we set up a confocal microscope system incorporating either of two lasers (405 and 470 nm). The dispersive element is a transmission grating, which provided adequate spectral resolution and high efficiency. The detector is a room-temperature charge-coupled device video camera with 1388 x 1040 pixels. To detect the Stark effects on dye molecules with the greatest sensitivity, we developed a voltage-modulation technique. Voltages ranging from millivolts to kilovolts can be applied to electrodes in an optically accessible electrochemical cell. The voltage is modulated on and off while fluorescence spectra are measured and the voltage-applied data are subtracted from the voltage-free data. With our microscope system we were able to take high-resolution (>1000 pts) fluorescence spectra of gold and indium tin oxide surfaces functionalized with electrochromic dyes at coverages of a small fraction of a monolayer. However, the point-to-point differences, on a submicron scale, in the fluorescence intensity and spectra obscure the relatively small expected Stark shift from the applied voltage. From atomic force microscopy measurements and visual inspection, we conclude that the commercial substrates used for this short-term project were not sufficiently uniform and showed too much surface roughness for the control experiments needed to demonstrate this method.

Significance

This project supports Sandia's energy and science missions through development of tools that enable the fundamental understanding of electrochemical interfaces. The results will have wide applicability to electrical energy storage and energy conversion technologies that are critical to creating a sustainable and climate-friendly transportation sector for the nation.

Nanoparticle Modification of Photodefined Nanostructures for Sensor and Energy Applications

148067
Year 1 of 2
Principal Investigator: R. Polsky

Project Purpose

The purpose of this project is to explore photolithographically definable pyrolyzed photoresist carbon films for possible energy applications. The key attributes that we intend to explore are nanoparticle-modification strategies to provide enhanced catalytic capabilities and increased conductivity, as well as photo-interferometric fabrication methods to produce highly porous (meso, micro, and nano) and 3D electrode structures. The resulting electrode can be tailored for specific applications and integrated into battery and sensing platforms. Different strategies to be investigated in this project involve the following: 1) Investigations of electrochemical techniques to deposit conducting polymers and metal nanoparticles (gold, platinum, and palladium) with tunable sizes, shapes, and densities and then growing nanowires using the nanoparticle "seeds" as catalytic sites; 2) exploration of interferometric and two-photon fabrication methods to create 3D and porous carbon surfaces; and 3) exploration of these platforms for battery and energy applications.

Summary of Accomplishments

We have examined diffusion-profiles of the redox analyte ferrocene inside the porous carbon and discovered that hemispherical diffusion dominates inside the structures. This results in increased mass transport throughout the pores, which should translate into higher power densities and energy outputs for batteries. This was confirmed by demonstrating enhanced catalytic methanol oxidation over analogous 2D electrodes. We also explored nanoparticle and conducting polymer modifications. We investigated different solvents to attempt to achieve homogeneous nanoparticle deposition with a 90:10 vol% acetonitrile:water solvent being chosen as optimum to result in complete homogeneous nanoparticle deposition throughout the structures. This was demonstrated for silver and palladium nanoparticles with the corresponding effects on surface area and catalysis being examined with possible implications in improved fuel cell performances. The same hemispherical diffusion/increased mass transport characteristics, described above, were shown to result in uncharacteristically smooth conducting polymer depositions. Basic characteristics of this result relating to mass deposition and pore size, and preliminary results for ultracapacitor applications were examined. Finally, we showed that the palladium-modified structures were also capable of being used as possible hydrogen storage devices.

Significance

The basic science, as well as the multidisciplinary engineering aspects of this project are in alignment with several laboratory DOE and DHS missions. In addition to applications in energy storage (Li^+ batteries, ultracapacitors), fuel cells, and hydrogen storage, the proposed pyrolytic carbon with hierarchical porosity has potential application in sensor technology, water purification, filtration, preconcentration, and chem/bio agent detection.

Refereed Communications

X. Xiao, M.E. Roberts, D.R. Wheeler, C.M. Washburn, T.L. Edwards, S.M. Brozik, G.A. Montano, B.C. Bunker, D.B. Burckel, and R. Polsky, "Increased Mass Transport at Lithographically Defined 3-D Porous Carbon Electrodes," to be published in *ACS Applied Materials and Interfaces*.

Room Temperature Detector Array Technology for the Terahertz to Far-infrared

149404
Year 1 of 2
Principal Investigator: E. A. Shaner

Project Purpose

The terahertz (THz) to far-infrared portion of the electromagnetic spectrum extends from roughly 100 GHz to 30 THz (where 1 THz corresponds to a wavelength of 300 microns and photon energy of 4.1 meV). From radio-frequency waves through x-rays, this portion of the electromagnetic spectrum is the least developed, and therefore, the least understood scientifically and technologically. Detection of THz radiation at elevated temperatures is complicated due to the low excitation energies involved (ruling out more standard semiconductor based detection schemes). Our goal in this effort is to develop a path towards room-temperature detector solutions that are amenable to integration in a focal plane array. While this is a somewhat daunting task, this research will leverage years of previous work and experience to progress towards this goal.

Summary of Accomplishments

We demonstrated, in collaboration with Boston University, the integration of a metamaterial absorber with a thermal detection element. We observed resonant photoresponse at 95 GHz and 693 GHz frequencies in two different designs.

We have also been working to verify detection in a Sandia technology using microphotonic resonators. This was a new area for us, and we recently observed a previously characterized photoresponse at 10 micron excitation.

Significance

Middle-infrared (mid-IR) and THz sensing supports numerous mission spaces within homeland security. High-speed mid-IR imaging has significant advantages in offering real-time security information for event avoidance. THz detection operates in a spectral range where complex compounds have unique fingerprints and many common materials are transparent. Mature technology in the THz should enhance the effectiveness of screening systems.

Attosat Lorentz Augmented Orbit (LAO) Flight Dynamics

150115
Year 1 of 2
Principal Investigator: J. A. Palmer

Project Purpose

The term attosat describes a novel category of microchip-sized satellite (with mass not exceeding 0.01 kg) currently under research and development. We are motivated by the desire to radically reduce size, weight, and power by maneuvering an attosat without stored liquid or gas-phase propellant. Propellant-less propulsion ensures access to high-payoff space protection, distributed sensing, and emplacement and sampling missions. An orbiting attosat moves with tangential velocity, vrel, relative to the earth's geomagnetic field that rotates with the planet. If the attosat acquires an electrostatic charge q, the moving geomagnetic field induces the Lorentz acceleration, aL, expressed as:

aL = (q/m)vrel x Bg = (q/m)(rdot-omegaB x r) x Bg,

where m is the mass of the attosat, r is the orbital radius, omegaB is the angular velocity of the geomagnetic field, and Bg is the local geomagnetic field strength. By this mechanism, the kinetic energy of the earth's rotation is indirectly converted to useful work. It follows that in specific orbits, an attosat may be propelled by modulating the electrostatic charge, the magnitude of which is impacted by mass, materials, geometry; and interactions with the ionosphere's neutral magnetized plasma. The purpose of this effort is to quantify traceable mission scenarios for attosat systems and to discover efficient mechanisms for positive and negative electrostatic charging of an attosat considering plasma interactions.

Summary of Accomplishments

In year one of the project, we achieved a particle-in-cell plasma physics model that predicts negative potentials on the attosat body due to passive charging mechanisms at the altitude of interest. Predicted results show good agreement with the literature. A simulation of active positive charging by field emission of electrons from a gated nanowire array was added to the model. We demonstrated that an equilibrium charge of positive ten volts or greater is possible in low earth orbit. We derived closed-form equations that relate charge-to-mass ratio to rates of change of altitude and inclination. Moreover, we completed an analysis of nonconservative forces acting on the attosat. A comprehensive attosat system design, mass, and power budget is complete. The mass budget conforms to the objective of an attosat system that does not exceed ten grams total mass. The design identifies the composition, arrangement, and electrical connectivity of key high secondary electron emission coefficient engineering materials leading to passive positive differential charging of isolated regions of the vehicle body.

Significance

Geomagnetic Lorentz force propulsion without stored liquid or gas-phase propellant is a key technology differentiator for attosats that allows Sandia to offer access to high-payoff missions including space asset protection, distributed sensing, and emplacement and sampling. Moreover, the design facilitates affordable life-cycle management through inexpensive mass production and storage with existing semiconductor fabrication infrastructure and rapid configuration and deployment. We proved by modeling that measurable positive charging of an attosat in low earth orbit is possible. This opens the prospect of a Lorentz augmented orbit flight controller that can utilize positive and negative charge to both increase and decrease orbital parameters such as inclination or right ascension of the ascending node.

STRATEGIC PARTNERSHIPS INVESTMENT AREA

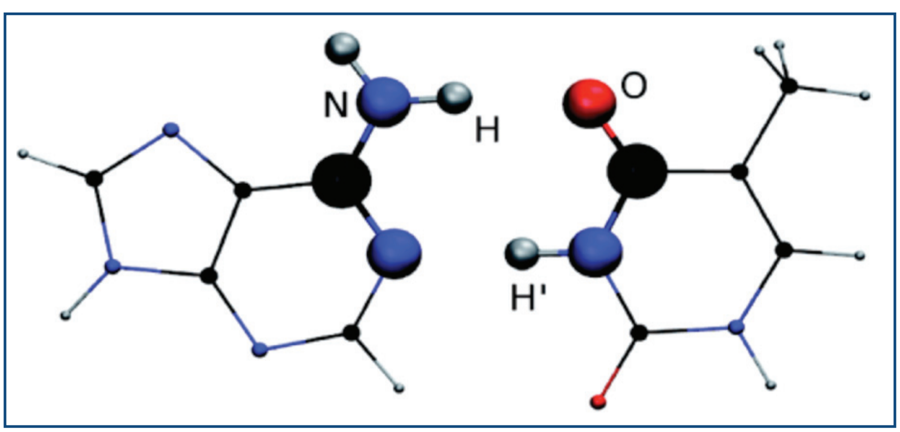
The common defining feature of projects in this investment area is a strong cooperative research endeavor with one or more academic or corporate partners. Because of Sandia's leadership in the multipartner National Institute for Nano Engineering (NINE), many SP projects are found in the nanotechnology arena. In addition, other projects within this IA, include the Sandia Fellows, and the President Harry S. Truman postdoctoral fellows, awarded annually to two or three recipients. In addition to being a great honor, the Truman is unique in that it supports a three-year initiative to pursue leading-edge research defined by the candidate's own proposal, which must be consonant with Sandia missions but which otherwise provides significant intellectual scope.

Multiscale Schemes for the Predictive Description and Virtual Engineering of Materials

Project 120209

The ability to accurately model atomic and molecular systems is key to predicting and designing materials for particular applications without conducting laborious experimental protocols. For example, the Sandia solar-thermal tower employs a molten salt to store thermal energy from sunlight, later releasing it to drive a mechanical engine that turns an electrical generator, thus converting sunlight to electricity. The salt can be heated to 600 °C, but at the top of the tower, temperatures at or above 1000 °C are reached; problematically the salt decomposes, losing its chemical structure above 600 °C. Additionally, the salt remains liquid — able to flow through the system's pipes — only above 100 °C, and it must be heated at night. What if a salt could be found that remained liquid at room temperature and absorbed the maximum amount of available solar thermal energy without decomposing? A daunting task to an experimentalist, it becomes more tractable with computational modeling, predicting desired properties directly from structural, bonding and quantum considerations.

Bridging statistical mechanics, density functional theory (DFT), and computer science, this young and highly interdisciplinary field of atomistic computational materials design has, in this project, been used to advance several important Sandia energy-security areas. The project investigated nanocluster metal catalysts for efficient conversion of carbon dioxide, methane, or oxygen for sustainable energy applications, and developed quantitative structure-property relationships for rapid but accurate predictions of charge transport properties in photovoltaic applications. At a more-fundamental level, high-dimensional property gradients in compound space were derived within density functional theory (DFT) and implemented and tested numerically. Interatomic three-body van der Waals forces were shown to be substantial in real materials. This research furthered the accuracy of computational materials modeling, a key step forward toward routinely engineering improved materials prior to attempting experimental realization.



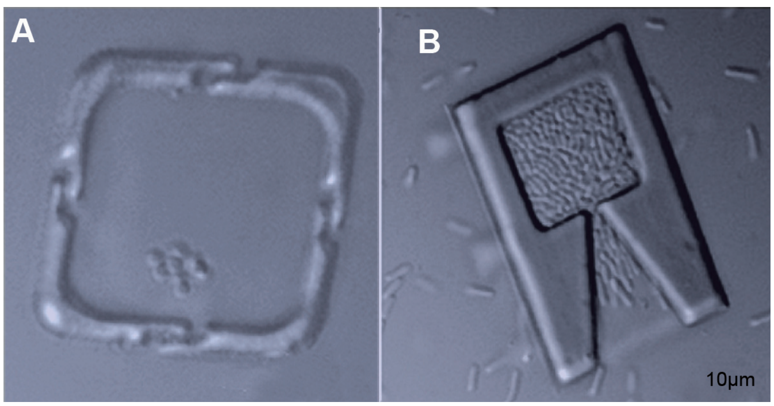
Purine-pyrimidine base-pairing in DNA, for which project results suggest a new understanding of what is sometimes described as the intrinsic mutation rate.

Development and Characterization of 3D, Nano-confined Multicellular Constructs for Advanced Biohybrid Devices

Project 130813

Over the course of evolution, Nature has perfected the design of a significant number of biological nanodevices, from sensors to molecular motors to catalysts, photovoltaics and other energy-transformative devices. In certain instances, current initiatives in nanotechnology could benefit from biological solutions. Although most biological devices are constructed entirely or partially of proteins, it should be possible to replicate such structures either completely or partially using inorganic constituents, while retaining functionality for such biohybrid (bio-organic-inorganic) devices.

In this project, mask-directed multiphoton lithography has been used to template biological protein synthesis into specific three-dimensional nanostructures (such as microcantilevers), which have then, in turn, been utilized as structural templates for the multistep conversion to silicon replicas, thereby forming silicon microstructures whose conformation is initially biologically directed. In addition, the mask-directed multiphoton lithography technique has been used to construct a diversity of microconfinement chambers for bacterial cells in order to elucidate several key hypotheses about bacterial pathogenicity, cell-to-cell communication, and cell-colony–material interactions.



Micrographs: A. In situ fabricated protein microenclosure with chicane ports, inside which seven *Staphylococcos aureus* (1-µm round cells) are trapped for a quorum sensing experiment. B. Microchamber filled with a colony of replicating rod-shaped (bacilli) bacteria, allowing mechanical analysis of pressure exerted by the colony.

STRATEGIC PARTNERSHIPS INVESTMENT AREA

Network Design Optimization of Fuel Cell Systems and Distributed Energy Devices

110404
*Year 4 of 4**
Principal Investigator: W. Colella

Project Purpose

A single poly-generative fuel cell system can provide electricity, heating, and cooling power onsite to local surrounding buildings. This research develops and applies analytic approaches to understand the design and performance space of networked stationary poly-generative fuel cell power plants against the electricity, heating, and cooling demand curves of the buildings they may supply. The aim of this research is to use relatively inexpensive simulation studies of energy system thermodynamics, chemical processes, and economic and environmental optimization to better design fuel cell systems. These energy systems and their supply chains are assessed against competing energy technologies based on their relative emissions, fuel use, energy security, and costs.

Of all distributed generators, this research focuses on fuel cell systems for several reasons. Fuel cell systems have a higher electrical efficiency and lower carbon dioxide and air pollutant emissions than all other types of distributed generators consuming the same fuels. By contrast, microturbines fueled by natural gas have very low electrical efficiencies (approximately 20%) and higher air pollution emissions than fuel cell systems fueled by the natural gas. Similarly, internal combustion engine systems fueled by natural gas have a relatively low electrical efficiency (approximately 30%), higher air pollution emissions than fuel cell systems, as well as noise abatement and maintenance concerns. Models of distributed energy systems and networks are being constructed that, on the supply side, describe fuel cell system operation and, on the demand side, describe the energy demand profiles of buildings that these fuel cell systems might serve. Key descriptions of fuel cell system thermodynamics, heat transfer, and test data are being incorporated.

This project combines Sandia's unique expertise in three main areas: systems engineering, the design of renewable and efficient energy technologies, and the design of national infrastructure to increase homeland security. The PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments

The noteworthy scientific/technical accomplishments and achievements over the life of the project include a modeling capability in advanced, next-generation poly-generative stationary fuel cell system design (PFCS). While most systems today only generate one product (electricity), future systems are expected to produce more than one output (heat, fuels, cooling power, etc.) to serve distributed markets. These models evaluate the techno-economic and environmental impacts of installing, design, and controlling advanced PFCS. They also evaluate the fundamental physics and thermodynamics of coupling fuel cells with other energy conversion devices (such as absorption chillers). Techno-economic models optimize advanced PFCS design for minimum carbon dioxide footprint, minimum human health impacts of air pollution, and minimum energy costs, among other objective functions. Thermodynamic models describe PFCS performance over a range of operating temperatures,

*This 36-month project spanned four fiscal years.

pressures, flow rates, and other engineering parameters. These models guide integration of PFCS with related technologies, and help identify more optimal design approaches and limitations. This new modeling capability within the DOE laboratory complex is being used to help guide both industrial and scientific research.

Significance

This research supports key DOE environmental and energy efficiency missions. It supports the goals of the Energy Efficiency and Renewable Energy Office, the Office of Electricity Delivery and Energy Reliability, the Office of Fossil Energy, and the Hydrogen Program, by developing fuel cells for distributed stationary power, making fossil energy systems more efficient, reducing carbon emissions, diversifying energy supplies, modernizing infrastructure, and ensuring optimal use of resources.

Aligned Mesoporous Architectures and Devices

118841
Year 3 of 3
Principal Investigator: C. J. Brinker

Project Purpose

During the last decade, mesoporous materials with tunable periodic pores have been synthesized using surfactant liquid crystalline templates, thus opening a new avenue for a wide spectrum of applications. However, potential applications for these materials are somewhat limited by their unfavorable pore orientation. Although great effort has been devoted to align the pore channels, fabrication of mesoporous materials with perpendicular pore channels remains a major challenge. For the final year's research in this project, we proposed to explore the use of the aligned architectures for ionic transport channels, which is of great interest for fuel cells and neuron signal transmission.

This work is performed by Presidential Early Career Awards for Scientists and Engineers (PECASE) awardee, Professor Yunfeng Lu, University of California, Los Angeles.

Summary of Accomplishments

Our previous years' work demonstrated that pore channels of mesoporous silica can be aligned by exploiting capillary forces; we successfully met the following milestones:

1. We optimized the synthesis conditions and successfully aligned the mesostructures. This was achieved by optimizing the pH, temperature and aging time, which allowed us to minimize the polymerization reaction kinetics and maximize the mobility of the building blocks.
2. We conducted both fluidic mechanical calculation and experimental studies to understand the aligning mechanism. Viscoelastic properties and contact angle of the nanocomposite were measured and used to calculate the capillary force and shearing force. A mechanism was proposed based on these studies.
3. We investigated the alignment of mesostructures within different-size alumina pore channels. Alumina membranes with different pore diameters were used as the template to allow an investigation of the assembly of the mesostructure within this confined environment.
4. We synthesized aligned metal and semiconductor nanowire arrays. This was achieved by electrochemical deposition using the aligned mesostructure as template.
5. We have set up a protocol for ion transport and neuron signal transmission experiments.
6. We have prepared a manuscript to be submitted to the *Journal of American Chemical Society* focusing on this work.

Significance

Demonstration and characterization of transport through aligned architectures that simulate ionic channels is key to applications in fuel cells and neuron signal transmission, in addition to potential applications in water purification separations, chem/bio sensors, microelectronics, and controlled drug release. Success of this work may provide new synthetic approach to novel architectures, as well as insight that may lead to enhanced materials for many energy-related or biological applications.

Refereed Communications

M. Yan, J. Du, Z. Gu, M. Liang, Y. Hu, W.J. Zhang, S. Priceman, L.L. Wu, Z.H. Zhou, Z. Liu, T. Segura, Y. Tang, and Y.F. Lu, "A Novel Intracellular Protein Delivery Platform Based on Single-Protein Nanocapsules," *Nature Nanotechnology*, vol. 5, pp. 48-53, January 2010.

Z. Chen, Y.C. Qin, D. Weng, Q.F. Xiao Y.T. Ping, X.L. Wang, H.X. Li, F. Wei and C.J. Brinker, "Design and Synthesis of Hierarchical Nanowire Composites for Electrochemical Energy Storage," *Advanced Functional Materials*, vol. 19, pp. 3420-3426, November 2009.

D. Pan, D. Weng, X. Wang, Q. Xiao, W. Chen, C. Xu, Z. Yang and Y.F. Lu, "Alloyed Semiconductor Nanocrystals With Broad Tunable Band Gaps," *Chemical Communications*, vol. 28, pp. 4221-4223, July 2009.

D. Pan, X. Wang, Z.H. Zhou, W. Chen, C. Xu, and Y.F. Lu, "Synthesis of Quaternary Semiconductor Nanocrystals With Tunable Band Gaps," *Chemistry of Materials*, vol. 21, pp. 2489-2493, 2009.

Rheological Properties of Nanocomposites

118842
Year 3 of 3
Principal Investigator: B. Simmons

Project Purpose

This project is performed in collaboration with Presidential Early Career Awards for Scientists and Engineers (PECASE) award recipient Professor Bill King at the University of Illinois at Urbana-Champaign, to develop an understanding of nanometer-scale polymer flow as a function of composition, shear, strain, and temperature.

Many creative approaches have been developed to fabricate nanostructures from nanoparticles (nPs) or nanoparticle composites, but there are also many common limitations. Nanolithography approaches have both advantages and apparent limitations. Our approach is maskless, patterns additively, avoids solution processing, and is exceptionally flexible in the range of materials easily deposited. It also achieves line widths for both nP rows and nanocomposite nanostructures that are much narrower than those in previous reports of directly written structures. For example, fabrication of gold nP patterns by nanoimprint lithography has been developed; however, the line width was >130 nm. Conventional dip-pen nanolithography (DPN) has been used to directly deposit functionalized gold nanoparticles by electrostatic interaction from single nanoparticles to its aggregates, but again, line widths generally exceed 100 nm. And although recent research showed that DPN could deposit rows of Au nPs that were roughly one nP wide (actual widths not reported), deposition was inhomogeneous leading to start-and-stop deposition.

In particular, most nanolithographies are developed for a particular material and require significant development for each new material or component. The required work for each new material significantly hinders fabricating devices that require multiple materials. A second hindrance is that many approaches for nanoparticle nanomanufacturing require prior deposition of a template or that the material first be deposited and then selectively removed. With polymers, these multiple processing steps or sequential depositions can generate cross-contamination or degrade previously deposited structures. We have explored additive maskless deposition of a wide range of nP types on multiple substrates with no solution processing and no sources of cross-contamination. This robust technique enables direct access to the exceptional properties of nanocomposites that promise significant advances in nanoelectronics, data storage, biosensors, mechanics, and optical imaging applications.

Summary of Accomplishments

To show that the nanoparticles remained functional after deposition, we deposited a line of pure polymethylmethacrylate (PMMA) next to a line of PMMA containing magnetic Fe_3O_4 nanoparticles. The magnetic response of Fe_3O_4-loaded polymer is clearly visible while, as expected, there is no magnetic response from the Fe_3O_4-free material. These results also demonstrate the ease with which a new structure may be placed next to an existing one without degrading the prior's performance. We observed full functionality in all inks tested. Polyethylene with CdSe/ZnS quantum dots fluoresced due to the quantum dots as did the metal organic tris(8-hydroxyquinolinato)aluminum mixed with the piezoelectric polymer poly(vinylidene fluoride-tetrafluoroethylene). Finally, a two-probe conductivity measurement showed that the inclusion of Au nanoparticles reduced the resistivity of the otherwise undoped conductive polymer significantly. The successful deposition of organometallic, oxide, semiconducting, and metallic nanoparticles demonstrates the flexibility of the technique. The functional nanocomposite lines may remain as deposited, or the polymer matrix may be removed with an oxygen plasma leaving solely the nPs. While analyzing the residual Fe_3O_4 nPs deposited with PMMA, we found that the nPs had formed rows significantly narrower than the overall deposit. Data show the dramatic reduction in line width when a PMMA/Fe_3O_4 composite was plasma-etched to remove the PMMA, thereby revealing a row of nanoparticles 10 nm wide. The plasma processing reduced the deposit cross sectional area by a factor of 993 which, when compared to the 0.1% particle loading, indicates that essentially all the nanoparticles are driven to the center line.

Significance

This project is focused on developing the next set of design rules for nanocomposites. These would enable the realization of nanocomposites relevant to many DOE and DHS missions, including the advent of next-generation renewable solar energy harvesting and electrical storage devices, advanced batteries, advanced materials, and next-generation sensing materials.

Refereed Communications

W.K. Lee, Z. Dai, W.P. King, and P.E. Sheehan, “Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies Using Thermal Nanoprobes,” *Nano Letters*, vol. 10, pp. 129-133, 2010.

A New Chamber Design for Aerosol Evolution Studies in the Ambient Environment

118843
Year 3 of 3
Principal Investigator: B. D. Zak

Project Purpose

Secondary organic aerosols (SOA) comprise a substantial fraction of the total global aerosol budget. While laboratory studies involving smog chambers have advanced our understanding of the formation mechanisms responsible for SOA, the processes leading to SOA production under ambient gaseous and particulate concentrations and the impact these aerosol types have on climate are poorly understood. Although the majority of atmospheric aerosols scatter radiation either directly or indirectly by serving as cloud condensation nuclei, soot is thought to have a significant warming effect through absorption. Like inorganic salts, soot may undergo atmospheric transformation through the vapor condensation of nonvolatile gaseous species that will alter both its chemical and physical properties. The purpose of this project is to understand the transformation of ammonium sulfate and soot seed particles in an environmental chamber designed to study this process under near-ambient conditions. The Ambient Aerosol Chamber for Evolution Studies (AACES) was field deployed during the summer of 2009. After injecting both inorganic salt seed particles and soot, we monitored evolution during the atmospheric aging process using a humidified tandem differential mobility analyzer (particle size and hygroscopic growth), an aerosol particle mass analyzer (particle mass), and a cavity ringdown/nephelometer system (particle optical properties). Data analysis over the course of FY 2010 revealed an increase in particle size as well as significant changes in the aerosol mass and optical properties, primarily for soot particles. Chamber verification experiments were conducted to determine the following:

- Size-dependent particulate deposition rates in chamber
- Various gaseous deposition rates in chamber
- Organic gaseous penetration across the membrane
- Mixing timescales under nominal chamber operation

Summary of Accomplishments

During the course of FY 2010, using various methods, we analyzed data collected from three separate field campaigns spanning four years. For the field projects conducted in both Oklahoma and Colorado, chamber measurements of particle size and hygroscopic growth factor were parameterized using log-normal fits to obtain geometric mean diameter and hygroscopic growth factor, as well as the standard deviation of the distribution representative of each stage of the aerosol aging process. These results indicate that significant growth occurs during the transformation and growth of seed particles under near-ambient conditions. Furthermore, chamber verification tests were designed and conducted to determine the loss of both particles and gases to the chamber walls. In order to measure the loss of particulates under chamber conditions, we injected monodisperse ammonium sulfate populations sized 0.50 µm, 0.075 µm, 0.100 µm, 0.150 µm, or 0.200 µm, and we measured their concentrations hourly, using a differential mobility analyzer system. Complementary measurements of the soot deposition rate were obtained at sizes equal to 0.100 µm and 0.150 µm. Overall, the particle suspension half-life was greater than 0.30 days, resulting in measureable particle concentrations well beyond 12 hours under normal chamber operation. We conducted similar experiments to determine the gaseous deposition of CO, O_3, SO_2, NO_x, toluene, and isoprene; the results yielded an operational concentration half-life roughly equal to 1.5 days for each species under investigation.

Because the operation of AACES requires the flow of ambient organic and other gases across an expanded polytetrafluoroethylene membrane, we measured the penetration efficiency of O_3, NO_x, CO, SO_2, toluene and isoprene. To this end, a known concentration was injected into the base of the chamber (below the membrane) and gases were allowed to penetrate, with consecutive measurements taken on the opposite side. The results revealed consistent penetration efficiencies above 96%.

Significance

This project relates to DOE's strategic goal: "improve the quality of the environment . . . from energy production and use . . . ." To ensure that the production of aerosols from energy-related processes is environmentally sound, we must understand the processes acting on these emitted aerosols. This project contributes to this goal by providing an innovative means to study the transformation and aging processes that energy-related aerosol undergo in an atmospherically relevant environment.

Applying a Sediment Mass Balance Approach to River Meander Migration Modeling: Predicting the Future Planform of the Middle Rio Grande

119634
Year 3 of 3
Principal Investigator: V. C. Tidwell

Project Purpose

River meander migration is one of the most perplexing and intriguing problems in open channel hydraulics. Significant progress in understanding this phenomenon has been accomplished only in the past few decades. While significant efforts toward understanding the relationships between sinuosity and sediment transport have led researchers to collect large datasets on natural rivers, relatively few laboratory experiments were conducted to date. The newly constructed sediment flume at the University of Arizona Civil Engineering and Engineering Mechanics Department offers a unique opportunity to shed insight onto these relations.

Several researchers found that bedload transport is the dominant mechanism driving planform evolution. As erosion occurs at the toe of the outer bank, adhesive forces holding the bank are overcome by gravitation forces on the bank block. Hydraulic forces then carry this new source of bed load downstream. Hydraulic forces are believed to be greatest at the concave bank resulting in growth of meander bends. Due to the complexity of meander geometry, transverse and downstream bed slope, as well as stratification, cohesion, and vegetation along stream banks, the mechanics of sediment transport in meandering streams is difficult to simulate.

The most commonly applied meander evolution model employs the product of a linear coefficient and an estimate of the downstream velocity around a meander bend based on the quasi-2D analytical solution to the Navier-Stokes Equation for incompressible and steady flow. This work couples laboratory and numerical experimentation to advance our understanding of this complex phenomenon and our ability to manage meandering rivers.

Summary of Accomplishments

In the past year we have built a quasi-2D numerical model to simulate river meander planform evolution. The bank erosion model is based on the most common form of meander evolution modeling, the linear bank erosion model. This model assumes that the distance of bank retreat and advance is linearly related to the near bank excessive velocity with a linear coefficient, which is considered as a stochastic variable. An important improvement to this approach was the incorporation of a Monte Carlo subroutine to the model to represent the uncertainty in bank geomorphological characteristics. This method yields a confidence interval within which the model predicts future planforms and a more realistic representation of our ability to model the meander evolution.

In addition, due to the asymmetry of meander bends, efforts to quantify model error are nontrivial. Therefore, a series of metrics to measure model error were developed, which can be used to optimize the model's predictive capabilities. To test this model, we used a prior set of experimental results. These experiments began with a symmetric planform, the sine generated curve. After a linear interpolation, the mean squared error of each node along the streamline was calculated. Then, each bend was treated as a random variable with mean, standard deviation, and skewness. Model errors were measured using these metrics. A manuscript of this work was submitted to the *Journal of Geomorphology* for a special issue on river meandering in May 2010.

Significance

River meander migration is one of the most perplexing and intriguing problems in open channel hydraulics. Some challenges in simulating river meandering processes include the distributions of streamwise and transverse velocity, sediment transport, and bank erosion. Traditional methods correlate meander geometry with flow hydraulic parameters based on regression analysis. With the advance of computing technology, analytical and computational models were applied to predict not only the amplitude and wavelength of meanders but also the evolution of meander planforms. Meandering channel migration models have advanced to consider downstream translation, lateral expansion, and downstream or upstream rotation. This study endeavors to review and integrate existing analytical and numerical models and test them against experimental data from controlled flume studies and basin scale field data from the Rio Grande. Improved understanding of the complex meandering evolution process is of both scientific and societal value as measured in terms of sustaining instream infrastructure, improving ecologic functions, and protecting water quality.

Using Reconfigurable Functional Units in Conventional Microprocessors

119638
Year 3 of 3
Principal Investigator: A. F. Rodrigues

Project Purpose

Scientific applications use highly specialized data structures that require complex, latency sensitive graphs of integer instructions for memory address calculations. In our prior work, we have demonstrated significant differences between Sandia's applications and the industry standard SPEC-FP (standard performance evaluation corporation-floating point) suite. The integer dataflow in Sandia's applications average 40% more instructions and 50% more operands than the SPEC benchmarks. Furthermore, 92% of the data produced by these graphs is used to generate a memory address. Therefore, integer dataflow performance is critical to overall system performance.

Previously, this problem could be handled with specialized address generation units. However, Sandia's large and complex applications do not have identical access patterns. We demonstrated that each application has between 16 and 32 unique important graphs. It is not feasible to implement unique address generation units for each graph type, and each new application may use a different set of graphs. Thus, a reconfigurable functional unit (RFU) is an attractive accelerator because its functionality can change to accelerate a variety of different graphs. In this work, we use an RFU tightly integrated with a microprocessor to accelerate integer dataflow, improve the number of outstanding memory operations and therefore improve overall system performance.

We have developed compile-time algorithms that detect and select common graphs for acceleration. In addition, we have developed an RFU execution model that efficiently encodes a large number of inputs and outputs (needed for the complex Sandia graphs) for execution in an RFU, through an interface which requires minimum modification to the CPU. The execution model also includes architectural techniques to improve RFU performance by improving issue time and output pipelining and minimizing register file bandwidth.

Summary of Accomplishments

This work has developed an RFU execution model that efficiently encodes a large number of inputs and outputs (needed for the complex Sandia graphs) for execution in an RFU, through an interface that requires minimum modification to the CPU. The execution model also includes architectural techniques to improve RFU performance.

An operating system (OS) for multitasking reconfigurable systems manages access to both CPU and reconfigurable hardware (RH) resources. As in traditional multitasking systems, the OS periodically performs a thread context-switch to time-share the CPU. Similarly, the RH allocator periodically reallocates RH resources based on the needs of active applications. There are multiple ways that a thread scheduler's behavior can impact the behavior of the RH allocator. Thus far, we have addressed two of these: the issue of hardware preemption in response to software context-switches, and the problem that knowledge of recent RH kernel requests near a context switch does not correctly predict near-future RH kernel needs. We have also developed alternative preemption techniques that yield the benefits of preemptable hardware, but without the overhead associated with full save and restore of configuration and data.

In developing these OS mechanisms, we have also defined a new method to calculate speedup in simulated hybrid multitasking systems. These techniques could also be applied to measurements such as power consumption or energy-delay product.

Significance

Sandia's missions in nuclear security and scientific discovery and innovation require high-performance science and engineering codes. A major obstacle to performance is the rate of memory addresses which can be generated. This work will address this bottleneck, and allow major improvements in the performance of Sandia's applications.

Heat Conduction and Particle Motion in Stationary Nanofluids

119639
Year 3 of 3
Principal Investigator: J. A. Zimmerman

Project Purpose

Fluidic cooling systems have been shown to remove more heat than conventional air systems while using less power than thermoelectric coolers. However, the demand for more heat removal necessitates advancements beyond existing technology. Nanofluids, nanoscale particles suspended in fluids, have been studied over the last decade for applications ranging from fluidic cooling to nanolubrication. Much of the research found thermal conductivity enhancements greater than predictions based on effective medium theory, at low concentrations. However, large variations in data and dependencies have been observed. By measuring the full-field temperature and thermal conductivity distribution of nanofluids in a temperature gradient, the goal of our measurements is to show how these variations can occur due to particle thermal diffusion away from the heated portion of the fluid and to particle aggregation over time.

To our knowledge, this is the first experiment to measure the impact on thermal conductivity distribution of thermodiffusion and aggregation of particles in a nanofluid. It is also the first experiment to temporally measure the effect of aggregation on a stable stationary nanofluid showing an increase in thermal conductivity during the course of natural aggregation. Through a more complete understanding of the complicated physical mechanisms governing nanofluids and the dependence of thermal properties on these mechanisms, the applicability to cooling solutions can be better understood.

Summary of Accomplishments

We completed dynamic light scattering measurements on a 0.05% by volume concentration stabilized alumina nanofluid showing the presence of 40-nm nominal diameter single particles and 125-nm nominal diameter permanent clusters. Scanning electron microscope images revealed permanent clusters, 100–200 nm in diameter with fractal dimensions of 2.5. Static light scattering measurements of the stabilized alumina nanofluid at 1%, 3%, and 5% by volume concentrations and at temperatures of 20, 40 and 60 °C, show initial fractal dimensions of 2.4 with the fractal dimension decreasing towards 1.8 as the aggregates grow. The aggregation progressed faster in higher-concentration and higher-temperature fluids. The fractal dimension of 1.8 is consistent with diffusion-limited aggregation. We performed isothermal Monte Carlo simulations showing the aggregation progression for each of nine cases of varying concentration and temperature, and the simulations agreed well with the static light scattering results.

We ran the Monte Carlo simulation to check agreement with infrared microscopy measurements of FY 2008. We showed that the spatially nonuniform temporal increases in thermal conductivity above effective medium theory can be well described by particle aggregation and thermal diffusion. The simulation showed large concentration distributions arising from thermal diffusion variations in aggregation and therefore thermal conductivity. However, in considering relations between viscosity and aggregation, predictions are that the aggregation will cause the fluid viscosity to rise much faster than the thermal conductivity, resulting in an unfavorable replacement for heat exchangers and fluidic cooling. An optimal nanoparticle diameter for these particular fluid properties is calculated to be 130 nm to optimize the fluid stability by reducing settling, thermal diffusion and aggregation in order to maintain conditions in the nanofluid favorable for fluidic cooling.

Significance

These measurements and simulations improve the understanding of nanofluid behavior due to particle diffusion and aggregation and show the importance of taking these effects into account. They provide insight into how nanofluids may behave in practical applications, including microscale heat exchangers. These results have allowed us to proposed an optimum particle size for nanofluids.

Refereed Communications

J. Lee, P.E. Gharagozloo, B. Kolade, J.K. Eaton, and K.E. Goodson, “Nanofluid Convection in Microtubes,” *Journal of Heat Transfer*, vol. 132, p. 092401, September 2010.

P.E. Gharagozloo and K.E. Goodson, “Temperature-Dependent Aggregation and Diffusion in Nanofluids,” to be published in the *International Journal of Heat and Mass Transfer*.

P.E. Gharagozloo and K.E. Goodson, "Aggregate Fractal Dimension and Thermal Conduction in Nanofluids," to be published in the *Journal of Applied Physics*.

Nanotransport and Control of Molecules Through Molecular Gates

119640
Year 3 of 3
Principal Investigator: K. Patel

Project Purpose

Development of sophisticated tools capable of manipulating molecules at their own length scale enables new methods for chemical synthesis and detection. Although nanoscale devices have been developed to perform individual tasks, little work has been done on developing a truly scalable platform: a system that combines multiple components for sequential processing, as well as simultaneously processing and identifying the millions of potential species that may be present in a biological sample. The development of a scalable micro-nanofluidic device is limited in part by the ability to combine different materials (polymers, metals, semiconductors) onto a single chip, and the challenges with locally controlling the chemical, electrical, and mechanical properties within a micro or nanochannel.

We have developed a unique construct known as a molecular gate: a multilayered polymer-based device that combines microscale fluid channels with nanofluidic interconnects. The molecular gate differs from other nanofluidic systems in that microfluidic and nanofluidic elements are assembled in a 3-dimensional construct where the nanofluidic connections are made with a nanoporous membrane, as opposed to single etched nanochannels. This allows for selective control of chemical and mechanical properties of each layer, and enables solution properties such as pH and ionic strength to be independently maintained in each layer. By utilizing dense arrays, nanofluidic transport phenomena can be exploited while maintaining high throughput. Molecular gates have been demonstrated to selectively transport molecules between channels based on size or charge. Processes have also been developed to metallize and modify the surface chemistry of the nanopores, changing the electrokinetic transport characteristics. Current research is focused on individually addressable nanopores for developing a scalable system to efficiently utilize nanoscale transport. The work is a collaboration with the University of Illinois at Urbana-Champaign (UIUC).

Summary of Accomplishments

We have developed a unique construct known as a molecular gate: a multilayered polymer-based device that combines microscale fluid channels with nanofluidic interconnects. Molecular gates have been demonstrated to selectively transport molecules between channels based on size or charge. In order to fully utilize these structures, we need to develop methods to actively control transport and identify species inside a nanopore. While previous work has been limited to creating electrical connections off-channel or metallizing the entire nanopore wall, we now have the ability to create multiple, separate conductive connections at the interior surface of a nanopore. These interior electrodes will be used for direct sensing of biological molecules, probing the electrical potential and charge distribution at the surface, and actively turning on and turning off electrically driven transport of molecules through nanopores. The overall goal is to create a system that can selectively move molecules based on size, charge, or structure, and can operate over a wide range of concentrations. Combining multiple materials into a single system is a key challenge to creating molecular gates. Changing bulk properties and surface chemistry within a device allows multiple components to be tailored for specific functions: transport, separation, filtration, concentration, etc. The overall goal of the project is to utilize molecular gates in a start-to-finish lab-on-chip device for transport, detection, and modification of proteins, peptides, or other biomolecules. Several key goals have been addressed: 1. integrating metal layers, multiple polymers, glass, and silicon onto a single platform; 2. selective coating or chemical modification of microchannel and nanopore surfaces; 3. using integrated electrodes inside a nanopore to measure electrical potential and serve as binding sites for various biomolecules; and 4. adapt the micro-nanofluidic molecular gate construct to perform on-chip separation and detection of molecules at low concentrations.

Significance

Development of molecular gates as a scalable architecture for controlling molecules and nanotransport is a vital part of DOE's mission to advance scientific understanding of nanoscale phenomena. Tools to help understand nanoscale transport will ultimately lead to the development of new diagnostic devices and methods to explore alternatives to environmentally sound energy sources. Despite this prevalence of nanostructured materials in numerous applications, relatively little is currently known about the fundamental behavior of fluids and charged species within the confinement of nanoscale structures having dimensions ranging from a few to several tens of nanometers. This works will benefit many cross-cutting investment areas by providing improved understanding of transport processes not just within a single nanopore, but also in a network. This new understanding will aid rational design of methodologies to selectively transport molecules relevant to Sandia's mission. The strategic partnership is viewed as an important step toward establishing a long-term partnership between Sandia and UIUC faculty aimed at enhancing the education of next-generation scientists and engineers and accelerating the development of innovative technologies supporting American competitiveness in the global economy. Pairing young, bright students to work closely with a Sandia staff mentor is vital to the success of Sandia mission in finding solutions to problems of national importance.

Solar Hydrogen Generation with Porous Semiconductor Electrodes

119644
Year 3 of 3
Principal Investigator: B. R. Antoun

Project Purpose

The large-scale utilization of solar energy to meet growing energy demands requires a viable method for energy generation and storage, and the direct conversion of solar energy to chemical fuels is a very attractive solution. Solar-driven photoelectrochemical production of hydrogen from aqueous solutions is especially appealing because it is an environmentally sustainable and carbon-free solar-to-fuel energy conversion process. However, the design of photoelectrodes for this application requires optimization of several, sometimes conflicting, materials properties. Many semiconductor systems have been investigated for this application but show limited efficiencies; more research is needed to establish economically viable photoelectrodes for efficient hydrogen production.

Fabrication of efficient photoelectrodes is well known to be a complex pursuit due to the demanding materials requirements, including specific electronic, optical, microstructural, and morphological characteristics. Traditional materials for photoelectrodes often have low charge carrier mobilities, and so nanostructured photoelectrodes with features of low dimensionality have emerged in the field to attempt to match carrier diffusion lengths to physical dimensions, as well as to increase internal light scattering and reduce reaction overpotentials. In addition, complex stoichiometries are often required to obtain the necessary electronic and optical properties. Multiple bandgap systems can be utilized to increase solar absorption as well as induce favorable interfacial charge transfer.

Pulsed laser deposition is a physical vapor deposition technique that is uniquely suited to fabricate and study photoelectrodes for solar-driven hydrogen production with the desired characteristics. The physical mechanisms of pulsed laser-material interactions offer a unique opportunity to optimize photoelectrode stoichiometry and nanoscale structuring simultaneously, which undoubtedly will be required to bring solar-driven hydrogen production to efficiencies required for large-scale applications. Through careful experimental design, one can achieve a wide variety of photoelectrode structures, which in turn, allows systematic study of chemical composition and electronic and optical properties.

This project is a collaboration with the University of California (UC) at Berkeley.

Summary of Accomplishments

In the previous year, the performance of several interesting photoelectrode material systems have been studied that were fabricated and characterized in FY 2009. We developed and tested the following systems: cation- and anion-doped niobium oxide films, nanostructured tungsten trioxide photoanodes, and nanostructured mixed oxide photoanodes incorporating combinations of titanium dioxide, niobium pentoxide, tungsten trioxide, and bismuth trioxide.

Measurements were made using a unique pulsed laser deposition system that was designed and constructed as a part of this project. This system allows deposition of photoelectrodes with complex stoichiometries and layered structures. Using this technique, we were able to systematically vary dopant and co-catalyst loading concentration, as well as vary layer compositions in multiple-bandgap heterostructure photoelectrodes.

We assembled a photoelectrochemical characterization system to study the performance of deposited electrodes. This system integrated potentiostatic control, artificial solar light simulation, and gas chromatography, in a setup capable of fully characterizing the photoelectrochemical properties and hydrogen production efficiency of a given material system.

An invited talk entitled “Metal Oxide Films and Nanostructures for Solar Energy Conversion and Storage,” was given at the Materials Research Society Spring Meeting, a symposium on *Functional Oxide Nanostructures and Heterostructures*. A paper has recently been prepared for submission to *Applied Physics Letters* entitled “Doped, Porous Iron Oxide Films and their Optical Functions and Anodic Photocurrents For Solar Water Splitting.” The fellowship student working with this project has completed all written and oral qualification exams and class requirements for a Ph.D. in Mechanical Engineering at UC Berkeley.

Significance

This research benefits DOE’s Science strategic goal by encouraging and developing scientists who can contribute to advancing scientific knowledge in the future. The renewable, solar-driven photoelectrochemical production of hydrogen fuel is directly consonant with the national security mission of DOE. This project will assist development of a technology capable of providing a diverse supply of reliable, affordable and environmentally sound energy source.

Physiological Models and Inference Based on Optical Imaging

119647
Year 3 of 3
Principal Investigator: C. F. Diegert

Project Purpose

The electrical and vascular activity of the brain are closely coupled. This project, a collaboration with Cornell Engineering and Cornell Weill Medical College, examines this coupling in the case where the electrical activity is due to epilepsy and the status of the vascular system is monitored by video optical reflectance spectroscopy. The purpose of the project is to develop mathematical models and video processing based on the relationship of electrical activity of the brain to video optical reflectance spectroscopy data. Since the spectroscopy data is directly related to the amount of hemoglobin present in each pixel of brain tissue and whether it is oxygenated or deoxygenated, the model is a description of the propagation of electrical activity and the neuro-vascular response of the brain. The model has two different mathematical forms depending on whether space is regarded as discretized or continuous, and these enable different types of computing and different relationships between the model and the experimental data, given that the experimental data is intrinsically spatially and temporally sampled. As an example of different types of computing, the continuous spatial models are partial differential equations that can be solved by finite element methods, where the elements need have no relationship to the discretization of the data. The project has broad implications. First, the neuro-vascular responses of the brain are not merely a consequence of epilepsy, but rather are always occurring in both normal and pathological brain states. Therefore the model also represents important characteristics of both normal brains and brains suffering from non-epileptic diseases. Second, the specific video optical reflectance spectroscopy data that is the focus of the project measures the same brain phenomenon, the amount of oxygenated and deoxygenated hemoglobin that is present in a volume of brain, which is measured by the BOLD (blood oxygen level-dependent) effect, the basis of functional magnetic resonance imaging (fMRI).

Summary of Accomplishments

As a part of our graduate student's Ph.D. thesis research, we have developed a model of the electrical and vascular behavior of brain cortex. The work is motivated by epilepsy, especially the use of video optical reflectance spectroscopy measurements to study epilepsy. The use of spectroscopy measurements requires a detailed vascular model that includes at least some metabolic characteristics because the measurements are primarily functions of the amount of oxygenated and deoxygenated hemoglobin present in each pixel of the video. The model is in the form of a circuit composed of parametrically controlled resistors and capacitors, so that it can describe both cerebral blood flow (resistors) and cerebral blood volume (capacitors), and Kirchhoff's circuit laws are used to enforce conservation laws. Because of the importance of oxygenated and deoxygenated hemoglobin, the circuit has the equivalent of two charge carriers that can interconvert. Using this model, the student has reproduced concentration curves measured by several research groups and published in the peer-reviewed journal literature.

The result is a framework for a class of models as well as a particular model in two senses: First, there is flexibility in certain control laws within the model, especially relating the amount of electrical activity to the contractility state of smooth muscle lining the walls of brain arterioles. Second, and more importantly, a regular topology is used for the vascular network. The regular topology does not reflect the anatomy of the brain's vascular system and induces symmetries that are not present in the brain's system. This has naturally led us to random graph topologies, which are the topic of the follow-on project. We anticipate synergy with Sandia's strategic investments in algorithms for large graphs as applied to cyber security, composite materials, etc.

Significance

The model has several features that set it apart from other models in the literature.

1. Neuroscientists are interested in both cerebral blood flow and volume and, in a circuit context, this requires both resistors and capacitors while other models try to make do with resistors only.
2. We focus on conservation laws while other models do not. In a circuit context, such as this model, conservation laws are imposed by using Kirchhoff's current and voltage laws, where current is blood flow and voltage is blood-pressure gradient.
3. The measurements are optical and are sensitive to the amounts of oxygenated and deoxygenated hemoglobin. Kirchhoff's laws are augmented to allow for what, in the electrical context, would be two charge carriers where one of the carriers (oxygenated) transforms into the other (deoxygenated) and this transformation is really the purpose of the system. Two charge carriers are incorporated without affecting the conservation laws and without increasing the basic complexity of the model, e.g., the order of the circuit.
4. The description of the vessels is based on mechanical principles, Laplace's Law and Poiseuille's Law, which result in having a small number of parameters, specifically, just the Young's Modulus of the wall of an elastic tube which models the circumferential smooth muscle that controls dilation/constriction of the vessel. A control law relates this modulus to the electrical activity of the tissue.
5. The model is really a framework for modeling the system since different control laws (especially connecting electrical activity with vascular smooth-muscle contractility) and different topologies for the vascular network can be explored.

In the initial project, all of the topologies considered for the vascular network were regular, i.e., the same at each pixel. This is not realistic. This is also not a good approximation because it leads to symmetries that are not present in the biological system. Generalizing the topologies led to our study of random graph topologies in the current project. At the simplest level, nodes in the graph are junctions between vessels and edges in the graph are the vessels. However, our random graphs are not just a set of nodes and edges. Rather, each node also has a geometric location and each edge has a variety of marks, such as the tortuosity of the vessel that makes the connection. We hope to be able to enforce global topological constraints, e.g., each node has three edges, but may have to do so approximately. We also hope to enforce geometric constraints, e.g., connected nodes have certain probabilistic distributions on their relative geometric locations, e.g., the Euclidean distance between them. We are pursuing two separate approaches, one based on Gibbsian Markov Random Fields and one based on multidimensional point processes. Algorithms for large random graphs are synergistic with Sandia's interests for a variety of applications including cyber security and composite materials.

Passive High-Flux Thermal Management of Electrochemical Systems with In Situ Microchannel Phase Change

120207
Year 3 of 3
Principal Investigator: C. Orendorff

Project Purpose

Energy-storing electrochemical batteries are the most critical components of hybrid and electric vehicles (HEV and EV). Lithium-ion batteries are proposed to improve the fuel economy of these vehicles because of their higher specific energy, but they face thermal management challenges. Thermal management to maintain a specific operating temperature window of individual cells and packs is essential to maintain the performance of these batteries. This research addresses the singular limiting feature of battery cooling systems — the cooling systems are external to the batteries, which implies that substantial temperature gradients exist between the heat generation location (the cells) and the skin of the battery. In addition, existing battery thermal models for lithium-ion batteries have not adequately addressed the impact of thermal management on electrochemical performance. In this project, a 2D fully coupled electrochemical and thermal model is developed for a flat spirally wound lithium-ion battery that can be readily used in HEV simulations to assess the impact of different thermal management strategies. This project is a collaboration with Georgia Technical University (Georgia Tech).

Summary of Accomplishments

Additional testing was completed on a new commercially available battery over a temperature range of 12 to 50 °C and current range of 0.25 to 5 C for both charge and discharge. Unlike previous experiments, these data were normalized for observed capacity fade. In addition, the reversible heating rate was determined over the range of 0.15–0.95 DOD (depth of discharge) for two samples, both of which show similar results. These new performance data were parameterized and incorporated into the existing 2D electrochemical-thermal model. Results from model simulations showed that external air cooling of batteries cause the peak temperature to rise more than external liquid cooling. However, liquid-cooled batteries develop larger thermal gradients, which affect the local current generation rate and DOD. As power or battery thickness increases, these differences become larger and significant.

A preliminary design for the internal cooling device for the battery has been completed using a system-level thermal-hydraulic model. However, flow characteristics inside the small diameter channels at the expected mass fluxes (G ~10 kg/m^2-s) are not well understood. Thus, a microscale flow visualization and phase-change heat transfer test facility for understanding system and evaporator performance has been designed and fabricated, and preliminary flow visualization results obtained.

Fluid screening based on the properties of interest (liquid and vapor densities and viscosities, as well as the enthalpy of vaporization) was also conducted to select the working fluid. Refrigerants that are flammable, acutely toxic in low concentrations, or deplete the ozone layer were removed from the list. Based on this, refrigerants under consideration are, in order of preference, R410a, R407c, R404a, and R134a. Since R134a has a saturation pressure much lower than the other refrigerants, it was selected as the working fluid.

Significance

The battery data collected in this study enable determination of the electrochemical heat generation rate over a wide range of currents, temperatures, and DOD. Because the battery loses capacity when cycled at high temperatures, there can be inherent errors in estimating this heat generation rate. However, the normalization procedure developed in this study accounts for the capacity fade, which facilitates data collection over a wider range of temperatures and rates. Furthermore, it was shown that the entropic heat rate was significant even at the highest rate and test temperature (e.g., 7.4% of total at ~5 C and 55 °C), and, therefore, should not be neglected.

The electrochemical-thermal model developed in this study is the first model that simulates the local variation of DOD for an HEV dynamic power profile. The results show that hotter, more-discharged portions of the battery readily accept current upon charging, and vice versa. This phenomenon causes hotter portions of the battery to be cycled more, which contributes to local degradation of the battery. Furthermore, the modeling studies show that external cooling is not sufficient to maintain either uniform temperature or DOD. The electrochemical heat generation rates observed in this study will be used in future phases of this research to design a representative battery for investigating the proposed internal cooling system. Due to the high-flux heat removal capabilities, this system will reduce the peak battery temperature while eliminating thermal gradients inside the battery.

The battery modeling technique developed in this study can be used in a wide variety of lithium-ion battery investigations. For example, the thermal response of the battery when abused via internal or external short circuit can be simulated. Furthermore, this model can be efficiently incorporated into large 3D models that simulate the impact of the current collection on local heat generation and charge maldistribution. Due to efficiently conserving computational resources, various thermal management strategies can be rapidly investigated, which allows for battery pack designs to be screened prior to fabrication and testing. Furthermore, the minimization of peak temperatures and gradients within batteries through passive, high-flux internal cooling will allow increased power and energy densities unencumbered by thermal limitations. These storage devices will also see application in the spatial and temporal concentration of renewable energy sources and in the harvesting of low-grade energy.

Cosmic-ray Hydrometrology for Land Surface Studies

120208
*Year 4 of 4**
Principal Investigator: D. Desilets

Project Purpose

Energetic cosmic rays continually bombard Earth, with implications important to humanity. For example, cosmic-rays interact with microelectronic components, generating soft errors in advanced computing systems and posing challenges to the design of reliable aerospace components. Cosmic-rays also interact with materials in the upper meter of the Earth's crust, producing rare radionuclides that are retained in the lattices of rock minerals. The buildup of these radionuclides (e.g., ^{10}Be and ^{36}Cl) can be used to determine numerical ages of previously undatable geologic hazards such as prehistoric earthquakes, volcanic eruptions and landslides. Cosmic-rays also produce rare radionuclides in the atmosphere, providing a valuable tracer for atmospheric transport and mixing processes. Investigators at Los Alamos National Laboratory have shown that highly penetrating cosmic rays can be used as an imaging tool to locate fissile materials hidden in shipping containers. More recently, the utilization of cosmic rays has been extended to the field of hydrology, where it has been discovered that measurements of slow cosmic-ray neutrons can potentially be used to remotely and passively monitor soil water content and snow water equivalence at a footprint not attainable by other instruments. This work, led by President Harry S. Truman Fellow Darin Desilets is centered on the novel application of cosmic-rays to remote sensing of soil water content and snow water equivalence — two of the most important variables in the hydrologic cycle. This new technology can be put to a variety of uses, including monitoring slope stability, forecasting spring snowmelt and flash floods, and monitoring soil moisture in croplands. In addition to exploring applications in hydrology, the proposed work will investigate fundamental aspects of cosmic-ray physics and neutron transport, and therefore provide ancillary benefits to all areas of applied cosmic ray research.

Summary of Accomplishments

Two field sites have been established in northern New Mexico. One site is on the Valles Caldera National Preserve, where neutron detectors are operating in a trailer adjacent to a snow pillow and buried neutron detectors. Neutron data have been collected over the 2008-09 winter season and are currently being analyzed. Algorithms for converting neutron count rates to snow water equivalent depth were tested and improved.

A second field site is located in a municipal watershed supplying the City of Santa Fe. We have conducted a survey of above-ground biomass density and canopy coverage. Analysis of neutron data suggests that forest thinning has little effect on soil moisture or snow accumulation dynamics in this watershed.

We have conducted roving measurements with a neutron detector across a transect stretching from southern MN to northern WY. This work was done in conjunction with an airborne gamma survey operated by the National Operational Hydrologic Remote Sensing Center at the National Aeronautics and Space Administration (NASA). Preliminary analysis shows a 40 percent increase in elevation-corrected neutron intensity from MN to WY, which is qualitatively consistent with observed dry soils in WY and wet soils in MN.

A manuscript for *Water Resources Research* is in press and other manuscripts are near completion. One manuscript discusses the cosmic-ray probe area of influence and another discusses calibration sampling strategies. Results have been presented at the European Geophysical Union 2010 spring meeting.

*This 36-month project spanned four fiscal years.

Significance

In this project we developed tools and techniques that are crucial to accurately understanding and predicting the availability of water for energy production and the myriad of other competing uses of this precious resource. The proposed research also has strong potential impact in other mission areas of importance to DOE, including climate change, homeland security (detection of trace radioactivity), and nuclear transport theory and application.

Multiscale Schemes for the Predictive Description and Virtual Engineering of Materials

120209
Year 3 of 3
Principal Investigator: O. A. Von Lilienfeld-Toal

Project Purpose

The predictive power of computational materials simulation shall be enhanced dramatically by delivering a tool that enables engineers and experimentalists not only to routinely characterize, but also to identify, customize, and subsequently, also synthesize from scratch new materials that exhibit valuable and desired properties. Such in silico rational compound design (RCD) efforts are not only hampered by the difficulty of reliably predicting macroscopic properties for any given material but also by the sheer size of chemical space, i.e., the mind-bogglingly large number of all the stable and potentially interesting chemical compositions which define a material. Methods from seemingly different areas and levels of theory, such as physics, chemistry, materials sciences, applied mathematics, and even molecular biology will be combined in order to account in a rigorous way for fluctuations in chemical composition and link them to their macroscopic properties that can be exploited for a purposefully guided exploration of chemical space. The feasibility and versatility of the underlying theory shall be evidenced by applying the devised RCD algorithms towards two prototypical materials discovery problems, namely the RCD of a photocatalyst for the efficient generation of energetically rich material such as methanol, methane, molecular hydrogen, or ammonia, as well as RCD of heat transfer fluids with optimized physical properties for enhanced efficiencies of solar power facilities. While there is great potential benefit of such a tool, for science, engineering, and eventually society, the technological and technical barriers on the way to its assembly are daunting because the involved research fields are only now on the edge of making such a project conceivable. The PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments

FY10 Accomplishments:

- The molecular grand-canonical ensemble (MGCE) density functional theory (DFT) scheme was furthered. A Monte Carlo protocol, devised for unified sampling of chemical space and phase space, has been extended toward drug design. Ongoing work with Mark Tuckerman, and Michel Cuendet of New York University (NYU).
- Interatomic 3-body dispersion forces have been computed for a variety of systems. These effects were shown to reach up to 50% of relevant energy contributions. This work was published with Alexandre Tkatchenko, Fritz-Haber Institute Berlin.
- Alchemical paths and finite difference derivatives, from the MGCE, were computed using VASP and tested for reactions, and catalyst design. Published with Daniel Sheppard and Graeme Henkelman.
- Development of a rigorous scheme for linearizing chemical compound space with intern Carolina Mattsson.
- Ongoing work on randomized aromatic hydrocarbons with variable number of atoms or beads for the development of quantitative structure–property relationships relevant for charge mobilities in photovoltaic candidate materials. With Denis Andrienko and Bjoern Baumeister, Max-Planck Institute Mainz, Milind Misra (Sandia), and Jean-Loup Faulon, Genopole, Paris.
- Publication of summer 2009 study on proton tunneling in DNA base pairs. With Alejandro Perez (summer student, FY 2009), Mark Tuckerman (NYU), and Harold Hjalmarson.
- New tangent method developed with Sandia's Sai Jayaraman and Aidan P. Thompson for the prediction

of molten salt eutectics from first principles. A manuscript is to be submitted shortly.

Significance

Enhancing the predictive power of computational materials simulation is instrumental to fulfill the national mission. The virtual tuning of material's properties through the engineering of the atomistic composition and structure carries a large potential impact. Entire technologies, e.g., involving biohazards, water purification, explosives, molecular electronics, or harvesting light for renewable energy stand to benefit from a successful outcome of this project.

Refereed Communications

O.A. von Lilienfeld, "Accurate Ab Initio Energy Gradients in Chemical Compound Space, "*Journal of Chemical Physics*, vol. 131, p. 164102, October 2009.

P.A. Schultz and O.A. von Lilienfeld, "Simple Intrinsic Defects in Gallium Arsenide," *Modeling and Simulation in Materials Science and Engineering*, vol. 17, p. 084007, December 2009.

S. Jayaraman, A.P. Thompson, O.A. von Lilienfeld, and E.J. Maginn, "Molecular Simulation of the Thermal and Transport Properties of Three Alkali Nitrate Salts," *Industrial and Engineering Chemistry Research*, vol. 49, p. 559, January 2010.

R.B. Lehoucq and O.A. von Lilienfeld, "Translation of Walter Noll's 'Derivation of the Fundamental Equations of Continuum Thermodynamics from Statistical Mechanics'" *Journal of Elasticity*, vol. 100, p. 5, April 2010.

R.H. French, V.A. Parsegian, R. Podgornik, R.F. Rajter, et al., "Long Range Interactions in Nanoscale Sciences," *Reviews of Modern Physics*, vol. 82, p. 1887, June 2010.

O.A. von Lilienfeld and A. Tkatchenko, "Two and Three-Body Interatomic Dispersion Energy Contributions to Binding in Molecules and Solids," *Journal of Chemical Physics*, vol. 132, p. 234109, June 2010.

A. Pérez, M.E. Tuckerman, H.P. Hjalmarson, and O.A. von Lilienfeld, "Enol Tautomers of Watson-Crick Base Pair Models are Metastable Because of Nuclear Quantum Effects," *Journal of the American Chemical Society*, vol. 132, p. 11510, August 2010.

D. Sheppard, G. Henkelman, and O. A. von Lilienfeld, "Alchemical Derivatives of Reaction Energetics," *Journal of Chemical Physics*, vol. 133, p. 084104, August 2010.

Fundamental Studies of Electrokinetic Phenomena in Polymer Microsystems

124007
Year 3 of 3
Principal Investigator: B. Simmons

Project Purpose

This project is the result of a Presidential Early Career Awards for Scientists and Engineers (PECASE) to Professor Brian Kirby of Cornell University. Polymers are increasing in popularity for microfluidics applications because of their low cost, ease of fabrication, and often favorable optical and chemical properties. Many polymers are hydrophobic, however, and the material properties of hydrophobic polymers relevant to electro-osmosis are in dispute; some researchers have reported that electrokinetic actuation in hydrophobic polymers is impossible or unpredictable, whereas others have measured significant z-potentials in hydrophobic substrates. The challenge in modeling and measuring electrokinetic phenomena in hydrophobic substrates stems from a poor understanding of the surface chemistry of water–hydrophobe interfaces. The uncertainty in the material properties of hydrophobic substrates limits predictive capabilities for device design, and complexities arising from poorly understood interfacial phenomena can lead to poor repeatability and accuracy of experiments.

Some of the complexity in understanding the origin of charge in hydrophobic electrokinetic systems arises from the molecular/supramolecular structure of water at the fluid–solid interface. Postulated structures include regions of reduced or depleted water density ice-like hydrogen-bonded water molecule networks, and nanobubbles. Depletion layers and water molecule networks impact ion adsorption onto the fluid–solid interface, and are therefore important factors in understanding the origin of charge. Nanobubbles are of particular interest, since their presence would affect both interfacial charge formation and the fluid mechanical boundary condition, and their thermodynamic instability could lead to unpredictable or fluctuating electrokinetic behavior in hydrophobic systems. This suggests that electrokinetic properties of hydrophobic systems may depend on the time history of the interface.

Summary of Accomplishments

We conducted experiments in both hydrophobic TOPAS® microfluidic channels and hydrophilic silica microchannels in order to measure their electrokinetic properties as a function of the time history of the fluid-solid interface. In particular, we measured the z-potential as a function of time:

1. in pressure-driven flow inferred from streaming potential measurements;
2. in electro-osmotic flow inferred from current monitoring experiments;
3. in pressure-driven flow after an initial exposure to an electric field; and
4. after exchanging ethanol as the solvent in the system for water.

In the TOPAS microchannels filled with 1mM phosphate buffer, the normalized z-potential was initially high, but it decayed to an equilibrium value. The transient is well fit by an exponential decay. The normalized z-potential for 10mM phosphate buffer in TOPAS had a very similar exponential decay; by contrast, in the silica microchannels, it showed constancy over a significant time period, with a time average that varied only slightly during that interval. The electric field magnitude was chosen so that the shear stress at the fluid-solid interface during the initial period of electroosmotic flow would be roughly a factor of two larger than in the current-monitoring experiments. The electric field was then switched off, flow actuated via a sinusoidal pressure waveform, and the streaming potential measured.

Significance

This project will underpin the fundamental science mission within DOE by developing a further understanding of electrokinetic flows at solid-liquid interfaces. This understanding will enable the further development and realization of optimal microfluidic devices that can meet DOE missions in energy security, and remote monitoring and sensing, as well as relevant DHS missions in the same technology space.

Refereed Communications

V. Tandon, S.K. Bhagavatula, and B.J. Kirby, "Transient Zeta-Potential Measurements in Hydrophobic, TOPAS Microfluidic Substrates," *Electrophoresis*, vol. 30, pp. 2656-2667, 2009.

Solid-Oxide Electrochemical Reactor Science

126613
Year 3 of 3
Principal Investigator: A. Ambrosini

Project Purpose

The topic area of this collaboration between Sandia and the Colorado School of Mines (CSM) is solid-oxide electrochemical reactors targeted at solid oxide electrolyzer cells (SOEC), which are the reverse of solid-oxide fuel cells (SOFC). SOECs complement Sandia's efforts in thermo-chemical production of alternative fuels. An SOEC technology would co-electrolyze carbon dioxide (CO_2), produced by and captured from coal-burning power plants or other CO_2 waste streams, with steam at temperatures around 800 °C to form synthesis gas (H_2 and CO). Synthesis gas forms the building blocks for a number of petrochemical substitutes which can then be used to power transportation vehicles or distributed energy platforms. In other words, SOECs afford the possibility of recycling CO_2 rather than emitting it or sequestering it. Thus there are societal, political, and environmental benefits to be realized by bringing the technology to the state where cost-effective commercial products are viable in the marketplace.

SOECs operate at high temperature, around 800 °C, which provides both challenges and benefits. Research is certainly needed to improve materials, optimize cell architectures, and produce cost-effective SOEC systems. The effort proposed here concentrates on research concerning catalytic chemistry, charge-transfer chemistry, and optimal cell-architecture. Other important considerations include degradation mechanisms, for example, carbon deposits or Ni electrode re-oxidation. The technical scope will include computational modeling, materials development, and experimental evaluation. The project engaged the Colorado Fuel Cell Center at CSM through the support of a graduate student at CSM and his advisors, in collaboration with the Sandia PI.

Summary of Accomplishments

Over the course of this project, the concept of and motivation for researching high-temperature solid-oxide electrolysis cells were developed. Synthesis gas production through high-temperature electrolysis was shown to be a viable option through exploration of and comparison with other existing technologies. We explored previous research that forms the basis of understanding for this project, including patterned anode experiments and modeling attempts.

We investigated the synthesis of both planar and tubular solid-oxide cells; however, difficulties in reliably sealing and testing planar cells, led to the use of tubular cells, which are easier to seal and more reproducibly produced. We used polarization measurements in a specially built test apparatus to characterize the performance of a tubular cell. The cell was supplied a gas mixture of varying composition of H_2, H_2O, CO, CO_2, and Ar. Experiments used carefully controlled gas-phase partial pressures to assist in understanding reaction orders. The partial pressure of one gas species was varied, while all others were held fixed by balancing with Ar. High flow rates were used to ensure low fuel utilization, thus matching the one-dimensional model with fixed fuel-channel mole fractions.

Experiments were interpreted via detailed reaction mechanisms. A model with fixed thermal chemistry and air-electrode charge-transfer chemistry and adjustable parameter charge-transfer mechanisms was used in matching experimental data. We found that a parallel system of hydrogen- and oxygen-spillover charge-transfer provided the best fit for the data over all operating temperatures and gas compositions. By studying the individual contribution of the rate limiting reaction for each charge-transfer pathway separately, we found that the oxygen-spillover mechanism is more important at high temperatures and high levels of CO_2. At low temperatures, the hydrogen-spillover mechanism is dominant. Further work must be done, however, to fully quantify the contribution of each separate mechanism and the sensitivity to various modeling parameters.

Significance

Sandia is establishing a leadership position in recycling CO_2 into liquid hydrocarbon fuels. High-temperature electrolysis from carbon-neutral electricity is a promising synergistic and complementary and possibly competitive approach to Sandia's unique efforts in its Sunshine to Petrol project. An effort such as the one described here would bring new capabilities to Sandia, build a strategic partnership with CSM in the science of high-temperature electrochemical reactors, and build on Sandia's considerable strengths in materials fabrication and experimental diagnostics. Electrolyzers offer the possibility of converting CO_2 to CO, and then to logistics fuels. Thus, there are societal, political, and environmental benefits to be realized by bringing the technology to the state where cost-effective commercial products are viable in the marketplace.

Refereed Communications

C. Moyer, N.P. Sullivan, H. Zhua, and R.J. Kee, "Polarization Characteristics and Chemistry in Reversible Tubular Solid-Oxide Cells Operating on Mixtures of H_2, CO, H_2O and CO_2," to be published in the *Journal of the Electrochemical Society*.

Computational Models of Intergroup Competition and Warfare

130810
Year 2 of 3
Principal Investigator: R. G. Abbott

Project Purpose

Warfare is an extreme form of intergroup competition in which individuals make sacrifices for the benefit of their nation or other group to which they belong. Among other animals, limited, nonlethal competition is the norm. It is not fully understood what factors lead to warfare, or to more moderate examples of intergroup competition like territorial fighting in social primates. Building on agent-based models of ant foraging, models of inter-colony conflict in ants will be developed, and later adapted to model conflict and warfare among human groups. A parallel genetic algorithm to model the coevolution of conflict behaviors in ant colonies and group-living humans will be developed. These powerful computational techniques give novel insights and allow us to test hypotheses about what drives intergroup competition and warfare.

Research will focus on the development of computational models of intergroup competition. In particular, we will study the conditions under which natural selection selects for optimal group size, balancing the need to disperse for access to new food sources against the benefits of living in large groups (such as information sharing and strength of numbers); individual sacrifice for the benefit of the group; and how change in the intensity of intergroup competition over time applies pressure for the attunement of effort devoted to individual vs. group goals, both over the course of generations, and within the lifetime of an individual. There is a tradition of examining these properties using mathematical and computational models. However these models have failed to take advantage of genetic algorithms to simulate the evolution of intergroup aggression by natural selection. The emergent properties of groups of organisms lend themselves to study with computational models because group properties are the result of the repeated interactions of discrete, individual members of those groups. This work is a collaboration with the University of New Mexico (UNM).

Summary of Accomplishments

Over the past year, we have extended our findings — that variation in the intensity of infectious disease predicts global and cross-national variation in the frequency of armed conflict and civil war in human societies — to other categories of conflict including clan warfare, revolutions and coups, and the Institute for Economics and Peace’s Global Peace Index of peace and conflict. We completed a path analysis that supports a causal model in which greater intensity of infectious disease leads to poverty and increased xenophobia, both of which cause increased frequency of conflict at lower latitudes, and especially in Africa, Southeast Asia, and equatorial South America.

We have expanded our models of ant colony foraging to include foraging ants’ memory of sites where food has recently been found, as well as pools of idle foragers that remain idle in the nest, awaiting activation by the discovery of sites with very large food sources or sites where control of food resources are contested by neighboring colonies. These behaviors may interact with the pheromone recruitment behaviors we have been studying by allowing effective solitary foraging until times when mass recruitment is required. We have also begun to collaborate with an interdisciplinary team of researchers at UNM, investigating analogies between population-level, distributed-search and problem-solving systems like ant colonies and organ systems, such as the human immune system, which also engages in distributed searching and problem-solving.

To extend the findings to resource compensation among humans, we also conducted a statistical analysis of historical data linking infectious disease to armed conflict and civil war. While it is well known that trade is essential to economic growth, inter-group interactions in evolutionary time also carried costs including risk of transmission of infectious disease. To quantify this link we examined differences in the occurrence of conflict as a function of climate and infectious agents.

Significance

This work will uncover the factors that contribute to the timing, intensity and distribution of warfare. These models will study the emergence of group properties and behavior as the result of the interaction of individuals, clarifying the contribution of individual psychology and motivation to the occurrence of warfare. The modeling techniques developed are also likely to apply to other computationally intensive, information-rich modeling projects.

Refereed Communications

K. Letendre, C.L. Fincher, and R. Thornhill, "Does Infectious Disease Cause Global Variation in the Frequency of Intrastate Armed Conflict and Civil War?" *Biological Reviews*, vol. 85, pp. 669-683, 2010.

K. Letendre, C.L. Fincher, and R. Thornhill, "Parasite Stress May Cause Non-State Wars, Revolutions and Coups, and the Absence of Peace Across the World," Presented at *The Human Behavior and Evolution Society Conference*, Eugene, OR.

Data-Driven Optimization of Dynamic Reconfigurable Systems of Systems

130812
Year 2 of 2
Principal Investigator: J. P. Eddy

Project Purpose

In this research, we define a System-of-Systems (SoS) as a dynamic, interdisciplinary network of individual communicating, collaborating entities with varying levels of autonomy and decision-making capability. Entities may be humans, autonomous machines, or human-operated equipment. The concept of a system-of-systems is different from that of a traditional large-scale system that is complex but static. To understand the nature and mechanisms of complex systems, researchers have addressed the core components of static, single-system design optimization using traditional systems engineering and mathematical programming for more than two decades. With the emerging notion of dynamic design and operations of an SoS, we are faced with an important generalization of the architecture and mechanism. Our vision of this research is to develop new methods for a quantitative reconfiguration of an SoS that can respond to unforeseen operating scenarios by integrating distinctive domains of knowledge in systems engineering, data management and mining, multidisciplinary optimization, and parallel computing. We identify key research themes: a) the dynamic aspect of systems architecture is modeled, b) the decision-maker remains in the loop for the coordination process, and c) the SoS optimization framework is easily scalable to model realistic operating conditions and models. The proposed research will transform the conventional paradigm for designing and operating multiple system infrastructures into a new paradigm of autonomous, reconfigurable SoS. The outcome of the research will potentially benefit areas such as homeland security, emergency response, and future combat systems, where the dynamic paradigm plays a key role. Human and capital losses from natural disasters, unforeseen attacks or system failure may be significantly smaller than those observed in the cases of hurricanes, tsunami disasters, or food contamination outbreaks. The collaboration between Sandia and the University of Illinois at Urbana-Champaign will leverage expertise in the core research areas addressed above.

Summary of Accomplishments

During FY 2009, we developed expertise in the areas of data mining and optimization. Each of these areas is critical to this project. We used Sandia tools for performing SoS analysis and optimization. We created a proof-of-concept example in data-mining, and it proved of benefit to our SoS analysis. These capabilities may prove valuable to some of our federal agencies such as army future combat systems and ground combat systems.

During FY 2010, we were able to leverage the algorithms and expertise developed in FY 2009 in the areas of data mining and optimization to create a prototype software application. Among other things, the application can perform the data mining, clustering, and regression techniques investigated.

While this software is only a prototype, it will serve as a means of testing the usefulness of the techniques it incorporates. It is our belief that these techniques will prove very useful at which time we intend to create a distributable, verified-and-validated version of the software for use by our analysts and other interested parties.

Significance

Sandia is engaged in SoS research as a tool for furthering its strategic goals. Examples include the US Army programs for defense, logistics modeling of disaster relief efforts for national security, and power grid analysis and water systems modeling for energy and security. This research is intended not only to improve our ability to model these kinds of systems but also to provide tools to aid in real-time operation of such systems for optimal decision-making and resource allocation.

The kinds of analyses performed in the Center for System Reliability invariably generate large amounts of data. These resultant data sets are representative of the behavior and performance of the systems studied. Ongoing challenges we face include how to identify trends in the output and how to relate features of the output back to features of the input (and vice-versa). These are exactly the kinds of questions answered by these data mining and related techniques.

In terms of how these techniques might be used, a number of new ideas for possible application have been identified. Examples include use of these techniques to guide optimization algorithms in real-time, provide real-time decision support to decision-makers embedded within SoS, and to provide a means of identifying and quantifying high-impact factors affecting the performance of an SoS.

Development and Characterization of 3D, Nano-Confined Multicellular Constructs for Advanced Biohybrid Devices

130813
Year 2 of 3
Principal Investigator: B. J. Kaehr

Project Purpose

Inspiration for the design of new materials and devices is increasingly found in biological systems where sensitive detection, energy conversion, and molecular-/nanomachinery have been continually improved upon by evolution. However, to impart the useful properties of biological systems into devices requires new ideas and technologies. Although there has been much focus on material functionalization using biomolecules, incorporation of self-sustaining and self-replicating components (e.g., biological cells and bio-catalysts) into solid-state platforms has received scant attention. Moreover, in order to bridge the organic structures and functionalities of cells to the inorganic, solid-state materials of modern devices, functional biotic/abiotic interfaces are required. The proposed research will address these problems using a breakthrough approach for the rapid-prototyping of 3D bio-interfaces and catalytic architectures.

In this project, recent breakthroughs — based on our previous work in 3D microfabrication — that enable the topographical and chemical microenvironments of developing cell populations to be precisely defined and analyzed will be employed to confine and direct the behaviors of developing cell populations. Patterning of biological architectures and multicellular constructs that can direct assembly of inorganic materials combined with the emerging tools of cellular (re)programming (i.e., synthetic biology) will permit the design of communication networks between engineered cell populations — enabling the development of cell-based circuitry. These efforts should expand the applications of biohybrid materials into new territories. For instance, sensing regimes based on precisely defined cell behaviors (e.g., cell motility) and networked cells communicating via innate and engineered pathways will enhance the range and sensitivity of biosensing devices to analytes in complex environments. The PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments

We have established a unique capability within Sandia for biological microprototyping and three-dimensional microfabrication that has enabled significant progress towards project goals, as follows:

- The development of an analytical strategy to measure mechanical properties of 3D microscale hydrogels comprised of proteins has been achieved. This extensive characterization of this new class of “smart” hydrogel materials provides a crucial foundation underpinning the goals of the proposed research (e.g., functional biotic/abiotic interfaces).
- Containment of viable bacterial strains engineered to report cell-cell communication (i.e., quorum sensing [QS]) was achieved using a biocompatible microfabrication approach. Chambers were microfabricated from a protein/photosensitizer solution to contain Staphylococcus aureus cells carrying the QS reporter gene/protein agr: P3-gfp. Preliminary results show cell behaviors are highly dependent on the diffusivity of the hydrogel chamber. Interestingly, single cells confined into low-diffusivity chambers undergo slight differentiation and report QS in 1 to 2 days under nutrient conditions. Cells confined in high-diffusivity chambers replicate to fill the chamber to a high cell density (~10^{13} cells/cm^3), but do not report QS.
- Investigations into protein-directed assembly of inorganic architectures have led to a bona fide breakthrough in biomimetic chemistry (Khripin Brinker and Kaehr, under review). A methodology

has been devised by which proteins incorporated into an arbitrary 3D microstructure direct silica polymerization. This precise control over template architectures enables complex structures to be generated, offering control over hierarchical features across approximately seven orders of magnitude and providing a bridge to further transformational chemistries. For instance, we have shown that protein-templated silica materials can be converted to silicon. These results provide access to substantial opportunities to develop 3D device materials with nanoscale precision.

Significance

If development of what is essentially a new class of materials is successful, potential applications will far exceed those that are proposed here (e.g., robust cell-sensors, biocomputers), benefiting DOE, DHS, national security missions involving bioterrorism, and biomedical and bionic technologies. Additionally, understanding of quorum sensing behavior and mechanisms using precisely defined microenvironments is important for human health and disease and currently these mechanisms, particularly the influence of mass transfer in confined environments, are poorly understood. Breakthrough developments reported in FY 2010 for rapid-prototyping of inorganic device materials in 3D will further enable Sandia thrust areas in photonics, plasmonics, and metamaterials.

Refereed Communications

B. Kaehr and C.J. Brinker, "Using Bacterial Growth to Template Catalytic Asymmetry," *Chemical Communications*, vol. 46, pp. 5268-5270, 2010.

C.Y. Khripin, C.J. Brinker, and B. Kaehr, "Mechanically Tunable Multiphoton Fabricated Protein Hydrogels Investigated Using Atomic Force Microscopy," *Soft Matter*, vol. 6, pp. 2842-2848, 2010.

J.C. Harper, C.Y. Khirpin, E.C. Carnes, C.E. Ashley, D.M. Lopez, T. Savage H.D.T. Jones, R.W. Davis, L.M. Brinker, B. Kaehr, S.M. Brozik, and C.J. Brinker, "Cell-Directed Integration into 3D Lipid-Silica Nanostructured Matrices," *ACS Nano*, vol. 4, p. DOI:10.1021/nn101793, 2010.

Development of a Structural Health Monitoring System for the Assessment of Critical Transportation Infrastructure

130814
Year 2 of 3
Principal Investigator: D. P. Roach

Project Purpose

Recent structural failures such as the I-35W Mississippi River Bridge in Minnesota have underscored the urgent need for improved methods and procedures for evaluating our aging transportation infrastructure. This research seeks to develop a structural health monitoring (SHM) system to provide more-quantitative information related to the structural integrity of metallic structures to make appropriate management decisions and ensure public safety. The system will employ advanced structural analysis and nondestructive testing (NDT) methods for sensing/measurement and decision-making purposes. Metal railroad bridges in New Mexico will be the focus since many of these structures are over 100-years old and classified as fracture-critical. Fracture-critical indicates that failure of a single component may result in complete collapse of the structure such as the one experienced by the I-35W Bridge. Failure may originate from sources such as loss of section due to corrosion and cracking due to fatigue loading. Because standard inspection practice is primarily visual, these types of defects can go undetected due to oversight, lack of access to critical areas, or, in riveted members, some defects may be hidden by the connecting members. Another issue is that it is difficult to determine the fatigue damage that a structure has experienced and the rate at which damage is accumulating due to uncertain load distribution to supporting members. A SHM system has several advantages for overcoming these limitations, primarily that critical areas of the structure are monitored more quantitatively under actual loading. The research needed to apply SHM to metallic structures will be performed and field demonstrations will be carried out to show the potential of SHM for assessing the condition of critical transportation infrastructure. This project will combine the expertise in transportation infrastructure at New Mexico State University with the expertise at Sandia in the emerging field of SHM.

Summary of Accomplishments

Over the life of this project, several significant accomplishments have been realized. A thorough literature review that included fatigue in steel structures, SHM, and bridge management has been completed and documented in a dissertation chapter. The literature showed that fatigue is one of the most common failure mechanisms in metallic structures, and that various methods have been developed in an attempt to identify failures in large structures using long-term monitoring with dynamic sensors. However, none of the methods could reliably and accurately locate and quantify damage of a structure outside of a laboratory setting. Also, common strain gauges are susceptible to significant random drift over time, which complicates long-term monitoring. Therefore, the direction of this research is to use short-term measurements to determine the service behavior and to validate a structural model that can be used to estimate the remaining fatigue life. This methodology allows for the analysis of an entire inventory of structures with minimum cost. A preliminary 3D finite element model (FEM) has been developed for two steel railway bridges in New Mexico that carry the RailRunner and Amtrack trains. One model was used to determine the placement of strain gauges for load testing, which involved measuring the response of one of the structures under six commuter trains. The load tests were performed in August under normal traffic at full speed (79 mph). For this load test, the data logger was manually triggered when visual contact was made with the trains. The load test data has been reviewed and the initial findings indicate the following: low dynamic impact on the structure, bridge behaved symmetrically about the longitudinal centerline, behavior of the girders was noncomposite, and some stringers acted as partially composite members due to the interaction with the timber deck.

Significance

SHM shows great promise for various DOE-related areas such as critical infrastructure assurance and homeland security. Although advanced methods and techniques are available to SHM professionals, deployment of SHM systems for in-depth evaluation has been slow due to the lack of specific procedures for properly designing, installing, and operating the SHM system for making decisions. This project will enable more widespread use of SHM to improve the assessment of our critical infrastructure.

Distributed Video Coding for Arrays of Remote Sensing Nodes

130815
Year 2 of 2
Principal Investigator: B. J. Merchant

Project Purpose

The focus of this research is the application of bitstream-based processing techniques to distributed video compression. The objective of distributed compression (distributed source coding) is to exploit the correlations between sensor measurements to reduce communications bandwidth required to transmit these measurements to a collection site. There has been a great deal of research related to distributed source coding in recent years, but virtually all of this work has assumed the availability of sensor correlation information at both the sensor nodes and the collection site. In reality, such information must be extracted by the sensors in the network and efficiently distributed as needed. Typically, this would require a sensor node exploiting the distributed coding paradigm to have essentially the same capabilities as the decoder at the collection site — i.e., it would have to be capable of fully decoding the transmissions that it picks up from all of neighboring nodes in the array and analyzing them to determine what, if any, correlations exist. In the case of video, this decoding process converts the very sparse compressed representation of the data into a very large number of image pixels, which must then be processed by the sensor node. Both the process of decoding the compressed bitstream and that of analyzing the reconstructed video sequence consume large amounts of computational bandwidth and node power, making sensor nodes more expensive and reducing their effective lifetimes in the field. The work is a collaboration with New Mexico State University.

Summary of Accomplishments

We have evaluated the performance of a distributed multiview coding system using an ideal conditional coding paradigm. In particular, we have considered the performance impacts of practical nonidealities such as block misalignments and additive noise. Finally, we have analyzed a real-world scenario that uses a low-complexity correlation detector on video with unknown (and varying) a priori camera field-of-view overlaps. When compared to motion-JPEG (Joint Photographic Experts Group) coding, it becomes evident that any bit-rate reductions (if they exist at all) are small. If any significant bit-rate reductions are to be made, then interpixel redundancies in the dependently encoded overlap regions must also be exploited. In the future, we will explore methods for exploiting these redundancies, mainly the runs of zeros of the coefficients, similar to JPEG and H.264 (advanced video coding) intra-coding.

Significance

Many Sandia mission areas utilize distributed sensor systems (monitoring for security, environment, production processes, etc). The DOE ground-based nuclear explosion monitoring research program is seeking unobtrusive sensors for deployment near testing areas. In some cases communications will be severely limited due to the location of these systems. This work will advance the technology available for application to these monitoring systems.

Evaluation of Baseline Numerical Schemes for Compressible Turbulence Simulations

130817
Year 2 of 3
Principal Investigator: J. Smith

Project Purpose

Numerical and modeling errors in turbulence simulations are difficult to isolate and quantify. An approach that has previously shown promise in this area is the Method of Nearby Problems (MNP), developed by Dr. Christopher Roy of Virginia Polytechnic University (Presidential Early Career Awards for Scientists and Engineers [PECASE] recipient). MNP is a novel approach that can be used to assess numerical errors in complex calculations. In MNP, exact solutions are generated by spline-fitting highly resolved numerical solutions. These solutions are "nearby" the numerical solutions from which they were derived, and thus are representative of the relevant physical and mathematical properties, yet they are exact and can thus be represented to machine precision. These exact solutions are solutions not to the original equation set, but rather, to a "nearby" equation set, with the same differential operator and a source term generated by applying the original differential operator to the exact solution. The source terms generated are small and distributed, preserving the "nearby" nature of the new equation set. Multidimensional MNP can be applied to problems in code and solution verification in many different areas of computational science and engineering. Last year's work focused on applying multidimensional MNP to 3D (2 spatial and 1 temporal) and 4D (3 spatial and 1 temporal) solutions to the Euler and Navier-Stokes equations. This allowed baseline numerical schemes for these equation sets to be evaluated. This year will extend this work for unsteady turbulent simulations. This will allow dissipative and dispersive errors to be quantified. Quantification and study of these numerical errors will lead to the development of new subgrid turbulence models which can account for the presence of numerical error, as estimated by MNP. This contribution will be particularly useful for modeling of compressible turbulent flows, since computer codes used for simulating compressible flows are often limited to second-order accuracy.

Summary of Accomplishments

Over the past year, we have accomplished a number of key objectives of this work. These accomplishments follow:

1. The spline-fitting approach has been extended from 2D to 3D and tested. This will now allow MNP to be applied to 3D steady-state flows as well as 2D unsteady flows.
2. The spline-fitting code has been rewritten to provide more accurate spline fitting of the underlying data. This has been accomplished by changing the order of operations in the weight function/local fit convolution and evaluation.
   - Updated results have been shown for the following problems:
   - 1D steady Burgers equation
   - 1D unsteady Burgers equation: shock coalescence and pulse decay
   - 2D Euler equations: manufactured solution on two different grid families
   - 2D Euler equations: Ringleb's flow
   - 2D Euler equations: subsonic airfoil

3. The MS student at Virginia Polytechnic University has successfully defended and published his masters thesis.

Significance

The proposed work will provide a platform for evaluating numerical schemes for compressible turbulent flows that are important in a number of transonic and supersonic weapons systems. The work will also advance the state-of-the-art in discretization error estimation, which indirectly impacts the predictive capability of modeling and simulation for the Stockpile Stewardship Program.

Refereed Communications

M J. Kurzen, “Discretization Error Estimation and Exact Solution Generation Using the 2D Method of Nearby Problems,” Masters Thesis, Virginia Tech, 2010.

Interfacial Electron and Phonon Scattering Processes in High-Powered Nanoscale Applications

130818
Year 2 of 3
Principal Investigator: P. E. Hopkins

Project Purpose

The objective of this project is to study heat transfer processes around structurally imperfect regions at interfaces involving both traditional and novel nanostructures used in high-powered nanoelectronic and energy conversion applications. Deposition, fabrication, and post-possessing procedures of nanocomposites and devices can give rise to interatomic mixing around interfaces of materials leading to stresses and imperfections that could affect heat transfer. As nanoapplications continue to decrease in characteristic sizes, the degree and depth of the interatomic mixing can be on the same order or greater than the sizes and length scales of the individual materials comprising the device. An understanding of the physics of energy carrier scattering processes and their response to interfacial disorder will elucidate the potential of applying these novel materials to next-generation high powered nanodevices and energy conversion applications. The PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments

We have set up three optical experiments to measure thermal properties of thin film systems: a phase sensitive thermoreflectance technique and two time-domain thermoreflectance (TDTR) techniques. We have extended the TDTR capabilities to temperatures from 80 to 500 K and wavelengths from 400 to 1200 nm, increasing thermal and spectral measurement ranges. We have also been studying thermal transport across traditional interfaces that are heavily disordered; we have studied electron–phonon coupling, thermal boundary conductance, and substrate thermal conductivity changes resulting from changes in the interfacial structure. The experimental capabilities that we have developed have been fully operational for over a year and have been used to test the thermal properties of various nanosystems and interfaces through extensive collaboration. In addition to these experimental initiatives, we have also progressed in modeling and simulation, studying upper and lower limits to electron and phonon scattering with various Boltzmann-based theories. We have also extensively examined the effects of interface structure and morphology on phonon transport at interfaces, developing new lower limits for thermal conductance across interfaces as a function of structure. In addition, we have outlined a phonon modeling technique for one-dimensional thermal transport, the nonequilibrium Green's function (NEGF) technique, and have used this method to predict new phonon transport mechanisms that result from interface scattering that parallels interference in optics. This phonon wave interference mechanism can be controlled to give rise to thermal rectification. The research accomplishments to date from this project have resulted in 25 refereed journal publications.

Significance

One key to continued success with national security and defense issues lies in improving the fundamental scientific understanding of the complex dynamic behavior in modern weapon and sensor systems. With the increased power requirements in these systems, the thermal processes across material interfaces are becoming more critical. This study is examining the effects of structural disorder around interfaces on electron carrier scattering events that contribute to thermal boundary conductance.

Refereed Communications

P.E. Hopkins and J.R. Serrano, "Phonon Localization and Thermal Rectification in Asymmetric Harmonic Chains Using a Nonequilibrium Green's Function Formalism," *Physical Review B*, vol. 80, p. 201408R, 2009.

T.E. Beechem and P.E. Hopkins, "Predictions of Thermal Boundary Conductance for Systems of Disordered Solids and Interfaces," *Journal of Applied Physics*, vol. 106, p. 124301, December 2009.

P.E. Hopkins, "Contributions of Inter- and Intraband Excitations to Electron Heat Capacity and Electron–Phonon Coupling in Noble Metals," *Journal of Heat Transfer*, vol. 132, p. 014504, 2010.

P.E. Hopkins, T.E. Beechem, J.C. Duda, and P.M. Norris, "Effects of Subconduction Band Excitations on Thermal Conductance at Metal-Metal Interfaces," *Applied Physics Letters*, vol. 96, p. 011907, 2010.

P.E. Hopkins, "Influence of Electron-Boundary Scattering on Thermoreflectance Calculations After Intra- and Interband Transitions Induced by Short-Pulsed Laser Absorption," *Physical Review B*, vol. 81, p. 035413, 2010.

P.E. Hopkins, "Thermoreflectance Dependence on Fermi Surface Electron Number Density Perturbations," *Applied Physics Letters*, vol. 96, p. 041901, 2010.

P.E. Hopkins, E.V. Barnat, J.L. Cruz-Campa, M. Okandan, and G.N. Nielson, "Excitation Frequency Dependence of Auger Recombination in Surface Treated Si Wafers," *Journal of Applied Physics*, vol. 107, p. 053713, 2010.

P.E. Hopkins and T.E. Beechem, "Effects of Propagating and Localized Modes on the Minimum Phonon Thermal Conductivity of Layered Solids Above the Plateau," *Nanoscale and Microscale Thermophysical Engineering*, vol. 14, pp. 51-61, 2010.

J.C. Duda, P.E. Hopkins, J.L. Smoyer, M.L. Bauer, T.S. English, C.B. Saltonstall, and P.M. Norris, "On the Assumption of Detailed Balance in Prediction of Diffusive Transmission Probability During Interfacial Transport," *Nanoscale and Microscale Thermophysical Engineering*, vol. 14, pp. 21-33, 2010.

J.C. Duda, J.L. Smoyer, P.M. Norris, and P.E. Hopkins, "Inelastic Phonon Interactions at Solid-Graphite Interfaces," *Superlattices and Microstructures*, vol. 47, pp. 550-555, 2010.

P.E. Hopkins, J.R. Serrano, L.M. Phinney, S.P. Kearney, T.W. Grasser, and C.T. Harris, "Dimensionality Analysis of Thermal Transport in Multilayer Thin Film Systems," *Journal of Heat Transfer*, vol. 132, p. 081302, 2010.

P.E. Hopkins, L.M. Phinney, J.R. Serrano, and T.E. Beechem, "Effects of Surface Roughness and Oxide Layer on Thermal Boundary Conductance at Aluminum/Silicon Interfaces," *Physical Review B*, vol. 82, p. 085307, 2010.

T.E. Beechem, J.C. Duda, P.E. Hopkins, and P.M. Norris, "Contribution of Optical Phonons to Thermal Boundary Conductance," *Applied Physics Letters*, vol. 97, p. 061907, 2010.

Nanocomposite Materials for Efficient Solar Hydrogen Production

130820
Year 2 of 3
Principal Investigator: J. E. Miller

Project Purpose

Materials that utilize concentrated solar energy to produce hydrogen will potentially enable a long-term viable alternative to fossil fuels. The goal of this project is to create novel ceramic composite structures that can be used to convert solar energy into chemical energy in the form of hydrogen in a more efficient, straightforward, and possibly more cost-effective manner than solar-driven electrolysis. Advanced ceramic manufacturing methods will be used to provide an improvement over the current generation of materials because the active exposed phase will have a higher surface area to volume ratio within the oxygen-conducting bulk phase that should allow for greater materials utilization within each thermochemical cycle. The composites will be fabricated into honeycomb structures with cell sizes of 2, 4 and 6 mm, and with controlled macroscale surface-to-volume ratios that can be evaluated and compared at the National Solar Thermal Testing Facility (NSTTF) at Sandia in a solar water-splitting reactor. Several known and novel formulations will be evaluated. Key metrics important to achieving high efficiency that will be considered include overall active phase utilization (reaction extent) and reaction kinetics as a function of honeycomb cell size and the composite composition. The processing of the materials will take place in the Materials Science and Engineering Department at the University of Arizona. This work will help create a partnership between Sandia and the Arizona Research Institute for Solar Energy, whose mission is to help create innovative collaborations in order to accelerate research, development, and practical implementation of solar energy solutions to our energy needs.

Summary of Accomplishments

During the previous project year, we accomplished the following objectives:

- Developed powder processing and polymer co-extrusion methods for Fe_2O_3-ZrO_2 with increasing yttria content from 3 to 8 mol% composites.
- Extruded and laminated structures into 1- and 2-cm honeycomb structures with 2-, 4- and 6-mm cell size with wall thickness ranging from 0.2-0.5 mm.
- Designed binder burnout and sintering heat treatments.
- Designed and tested 1-cm test parts in lab scale reactor configuration.
- Analyzed CO production efficiencies of honeycomb test substrates as a function of surface area.
- Designed solar test cycles in order to evaluate honeycomb structure, geometry, and composite thermochemical efficiencies at NSTTF.
- The 2-cm-diameter test parts are currently still under investigation and require additional time in order to densify into larger-scale reactor test parts.

Significance

The design and implementation of new thermochemical materials that have ideal compositions and structures will enable cutting-edge technology for producing alternatives to fossil fuels. This work on sustainable energy sources supports the goals all four of the DOE strategic areas including Defense, Energy, Science and Environment and will help to strengthen our nation's long term energy independence and national security.

Nanotexturing of Surfaces to Reduce Melting Point

130821
Year 2 of 3
Principal Investigator: E. J. Garcia

Project Purpose

The reduced melting point of nanotextured silicon surfaces is far below theoretical prediction and has practical application for bonding in microsystems packaging. This three-year investigation focuses on: the following goals: Year one, advancing the science and technology of reduced melting point (RMP) in nanotextured silicon-on-insulator (SOI) wafers; year two, using RMP for bonding applications; and year 3, implementing the RMP bonding technique for microsystems. Year 1 research focuses on comparing theoretical predictions to results from melting experiments in which the geometry and size of the surface silicon on SOI wafers is varied. Preliminary experiments have shown that the melting point of silicon nanocrystals measuring 100 nm in diameter and 40 nm in thickness but with very fine features (< 5 nm) is reduced from its bulk value of 1412 °C to 1055 °C. This reduction deviates strongly from simple theoretical modeling that predicts that for a melting temperature of 1055 °C, the particle diameter would have to be ~0.8 nm. In this project, theoretical models will be adapted and used to predict the size-dependent melting of nanostructured silicon crystals using the appropriate characteristic dimension such as the size of fine features. An experiment will be designed to nanopattern the surface silicon on SOI wafers and heat the samples to determine their size-dependent melting point. The silicon nanocrystals will be characterized for morphology, size and crystallography, before and after heat treatment. Experimental results will be analyzed relative to theoretical predictions. Year 2 research will study the effect of doping the surface silicon to further reduce the melting point. Localized heating via electrical current through doped regions will be attempted. Bond strength and character will be studied as a function of temperature, pressure and other critical parameters. Year 3 will implement the RMP bonding technique on actual microsystems chips. This work is a collaboration with the University of Texas, El Paso (UTEP).

Summary of Accomplishments

We performed various heating experiments of sharp diamond-like shaped structures using various gases, pressures and furnaces. The gases used were nitrogen, hydrogen, argon, and 5% hydrogen in 95% nitrogen. The pressures used were 10 µtorr, 100 torr and 760 torr. Box, tube and vacuum furnaces were used. We discovered that oxygen and nitrogen are not suitable gases for shape transformation of the silicon nanostructures. Heating in oxygen creates silicon-dioxide. The data indicates that heating in nitrogen creates silicon-nitride that acts to stabilize the shape of the nanostructure. Therefore oxygen and nitrogen should be avoided. Moreover heating in high vacuum (10 µtorr) up to 1300 °C did not result in shape change. In contrast, heating in pure hydrogen or argon up to 1100 °C successfully resulted in dramatic shape change. We discovered that heating in hydrogen at 100 torr produced a sharp morphological transition in the temperature range between 945 °C and 996 °C. Samples heated at 945 °C did not demonstrate any change in shape while those heated at ≥ 996 °C showed a gross morphological transformation: Sharp features were smoothed out and the diamond-like structures were transformed to semispherical shapes. Samples heated in argon also demonstrated morphological change at 1100 °C at atmosphere pressure. However, these samples also showed undesirable surface pitting. We attempted initial bonding experiments, however, the nitrogen gas ambient prevented the samples from bonding. The effect of shape transformation in hydrogen may be strong enough for micrometer size features. The effect of patterning size, doping, and hydrogen concentration will be further explored to create unique fabrication paths for various functional structures. A new vacuum, hydrogen furnace will be installed at UTEP to facilitate the experiments. We will perform further bonding experiments in argon or hydrogen. We will attempt shape transformation of microsystem components.

Significance

This research will benefit our efforts to develop microsystem-based components for application to sensing and switching functions. The work is furthering the development of advanced microsystem packaging methodologies, in particular, how we can achieve hermetic bonding of packages in reduced temperature processing environments. Such environments will lesson the deleterious effects of high-temperature processing on microdevices during the packaging stage.

Neural Correlates of Attention

130823
Year 2 of 3
Principal Investigator: T. J. Shepodd

Project Purpose

Decision-making is a spatiotemporal process, requiring spatial elements of sensory information and motor planning as well as temporal elements of reward expectancy and learning (error-correction). Prior research at the Calfornia Institute of Technology has shown that the posterior parietal cortex is necessary for such sensorimotor integration, representing target locations, intended actions, and even reward-related signals. In this study, recent techniques of selective, reversible cortical lesioning combined with neurophysiological and behavioral monitoring will help elucidate the causal relationships of various functional areas within the intraparietal sulcus during voluntary decision-making behavior. In primates, GABAa agonists will inactivate either the parietal reach region (PRR), an area encompassing the medial intraparietal area, or the lateral intraparietal area (LIP) while the other region is monitored with electrophysiological recording and functional magnetic resonance imaging (fMRI). In humans, an analogous technique of repetitive transcranial magnetic stimulation (TMS) will be employed to create temporary, virtual lesions in the homologous parietal regions while reach and saccade decision tasks assess any behavioral deficits and simultaneous fMRI reveals the underlying neuronal changes responsible for any such behavioral changes. The purpose of these studies is to determine what kind of information flows between parietal areas LIP and PRR, and in what direction(s), as well as to or from other prefrontal and subcortical structures in the sensorimotor decision-making circuitry.

Summary of Accomplishments

In this study, recent techniques of selective, reversible cortical lesioning combined with neurophysiological and behavioral monitoring will help elucidate the causal relationships of various functional areas within the intraparietal sulcus during voluntary decision-making behavior. We have recruited 10 additional human subjects for functional and anatomical magnetic resonance imaging, and we have acquired data for these new subjects for all three tasks (retinotopy, topography, and choice). Preprocessing of all new these datasets and completed general linear modeling of seven of the datasets are complete. We will finalize the remaining datasets shortly. Dynamic causal modeling on all the new datasets as well as the initial pilot datasets has begun and will be completed shortly. The task is transitioning to the transcranial magnetic stimulation environment, and the program being rewritten to acquire eye data real-time using an EYELINK™ system in the TMS eyetracking environment — rather than the ISCAN™ system used in the fMRI environment. We are integrating the fMRI regions of interest identified from the prior data analyses into the infrared frameless stereotactic TMS system.

Significance

The project supports our mission in cognitive science. The work with monkeys and humans seeks to discover fundamentals about how the brain functions and the spatial relationship between cognition and the decision-making process. Understanding this process could enable us to impact fields as different as "controlling artificial limbs" to "understanding the enemy's thought processes."

The transition to human subjects has been successful; the studies in the upcoming year will be the most significant.

Particle Image Velocimetry Investigation of the Richtmyer-Meshkov Instability after Reshock

130826
Year 2 of 3
Principal Investigator: B. B. Cipiti

Project Purpose

Inertial confinement fusion (ICF) is hampered by a hydrodynamic instability, whereby any imperfection on the interface between the ablator and deuterium-tritium (DT) fuel is impulsively accelerated, resulting in mixing between the fuel and the ablator. The mixing can reduce the yield of the fuel and distort the converging shock wave so thermonuclear conditions are not reached. In ICF experiments, such as the Z Machine at Sandia and the National Ignition Facility at Lawrence Livermore National Laboratory, a thorough understanding of this instability is crucial to successful advancement of controlled nuclear fusion. This phenomenon is also important in stellar evolution behind a supernova and in the mixing of fuel and oxidizer in hypersonic vehicles. Known as the Richtmyer-Meshkov instability, it has been studied in shock tubes by observing the growth of the interface between a pair of gases. The proposed work will advance this research by using a membrane-less interface accelerated by a strong shock and reshock using the facilities at the University of Wisconsin-Madison Shock Tube Laboratory. Reshock represents an important physical condition because the shock wave will pass from the heavy gas into the light gas, analogous to a shock wave passing from the heavy ablator to the light DT fuel. After this heavy-to-light transversal, the perturbation reverses phase and continues to grow in amplitude with enhanced turbulent mixing. The work will utilize the Mie scattering of solid particles entrained in one of the gases to clearly distinguish the interface and to obtain density measurements from the spatial concentration of the particles. With this setup, a portion of the field will be imaged and successive images will be used for particle image velocimetry (PIV) analysis. The velocity field from PIV will resolve the location of vortex cores and produce turbulence statistics.

Summary of Accomplishments

Work over the past year has focused on studying the Richtmyer-Meshkov instability using PIV. One set of experiments used an interface of helium over sulfur hexafluoride with a near-single-mode, 2D perturbation. The interface was accelerated by a M = 1.14 shock wave and a pair of planar images were processed to produce a velocity field in the seeded helium gas. The bubble and spike growth rates, velocity distribution, vorticity fields, and circulation were obtained from these velocity fields. Numerical simulations were performed and compared favorably to the experimental results. The simulations confirmed the trends observed for the bubble and spike growth rates and the circulation. The simulations also showed the relation between vorticity distribution and SF_6 concentration, which helps identify the diffusion thickness of the experimental interface.

At higher Mach numbers, M = 1.7 for He/SF_6 and M = 2.1 for N_2/SF_6, mixing between the two gases caused index of refraction gradients near the interface. The planar images from these experiments were blurred near the interface, so individual particles could not be discerned. Interest was instead focused on the region above the interface where distortion was not occurring. PIV analysis in this region produced fluctuating kinetic energy spectra and gave evidence that the presence of the perturbation increases anisotropy between the streamwise and transverse directions.

Significance

The advancement of energy technology is one of the key missions of DOE. Fusion energy systems have been held back due to a number of engineering issues. Inertial confinement fusion faces a large challenge of withstanding the shock induced by the fusion ignition. This project seeks to gain new understanding in shock physics to allow for the design of advanced systems in the future.

Relating Polymer Dynamics to Molecular Packing

130827
Year 2 of 3
Principal Investigator: A. Frischknecht

Project Purpose

Our primary goal is the understanding of the interplay between molecular level structure/dynamics and the macroscopic, dynamic response of bulk, viscoelastic materials such as plastic bonded explosives (PBX). The most obvious application is the prediction of aging of, for instance, shaped charges as creep degrades their reliability. Although, in this case, the creep is due almost entirely to the polymeric binder, the general issues are relevant to more traditional glasses. We focus primarily on short polymer chains that are suitable models for PBX binders. In addition, we investigate a common spin model as an extreme case at the molecular level. This work is a collaboration with New Mexico Institute of Mining and Technology.

Experimental probes of dynamics response are often in the frequency domain. Mechanical spectroscopy probes explore structural rearrangement in a fairly direct manner. A sample is sheared in a sinusoidal manner, and the stress response is found to lag in a frequency-dependent manner. This leads to a storage and loss contribution of the dynamic modulus which can be used to predict the characteristic time and shape of the creep behavior. A related technique is dynamic calorimetry. The temperature is varied sinusoidally, and the energy response is found to lag, resulting in a dynamic heat capacity. Although experimentally less clear, dynamic calorimetry has a degree of computational convenience. In particular, it provides a direct link to potential energy rearrangement. Potential energy density, in turn, has been found to be useful in the finite element modeling of viscoelastic materials (particularly, the modeling and design of tires).

Questions addressed are the following: 1. How similar are structural and energetic rearrangements? 2. What signatures of molecular structure are in the dynamic heat capacity? 3. How does potential energy "clump"? 4. How do functional shape and relaxation time vary with temperature and density?

Summary of Accomplishments

We have investigated three system types in great detail: freely jointed, freely rotating, and torsional polymer chains. The first enforces bond lengths; the second enforces bond length and angles; the third includes a rotational potential in addition to bond length and angle restrictions. Bulk system dynamics have been probed in a variety of manners. Currently, the dynamic heat capacity has been the focus. We have developed a new simulation methodology for this and published a paper highlighting the approach. In these simulations, the temperature is varied in a sine wave and the in-phase and out-of-phase components of the energy response are tracked. In addition, we demonstrated that the technique could also be applied to spin models of the glass transition. Detailed analysis of the dynamic heat capacity of the aforementioned polymer systems is largely complete and a draft of the paper is expected in the near future.

Explanation of whole system dynamics is often expressed in the language of the potential energy landscape, which envisions the system as a single multidimensional "point." The underlying potential energy surface dictates the difficulty the system has moving from place to place. Our simulation method is well suited to probe the dynamics of the system specifically related to meta-basin transitions in the potential energy landscape. (paper in preparation). Finally, nonlinear behavior was investigated. This aspect of the project is still in its early stages; however, because of the important technological aspect of nonlinear effects, we plan to dedicate considerable time to this in the upcoming year. To date, our results are consistent with other experimental findings, and we plan to explore the sensitivity to molecular structure.

Significance

The project benefits the DOE science mission and national security by addressing the time/frequency rheological response of plastic-bonded explosives (PBX). Although a small percentage of the whole, the polymer binder has a marked effect on properties. Understanding the relationship between the molecular structure of an elastomer and its complex modulus (viscoelastic behavior) would, for example, permit the chemical aging of PBX to be linked to the mechanical properties of the material.

Refereed Communications

J.R. Brown, J.D. McCoy, and B. Borchers, “Theory and Simulation of the Dynamic Heat Capacity of the East Ising Model,” *Journal of Chemical Physics*, vol. 133, p. 064508, 2010.

High-Fidelity Nuclear Energy System Optimization

131333
Year 2 of 2
Principal Investigator: S. B. Rodriguez

Project Purpose

Nuclear technology sustainability and nuclear waste management are the key challenges for nuclear energy technology on its path towards broad acceptance and deployment. Minimization or elimination of high level waste (HLW) inventories (transuranics [TRUs] and long-lived fission products) warrants expansion of nuclear energy as a sustainable energy source ensuring energy independence and security. This project is focused on high-fidelity nuclear energy system optimization towards an environmentally benign, sustainable, and secure energy source. The analysis takes advantage of Generation IV reactor technologies and advanced fuel cycle options. This project defines a nuclear energy system as a configuration of nuclear reactors and corresponding fuel cycle components. The nuclear energy system performance is optimized under constraints of nuclear waste minimization and sustainability requirements targeting an environmentally benign energy source limit.

Recognizing the difficulties of spent nuclear fuel reprocessing and the virtual technical impossibility to reprocess transmutation fuel compositions containing higher actinides after their first irradiation cycle, it is desirable to assess technical characteristics of a nuclear system that would achieve the highest incineration rate of spent nuclear fuel compositions as a result of one-cycle irradiation. This project will identify system needs and performance requirements leading to the actinide-free high-level waste and perform technology optimization studies towards an environmentally benign system.

The analysis focuses on Generation IV VHTRs (very high temperature reactors) operating in an OTTO (once-through-then-out) mode with 3D reloading schemes in combination with fast spectrum systems (VHTR-FR scenarios), specifically accounting for performance optimization and nuclear waste management including nuclear waste minimization. The analysis will be performed for technologically feasible configurations with full accounting for the core physics in the 3D whole-core exact-geometry fuel cycle analysis using hybrid Monte Carlo methods. The modeling approach will be validated in experiment-to-code benchmark studies. The work is a collaboration with Texas A&M University.

Summary of Accomplishments

1. We have developed and implemented new high-fidelity integrated system method and analysis approaches for consistent and comprehensive evaluations of advanced fuel cycles leading to minimized TRU inventories.
2. We have developed detailed 3D whole-core models for analysis of the individual reactor systems of the nuclear energy system (NES). The models were validated and verified by performing experiment-to-code and/or code-to-code benchmarking procedures.
3. We performed and analyzed reactor core physics and material depletion calculations.
4. We assessed integrated safety management (ISM) performance by comparing it to standalone results acquired by manually linking the individual 3D whole-core models.
5. We implemented a method for assessing how variations in key system parameters affect the NES on multiple levels.
6. We have demonstrated the potential for implementing multi-objective optimization techniques within the ISM structure.
7. We performed parameter minimum/maximum searches and applied a method for weighting system

variables.

8. The NES has demonstrated great potential for providing safe, clean, and secure energy and doing so with foreseen advantages over the low enriched uranium once-through fuel cycle option.
9. Calculations for NES scenarios estimate that the HLW will decay to radiotoxicity levels matching the originating uranium ore in about 2,000 years.
10. The yearly savings in emissions for the replacement of coal would be 47.8 million metric tons of CO_2. For natural gas, it would be 19.1 million metric tons of CO_2 and for petroleum it would register at 40.2 million metric tons of CO_2. In more relative terms, the NES CO_2 emissions savings would be equivalent to taking 10.5 million cars of the road.

Significance

The proposed research is directly relevant to a variety of research programs led by the Department of Energy and Sandia, in particular, in the areas of modeling and systems analysis targeting high-fidelity analysis of nuclear systems capturing their physics features and environmentally benign energy technologies for secure energy future. The focus on nuclear fuel cycles directly addresses the grand challenge of nuclear technology — nuclear waste management.

A standalone configuration of the integrated safety management document is in preparation for submission to the Radiation Safety Information Computational Center for broad nuclear engineering community use.

Nanostructured Material for Advanced Energy Storage

135569
Year 2 of 2
Principal Investigator: N. S. Bell

Project Purpose

The purpose of this project is to create a magnesium ion battery cathode from a sol-gel precursor solution using the process of electrospinning. Magnesium batteries are a possible alternative to lithium ion and nickel metal hydride secondary batteries, both from scientific and applied perspectives. Magnesium has the second highest specific charge of all materials, is widely abundant and offers scientific challenges and opportunities due to its increased ionic diameter and dual charge. It also offers increased safety, reducing the risk of explosion or burning of batteries. The electrospinning technique can be applied to the rapid production of nanosized, fibrous precursors for an active cathode phase. We selected the Chevrel phase as cathode and use a recently established method to turn these materials into fibers with diameters ranging from 10 micron to sub-one-micron with Feret diameters of grains ranging from micrometers to nanometers. After processing, the submicron-sized fibers are of the composition $Mg_xMo_6S_8$. In this work, scanning electron microscopy, transmission electron microscopy, and electrochemical cycling testing are used to characterize the structure, morphology and performance of the fibers. We anticipated that the fibers with nanosized grains should have increased capacities and faster charge/discharge rates.

Summary of Accomplishments

We were successful in implementing the electrospinning process to develop cathodes with a high degree of cyclability. An electrospinning solution was prepared, and the electrospun material characterized and then constructed into a working battery cell to determine its electrochemical properties. We observed long-term stability with a 66% remaining capacity after 50 cycles at high temperatures. Because polyacrylonitrile was used in the precursor solution, the resulting fibers contained a large amount of carbon, post-heat-treatment. We obtained an improved match with x-ray diffraction Chevrel peak positions for a reacted sample without polyacrylonitrile.

Further work must be undertaken to increase the active mass content of the electrospun material. Currently, the active mass content is only 25% of the cathode disk. We also need to investigate the reasons why performance was significantly lower than theoretical predictions. This includes determining macrostructural effects on capacity, such as the grain size of the magnesium-Chevrel phase, identifying the presence of surface films post-storage or the formation of deposits during intercalation of the cathode that might hinder further intercalation of the Chevrel phase, and examining the products of the degradation from tested cells. In summary, the milestones were reached in synthesizing and conducting preliminary tests on magnesium-based nanoscale fibrous cathodes; however, more research on intercalation mechanisms and degradation mechanisms is needed to enhance and optimize the cathode material towards its theoretical performance values.

Significance

This research ties jointly to the DOE Missions of Energy and Science. Research on the development of secondary, i.e., rechargeable, batteries is being avidly pursued due to the prevalence and ubiquity of mobile devices and the need for energy storage from renewable resources. Magnesium-ion batteries show promise as an alternative. They have a high specific charge compared to materials beyond lithium, and magnesium is abundantly present in nature. Further benefits result from decreased risk of exploding or overheating of the batteries since magnesium is relatively inert compared with lithium.

This project applied processing methods to create a high surface area cathode for the Chevrel phase $Mg_2Mo_6S_8$ material and was successful. Many challenges remain for the adoption of magnesium-based batteries, primarily related to the prevention of surface film formation upon the magnesium anode, the volatility and anodic stability of electrolytes, and the development of cathodes with a high degree of magnesium intercalation and kinetics to yield high capacities. Research must explore the prevention of surface films either in terms of electrolyte composition, film removal from fibers by acid treatment, or electrospinning of Cu chevrel phase precursors to avoid the MgO surface film formation. Varying the heat treatment schedule to determine the effects of grain size on capacity or measuring the impurity concentrations and comparing them with electrochemical performance should also be actively pursued research areas.

Because the project is focused on the development of a novel battery chemistry based on magnesium ion conduction, successful outcomes will ultimately impact energy storage by increasing electron storage density in battery devices. This type of battery chemistry is novel and in very early stages of technological development. Therefore there is also significant potential for impact on fundamental science understanding.

Hazard Analysis and Visualization of Dynamic Complex Systems

135790
Year 2 of 3
Principal Investigator: N. N. Brown

Project Purpose

This project will seek to apply recent results toward two efforts: (1) the development of visualizations for the Systems-Theoretic Accident Modeling and Processes (STAMP) framework and (2) the development of a preliminary STAMP-based Hazard Analysis (STPA) methodology. These efforts are described below.

The first effort follows previous work suggesting possibilities for advancement by developing visual representations within the STAMP framework. This would assist in creating and understanding the analysis by simplifying the mental effort required — especially when communicating the results to people with diverse backgrounds. This visualization can be used later to construct an interactive STAMP tool to reinforce the creative analysis process and to present the analysis in a concise format. Because STPA and STAMP share similar structures, this visualization can later be adapted to the STPA method under development.

Another effort will involve applying a preliminary form of STPA to a real-world example by working with engineers unfamiliar with this approach. The focus will be on evolving this conceptual approach into a framework through an iterative process of observing the way it is used by humans and adapting the methodology to maximize its effectiveness. This plan is based on the idea that theoretical concepts are necessary but insufficient when considering the practical implementation of an approach. The ultimate goal is to develop a methodology with both solid theoretical concepts and practical implications for system safety engineering.

The work is a collaboration with the Massachusetts Institute of Technology.

Summary of Accomplishments

The following visualizations were developed: a) a time and control diagramming format that visualizes control actions from a STAMP analysis and clearly illustrates how and when information is distributed throughout the system; b) a flexible control structure representation that incorporates detailed internal structures for both human and physical components; c) an enhanced representation to convey not just differences between the intended control structure and the actual system control structure, but also the control structure that is perceived by humans in the system (i.e., the human operators).

We also conducted the preliminary application of an STPA methodology to an exemplary system. To address this milestone, a preliminary form of STPA was applied to an existing unmanned transfer vehicle system. The results were compared to a previous independent Fault Tree Analysis (FTA) of the system, and the preliminary STPA methodology was found to identify all the hazard causes of the FTA, as well as causal factors not found in the FTA.

We accrued accomplishments beyond the required milestones. As the research progressed, we discovered that the underlying models used by both STAMP and STPA might be further improved by exploring the inferred process state and the control algorithms used. A preliminary analysis was performed on an existing socio-technical system, and the potential improvements appear to be feasible and applicable to both human and non-human systems. As a result, more-detailed models are currently being developed and may be formally evaluated during the project's next year.

Significance

This proposal develops a model for social and organizational effects on safety that are necessary but not currently available. As such it is broadly applicable to diverse aspects of Sandia's and DOE's national security missions.

Processor Modeling for Use in Large-Scale Systems Models

137299
Year 2 of 3
Principal Investigator: E. DeBenedictis

Project Purpose

The complexity of contemporary and future computer processors has changed the methodology and tools that have been traditionally used for performance and design space analysis. Multicore, multithreaded architectures cannot be designed solely using cycle-accurate simulation, which is commonly used as a design tool for next-generation processors. Cycle-accurate simulation is very accurate and robust, but prohibitively slow, with slowdowns on the order of 10^4. Therefore, new techniques and tools must be developed for the design and analysis of processors and processor systems.

We are currently developing a Monte Carlo-based processor modeling technique that can be used for performance analysis and prediction of contemporary and future processor architectures. These models abstract the execution pipeline into a stochastic model using both processor and application characteristics. To date, we have developed models of the IBM Cell Broadband Engine, the Sun Niagara 1 and Niagara 2, and the Intel Itanium processors. This methodology is in its infancy and must be matured to enable the modeling of complex future architectures. Currently, we are only able to model in-order execution, single-threaded processors.

This is a project in collaboration with Presidential Early Career Awards for Scientists and Engineers awardee, Dr. Jeanine Cook of New Mexico State University.

Summary of Accomplishments

We have completed another iteration of validation on the single-core Opteron Monte Carlo processor model (MCPM), and are currently working on final validation. We integrated this model into the Sandia Structural Simulation Toolkit (SST). However, the SST simulator core was recently changed and we are now re-integrating all of our processor models back into SST. During the past year of this project, we developed a methodology to enhance our current modeling technique with the capability to model multicore processors. We implemented this methodology into our Niagara 2 processor model and are working on implementing the multicore Opteron model. Monte Carlo processor models developed in the past did not actually execute application instructions. In order to use these models in a larger SST simulation, we have been working on the development of a functional simulator front-end to MCPMs that will execute application instructions, store results, and pass these on to other system model components as necessary. This front-end is approximately 50% complete.

Our paper on the Niagara 2 processor models was published in the *International Conference on Parallel Processing*. We submitted a paper to the *International Workshop on Performance Modeling, Benchmarking, and Simulation of High Performance Computing Systems.* We are preparing another paper for submission to the same workshop on the Opteron model.

Significance

Microarchitecture simulation applies immediately to the design of high performance computers. These types of computers will be used by the Advanced Simulation and Computing initiative and other DOE missions for nuclear weapons simulation, extreme scalability initiatives for scientific research, in manufacturing facilities like the Microsystems and Engineering Sciences Applications facility and the Center for Integrated Nanotechnologies, and for intelligence community problems, and space computing. The tools developed will help evaluate designs that will become the basis of procurements, R&D contracts, and lab products.

Development of a System for Identification of Data

139708
Year 2 of 2
Principal Investigator: R. Custer

Project Purpose

The purpose of the project is to protect Sandia's most sensitive data. Loss of data confidentiality is a fundamental risk to any program. We do not currently have adequate tools and techniques to manage this risk. We must investigate new data confidentiality approaches that allow us to detect and attribute data leaks.

Electronic files can be copied infinitely and instantaneously. Electronic logs can be easily modified. Even if we are lucky enough to detect that the confidentiality of our electronic information has been compromised — a skilled attacker leaves no trace — finding the source of the compromise is all but impossible.

The purpose of this work is to create a comprehensive system for detecting information compromise. The goal of this system would be to address the complete information lifecycle, from creation to destruction.

Summary of Accomplishments

We designed and implemented a system for data identification that is easy to extend and augment. We developed new techniques for identifying data based on solutions suggested by subject matter experts from multiple organizations within Sandia. We implemented a system for data identification that utilized these techniques.

Significance

The development of new techniques to protect and track sensitive data will benefit Sandia, DOE, and the greater federal government community, while advancing the skills and state of the art. This work will provide the larger government complex with a unique capability to protect classified information.

Responsive Nanocomposites

141076
*Year 2 of 4**
Principal Investigator: T. J. Boyle

Project Purpose

The creation of environmentally responsive nanocomposites will result in materials that are much more robust and stable. To produce such nanocomposites requires that the surface interaction between functionalized nanoparticles and the matrix be better understood and controlled. This project will attack this mission related problem of interest by invoking a multidisciplinary approach based on predictive computational models and experimental verification using a series of well-controlled complex nanomaterials dispersed in a variety of elastomeric or soft materials. We will determine the proper chemical species and length of the functional groups and the required surface coverage density of morphologically and compositionally varied nanomaterials dispersed in these matrices. Our initial response stimuli will focus on temperature or hydration since these are two major areas of interest to Sandia's missions as well as our industrial collaborators. The project will be initiated by building on Sandia's expertise in the synthesis of size- and shape-controlled nanomaterials of varied compositions and functionalizations, nanocomposite self-assembly, and computational modeling of nanocomposites aided by several key university (Columbia University, Cornell University, University of Florida, Harvard University, University of New Mexico, Northwestern University, University of Texas, Washington University) and industrial partners with expertise in nanocomposite testing. Together, a model for nanocomposite mixtures that possess active or applied responses to temperature or hydration environmental changes will be developed.

Summary of Accomplishments

<u>Task 1 — solution synthesis nano (Boyle)</u>

- Produced uniform 5–10 nm charged δ^- (-COOH), δ^+ ($-NH_2$), neutral (-R) Au nanodots, functionalized graphene oxide platelets, CdE of different morphologies for interaction with elastomer
- Produced high-aspect-ratio nanowires and varied morphologies of TiO_2.
- Established baseline electrospinning processes of variety of polymers.
- Incorporated nanoparticles into electrospun polymers at low loads: Au in polyvinylpyrrolidone (PVP), CdE in PVP, graphene oxide platelets.
- Developing methods for removal of nanowires using electrostatic process for controlled delivery (Harvey Mudd interaction).
- Reversible and switchable surface properties of electrospun poly(N-isopropylacrylamide) functionalized with spirobenzopyran chromophore (PS-poly-NIPAM) and PS-poly-NIPAM-Au composite were achieved that showed surface properties between superhydrophobic and superhydrophilic.

<u>Task 02 – soft-templating nanosynthesis (Shelnutt)</u>

- Shaped Cu and Pt nanostructures produced by soft-templating and photocatalytic growth.
- Poly-3-hexylthiophene P3HT hole conductivity enhanced by metal dendrites at low loading.

<u>Task 03 – interfacial assemblies (Brinker)</u>

- For the first time in the highly crowded NP assembly arena, used in situ grazing incidence small angle X-ray scattering to follow NP/polymer self-assembly on an evaporating water droplet.
- Demonstrated poly(N-isopropylacrylamide) (poly-NIPAM) interfacial film formation at a water interface.

*This 36-month project spanned four fiscal years

- Developed a hydrogel polymerization approach compatible with multiphoton excited photochemical processing to achieve high resolution, 3D responsive hydrogel structures from the reaction mixture of acrylamide, acrylic acid, N,N'-methylenebisacrylamide, Igracure 819 in a ratio of 20:20:5:2 (w/v) dissolved in ethylene glycol.

Task 04 – graphene functionalization (Lambert)

- Prepared M_xCo_3-xO_4 nanoparticles (M = Cu, Ni, Fe, Mn and x = 0–1.0).
- Prepared reduced graphene oxide using aerosol-through-plasma.

Task 05 – computational calculations (Grest)

- Determined forces between coated silica nanoparticles in water.
- Determined structure of alkylsilane coated silica nanoparticles in polymers.
- Used primitive path analysis to determine entanglements between polymer grafted nanoparticles in polymeric matrix.

Significance

- Nanoparticle charged functionalization variations may lead to new discoveries in terms of determining the effectiveness of controlling dispersion in nanocomposites.
- The work is very relevant to chemically modified graphene (CMG)-based materials, which is a rapidly-growing field.
- We extended hydrogel chemical systems into 3D photopatterning, thereby providing the foundation to achieve precise, autonomous actuation of micro-mechanical components using environmental stimuli.
- PS-PNIPAAm and PS-PNIPAAm-Au composite responsive systems would be an interesting material in temperature dependent systems (i.e., car tires, chip manufacturing, wells).

Refereed Communications

T.J. Boyle, L.A.M. Ottley, and S.M. Hoppe, “pH Dependent Group 4 Nanoceramic Morphologies Generated from a Series of Comparable Dinuclear Group 4 Neo-Pentoxide Precursors,” to be published in *Inorganic Chemistry*.

P. Kim, L.D. Zarzar, X. Zhao, A. Sidorenko and J. Aizenberg, “Microbristle in Gels: Toward All-Polymer Reconfigurable Hybrid Surfaces,” *Soft Matter*, vol. 6, pp. 750-755, 2010.

T.J. Boyle, T.N. Lambert, H.D. Pratt, P. Lu, J.J.M. Griego, N. Bush, C.A. Chavez, and M. Welk, “Morphological and Phase Dependence of Nanotitania Materials Generated Under Extreme pH Conditions for Large Scale Production of TiO_2 Nanowires (basic) and Nanosquares or Nanrods,” *Journal of Materials Science*, vol. 45, p. 1744, 2010.

T.N. Lambert, C.A. Chavez, B. Hernandez-Sanchez, P. Lu, N.S. Bell, A. Ambrosini, T. Friedman, T.J. Boyle, D.R. Wheeler, and D.L. Huber, “Synthesis and Characterization of Titania-Graphene Nanocomposites,” *Journal of Physical Chemistry C.*, vol. 113, pp. 19812-19823, 2009.

T.N. Lambert, C.C. Luhrs, C.A. Chavez, S. Wakefield, T. Alam, and M. Brumbach, “Graphite Oxide as a Precursor for the Synthesis of Disordered Graphenes Using the Aerosol-Through-Plasma Method,” *Carbon*, vol. 48, pp. 4081-4089, 2010.

D.R. Heine, M.K. Petersen, and G.S. Grest, "Effect of Particle Shape and Charge on Bulk Rheology of Nanoparticle Suspensions," *Journal of Chemical Physics*, vol. 132, p. 184509, 2010.

M.K. Petersen, J. Matthew, D. Lane, and G.S. Grest, "Shear Rheology of Extended Nanoparticles," *Physical Review E*, vol. 82, p. 010201, 2010.

A. Miranda, E. Malheiro, E. Skiba, P. Quaresma, P.A. Carvalho, P. Eaton, B. de Castro, J.A. Shelnutt, and E. Pereira, "One-Pot Synthesis of Triangular Gold Nanoplates Allowing Broad and Fine Tuning of Edge Length," *Nanoscale*, vol. 2, pp. 2209-2216, 2010.

Thermokinetic/Mass-transfer Analysis of Carbon Capture for Reuse/Sequestration

141078
Year 2 of 2
Principal Investigator: C. Staiger

Project Purpose

Capture of CO_2 from the atmosphere is increasingly seen as an enabling technology for net neutral recycling of carbon dioxide, and as a potentially important tool for mitigating climate change. The technical feasibility of atmospheric carbon dioxide capture has not yet been unambiguously quantified, however. We propose to establish the boundary conditions and performance metrics of atmospheric CO_2 capture by: 1) analyzing the thermodynamic and kinetic controls over CO_2 uptake and release by sorbent media; 2) quantifying air flux constraints over achievable mass transfer; and 3) developing a detailed preliminary process model for CO_2 capture from air. The thermo-kinetic analysis of sorbent performance will seek to provide a technical basis for selecting and optimizing new capture or separations media. The examination of the physical constraints over engineered air fluxes will result in the development of a portfolio of wind control approaches that might be applied. The process model will provide a starting point for improving component performance. The media, wind engineering, and process analyses should together establish the achievable performance window for all atmospheric CO_2 capture approaches for reuse, recycling, or sequestration. This will enhance Sandia's efforts to develop low-net-carbon hydrocarbon fuels and build Sandia's reputation as a provider of a wide-range of climate mitigation tools.

Summary of Accomplishments

Our analysis suggests the following technical challenges must be met before capture of atmospheric CO_2 for conversion and recycle to hydrocarbon fuels or for re-use options can be considered plausible at the industrial scale.

1. Low-energy input air processing approaches must be pioneered to ensure regular and effective air flows through CO_2 sorbent media to ensure high production rates. Ideally these will take advantage of, or be engineered enhancements of, natural wind-generating thermal gradients. Air flows must be over-pressured to compensate for pressure drops or deflection that will naturally occur during passage through or around the media.
2. For aqueous CO_2 sorbents, air-water CO_2 transfer may be the step that limits overall process success. Using carbonic anhydrase or a similarly effective CO_2 hydration/dehydration catalytic agent is a potential enabler for an industrial scale CO_2 capture process.
3. Less-expensive solid CO_2 sorbents must be developed that are stable over very many catch and release cycles, have higher CO_2 capacities, and lower non-recuperable swing energies. Media and/or its support must be designed to minimize the pressure drop associated with the air processing.
4. Atmospheric CO_2 capture systems must be objectively evaluated, first at the bench scale and later at the pilot scale. A host of bench and pilot-testing has built confidence in flue gas capture approaches and driven significant progress. No such track record exists to benchmark and accelerate the development of atmospheric CO_2 capture approaches.

Significance

Establishing the fundamental thermodynamics and kinetic of atmospheric carbon capture will accelerate development of effective means of separating CO_2 from the atmosphere for beneficial reuse and sequestration. Both would contribute to the mission of achieving US energy and climate security.

Improved High-Temperature Solar Absorbers for use in Concentrating Solar Power Central Receiver Applications

141359
Year 2 of 2
Principal Investigator: A. Ambrosini

Project Purpose

Concentrating solar power (CSP) systems use solar absorbers to convert sunlight to electric power. Increased operating temperatures of the central receiver CSP process are necessary to lower the cost of the solar generated electricity by improving power cycle efficiencies and reducing thermal energy storage costs. In order for CSP to meet an electricity cost target of \$0.055/kWh, durable new materials are needed to cope with operating temperatures >600 ºC. Ideal absorbers must have high solar absorbance (>0.95) in the visible region and low thermal emittance (<0.05) in the IR region, be stable in air, and be low cost and readily manufacturable. In the case of central receivers, little effort has been invested in this area. The current coating technology (Pyromark High Temperature paint) has a solar absorbance in excess of 0.95 but a thermal emittance greater than 0.8 which results in large thermal losses at high temperatures. In addition, because solar receivers operate in air, these coatings have long-term stability issues that add to the operating costs of CSP facilities. This project will utilize solution-based synthesis techniques to prepare promising intrinsic absorbers (e.g., Si_3N_4-ZrB_2) and cermets and evaluate their efficacy as solar-selective coatings. Success in producing more-efficient solar-selective coatings for central receivers can help reduce costs and bring solar closer to cost parity with fossil fuels, a necessary factor for widespread implementation of alternative energy production technologies.

Summary of Accomplishments

In the course of this project, we have begun to develop film deposition methods onto stainless steel (SS304L) coupons using spin coating and dip coating techniques. In addition, we screened both commercially available materials (polysilazane, Co_3O_4) and lab-synthesized materials (spinels) for their optical and structural properties. Spinel oxides were chosen for their inherent high temperature and oxidation stability and their amenability to doping and substitution of a large number of transition metal cations, which should allow us to chemically tailor their properties. Durability tests have also been initiated with some preliminary success, in that the spinel coatings are stable in air at temperatures up to 600 °C, although they do begin to suffer from optical degradation at 800 °C. The oxide spinel materials continue to show promise as intrinsic solar-selective absorbance materials. They display relatively high absorbance and stability at high temperatures and in air. Their emittance values are still higher than preferred, but doping and cation-substitution strategies may still lead to lower values.

Significance

Cost parity with fossil-based power generation is a critical factor for widespread implementation of alternative energy production technologies. Such implementation benefits the US from both a national security and climate change perspective. The proposed work directly addresses the goals of the Energy, Resources, and Nonproliferation investment area by improving the costs and efficiencies of concentrating solar power for carbon-neutral electricity generation. The synthetic methods and new materials developed herein can be leveraged by other materials groups at Sandia. Success in solar selective coatings for central receivers can also be leveraged for other types of CSP, such as parabolic troughs.

Three Pathways to Enhanced Energy Storage

141370
Year 2 of 2
Principal Investigator: K. R. Zavadil

Project Purpose

The proposed project will evaluate three novel strategies to enable a five-fold improvement in battery performance. This work is proposed in response to a need for transformational changes in electrochemical energy storage devices (EESDs) for both transportation and stationary applications; applications that require specific energy and power densities that currently cannot be realized in a time- or cost-efficient manner. We contend that the path toward transformational advances lies in addressing three critical issues that promise to individually produce five-fold performance increases: 1) controlling passivation to better utilize the capacity available in developing materials systems; 2) development and control of novel electrode structures that minimize charge transport lengths and reduce parasitic interfacial loss; and 3) new energy storage reservoirs with greater capacity.

High-energy-density electrodes are passivated in battery systems by decomposition of the electrolyte leading to the formation of a solid electrolyte interphase (SEI) which dictates the resulting performance of the system. We propose to test a concept of using inorganic modification to produce stable SEIs whose properties can be investigated to establish the ground rules for passivation of a broader range of electrode materials. Capacity gains can also be achieved by minimizing the charge transport lengths allowing for more of the theoretical capacity to be used in a storage material at higher rates and at higher cell voltages. We propose to test the concept of fabricating three-dimensional electrode architectures based on extended pairs of electrode separated by tens of nanometer dimensions using templated synthesis. Alternate energy storage media based on multivalent electroactive materials represent an alternate approach to achieving stable, cost-effective, and safe storage systems. We propose to test the concept of using the multi-electron reduction of nitrogen to a nitride as an alternate storage scheme.

Summary of Accomplishments

The feasibility of sodium birnessite ($Na_2Mn(III)_2Mn(IV)_6O_{16}$) was studied as a negative electrode for rechargeable battery technology based on Li and Na ion insertion. Results showed that a Sandia synthesized birnessite initially exceeds its theoretical capacity for both Na and Li ions with initial cell discharge/recharge cycling. Low-rate cell cycling shows the Li ion capacity decreases to theoretical values, while an accentuated Na ion capacity is observed. Extended cell cycling at higher rates results in continued capacity fade with the Na ion exhibiting the better performance. The stability of NaSICON, a sodium super ion conductor, was explored through its surface reactions with metallic alkali metals, including Na and K, and with aqueous alkaline solutions. Results showed that the ceramic surface composition is stable to Na and K at the melting point of these metals. Thermodynamic calculation of the aqueous stability diagram was performed and predicted dissolution of the ceramic, increasing in degree with decreasing pH from highly alkaline to acidic and driven by the stability of a zirconium hydroxide cation. NaSICON surface analysis after extended variable pH aqueous exposure confirms this prediction, showing a divergent surface composition from the base ceramic composition driven by dissolution. Accelerated aging confirms that the formation of zirconium hydroxide surface layer plays a key role in the dissolution mechanism. Isotopic exchange studies with deuterated water were used to show that, despite these surface chemical changes, the ceramic is not susceptible to proton transport. The potential for using NaSICON as a separation membrane was demonstrated by developing a novel secondary Na:Iodine cell using ionic liquids. Cell operation at 45 ºC showed reversible cell cycling with reasonable cell voltages. Specific nanostructures such as copper and aluminum nanowire assemblies have been synthesized and explored as a stable current collector and an alloying matrix, respectively, for alkali metal anode chemistries.

Significance

The demonstration of Na birnessite as a viable cathode for rechargeable, nonaqueous, sodium battery chemistry is, to our knowledge, a previously unpublished accomplishment. The abundant presence of naturally occurring birnessite minerals coupled with widespread availability of sodium creates the possibility of developing a low-cost battery chemistry that competes quite favorably against Li ion technologies for stationary storage. The successful use of NaSICON as a viable solid electrolyte and separation membrane demonstrates that a core materials set exists and can be exploited for Na ion–based cell chemistries. The demonstrated sodium–polyiodide cell highlights the flexibility possible with developed cores materials allowing for the combination of seemingly incompatible half-cell chemistries. These collective accomplishments raise the possibility of additional coupling of metallic sodium with aqueous-based electrochemistry to greatly improve the energy and power densities by transitioning to batteries based on either Na ion insertion or oxygen negative electrodes, specifically metal-air cells.

The reality of achieving cost-effective electrical energy storage is that a suite of battery chemistries will be required to meet the nation’s needs for energy security. These battery chemistries, including the metallic sodium, show promise, with further development, in achieving long-term DOE cost goals of <$100/kW. Our stability studies with NaSICON focused on examining the surface stability with molten alkali metal and aqueous exposure show that the ceramic holds promise in enabling facile Na ion selective transport and stable barrier attributes. Our thermodynamic computation for NaSICON does raise some concerns over long-term stability of the ceramic for aqueous applications, but clearly delineates the future research requirements in this critical area of ensuring mechanically stable, perm-selective ionic transport required for realizing the alkali metal:air chemistries. Thermodynamic computation involving the metastability of birnessite highlights the importance of surface passivation layers and provides interesting insights into how electroactive materials for ion insertion or for electrocatalysis (i.e., manganese oxides are demonstrated oxygen reduction and oxygen evolution electrocatalysts) might be stabilized for longevity. Our work on nanowire assemblies indicates the potential for the discovery of unanticipated reversible and stable activity based on size reduction. With the exception of tin oxide, alkali metal alloy formation concept developments have stalled due to the absence of mechanical stability in these systems. The ability to synthesize hybrid structures where the shape anisotropy is an advantage and materials and processing costs are low raises intriguing possibilities for expanding alkali anode half cell chemistries beyond solid or molten sodium. The demonstrated nanostructure assemblies potentially lead to novel integration strategies for combining our core materials set in ways that promise enhancement in energy storage capability and efficiency.

Innovative Electric Power Grid Architecture for High-Penetration Distributed Renewable Energy Generation

141679
Year 2 of 2
Principal Investigator: A. L. Lentine

Project Purpose

Increasing renewable energy generation is a key element in gaining energy independence and decreasing global warming. Within ten years, distributed renewable generation (for example, solar photovoltaic), is expected to be cost competitive with centralized coal generation, yet the current electric power grid is ill-equipped to handle a large penetration of distributed renewable generation. This is largely because the control algorithms, hardware, and software do not exist to maintain stability of the power grid in the face of the variable supply of electricity from changing weather conditions. In addition, today's grid cannot safely and securely allow the bidirectional power transport in the distribution layer that optimizes efficiency and reliability in the absence of a strong grid connection.

We propose a new grid architecture very different from today's and well beyond industries' version of the "smart grid" of tomorrow. It will actively manage generation, storage, and loads in a distributed manner to avoid the vulnerabilities and single points of failure common to centralized control approaches. The control algorithms will rely on a low-power, high-security sensing network to route the required measured information to the control hardware. A new class of voltage control devices is needed at all points in the grid hierarchy, controllers that adjust voltage magnitudes and phases continuously in response to changing renewable generation, replacing the mechanical relays of today's voltage regulators and reactive power compensators that would quickly wear out under such conditions. In this project, we will complete a preliminary high-level design of the architecture, control algorithms, power electronics, communications, sensing, element models, and scaling analysis for this new grid paradigm.

Summary of Accomplishments

- Gained a thorough understanding of the grid control problem in a scenario with high penetration of renewable energy resources (wind and photovoltaic)
- Developed a reference network and identified hardware sensing and control elements
- Identified key technologies for power electronics elements
- Identified key areas for further study of control of these networks

Significance

Transitioning the grid from its current centralized structure to a distributed intelligent grid enables the transition of society from fossil-fuel-based energy to a carbon-neutral, sustainable, and secure energy infrastructure. This project and interdisciplinary program will utilize Sandia's leadership position in nonlinear control theories, high performance computing, semiconductor devices, energy systems, and secure communications to contribute to that goal.

Nature Versus Nurture in Cellular Behavior and Disease

141704
Year 1 of 3
Principal Investigator: C. J. Brinker

Project Purpose

Microenvironmental effects on cellular behavior are recognized as crucial to the understanding of a diverse spectrum of problems including onset of infection, cancer metastasis, drug resistance, TB dormancy, and nanoparticle toxicology. Progress on understanding environmental effects, however, is hindered by an inability to incorporate cells into 3D-architectures that better represent the nanostructured extracellular matrix, tissues, or niches, where cells may reside in vivo. Also, there is limited understanding of strategies needed to target, deliver drugs, and kill dormant, drug-resistant and other rare cellular states induced by environmental factors. The purposes of this project are two-fold. First, we will discover and understand how engineered 3D microenvironments influence the behavior of bacterial, yeast, and mammalian cells. Second, we will use this understanding along with our expertise in nanofabrication to create new classes of targeted nanoparticle delivery agents. These purposes are strongly interrelated because our ultimate goal is to use engineered 3D-environments to induce uniform populations of dormant or drug resistant cells as targets for drug delivery strategies. Our approach uses self-assembly and two-photon protein lithography to create 3D nano-to-microscale matrices engineered to mimic specific in vivo environments. Adaptation/differentiation of cells (bacteria, yeast, and cancer) integrated within these matrices will be followed by fluorescent molecular markers of cell cycle, metabolic state gene profiling, etc. For cancer, induced drug-resistant states will be used as targets for phage display affinity studies and will also be reintroduced into lithographically defined tissue replicas to simulate metastatic recolonization. Phage display identified peptides will be used to create new nanoparticle vectors, protocells and virus-like particles (VLPs), designed to selectively deliver drugs, imaging agents, or other cargo to arbitrary cancer cell types including dormant, metastatic, or cancer stem cells. The integrated cellular systems we propose will also be relevant to the development of next-generation platforms for assessing nanoparticle toxicology.

Summary of Accomplishments

During the past year we have achieved the following: 1) We have adapted our tailorable hybrid bio/inorganic 3D matrices, known to induce long-term non-replicative viability in microbes to cancer hepatocarcinoma (HCC) cells. Our approach enables isolation of individual cells and induces a synchronous population of dormant, drug-resistant cells. 2) We demonstrated the ability of two-photon protein lithography to define arbitrary protein-based scaffolds and compartments with gray-scale, i.e. exposure-based optical control of the elastic modulus (measured in situ using a cantilever beam technique). The modulus can be tuned over the complete range relevant for physiological tissues. 3) We developed porous nanoparticle-supported lipid bilayers (protocells), a new class of targeted nanocarriers that, due to a unique set of biophysical properties, simultaneously addresses multiple challenges associated with targeted delivery, including specificity, a high capacity for disparate cargo types, controllable cargo release, stability, solubility, biocompatibility, and lack of immunogenicity. Protocells, when modified with a low density of targeting peptide (SP94) that binds to HCC, exhibit a 10,000-fold greater affinity for HCC than for normal human hepatocytes, endothelial cells, and immune cells. We show that this enhanced binding affinity is due to multivalent interactions of targeting ligands with cancer cell surface receptors, enabled by the fluidity and stability of the supported lipid bilayer on the protocell surface. 4) We encapsidated representative types of cargo (drugs, siRNA, and protein toxins) and imaging agents (quantum dots) within the interior volume of MS2 VLPs and showed that MS2 VLPs are capable of simultaneously encapsidating and delivering a variety of therapeutic and diagnostic agents selectively to HCC. 5) We initiated nanoparticle toxicology studies within a 3D microenvironment.

Significance

Significance to targeted drug delivery It has been long recognized that the pharmacological properties of conventional free drugs can be improved through their targeted delivery using nanocarriers. To date, passive targeting strategies employing liposomes or polymer-protein conjugates for drug encapsulation or complexation are the basis for several families of commercially available drugs and therapeutics, but there are only a few clinically approved drugs that selectively target diseased cells through specific biomolecular interactions. During the past year we developed porous nanoparticle-supported lipid bilayers (called protocells) as a new class of targeted drug delivery nanocarrier that meets the current primary challenges for selective drug delivery and that promises to serve as a universal platform enabling delivery and controlled release of the diverse spectrum of drugs, therapeutics, and imaging agents currently being pursued in biomedical research. Protocells synergistically combine the properties of liposomes (un-supported spherically shaped lipid bilayers) and porous silica nanoparticles, each of which represents an emerging strategy for drug delivery. In combination, we harness the enormous cargo capacity and stability of the porous silica nanoparticle and the biocompatibility and fluidity of the lipid bilayer. We find that conjugation of a low density of targeting peptides to the fluid lipid bilayer fused to the porous nanoparticle core effects highly specific binding to and internalization within hepatocarinoma (Hep3B) cells through a multivalency effect enabled by ligand mobility and peptide recruitment to cancer cell surface receptors. However, the low density of binding peptides minimizes nonspecific binding to hepatocytes and epithelial cells and suppresses the immune response. Exploiting the high adsorption capacity of the nanoporous particle core, we demonstrated efficient loading and delivery of chemotherapeutic agents, toxins, siRNA, plasmids, nanoparticles, and cocktails to Hep3B. Compared to corresponding state of the art, targeted liposomes, protocells are shown to exhibit higher selectivity, stability, and cargo capacity, and multicomponent cargo loading and delivery is easily accomplished. In combination, these advantages result in a million-fold greater cytotoxic efficiency of protocells. Furthermore our generic system should be easily adapted to arbitrary cell types by identification and implementation of new targeting ligands. Because the supported lipid bilayer can be conjugated with multiple ligands and is reconfigurable, a single protocell might be able to target the multiple subtypes of a heterogeneous cancer cell population, necessary for curing cancer.

Significance to 3D Microenvironments Cellular integration into self-assembled/lithographically defined matrices has the potential to create new biotic/abiotic functional nanocomposites for ultrasensitive cell-based environmental sensors or platforms for detecting disease outbreak and mimicking metastasis. We have developed two unique types of engineered cellular microenvironments (via cell-directed integration and two-photon protein lithography) and have shown heretofore unknown cellular behaviors like uniform cell cycle synchronization, induction of drug resistance, and quorum sensing at the individual cell level. The promise is that we can exploit our discoveries to make new types of platforms to understand and direct biology. These strategies are also promising for the development of next-generation nanotoxicology platforms to allow testing within engineered 3D matrices, which better represent in vivo conditions.

Refereed Communications

J.C. Harper, C. Khirpin, E.C. Carnes, C.E. Ashley, D.M. Lopez, T. Savage, H. Jones, R. Davis, D. Nunez, L.M. Brinker, B.J. Kaehr, S. Brozik, and C.J. Brinker, "Cell-Directed Integration into 3D Lipid-Silica Nanostructured Matrices," *ACS Nano*, vol. 4, pp. 5539-5550, September 2010.

Z. Chen, Y.B. Jiang, D.R. Dunphy, D.P. Adams, C. Hodges, N.G. Liu, N. Zhang, G. Xomeritakis, N.R. Aluru, S.J. Gaik, H.W. Hillhouse, and C.J. Brinker, "DNA Translocation Through an Array of Kinked Nanopores," *Nature Materials*, vol. 9, pp. 667-675, August 2010.

B.J. Kaehr, and C J. Brinker, "Using Bacterial Cell Growth to Template Catalytic Asymmetry," *Chemical Communications*, vol. 46, pp. 5268-5270, June 2010.

C.Y. Khripin, C.J. Brinker, and B.J. Kaehr, "Mechanically Tunable Multiphoton Fabricated Protein Hydrogels Investigated Using Atomic Force Microscopy," *Soft Matter*, vol. 6, pp. 2842-2848, July 2010.

E.L. Kendall, E. Mills, J.W. Liu, X.M. Jiang, C.J. Brinker, and B.J. Kaehr, "Salt-Induced Lipid Transfer Between Colloidal Supported Lipid Bilayers, " *Soft Matter*, vol. 6, pp. 2628-2632, June 2010.

T.L. Ward, Y.S. Cheng, J.W. Liu, and C.J. Brinker, "Aerosol Fabrication of Hollow Mesoporous Silica Nanoparticles and Encapsulation of L-Methionine as a Candidate Drug Cargo," *Chemical Communications*, vol. 46, pp. 3019-3021, March 2010.

E.C. Carnes, D.M. Lopez, N.P. Donegan, A. Cheung, H. Gresham, G.S. Timmins, and C.J. Brinker, "Confinement-Induced Quorum Sensing of Individual Staphylococcus Aureus Bacteria," *Nature Chemical Biology*, vol. 6, pp. 41-45, January 2010.

Understanding the Fundamentals of Plastic Deformation

141712
Year 1 of 3
Principal Investigator: C. R. Weinberger

Project Purpose

Predicting material response from fundamental physics has been a major goal of science and engineering for the last 70 years. This basic problem is important to Sandia due to its need to predict the material response for a wide range of applications including nuclear stockpile stewardship, Department of Defense technologies, and fundamental science. However, predicting how a material will deform based on its microstructure and loading conditions is still a very challenging problem. This project is aimed at building models to answer a few key questions regarding predicting the mechanical response of materials. This work will investigate three areas important to modeling material mechanical behavior: dislocation nucleation, dislocation multiplication, and the homogenization of dislocation ensembles. All three of these aspects involve dislocations, which are the fundamental carriers of plastic deformation in metals. Dislocations are line defects in crystals and are boundaries between regions of relative slip in the crystal lattice. Studying dislocations in metals is fundamentally important because their behavior directly governs the plastic behavior of the material under a wide range of loading conditions and temperatures. They also are involved in the ductile-to-brittle transition of metals and semiconductors, and plastic motion is important in fragmentation. Therefore, understanding dislocation behavior is tantamount to understanding a material's mechanical response. The focus of this work will be on micro- and nano-scale systems such as micropillars and nanoscale crystals.

Summary of Accomplishments

The first milestone concerns dislocation motion and multiplication in thin films and other small volumes. We have investigated initial dislocation motion in thin films in order to determine forces, in addition to image forces, that act on a dislocation. Our findings indicate that, for edge dislocations oriented perpendicular to the film's surface, that additional drag forces do exist and scale inversely with length. These results also show for dislocations parallel to the film surface, that thickness of the film does not change the motion significantly until the film is less than 5 nanometers. This result is important because it contradicts previous work on mobility at the nanoscale, and a comment to *Physical Review Letters* was submitted to clarify this contradiction.

Collaboration with the Center for Integrated Nanotechnologies (CINT) has been established for dislocation nucleation modeling. The researchers at CINT are doing high-resolution transmission electron microscopy (HRTEM) investigation of plasticity in gold nanowires, which is dominated by dislocation nucleation. This will provide an excellent opportunity to gauge the success of computational models.

We have also made progress toward homogenization. An initial study into the collective behavior of screw dislocations in a rod under torsion is nearly completed. In this study, we developed a continuum model for the structure, energy, and plasticity of these types of dislocations. We compared this model against atomistic simulations to verify the energy of collections of these dislocations. We also compare the plasticity caused by these dislocations from a molecular dynamics, discrete dislocation dynamics and semi-continuum point of view. One specific finding is a relationship between the plastic twist and the number of dislocations and effective dislocation distribution size. This work is a first step in homogenization because it shows a link between the dislocation distribution, plastic twist, and the torque in the rod.

Significance

Sandia's success relies on being at the forefront of materials characterization, modeling and development. The proposed work will provide an improved fundamental basis for the development of materials models for the full range of Sandia programs. These capabilities are important for a wide range of applications in our national security missions, including nuclear stockpile stewardship, Department of Defense technologies, and fundamental science.

Refereed Communications

C.R. Weinberger, "Comment on 'Lattice Resistance to Dislocation Motion at the Nanoscale,'" *Physical Review Letters*, vol. 105, p. 099601, August 2010.

C.R. Weinberger, "Dislocation Drag at the Nanoscale," *Acta Materialia*, vol. 58, pp. 6535-6541, November 2010.

Development of First-Principles Methodologies to Study Electro-Catalytic Reactions at Metal/Electrolyte Interfaces

141927
Year 1 of 3
Principal Investigator: B. Debusschere

Project Purpose

The purpose of the project is to understand electrochemical reactions occurring at interfaces of electron- and ion-conducting materials. These reactions are critical for many devices associated with the conversion between different forms of energy (mainly electrical, chemical, and solar). For example, electrochemical reactions at metal/electrolyte interfaces are important for fuel cells, electrolyzers, batteries, and photo-electrochemical cells. These processes involve direct conversion between chemical and electrical energy. Fuel cells operate by electrochemically oxidizing a fuel (such as hydrogen, fossil, or even bio-renewable fuels), which is rich in chemical energy, converting its chemical energy into electricity. While the electrochemical reactions are important, the molecular mechanisms that govern these transformations are poorly understood, leading to suboptimal device design and performance. The main difficulties in the development of an improved molecular understanding stem from an inherent inaccessibility of the metal/electrolyte interface sites to experimental probes. Additional complications are related to the presence of high electric fields and high potential biases at the interfaces.

To address these issues, this project, in collaboration with the University of Michigan, will develop a computational approach, based on first-principles calculations, which will allow the probing of electrochemical reactions at metal/electrolyte interfaces. The proposed approach will incorporate the effects of potential bias and electric fields, treated with first-principles methods. This framework will allow us to obtain molecular information that is virtually impossible to obtain through other means. We anticipate that the project will, on one hand, advance our ability to model molecular electrochemical transformation from first principles and on the other hand provide us with molecular information that is critical for the formulation of superior new materials for electrochemical transformations, including materials for fuel cells, electrolyzers, and batteries.

Summary of Accomplishments

A general framework was developed to study electrochemical transformations at solid/electrolyte interfaces. We demonstrated our approach in the context of the oxygen evolution half-reaction (OER) in water splitting processes and the oxygen reduction reaction (ORR). Quantum Density Functional Theory (DFT) provided insights on the potential energy surfaces of these reactions for a very small length scale. Metropolis Monte Carlo simulations increased the length scale by an order of magnitude, and determined oxygen and hydroxide coverage on a Pt(111) surface for varying operating potentials of a water splitting device. At low operating potentials near the standard hydrogen electrode (0 V), there is no driving force to split water on the surface and therefore the surface is clean. As the potential increases, water begins partially dissociating, populating the surface with hydroxide. At higher potentials around 1 V, atomic O begins forming by deprotonation of hydroxide. Around 1.23V, the surface of Pt has a high concentration of both hydroxide and O adsorbates. The presence and amounts of these adsorbates at operating potentials affects the kinetics of ORR and OER. Therefore the ability to know the coverage values is critical for the current goals of assessing the kinetics.

We have accomplished two major goals: 1) we have developed a general methodology that will allow us to study heterogeneous electrocatalytic reactions from first principles using DFT calculations, and 2) we have combined the first principles DFT studies with lattice gas Hamiltonian cluster expansion methods to extend our studies to larger length scales. These goals lay the groundwork for extending the theoretical studies to include reaction kinetics and for generalizations to include other materials and devices.

Significance

Modern first-principles theoretical tools have already had a significant impact in the discovery of new solid catalysts for ammonia synthesis, ethylene epoxidation, and hydrocarbon reforming. The impact of these techniques in the field of electrochemical conversion is significantly less pronounced. The proposed computational approach will be employed to study the basic molecular processes governing the behavior of various electrochemical systems and to unearth the critical sources of energy losses in electrochemical devices.

This work will yield a computational approach that will easily be used in the analysis of any system where chemical transformations at metal/electrolyte interfaces are important, including batteries, fuel cells, and electrolyzers. This work will enable the performance optimization of these devices through the choice of proper materials and operational conditions. The key accomplishments will allow us to move towards systematic knowledge-based approaches to discovery of new materials for electrochemical conversion, rather than empirical trial-and-error experimental approaches.

By providing fundamental insight, this work will support the DOE missions in terms of better science, improved energy efficiency, pollution reduction, and enablement of renewable energy. This will allow better environmental stewardship, and support DOE’s national security goal by reducing the dependence on fossil fuels and reducing the impact of energy use on climate change.

Covalently Cross-Linked Diels-Alder Polymer Networks

141928
Year 1 of 3
Principal Investigator: B. J. Anderson

Project Purpose

The polymer networks formed by traditional covalent linkages, such as those in novolac and epoxy thermosets, are nearly indestructible under most environmental conditions; however, this stability renders them intractable to post-polymerization manipulation. Incorporation of labile covalent bonds that can be irreversibly degraded extends the utility, but at the cost of permanent destruction of the material. The incorporation of covalent bonds that can be reversibly broken or rearranged into the network allows for the creation of living polymers that can be readily, and repeatedly, manipulated post-polymerization. Unlike many conventional gels, these reversible gels display capabilities such as mechanical actuation, stress relief, and a reversible gel-to-sol transition. The selection of appropriate reactions is the key aspect of design. Such reactions must be readily controllable through external means (e.g., temperature, pH, concentration, or illumination) and highly selective to avoid side reactions. One such reaction is the Diels-Alder (DA) reaction, a [4+2] cycloaddition that is readily reversible at elevated temperatures. Our partners at the University of Colorado have explored the use of the DA reaction in polymer networks formed by the condensation of multifunctional monomers. Using a combination of kinetic studies and rheological measurements, the DA reaction was shown to exhibit an Arrhenius dependence on temperature enabling the extent of reaction to be readily controlled. When heated to elevated temperatures, the material transitions from a network polymer to a liquid composed of oligomers. The proposed work is directed towards the control of the temperature activated gel-to-sol transition by studying the reaction thermodynamics and network architecture.

Summary of Accomplishments

A paper entitled “Externally Triggered Healing of a Thermoreversible Covalent Network via Self-limited Hysteresis Heating” was accepted for publication in *Advanced Materials*. This communication demonstrated the ability of a thermally reversible covalent network to heat via hysteresis in a radiofrequency electromagnetic field and heal damage via polymer network rearrangement. The use of chromium oxide particles as a magnetic susceptor allowed the material to heat above the sol-gel transition temperature and readily flow to heal fractures; however, the self-limiting nature of the heating mechanism prevented the material from heating to a temperature where destruction decomposition would occur. We demonstrated that the material could be fractured and healed at least ten times with no change in either the modulus or ultimate strength. Healing was rapid, requiring only 100-second exposure to the field. Furthermore, while the full value of the strength took 12 hours to recover, a significant portion was recovered within minutes.

A manuscript entitled “Photoinitiated Click Reactions: Spatial and Temporal Control of the Alkyne—Azide Reaction,” has been submitted to *Nature Chemistry*. This communication describes a photochemical process enabling the spatial and temporal control of the copper catalyzed azide-alkyne cycloaddition (CuAAC reaction). In this paper, the copper(I) catalyst was generated by the radical mediated reduction of copper (II). Nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy confirmed the reaction mechanism and the temporal control of small molecule reactions. We demonstrated the spatial control of the reaction by patterning the formation and in situ labeling of hydrogels. This procedure appears to be readily extendable to other azide and alkyne species, allowing the patterning of a vast library of developed materials.

Significance

The project benefits the DOE science mission and national security by developing covalently cross-linked polymer networks that can be used in a variety of nuclear weapons, defense, and energy applications. Further, the research will begin the process of developing a fundamental understanding of the materials properties and of the aging behavior in relevant environments. Specifically, cycloaddition reactions are explored as a means for producing materials with novel properties.

Cycloadditions are a broad class of reactions where unsaturated species combine to form a cyclic adduct with reduced bond multiplicity. Consequently, unlike condensation reactions, no small molecule species are produced, permitting the formation of high molecular weight species and avoiding plasticization. Furthermore, problems plaguing addition polymerization mechanisms such as reactions with water and oxygen are avoided. As such, cycloadditions are well suited to both the synthesis and modification of polymers. Despite such inherent advantages and widespread use in small molecule synthesis, cycloadditions have been seldom utilized by the polymer community as evidenced by their near or complete omission in the literature of the field. Unlike many other reactions, the DA reaction is often reversible and can be used for synthesizing materials containing dynamic covalent bonds. While all bimolecular reactions are, in principle, reversible, few reactions are robust enough to synthesize a polymer that can be repeatedly polymerized and depolymerized. Often, the chief difficulties are the high-temperature decomposition reactions common to all organic materials, e.g., the ceiling temperature often exceeds the decomposition temperature of many polymers formed via addition mechanisms. Synthesizing materials using the Diels-Alder reactions presents the possibility of creating novel materials such as weak chemical gels, self-healing materials, and shape memory materials.

While the Husigen cycloaddition of azides and alkynes is typically sluggish, a rate acceleration of approximately 10^7 is achieved by the addition of Cu(I), and high yields are readily obtained. Furthermore, the invisibility of azides and alkynes to many functional groups, the ability to use a variety of solvents, and the reaction's tolerance of a wide pH range enable reliable results in diverse applications. Telechelic azide and alkyne polymers are readily synthesized by controlled radical polymerization techniques such as atom transfer radical polymerization and reversible addition fragmentation chain transfer polymerization. These advantages have led to a "Lego-like" approach to the fabrication of complex macromolecular structures, and the CuAAC reaction has become ubiquitous. Unfortunately, spatial control of the CuAAC reaction has been limited to surfaces, using techniques such as microcontact printing and scanning-probe lithography. Methods for patterning the CuAAC reaction would both greatly increase the utility of the CuAAC reaction and increase the amount of materials that can be patterned using photolithographic techniques.

Refereed Communications

B.J. Adzima, C.J. Kloxin, and C.N. Bowman, "Externally Triggered Healing of a Thermoreversible Covalent Network via Self-Limited Hysteresis Heating," *Advanced Materials*, vol. 22, pp. 2784-2787, July 2010.

Effect of Doping on the Performance of Solid-Oxide Fuel Cell Electrolytes Produced by a Combination of Suspension Plasma Spray and Very Low Pressure Plasma Spray

141929
Year 1 of 3
Principal Investigator: A. C. Hall

Project Purpose

Meeting increasing worldwide energy demands will require every available energy technology, including nuclear, solar, wind, clean-burning coal, and hydrogen. Solid oxide fuel cells (SOFCs), which are powered by hydrogen, provide a direct mechanism for converting fuel into electrical energy. SOFCs have a relatively simple design: oxygen from air is supplied to a cathode where O_2^- is formed, O_2^- molecules then diffuse through an oxygen conducting electrolyte to the fuel cell anode. Hydrogen fuel supplied to the anode reacts with O_2^- to form H_2O, releasing electrons, and generating electricity. Advantages of SOFCs include no moving parts, no expensive platinum catalysts, and no emission of SO_x and NO_x.

Despite the successes of developing SOFCs, there is still a need for improvement of SOFC technology, particularly the electrolyte materials. The ideal electrolyte meets the following criteria: (1) it is applied easily to nonplanar shapes, (2) it is both dense and thin (<50 microns), and (3) it has optimized oxygen ion conductivity. Plasma-spray coating techniques are a very promising way to prepare electrolytes on complex surfaces. However, conventional plasma-deposited coatings have high porosities and cannot be applied in thin layers (<50 microns) suitable for electrolytes. Also, control of the final composition of the electrolyte is limited to the composition of the starting feed stock powders that are plasma-sprayed.

We propose investigating SOFC electrolytes by combining suspension plasma spray (SPS), a new spray technique being developed by Purdue University, with a unique plasma spray process (very low pressure plasma spray) available at Sandia. Combination of these two processes will allow preparation of thin (<50 microns) dense coatings with highly controlled compositions, thus allowing better understanding of, and improvement to, SOFC electrolytes.

Summary of Accomplishments

Feasibility of the combined suspension plasma spray (SPS) and a very low pressure plasma spray (VLPPS) coating preparation process has been demonstrated. This includes the preparation of thin and dense electrolyte coatings, the preparation of doped electrolyte coatings, as well as the fabrication and use of a solid oxide fuel cell (SOFC) test rig to evaluate the electrolyte performance. The SPS/VLPPS process has been proven capable of consistently producing well-adhered coatings in thicknesses of 5-10 µm. The SOFC test results show improved performance with scandium doping of yttria stabilized zirconia (YSZ) relative to the un-doped YSZ, though performance is not yet competitive with leading electrolyte research. Significant information has been gathered by using experimental approaches to explore process parameters, including plasma torch power, standoff distance, dopant concentration, spray time, and powder loading.

Clogging in the suspension spray nozzle, the primary technical problem with this process, has been resolved through the development of improved operating techniques for the SPS/VLPPS equipment, as well as by refining the suspension preparation process. Also, a water cooled copper cold plate has been fabricated to resolve overheating problems caused by the high heat flux from the plasma that had previously limited plasma torch power to 70 kV at a 43-inch standoff distance. This cold plate will also allow exploration of the effect of substrate temperature on the coating process, as well as permit the testing of both higher plasma torch powers and shorter standoff distances.

Significance

This project ties to DOE's Energy Security mission by furthering our understanding of SOFC electrolytes and improving fuel cell performance. Fuel cells offer realistic, low emission, high-energy-density, portable power, potentially suitable for automobiles. Providing portable power sources for transportation needs is critical to energy security in the US. This project will also advance Sandia's VLPPS capabilities. VLPPS is an emerging coating technology that can prepare coatings in thickness/density regimes not currently accessible with conventional thermal spray or thin film processes. Improved ability to effectively prepare dense coatings in the 1 – 100 µm thickness regime with a wide range of compositions also allows for new coating solutions to be realized for broad-based application across DOE mission space, including work associated with nuclear weapons, energy, and national security missions, as well as support of other federal agencies.

The specific focus of this coating program on SOFC electrolytes has the potential to significantly improve SOFC performance and efficiency, thus directly impacting Sandia's mission to develop improved energy technologies. By combining SPS with VLPPS, thin and dense electrolytes of ideal composition for SOFCs are possible. SPS feeds a suspension of nominally micron-sized powders within a solvent into the plasma. The solvent is evaporated, and the powders are melted and propelled toward a substrate. By operating at pressures of 2.4 Torr, energy partitioning in the plasma and its interaction with the surrounding chamber atmosphere is dramatically reduced. The result is a significant increase in plasma mean free path length and plasma velocity. This causes the plasma to remain coherent longer and deposit uniformly over larger areas. It also increases the total time that particles are entrained in the plasma, and consequently, the amount of energy these particles absorb. The increased residence time in the plasma ensures that dopants diffuse into the powder before reaching the substrate. It has been shown that other compounds dissolved in the suspension (i.e., dopants) are incorporated into the coating during plasma spraying. Thus, it is possible to change the chemistry of the micron-sized powder during the short millisecond time the powder/dopant is in the hot spray plume. This means that it is now possible to quickly and systematically change the composition of the sprayed SOFC electrolyte to optimize its oxygen-ion conductivity by simply adjusting the suspension composition. SPS therefore confers the ability to compositionally design electrolytes that maximize their performance as part of a SOFC system. This coating control capability has the potential to significantly improve the state of the art in SOFC electrolyte production and efficiency.

A Quantum Network Based on Telecomm Interconnects for Secure Communications

141930
Year 1 of 3
Principal Investigator: G. Biedermann

Project Purpose

In this project, we propose to build a quantum repeater network for secure communications (quantum key distribution) that consists of a single laser-cooled rubidium atom trapped in a high finesse optical cavity. Quantum information science offers unmatched potential for secure communications, and to realize this potential, networks must be built that can faithfully transfer the quantum information over large distances. A typical quantum network is composed of matter nodes that are interconnected via photons. The matter is typically a laser-cooled atom or ion, while the photon interconnect is an optical or UV photon that is emitted by the matter. The short wavelength of the emitted single photon limits current state of the art quantum repeaters due to the associated large attenuation loss in optical fiber. If the atom could be made to emit a telecommunication-wavelength photon then the attenuation in the optical fiber is greatly reduced. Using a two-photon transition between the $5S_{1/2}$ and $4D_{5/2}$ state, a single Rubidium atom will emit two photons via a cascading transition. One photon is at 1530 nm and the other is at 780 nm. The telecomm wavelength, 1530 nm photon acts as a flying qubit to connect two distant nodes of our quantum network. The work is a collaboration with the University of New Mexico.

Summary of Accomplishments

In previous work, we investigated quantum-enhanced communications in the form of a quantum repeater using the system of neutral atoms in an optical cavity. We had previously designed and fabricated a high-reflectivity mirror in Si. We demonstrated that the resulting Fabry-Perot cavity is capable of a finesse of 64,000, which is the highest of its kind. The coupling strength of a cavity photon to an atom is characterized by the single atom cooperativity, C1, which in general should be a value much larger than unity. For this system, we found C1 = 100-200 depending on cavity length. This suggests a strong response from the cavity in the presence of an atom. We also designed a layout that will magnetically trap the atoms, and use an atom conveyor belt design to transport them into a network of on-chip optical cavities, forming the quantum repeater. In this work, using a pre-existing atom chip with a simplified conductor pattern, we developed and demonstrated the ability to magnetically trap neutral atoms with a trap lifetime exceeding 1 second. We also demonstrated the ability to do qubit rotations with resonant microwave fields. Given these results, we are confident that we should be able to demonstrate strong atom-photon coupling in the future.

Significance

This work will make progress toward an integrated solution for secure communication with strong applications for national security and can enable distributed/parallel quantum computing. Quantum communication is a new physical basis for secure communication, because accurate copying is impossible, and the changes caused by eavesdropping can be detected. Bringing quantum repeaters to the point of viability is a recognized technology milestone for quantum communication.

Multicomponent Approach Calculations of Electromagnetic Scattering in Turbid Media

141931
Year 1 of 3
Principal Investigator: M. Pack

Project Purpose

Remote sensing of clouds using optical radiation (i.e., lasers) is a relatively mature research field, but there are significant fundamental questions that remain to be answered. For example, how well can two clouds containing different particles be differentiated using parameters such as depolarization ratios, and their variations as a function of angle. The fast accurate modeling of cloud scattering plays a vital role in answering these questions. One promising method of calculating radiative transfer for plane-parallel layers is the multicomponent approach (MCA). The MCA is a semi-analytic small-angle scattering approximation. What makes the MCA different from other approaches is that the small-angle scattering component can be solved very efficiently by using an analytic solution given in the previous publications; indeed, it exhibits incredible advantages in terms of computational time and exhibits comparable accuracy when pitted against more conventional methods.

We propose to develop an MCA program for the scalar radiative transfer equation, and to build on this code in order to calculate the full Stokes parameterization of scattered radiation. We will then take the method to the next level and include the k-distribution method and other modern developments. This code will allow us to calculate the internal field structure of particles in clouds that will lead to a better understanding of both fluorescence and Raman scattering. A potential ancillary benefit is that this research could provide insights into bio-inspired materials by aiding in the understanding of how cephalopod mollusks (e.g., octopus, squid) use chromatophores and iridophores for camouflage. The work is a collaboration with Texas A&M University

Summary of Accomplishments

We have several distinct results reflecting the multiple well-defined thrust of this project. We have explored the existence of nonlinear effects in the propagation of ultrashort laser pulses through water. Our results confirm that ultrashort laser pulses in water do obey the Bouguer−Lambert−Beer law. We have also developed some scalar models to simulate linear electromagnetic scattering in clouds, and have partially validated these codes against established Monte-Carlo and Delta-M method codes.

Significance

In January of 2010, we published a paper correcting and clarifying some errors in the literature concerning integrating cavities. In this work, we pointed out that one must be very careful in making approximations involving the reflectivity and average path length in an integrating cavity. We developed a Monte Carlo code to simulate ring-down spectroscopy and to confirm the some of the derivations included in the paper, although the paper does not mention the code. Later in the year, we altered our research focus to experimental optics, particularly aspects dealing with nonlinear optics and optical filaments. Thus far, we have investigated the energy coupling between two filament-forming beams in liquid methanol and have identified a phenomenon not previously reported in the literature. This finding is soon to be published; we have also begun researching various applications of optical filaments, such as remote imaging on a very fine spatial scale. In addition, we have initiated a study of the acoustic signature of filaments in water and how these acoustic signatures may help in determining the speed of sound in liquids. Future research efforts may reflect various new applications of nonlinear optics in the atmosphere and oceans.

Refereed Communications

A.V. Sokolov, L.M. Naveira, M.P. Poudel, J. Strohaber, C.S. Trendafilova, W.C. Buck, J.Y. Wang, B. D. Strycker, C. Wang, H. Schuessler, A. Kolomenskii, and G.W. Kattawar, "Propagation of Ultrashort Laser Pulses in Water: Linear Absorption and Onset of Nonlinear Spectral Transformation," Applied Optics, vol. 49, pp. 513-519, 2010.

Modeling and Simulation of Explosive Dispersal of Liquids

141932
Year 1 of 3
Principal Investigator: A. Brown

Project Purpose

This project is intended to expand capability and knowledge around the explosive dispersal of liquids. This is a very complex problem, and has many national security related applications. It is complex not only because the environment is very difficult to measure, but also because of the nature of the classical Richtmeyer-Meshkov and Rayleigh-Taylor instabilities that seem to control the atomization process in many cases.

Summary of Accomplishments

This year a new Ph.D. student at the University of Florida has been actively assessing theoretical methods used to predict simplified problems of this nature. There was a successful verification and validation effort performed on some simulation models developed, and they are progressing to more complex scenarios. They have been interfacing with a team at Sandia that is focused on high-fidelity modeling of the same class of problems.

Significance

Successful conclusion to this work will hopefully provide guidance on how to formulate accurate subgrid models for atomization and break-up without having to resort to detailed simulation. Such a capability will affect the accuracy and capability of Sandia modeling tools.

MBE Growth and Transport Properties of Carbon-Doped High-Mobility Two-Dimensional Hole Systems

141933
Year 1 of 3
Principal Investigator: J. L. Reno

Project Purpose

Utilizing a new high-mobility GaAs growth facility under construction at the Birck Nanotechnology Center at Purdue University, we propose to systematically investigate molecular beam epitaxy (MBE) growth of carbon-doped high-mobility two-dimensional hole systems (2DHS). New physics and new device applications often follow from advances in material synthesis. The recent development of efficient resistive carbon doping filaments allow for the construction of extremely high-quality 2DHS on the high symmetry (100) face of GaAs. Yet there is still much to learn about structure optimization, and many physical phenomena remain to be explored. Our initial studies will focus on determining the parameters that presently limit low-temperature mobility in carbon-doped 2DHS. The proposed work will include MBE growth, structure modeling, and low temperature transport measurement of MBE-grown samples. Furthermore, we anticipate that samples grown in the course of this study will find utility for experiments studying electron-electron interactions in low-dimensional systems.

Summary of Accomplishments

In the first year of the project, we developed and baselined analytical techniques on prototype quantum structures used to determine their transport properties. These samples were grown in collaboration with Bell Laboratories and PurdueUniversity. The analysis involved low-temperature magneto-transport measurements to be used as initial input for samples grown with the new MBE. The analysis technique was benchmarked using several samples. A significant amount of valuable data was collected from these samples, which will be directly implemented in the benchmarking and analysis of the next generation of samples. The analysis of these samples was presented at the American Physical Society March Meeting in Portland, Oregon. In analyzing the transport data, we found that hole mobility drops off at low density faster than we can account for theoretically, in a manner very similar to that observed by other researchers at Sandia in an electron-hole bilayer. The development of these analytical techniques and baselining of the materials properties is a key outcome.

Significance

The proposed work is aligned with the DOE's mission of advancing basic science in support of national security. Several proposed schemes for solid-state quantum computation rely on development of GaAs-based technology. Our work dovetails nicely with these approaches, and as such, should be of interest to DOE. The benefits of the proposed research are numerous. The rich spin structure of the GaAs valence band will be of interest to physicists studying spin related phenomena in lower-dimensional systems. Samples grown during the course of this work may allow for the exploration of new 2DHS-based semiconductor nanostructures. Such nanostructures have not been as widely investigated as electron systems. In addition to being of fundamental interest, these GaAs hole systems may have many applications in next-generation technologies. For instance, the lower hyperfine coupling of holes (e.g., as compared to electrons) to atomic nuclei is of great importance for schemes for solid state quantum computation that require spin systems largely decoupled from their environments.

Power Reduction Techniques for Modern Modulation Schemes

142044
Year 1 of 3
Principal Investigator: R. J. Punnoose

Project Purpose

There are many challenges and opportunities in increasing spectral and power efficiency in modern wireless digital communication systems. For this work, in collaboration with the University of California-Davis (UC-Davis), we plan to extend existing work on power reduction techniques developed at UC-Davis as applied to radio-wave modulation. Work on power reduction pertains to a computationally efficient technique to reduce peak-to-average power ratio (PAPR) for the orthogonal frequency division modulation (OFDM), while maintaining spectral efficiency.

The initial work addresses single-input single-output (SISO) systems (i.e., one transmit and one receive antenna). Previous UC-Davis work has used the open source GNU Radio project to implement a simple SISO communication system in hardware. We will extend the PAPR reduction work for OFDM to the multiple-access OFDMA case. We also plan to expand the SISO software radio system to a multiple-input multiple-output (MIMO) system using space-time block coded (STBC) OFDM. STBC-OFDM has shown great promise for dealing with wide-bandwidth, frequency selective channels in a computationally efficient way. We hope to extend the benefits of power reduction to larger and more efficient MIMO systems in this work. This work can also potentially serve as the basis for the development of a cognitive radio testbed that will be investigated in the future.

Summary of Accomplishments

This work has focused on PAPR reduction and its efficient and practical implementation for OFDM data transmission. The method is a novel tone insertion / constellation expansion method which lowers the transmitted PAPR in OFDM systems without incurring bandwidth overhead or transmission of side information. The key accomplishments have been to formulate and refine the problem as a tractable convex optimization problem and extend the method to multi-user OFDMA and MIMO systems using STBC-OFDM. In its original form, the tone insertion problem is a combinatorial optimization problem that is known to be NP-hard (non-deterministic polynomial-time hard). In this work, a semi-positive definite relaxation technique was applied that formulates a relaxed problem that can be solved with convex programming methods. Numerical experiments showed that this method provides excellent performance at reasonable computational complexity for small- to medium-sized OFDM frames (16-64 subcarriers). However, for large OFDM systems (standards exist utilizing 2048 subcarriers), the complexity of the method will not allow for rapid online solutions in reasonable time. Therefore, recent attention has been re-focused on lowering the computational complexity of the underlying algorithm using these approaches:

1. Tone-injection on a subset of subcarrier symbols and using heuristic or greedy algorithms
2. Numerical techniques for solving a related dual problem using spectral bundles.

Results show that moving a small fraction of subcarrier symbols can lead to significant PAPR reduction at greatly reduced computational complexity. Though promising, additional work is needed to identify the subcarriers to be selected.

Experimentation with GNU Radio has not shown promising results for high-speed datalink and other software-defined radio (SDR) systems are being investigated. The more recent open-source SDR platform, OSSIE (Open-Source SCA Implementation – Embedded), which is also compatible with previously-obtained Universal Software Radio Peripheral hardware has demonstrated greater capabilities in the literature and will be the focus, moving forward.

Significance

This work supports DOE's defense strategic goals by developing communications technology that can be beneficial in enhancing collaboration and telemetry systems. This will help to enhance the reliability of the stockpile. This work will also help to enhance the safety and security of sensitive material.

Metrology of 3D Nanostructures

142440
Year 1 of 3
Principal Investigator: P. Davids

Project Purpose

The goal of this project, a collaboration with the University of Colorado at Boulder, is to develop improved techniques for inspection of 3D nanostructures. Such structures are widely useful in optics and potential applications include metamaterials, volume holograms, nano-electrical-mechanical systems, photonic crystals, optical circuits, and any other devices that control light propagation. However, better metrology methods are necessary to properly analyze their design and fabrication, particularly as these structures expand in volume and shrink in feature size. Already, the size of features that can be fabricated is several times smaller than the wavelength of visible light, and therefore are beyond the resolution limit of a standard microscope (scanning electron microscopes can be used to form high-resolution images, but are limited to measuring the top of a sample).

Attempts to achieve super-resolution images take advantage of all information available. This often reduces to solving an inverse problem; using the results of a measurement and detailed knowledge of the detection system, one can obtain information about the object that yielded the measurement. Prior knowledge of the sample can be used to increase the accuracy of the measurement. Super-resolution microscopy is experiencing a revolution as new approaches are applied to biological samples. In a process called PALM (photoactivated localization microscopy), sparse arrays of fluorescent molecules are sequentially photoactivated within a sample in a wide filed of view. When light from a single fluorophore is collected, knowledge of the system's point spread function (PSF) enables super-resolution to ~20 nm. A related technique, called STORM (stochastic optical reconstruction microscopy), uses a different type of emitter that enables controlled photoswitching to achieve similar resolution. More recently, attempts to achieve optical sectioning, and thus depth resolution, in a wide-field technique use spatiotemporal focusing of short pulses in combination with two-photon excitation fluorescence.

Summary of Accomplishments

Demonstrate optical resolution of two small objects located deep inside a transparent material and measure their distance and location using wide field imaging: Progress towards this milestone is promising; we have acquired the emitters, and we have developed sample preparation techniques to make samples that contain closely spaced emitters. We have constructed and tested the imaging system for performing these 3D measurements and have performed numerous upgrades to improve measurement quality. Several algorithms have been explored for achieving source separation of closely spaced objects.

Significance

This project will advance the DOE's goal of improving nanophotonics technology by improving 3D inspection techniques, as well as increasing Sandia's expertise in creating large nanostructured samples that requires matching techniques for inspection and metrology in 3D. Moreover, optical imaging with 3D super-resolution well beyond the wavelength of light has applications in medicine, biology, materials science, and nanofabrication inspection in both research and industrial settings.

Genetic Engineering of Cyanobacteria as Biodiesel Feedstock

142441
Year 1 of 3
Principal Investigator: A. Ruffing

Project Purpose

The purpose of the project is to genetically engineer cyanobacteria for the production of hydrocarbons to be used for biodiesel feedstock. While most efforts in biofuel production from photosynthetic microorganisms focus on the natural oil-producing eukaryotic algae, this project investigates the use of fast-growing, prokaryotic photosynthetic organisms with established methods of genetic engineering. Moreover, cyanobacteria have been shown to naturally secrete hydrocarbons such as free fatty acids and alkanes, simplifying the downstream collection and purification of the biodiesel feedstock. This is advantageous compared to the intracellular accumulation of triacylglyceride (lipid) in eukaryotic algae, which is difficult to extract.

We are genetically engineering a well-studied cyanobacterium, *Synechococcus elongatus PCC 7942*, for the production of both free-fatty acids (FFA) and long chain alkanes, two potential biodiesel feedstocks. For FFA production, the engineering strategy includes four main steps: 1) elimination of FFA metabolism, 2) removal of feedback inhibition of the fatty acid (FA) biosynthesis pathway, 3) improving carbon flux through the FA biosynthesis pathway, and 4) enhancing carbon fixation. The engineering strategy for long-chain alkane production includes steps 3 and 4 along with overexpression of the alkane biosynthesis pathway. Both engineering strategies utilize novel genes cloned from the green alga, *Chlamydomonas reinhardtii*. As *C. reinhardtii* is a natural oil producer, the FA biosynthesis enzymes from this organism may have greater activity than the native enzymes. Genetic engineering of the natural fatty acid pathway may lead to changes in the cell and photosynthetic membranes. We are using several techniques to characterize changes in membrane composition and photosynthesis, including electrospray ionization-mass spectroscopy (ESI-MS), confocal hyperspectral fluorescence imaging, and pulse-amplitude-modulated (PAM) photosynthesis yield analysis. The PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments

The technical accomplishments for FY 2010 are as follows.

<u>Goal 1: Cyanobacterial strain selection and cultivation</u>

- We selected a model cyanobacterium, *Synechococcus elongatus* PCC 7942, for genetic modification due to the availability of its genome sequence, its metabolic network, and the established tools for genetic engineering.
- We obtained *S. elongatus* and established techniques for cultivation and cryopreservation.
- We designed an experimental test set-up for cyanobacterial cultivation and free fatty acid production.

<u>Goal 2: Elimination of free fatty acid metabolism</u>

- We obtained plasmid pAM2991 from the University of California at San Diego for genetic engineering of *S. elongatus*.
- We modified pAM2991 for gene knockout of acyl-acyl-carrier-protein (acyl-ACP) synthetase in S. elongatus to eliminate the metabolism of free fatty acids.
- We introduced the modified plasmid (pSE15) was into *S. elongatus* and confirmed successful knockout of acyl-ACP synthetase, thereby generating the engineered strain SE01.

Goal 3: Removal of feedback inhibition of free fatty acid biosynthesis pathway

- We cloned a truncated thioesterase from *E. coli* into pSE15, yielding the plasmid pSE16.
- We introduced pSE16 was into *S. elongatus* for simultaneous gene knockout of acyl-ACP synthetase and genome integration of the truncated thioesterase.
- We cultivated this second engineered strain (SE02) to measure cell growth and free fatty acid production, and showed that SE02 successfully produced free fatty acids and secreted them into the extracellular medium.

Goal 4: Measurement of free fatty acids produced by engineered strains

- We adapted a fluorescence method for quantifying free fatty acid levels in mammalian tissue to quantify free fatty acids in the extracellular medium of *S. elongatus* cultures.

Significance

The initial R&D accomplishments of this project demonstrate that cyanobacteria can be genetically engineered for hydrocarbon production. While it remains to be seen whether the engineered cyanobacteria can produce hydrocarbon at the high levels required to support biofuel production, the construction of two FFA-producing cyanobacteria illustrates the potential for biofuel production. This introduces a new photosynthetic candidate for hydrocarbon production, one that was previously overlooked due to its low level of natural lipids. With genetic modification, cyanobacteria can compete with the natural oil-producing algae that are the focus of the majority of biodiesel research efforts in the scientific community. This project also contributes to the fundamental understanding of the physiological changes that accompany hydrocarbon production. After thioesterase induction in the SE02 strain, the culture changed color from green to blue, indicating a change in the photosynthetic pigments of the cyanobacterium. This phenomenon is currently under investigation to determine which pigments are changing and if there is any affect on the photosynthetic process. The accomplishments of this project contribute to Sandia's Energy and Infrastructure Assurance mission and two themes of the DOE's strategic plan: Theme 1, Energy Security and Theme 3, Scientific Discovery and Innovation.

This project provides a foundation for the advancement of biofuel production using genetically engineered cyanobacteria. The engineered strains developed in this project may be further modified to optimize the potential for large-scale biofuel production. The novel genes cloned from *C. reinhardtii* may be used to enhance hydrocarbon production in other photosynthetic microorganisms, including other cyanobacterial strains and eukaryotic algae. Furthermore, the genetic engineering strategy employed in this project may be applied to improve hydrocarbon production in other microorganisms. In addition to advancing the development of hydrocarbon-producing strains, this project may also be leveraged to support the investigation of downstream processing including separation techniques, conversion to fuel, and analysis of fuel properties. The strains developed in this project, having the capability to produce and secrete FFA into the extracellular culture, may be leveraged to develop new technology for the separation and purification of FFA from the liquid culture. This project may also be leveraged to support the investigation of new techniques for converting the cyanobacterial FFAs into hydrocarbons with better fuel properties. Lastly, the combustion properties of the fuels developed from the cyanobacterial FFAs must be characterized.

Enabling Self-Powered Ferroelectric Nanosensors: Fundamental Science of Interfacial Effects Under Extreme Conditions

142543
Year 1 of 3
Principal Investigator: J. Ihlefeld

Project Purpose

The purpose of the project is to understand the role of extreme environments on the mechanical, electrical, and chemical properties of ferroelectric-based self-powered nanosensors. Development of self-powered nanosensors will be of great interest to DOE defense, national security, and energy missions. The technical problem at the device level is to enable the fabrication of small, unobtrusive sensors that can communicate back to control systems, and can function under the kinds of environments often encountered in, for example, downstream refining, engine/turbine health monitoring, and space-based communications. Environmental conditions including temperature, pressure, illumination, and even chemical surroundings can be detected based upon ferroelectric material response, and such information can be stored and/or communicated using energy harvested by the same material from ambient vibrations, light, and/or thermal variations. Progressing from basic material response to functional sensor involves materials integration challenges and a thorough understanding of how the entire system behaves in the application environment over the desired sensor lifetime. Our team will address the effect of corrosive, pressure and temperature, and radioactive environments on model ferroelectric-based structures and develop materials and synthesis techniques consistent with minimizing these environments on performance. We propose to study the performance and degradation mechanisms involved in ferroelectric materials under these conditions to understand the principal mechanisms for degradation. The basic science understanding that we will achieve will allow the design of more-robust materials that can better tolerate these environments.

Summary of Accomplishments

- We discovered via in-situ x-ray diffraction experiments that niobium additions minimizes electrode-film interactions presenting a potential route toward controlled nucleation, growth, and crystallographic texturing.
- We demonstrated via synchrotron x-ray diffraction experiments that heating rates during ferroelectric film preparation affects crystallographic texture and potentially device performance.
- We demonstrated via neutron irradiation experiments that radiation affects both macroscopic ferroelectric response and small signal response. This has broad implications for the study of the effect of defects on the properties of piezoelectric films.
- We developed test stands and methods to measure the electrochemical response of ferroelectric films in corrosive environments.
- We developed a substrate electrode adhesion layer technology that enables improved piezoelectric performance.

Significance

Developing a fundamental knowledge base of the effect of extreme environments on ferroelectric nanostructural interfaces in this project is of great importance for DOE nuclear weapons and pulsed power missions. Integrating complex oxide nanomaterials into functional systems is also of considerable interest for DOE energy programs that include enhanced high-energy dielectrics for the nation’s power grid, FreedomCAR power electronics and environmental material replacement of battery components.

Accomplishments for FY 2010 directly impact the science and technology community by providing controlled studies demonstrating a range of relevant extreme environments on the structure-property relations of ferroelectric thin films. This project is developing cutting-edge analysis techniques for measuring the effect of processing conditions and environments on device properties. Specifically, the in-situ processing monitoring is leading discoveries of phase development in these materials that has not been accessible to previous researchers. The corrosive environments experimental techniques have not been previously applied to these kinds of materials, and all newly acquired information will be novel to the scientific community. Irradiation experiments enable controlled defect formation in these materials and facilitate direct measurement of the role of these defects on the ferroelectric and piezoelectric properties. Combined with Sandia's advanced microscopy and additional characterization techniques, we are well positioned to provide structure-property relations not previously reported in the scientific literature.

As these materials and structures are utilized in energy harvesting and sensing applications the acquired knowledge enhances Sandia's national security missions by providing fundamental background information on the effects of a broad range of environments and processing conditions on device performance. All information learned will enable robust energy harvesting and sensor development across a broad range of environments.

Integration of Block-Copolymer with Nanoimprint Lithography: Pushing the Boundaries of Emerging Nanopatterning Technology

145832
Year 1 of 3
Principal Investigator: G. L. Brennecka

Project Purpose

The rapid pace of innovation enabling Moore's Law (doubling transistor density every ~1.5 years) is critical to our nation's technological leadership and economic security. To maintain this pace, the *International Technology Roadmap for Semiconductors* (ITRS) prescribes an 11-nm half-pitch for dense patterns and 4.5-nm critical dimensions by 2022. Current 193-nm immersion optical lithography can print ~40-nm half-pitch and may reach 20 nm with double patterning. Extreme ultraviolet (EUV) lithography persistently raises doubts due to the costly complete change of infrastructure. Therefore, alternative lithographic pathways to the extreme nanoscale ITRS goals are needed. We propose to direct the self-assembly of block copolymers (BCP) into device-oriented patterns fabricated by optical interference lithography (IL), use those self-assembled BCP patterns as masks to create nanoimprint lithography (NIL) masters via plasma etching, and fabricate prototypical devices with the combined "top-down" and "bottom-up" approach. Our principle goals include, 1) employ optical interference lithography to direct large area (>4 cm^2) assembly of BCP with device relevant patterns, having critical dimension ranges of 10-50 nm with half-pitch < 11nm; 2) fabricate NIL templates based on the IL-BCP pattern formation, characterize the long-range uniformity, defect density and line-edge roughness (LER) of the resulting imprints, and demonstrate reliable pattern transfer; 3) demonstrate prototypes of at least three devices using the above integrated approach. This project is the first combination of IL with BCP and NIL technologies. The benefits of this project will define the limits of a combined top-down/bottom-up lithography approach for use in commercial applications including integrated circuit manufacture.

Summary of Accomplishments

University of New Mexico (UNM)-fabricated interferometric lithography (IL) patterns have directed the self-assembly of University of Wisconsin BCP features, and we have demonstrated 4× feature density multiplication, assembling BCP features with ~20-nm pitch over large areas (tens of microns) defined by IL patterns having ~100-nm pitch. This advanced involved development of an integration scheme to combine 193-nm immersion interference lithography with directed self-assembly using cross-linkable mats and hydroxyl-terminated brushes with an inorganic antireflection coating. In addition, BCP-defined patterns have been transferred into Si and used as templates for NIL master fabrication and subsequent patterning, which have produced nanofeatured substrates that have successfully demonstrated improved surface enhanced Raman scattering (SERS) response.

The unique capabilities of Sandia's FEI® Magellan scanning electron microscopy allow us to achieve quantitative size, shape, and distribution information on sub-20 nm features without coating the sample, as is typically required for high-resolution imaging. Combined with advanced statistical tools that we are still optimizing, this allows quantitative description of pattern and feature quality and variation at each stage of the process without altering the sample. Additionally, industrial partner Intel shared with us some process development wafers that allowed demonstration of the consistency of approaches, values, and parameters between Sandia and Intel. We now have an Intel-approved metrology system in place that will allow us to quantitatively analyze feature and pattern fidelity throughout all processing steps.

Modeling and simulation efforts have already demonstrated how the substrate-BCP interface alters the thermodynamic stability of the BCP thin film system relative to the bulk sufficiently to describe and predict various previously unexplained unusual morphologies experimentally observed under certain conditions.

Significance

The entire integrated circuit community is trying to determine how to cheaply and reliably pattern materials at the 10–30 nm level in an attempt to squeeze more life out of Moore's Law. Lithography techniques based on the self-assembly of block copolymers have received significant interest for this purpose, and are viewed as promising enough to be explicitly listed on the ITRS roadmap. However, before any serious attempts are made to implement block copolymer directed self-assembly (BCP-DSA) lithography, several important issues need to be addressed, such as the following:

- What is the minimum feature size that can reliably be formed by BCP-DSA?
- What is a feasible defect density that can be achieved by BCP-DSA?
- Over what areas is such a patterning technique feasible?
- How well can multiple BCP-DSA pattern types be integrated into a single master?
- What parameters are coupled (for example, annealing time and defect density, feature size, and order area, etc.) and what are their relationships?

This project is attempting to address these and many other related questions about BCP-DSA, in part, because the scientific knowledge gained will allow us to improve related processes, in part because this groundwork type of research is critically important for US-based semiconductor device manufacturers and therefore for the US economy, and in part because bringing the most advanced lithography and fabrication capabilities to Sandia will expand the capabilities of Sandia device makers.

Developing nanopatterning capabilities for Sandia will enhance or enable a variety of programs that may directly impact the missions of NNSA (trusted microdevices for nuclear weapons, surveillance for nonproliferation) and DHS (security and awareness), while also addressing the DOE science directive by advancing the frontiers of scientific knowledge and exposing top-tier graduate students to national security career opportunities while building skills and capabilities related to nanoscience.

Refereed Communications

C. Liu and P.F. Nealey, “The Integration of Block Copolymer With 193i Lithography,” to be published in the *Journal of Vacuum Science and Technology B*.

E. Yang, C.C. Liu, C. Steinhaus, C.Y. Yang, P.F. Nealey, and J. Skinner, “Nanofabrication of SERS Device by an Integrated Block-Copolymer and Nanoimprint Lithography Method,” to be published in the *Journal of Vacuum Science and Technology B*.

D.B. Burckel, C.M. Washburn, D.D. Koleske, and R. Polsky, “Pyrolysis of 2D and 3D Interferometrically Patterned Resist Structures,” to be published in the *Journal of Vacuum Science and Technology B*.

Online Learning Techniques for Improving Robot Navigation in Unfamiliar Domains

145969
Year 1 of 1
Principal Investigator: C. Q. Little

Project Purpose

This project, a collaboration with Carnegie Mellon University, explores how self-supervised online learning techniques can be applied to robotics, particularly autonomous outdoor navigation, in order to allow robotic systems to improve their performance over time. While roboticists do everything they can to equip robots with capabilities relevant to a wide range of domains, in order for real-world applications of mobile robots to increase, they must be able to adapt to changing and unfamiliar aspects of their environments. In many domains that are prime candidates for mobile robotic applications, the risk of catastrophic failure, however small, is a primary reason why autonomous systems are still underutilized despite already demonstrating impressive abilities. The techniques developed throughout this project aim to improve the effectiveness and range of the robot's perception system, dramatically reduce the number of mission-ending errors by identifying potentially hazardous unfamiliar situations, reliably detect unexpected changes in previously traversed environments, and allow better utilization of the availability of limited human assistance.

Summary of Accomplishments

Mission-ending mistakes are a key concern in deploying mobile robots. One approach to facilitating safe traversal is for a unmanned ground vehicle to be able to identify situations that it is likely untrained to handle before it experiences a major failure. We addressed this problem by developing a variety of algorithms for enabling online novelty and change detection, and we explored applications for these algorithms in mobile robotics. Our novelty detection algorithm addresses several significant limitations of most novelty detection approaches. This algorithm creates and operates within a feature space that is more conducive to viewing novelty as a distance metric, and is therefore more resistant to many of the issues associated with high-dimensional feature spaces. Additionally, this algorithm's adaptive abilities, computational bounds, and anytime properties make it a logical choice for many online novelty detection tasks including those valuable for mobile robots. We then extended this online novelty detection algorithm to deal with the problem of online change detection (detecting when a scene has changed with respect to a previous traversal). By using an online scene segmentation system, the change detection system was able to achieve further improvements to accuracy and robustness. We tested the robustness and accuracy of these systems onboard several large outdoor robots.

Significance

Autonomous robot navigation is a critical technology for several Sandia mission areas. These include nonproliferation and assessments, military technologies and applications, and homeland security. Under nonproliferation and assessments, autonomous robot technology can be used to aid robots performing site assessments. For homeland security, robots are used in a wide range of activities that include emergency response and physical security. The autonomous navigation technologies developed under this project will enhance robot performance for this wide range of applications, particularly when high degrees of reliability are necessary and single human operators must supervise many robots simultaneously.

Refereed Communications

J.A. Bagnell, D. Bradley, D. Silver, B. Sofman, and A. Stentz, "Learning for Autonomous Navigation: Advances in Machine Learning for Rough Terrain Mobility," *IEEE Robotics and Automation Magazine*, vol. 17, pp. 74-84, June 2010.

Performance Monitoring and Enhancement in Data Center

145970
Year 1 of 3
Principal Investigator: Y. R. Choe

Project Purpose

With the growth of data and the need to process them, data center (DC) has become an important computational paradigm to deal with this data explosion. Whether offered as an open cloud service or running proprietary solutions, services offered by data center are important selling points for data center owners. Here we are concerned with services offered that can enhance the performance and ability of users. We propose a project to examine fault diagnosis under conditions of limited resource consumption.

One way to enhance data centers' performance is to ensure they can react to faults. Fault scenarios can be complicated, however. Other than hardware failures, services within the data center can fail without notice due to software bugs or network conditions (e.g., high congestion). The ability to monitor DC environment, at the hardware and service level, and to react to anomalous behaviors is essential to ensure DC remains a high-value asset. It is also important that DC operators and users are aware of failures, and can react to failures independently to ensure their operations can either continue or degrade gracefully. It is then important to offer monitoring, detection, and recovery of failures as services to both network operators and users.

Another vector to enhance performance is to allow the network components to be offered as an "open platform." By open platform we mean that users can easily and expressively indicate the requirement for their services, and the network can automatically adjust the service (by moving them within the DC, for example) to satisfy the requirement. The issue here is the implementation of a service in the network that would allow such a dynamic change to users' services. Offering network as a service, beyond the traditional packet delivery, is an important value-added service that could benefit network operators and users.

Summary of Accomplishments

We observed that high traffic rate poses a significant problem for measurement. Our tests indicate that above 100 Mbps, CPU load for packet capture exceeds 20% even if captured packets are not saved to disk. In addition to the inherent load that packet capturing requires, external influence can also limit the resource usage allowed for traffic monitoring. For one, traffic monitoring is considered a secondary task when it is collocated within the production servers (unless the machines are dedicated for monitoring). Thus it is desirable to place an artificial resource bound on monitoring tasks.

Our first task involved constructing dependency graphs under processing constraint. A dependency graph is a fundamental building block in fault diagnosis systems, in which the dependencies for accessing various networked services are automatically recorded by the system. When certain networked services are deemed faulty, the fault diagnosis system leverages the learned dependencies to discover possible root causes.

We developed a dependency graph system following these principles:

1. A centralized controller is assumed to coordinate the monitoring efforts at remote servers.
2. Instead of capturing packets, each monitoring node immediately processes the occurring network events and constructs the dependency graph. The monitoring node captures socket creation events and uses the process ID and outgoing IP address and port to construct a local dependency graph.
3. Periodically, the monitoring nodes export the local dependency graph to the central controller. To ensure network overhead is low, distributed triggers are used.

We are in the process of constructing the system for the monitoring agent, and have developed the agent so that it can process network events immediately and construct the dependency graph via the recorded network events.

Significance

With the explosive growth in computing power and storage capacity, DC management has become more difficult. In this project, identifying the bottlenecks and designing an automated method to enhance them are being explored. This work can benefit cloud computing and also directly benefit Sandia, as well as having the potential to benefit key agencies. Our accomplishments thus far demonstrate a prototype that, in theory, is capable of dynamically handling a large amount of information, and ultimately using it to build dependency graphs in a relevant DC environment — through a hybrid local/centralized processing approach.

Using the prototype to develop a system for constructing an application dependency graph in the short term is aimed at improving the existing techniques, but the long-term goal is to integrate the system into a fault management and detection system. One of the ways the application dependency graph system can be applied to fault management is to use the graph to mine for fault patterns, thus automatically grouping faults into several classes. This can be useful for operators to approach fault management from a holistic perspective, instead of dealing with individual faults. In addition, grouping faults into classes can also help evaluate the impact of fault mitigation. For example, if faults are found to only occur within a certain virtual local area network (VLAN), this would give operators a better idea about the impact to users and future data center loads were the VLAN to be reassigned as the mitigation strategy. More interesting scenarios could involve examining temporal variation in the application dependency to detect changes in application behavior, for example, when new patches are being applied, and the patches affect the communication behavior of the patched applications. More generally, the application dependency graph system is one specific example of modeling the behavior of DCs. The collection technique can be generalized to collect any information about the DC to aid in building a DC model.

Fouling-Resistant Poly(ethylene glycol)-Grafted Polyamide Desalination Membranes for Produced Water Purification

145997
Year 1 of 1
Principal Investigator: S. J. Altman

Project Purpose

The desalination market, using polyamide reverse osmosis membranes, is growing steadily around the world. However, these membranes are limited by their susceptibility to fouling, a phenomenon that decreases water flux and membrane lifetime, thus increasing the cost of the desalination process. Alternative water sources such as produced water, a byproduct of oil and gas production, present even more potential for fouling, but are of interest due to growing water shortages and the resulting need to consider previously unused water sources. Depending on the level of purification achieved, produced water could provide a new water source for agricultural irrigation, livestock watering, process water, or even human consumption. The objective of this project is to modify the surface of commercial polyamide desalination membranes to make them more resistant to fouling by produced water. Surface modification with neutral, hydrophilic poly(ethylene glycol) (PEG) has been shown to reduce biological fouling of membranes, and could also help alleviate fouling by produced water. The interfacial polymerization used to form the polyamide membranes leaves residual surface carboxylic acid and amine groups, thus a PEG with reactive epoxide endgroups, poly(ethylene glycol) diglycidyl ether (PEGDE), has been chosen for surface modification. This project is a collaboration with the University of Texas, Austin (UT).The proposed project supports technology and materials testing capability development in the area of water purification which is of strategic interest to Sandia and may provide future opportunities for programmatic work. Additionally, creating opportunities for graduate student training and opening future avenues for UT students at Sandia is of key importance in this university collaboration.

Summary of Accomplishments

Characterization of commercial polyamide membrane performance was a necessary first step before undertaking surface modification studies. Membrane performance was found to be sensitive to crossflow testing conditions. Concentration polarization and feed pH strongly influenced NaCl rejection, and the use of continuous feed filtration led to higher water flux and lower NaCl rejection than was observed for similar tests performed using unfiltered feed.

Two commercial polyamide membranes, including one reverse osmosis and one nanofiltration membrane, were modified by grafting PEGDE to their surfaces. Two different PEG molecular weights (200 and 1000) and treatment concentrations (1% [w/w] and 15% [w/w]) were studied. Water flux decreased and NaCl rejection increased with PEGDE graft density ($\mu g/cm^2$), although the largest changes were observed for low PEGDE graft densities. Surface properties including hydrophilicity, roughness, and charge were minimally affected by surface modification.

The fouling resistances of modified and unmodified membranes were compared in crossflow filtration studies using model foulant solutions consisting of either a charged surfactant or an oil in water emulsion containing n-decane and a charged surfactant. Several PEGDE-modified membranes demonstrated improved fouling resistance compared to unmodified membranes of similar initial water flux, possibly due to steric hindrance imparted by the PEG chains. Fouling resistance was higher for membranes modified with higher molecular weight PEG. Fouling was more extensive for feeds containing the cationic surfactant, potentially due to electrostatic attraction with the negatively charged membranes. However, fouling was also observed in the presence of the anionic surfactant, indicating that hydrodynamic forces are also responsible for fouling.

Significance

This university collaboration will benefit the national security mission of the DOE by creating technology that is targeted toward maintaining a sustainable and secure water supply for human use. This is a key component of the current Sandia water initiative. New science will facilitate lowering the energy requirements for water purification.

Refereed Communications

E.M. Van Wagner, A.C. Sagle, M.M. Sharma, and B.D. Freeman, “Effect of Crossflow Testing Conditions, Including Feed pH and Continuous Feed Filtration, on Commercial Reverse Osmosis Membrane Performance,” *Journal of Membrane Science*, vol. 345, pp. 97–109, December 2009.

A.C. Sagle, E.M. Van Wagner, H. Ju, B.D. McCloskey, B.D. Freeman, and M.M. Sharma, “PEG-Coated Reverse Osmosis Membranes: Desalination Properties and Fouling Resistance,” *Journal of Membrane Science*, vol. 340, pp. 92–108, September 2009.

E.M. Van Wagner, “Polyamide Desalination Membrane Characterization and Surface Modification to Enhance Fouling Resistance,” Ph.D. Thesis, Department of Chemical Engineering, The University of Texas at Austin, 2010.

Advanced Constitutive Models for Thermally Activated Shape Memory Polymers: Connecting Structure to Function

146013
Year 1 of 3
Principal Investigator: J. A. Zimmerman

Project Purpose

Thermally activated shape memory polymers (SMP) can be manufactured to memorize a permanent shape, programmed thermo-mechanically to hold a temporary shape, then deployed back to its permanent shape in response to a specific temperature event. Compared to shape memory alloys, SMPs are inexpensive to manufacture. They are malleable and damage tolerant, and can undergo large, controllable shape changes in excess of 100% strain. SMPs are being investigated for a variety of uses, including temperature sensors and deployable and morphing structures for aerospace and biomedical applications. The shape memory performance depends on the complex interactions of many microstructural and thermomechanical factors, and considerable opportunities exist to tailor the polymer structure and the thermomechanical programming procedure to achieve the desired shape memory performance.

Our work initially focused on type I SMPs described by covalently cross-linked amorphous networks. The shape memory effect is provided by the equilibrium configuration of the cross-linked network. Shape storage and recovery is achieved by the glass transition and is strongly influenced by viscoelastic relaxation. While the thermomechanical properties of SMPs are highly customizable, the connections between thermomechanical properties and shape memory performance are unclear. Our goal is to develop advanced constitutive models for SMPs to study the connection between polymer structure, thermomechanical properties, and shape memory performance.

Summary of Accomplishments

In the first year of the project, we developed a finite deformation thermoviscoelastic model of tBA-co-PEGDMA (tert-Butyl acrylate poly[ethylene glycol] dimethacrylate) copolymer that incorporates stress and structural relaxation at temperatures near and above the glass transition temperature (Tg) and viscoplastic flow at temperatures below Tg. Specifically, the models for stress and structural relaxation models incorporated a broad spectrum of relaxation times. This represented a significant improvement from previous thermoviscoelastic models and allowed the model to predict realistic recovery rates measured in unconstrained recovery tests. Nonlinear viscoelastic behavior at finite strains was modeled using a discrete relaxation spectrum with N relaxation processes, each characterized by nonlinear temperature dependent flow rule with a characteristic relaxation time. To determine the N parameters of the discrete relaxation spectrum, we developed a corresponding small strain model with a continuous relaxation spectrum. The latter was described by two parameters for characteristic relaxation time and breadth of the relaxation spectrum. The parameters of discrete model were determined to approximate the cumulative relaxation spectrum of the continuous model for the limiting case of small strain and structural equilibrium.

A parameter study was developed to compare the effects of the thermoviscoelastic properties (e.g., glassy and rubbery modulus, characteristic relaxation times) and the thermomechanical programming conditions (e.g., cooling rate, heating rate) on the recovery rate of the unconstrained recovery response and the stress hysteresis of the constrained recovery response. The unconstrained recovery response was most sensitive to the viscoelastic parameters. The recovery rate correlated directly to the temperature range of the glass transition observed in the temperature dependence of the storage modulus. The stress overshoot observed during constrained recovery was caused by the constrained thermal expansion of the stiff unrelaxed material. The maximum stress obtained during recovery scaled nearly linearly with the glassy coefficient of thermal expansion and correlated with the glassy modulus.

Significance

The modeling studies provide a fundamental understanding between the thermoviscoelastic properties and thermomechanical loading conditions, and the recovery behavior of shape memory polymers, which is needed for the developmental of computational tools for the efficient design and optimization of SMP materials and devices. Moreover, the modeling studies advance the development of a continuum modeling framework for finite deformation thermoviscoelasticity. This work supports the mission of the Department of Energy through scientific discovery and innovation in physical science, engineering and emerging scientific disciplines by developing advanced models for the physical response of polymers and polymer composites. When coupled with models for piezoelectric materials, this effort presents unique possibilities for the design and development of unpowered, self-aware sensors suitable for DOE, DoD and DHS applications.

Refereed Communications

T.D. Nguyen, C.M. Yakacki, P.D. Brahmbhatt, and M.L Chambers, “Modeling the Relaxation Mechanism of Amorphous Shape Memory Polymer,” *Advanced Materials*, vol. 22, pp. 3411-3423, 2010.

Scalable Assembly of Patterned Ordered Functional Micelle Arrays

146152
Year 1 of 3
Principal Investigator: H. Fan

Project Purpose

Successful multiscale patterning (micro- to nanometer) with precision, speed, and reproducibility at the nanoscale is crucial for rapid evolution in computer logic, memory, metamaterials, photonic crystals, plasmonics, energy harvesting and storage, and nano-bio applications. Significant advances in nanopatterning technology combine "bottom-up" directed self-assembly with "top-down" lithographies, producing sub-100 nm features. However, control of nanoscale structures in the third dimension remains an unsolved challenge. Significant technical difficulties include scalable, cost-effective, and rapid fabrication of reliable patterns with low defect densities and long-range order in various materials systems. We propose to study self-assembly of amphiphilic molecular micelles to form large-area arrays on patterned surfaces, and in 3D nanoscale templates with an emphasis on compatibility with semiconductor processing for future device integration. Amphiphilic molecules form monodisperse micelles with sizes precisely defined by the molecular chain length of each amphiphilic molecule, ranging from 5–50 nm. Evaporation of micellar solutions leads to highly ordered large-area micelle arrays. Dynamic micelle assembly operating under the influence of physical 1D-3D topographical templates with characteristic dimensions having integer multiples of one- to five-times the micelle diameter will provide a means to spatially control long-range order and to direct micelle assembly into predefined hierarchical configurations. Through encapsulation, various metal, semiconductor, or magnetic nanoparticles can be introduced into the hydrophobic interior, providing unprecedented engineering of robust hybrid functional 1D-3D micelle arrays and their collective electronic, optical, or magnetic behaviors. For example, although the behavior of periodic dielectric structures, so-called "photonic crystals," are quite well understood, the response of metallo-dielectric structures with coupled collective plasmonic and dielectric responses are quite poorly understood, despite their great potential application in advanced devices. Precise nanoscale patterning of these arrays will enable fabrication of controlled nanostructures for devices such as surface enhanced Raman sensors and photonic crystals.

Summary of Accomplishments

1. Developed a cooperative self-assembly process to synthesize monodisperse polymer micelles with narrow size distributions. We used amphiphilic polstyrene-b-polyvinylpyridine (PS-PVP), as a main structure-directing agent. We used optically active molecules such as porphyrins (Prs) as building blocks with controlled hydrophilic groups such as -OH, -COOH, etc. that are capable of forming hydrogen bonds with PVP of the block copolymer to form monodisperse core (PVP) – shell (PS) micelles in hydrophobic solutions. Conversely, the same amphiphilic block copolymer was used to synthesize the inverse, core (PS) – shell (PVP) micelle structure dispersed in aqueous solutions. The dynamic PVP shell can swell and condense over a range of ~200 nm offering unique assembly opportunities not attainable with rigid nanoparticles.
2. Fabricated large-area array of ordered polymer micelles. Through a solvent evaporation process, we were able to form large-area arrays of these nanoparticles on planar substrates (e.g., Si wafer, glass slide, etc.).
3. Fabricated 2D patterned structures. Using nanoimprint lithography and a custom tip based imprint patterning approach, we have fabricated 2D patterned structures for use as micelle assembly directing agents. Nanoimprint lithography offers rapid fabrication of large-area substrates that can direct the assembly of micelle nanoparticles. The tip based imprint method offers the possibility to create virtually any topographic structure.

4. Performed initial work on direct assembly of polymer nanoparticles on these patterned structures. Through dip-, cast-, spin-coating, we are developing methods to fill the patterned substrates in a highly controlled fashion. Initial work thus far has focused on the assembly of micelle nanoparticles in 2D hole arrays in SU8. We demonstrated exceptional control over template hydrophobicity and surface charge using self-assembled monolayers to optimize the template directed assembly. We expect that our developments and procedures used for 2D assembly will directly extend to assembly in the third dimension.

Significance

This work provides bottom-up methods in the synthesis and control of matter on multiple length scales. The new nanostructures and the degree of control would provide benefits to energy and national security applications. Fabrication of scalable patterned structures and facile and scalable self-assembly processes for ordered arrays, and their use as templates for metallic nanostructures in energy storage, photonic, and sensor applications, will impact DOE/DHS missions in national security.

Discovering Tensor Structure via Higher-Order Eigen-Decompositions

147296
Year 1 of 1
Principal Investigator: T. G. Kolda

Project Purpose

Numerical multilinear algebra (so-called tensor computations) is an emerging field that considers mathematical objects having three or more modalities or dimensions. In 2005, two groups of researchers in the US and China defined the novel concept of tensor eigenvalues and eigenvectors. Though initially just a theoretical concept, an application for tensor eigen-computations has already emerged in medical imaging and more applications are anticipated in physics, network science, biology, etc. The goal of this project is to discover computational methods for computing tensor eigenvalues and eigenvectors. Although there have been a number of papers on this topic, only analytical methods for tensor eigen-calculations have been considered thus far. There is a critical need for numerical methods to address these problems. A challenge is that the full characterization of the tensor eigen-problem still eludes researchers, thus, we will need to address fundamental mathematical questions in order to develop reasonable computational methods. For example, it is unknown how to calculate the number of eigen-pairs that a tensor may have. Further, different versions of the tensor eigen-problem are characterized by different choices of the definition. We propose to leverage Sandia's extensive expertise in tensor computations and numerical linear algebra in order to address this challenging and important problem. Calculation of even one such pair is a nonlinear global optimization problem. This is an emerging and challenging field of research that is high risk not only due to its difficulty but also because it does not yet have many applications, but we anticipate that early work in this field will establish Sandia's leadership in this domain.

Summary of Accomplishments

We have accomplished our goal of developing a computational method for computing tensor eigenpairs; it is called the shifted symmetric higher-order power method. It is a simple method and guaranteed to converge to a tensor eigenpair. It is a novel contribution to the field. Through an informal collaboration with researchers in the Mathematics Department of the University of California, Berkeley, we have also discovered the exact number of eigenpairs for a given tensor.

Significance

The project is relevant to the DOE's mission of Scientific Discovery and Innovation. It is high-risk fundamental mathematical research that has limited applications, thus far. However, based on early applications in medical imaging, we expect that the tensor eigen-problem will have a wide range of potential applications with the DOE, including other types of imaging (underground, outer space, etc.). We have been working with Sandian David Rogers in applications to molecular conformation.

Self-Activating and Doped Tantalate Phosphors

147298
Year 1 of 1
Principal Investigator: M. D. Nyman

Project Purpose

Luminescent materials (phosphors) play an important role in multiple advanced-technology applications including solid-state lighting, energy and matter detection, medical imaging, and displays. Given this range of utility, properties — including color and brightness, excitation energy, compatibility with biological systems and the environment, and morphology — must be highly tunable. We have discovered a class of Eu-doped rare-earth tantalate materials that have ideal characteristics for multiple applications. They are bright (>75% quantum yield), are excited by a variety of wavelengths (UV, blue and green), can be produced as highly dispersible nanoparticles, and are incredibly inert and stable. In particular, these materials are promising candidates for blue-pumped LEDs for solid-state lighting. In the proposed project, we will expand the class of tantalate phosphors through development and optimization of novel materials, and characterization of the luminescence that results from both doping and self-activation of tantalate anions. We are focusing on the unexplored lithium lanthanum tantalates. The most promising materials will be further pursued for applications such as biomedical imaging and solid-state lighting.

Lithium lanthanum tantalates have been investigated in-depth as electrolytes, but their luminescent properties are virtually unexplored. These materials offer unprecedented compositional and structural flexibility that directly influences luminescent behavior. Variations we will pursue include the following: 1) lithium vacancies that produce corresponding lattice distortions and metal oxidation state changes; 2) lithium-tantalum disorder on the octahedral lattice sites; 3) rare-earth (Eu, Tb) doping on the lanthanum site and transition-metal (Cr) doping on the Li-Ta sites; and 4) phase changes induced by lithium extraction from the lattice. We have also observed a self-activated tantalate ion luminescence in lithium lanthanum tantalate materials that has never been reported previously. As part of this study we will investigate the origin of this behavior, and determine if it can be utilized to enhance the emission of dopants.

Summary of Accomplishments

The primary goal we pursued was determining the origin and mechanism of self-activating blue-excited, red emission from La_2LiTaO_6-perovskite (LiLaTa-perovskite). It is likely a self-activating mechanism of the tantalate ion. It has never been reported before and could represent an important new phenomenon that may be exploited. For example, this self-activation coupled with a Eu-dopant may produce the thus far elusive red phosphor for blue-pumped LEDs. We determined that direct synthesis of LiLaTa-perovskite does not exhibit the strong red emission. Rather, the LiLaTa-perovskite must be formed from $La_3Li_5Ta_2O_{12}$ (LiLaTa-garnet). In this process, the Li of the garnet is partially exchanged for H^+ by an acidic ion-exchange, and then is converted to the perovskite by heating above 600 °C. The La:Ta ratio of the garnet is 1.5:1 and the La:Ta ratio of the perovskite is 2:1, and the conversion of garnet to perovskite as described above does not change the La or Ta content, this suggests that the perovskite formed via the garnet has a formula of $La_2(Ta)(Ta_{0.33}Li_{0.67})O_{6.67}$. In other words, there must be vacancies in the lithium site, and substitution of Ta onto the Li site. This is probably related to the red emission. Another reasonable formula might be $La_2(Ta)(Ta_{0.1}Li_{0.5}V_{0.3})O_6$, or something in between. These formulations are being explored by direct synthesis to gain more control (rather than the acidic aqueous treatment followed by heating). The excitation spectra of red-emitting LiLaTa-perovskite revealed a broad adsorption band (~100 nm wide) that peaks around 500 nm. Its emission spectrum is also broad (~80 nm) and peaks around 710 nm. The very broad adsorption band is particularly interesting for blue-pumped LED applications, in that variation in the blue LED emission can be more easily tolerated.

Significance

This work represents advances in fundamental science (new luminescence mechanisms) and functional materials that can be applied in a number of DOE mission areas. Development of alternative energy-efficient lighting sources is a high priority mission to both Sandia and DOE. Relevant DHS mission includes defense, in that these materials might be applied in radiation detection or material tracking.

The most immediate application we are investigating is in the area of solid-state lighting, under the auspices of the Energy Frontier Research Center (EFRC) solid-state lighting program. We are continuing these studies in the EFRC program. Every solid-state lighting company with whom we have communicated has stated that the red phosphor for LED devices is one of the highest priority technologies for lighting devices. It must specifically emit red with blue excitation. Another valuable feature of this phosphor is that it is a chemically and physically robust, nontoxic oxide. Furthermore, fundamental science is the key product of the EFRC programs. This phosphor has an unprecedented mechanism of luminescence, the nature of which we do not completely understand yet. It is likely Ta in an unprecedented geometry such as tetrahedral, or related to oxygen vacancies within the oxide lattice. We have ruled out the possibility of reduction of Ta(V) to Ta(IV) as a mechanism. Thus, determining this mechanism will be an extremely interesting fundamental result for this Basic Energy Sciences program. Furthermore, understanding this mechanism will allow us to develop more tantalate-based phosphor materials. Tantalates are incredibly robust and inert and therefore of particular interest for industrial applications.

Application of Multivariate Analysis Techniques to Measurements in Optically Thick Environments

148896
Year 1 of 1
Principal Investigator: T. A. Reichardt

Project Purpose

Fluorescence excitation-emission data are utilized in the fields of medicine and analytical chemistry, as well as for scientific studies focused on the environment, defense/security, and energy. Specifically relating to energy research, Sandia has recently begun an effort to characterize the fluorescence signatures of bulk algal samples for assessment of both local and remote approaches for appraisal of algal health for biofuel production. Considering a matrix of excitation-emission data, the norm of the matrix is ideally proportional to the outer product of the excitation spectrum and emission spectrum. However, nonlinear deviations, also known as inner filter effects, can result from absorption of both the excitation (termed "primary absorption") and fluorescence (termed "secondary absorption"), with both effects increasing with increasing concentration.

The purpose of this project is to acquire a dataset for evaluating the ability of multivariate approaches to account for inner filter effects. We anticipate that such effects will be important when probing algal samples, for which the absorption and emission spectra of different pigments significantly overlap. Sandia is a recognized leader in developing and applying multivariate approaches, using such techniques to quantify the relative components in time-of-flight secondary ion mass spectrometry (TOF-SIMS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy, X-ray diffraction, and spectrally resolved laser-induced fluorescence (LIF). Applying multivariate approaches to data collected from the cuvette-contained samples will allow extrapolation of the cuvette results to a fieldable LIDAR (light detection and ranging) system. More generally, the methods discussed here could have much broader applications in the field of remote sensing, where nonlinear effects routinely degrade the fidelity of analysis by linear spectral unmixing.

Summary of Accomplishments

We acquired 688 spectra by measuring 11 different cuvette-contained Coumarin/Rhodamine mixtures at different (x,y) spatial locations, where the x-coordinate corresponds to the penetration of the laser into the sample (associated with primary absorption) and the y-coordinate corresponds to the path length through which the emission must pass (associated with secondary absorption). From the acquired spectra, spanning the spatial range x = 0.0–7.0 mm, y = 0.0–7.0 mm, with a 1.0-mm grid spacing, we made several observations.

1. The self-absorption over the 460–600 nm wavelength range matches the primary absorption feature of rhodamine.
2. For each value of x, the spectrum for pure coumarin is independent of the y-coordinate, demonstrating that coumarin does not exhibit self-absorption. In contrast, the opposite is true for pure rhodamine.
3. The fluorescence spectra were recorded with adequate signal-to-noise ratio even while spanning two orders of magnitude in signal strength. We anticipate that the absorption of 355-nm light could likely be calculated from the spectrally integrated signal strength as a function of x for a given value of y.
4. Fluorescence LIDAR measurements might be subject not only to the absorption of the initial fluorescence, but to the re-emission of that absorbed light as well. We have evidence that such re-emission is present in our laser-dye data. The 530–570 nm absorbance decreases with increasing values of y, resulting from photons absorbed at shorter wavelengths being subsequently emitted at longer wavelengths — an effect which becomes more pronounced with increasing path length of the emission through the sample.

Significance

This work has resulted in a data set rich in nonlinear effects to which we can apply multivariate approaches. With these data, we will assess the ability of principal component regression (PCR), partial least squares (PLS), classical least squares (CLS), and multivariate curve resolution (MCR) to understand linear and nonlinear effects when evaluating the fluorescence LIDAR signal return from optically thick media.

While this project focused on interpreting data acquired through laser-based measurements, any mathematical approaches developed to account for nonlinear effects in these data would have applications well beyond LIDAR. In particular, the interpretation of multispectral/hyperspectral data for classification or target detection is hindered by nonlinear effects such as Fresnel reflection, absorption, re-emission, scattering, and diffraction. As with laser-induced fluorescence, forward models can be used to predict these effects, but improving solutions of the inverse problem is of high value. If multivariate approaches could account for nonlinear effects in a rigorous manner, this added capability would likely find broad use in the sensing community.

Influence of Point Defects on Grain Boundary Motion

149049
Year 1 of 1
Principal Investigator: S. M. Foiles

Project Purpose

Understanding and controlling the evolution of materials microstructure, including grain size, is key to the development and evaluation of novel materials especially in extreme environments. This, in turn, requires a quantitative understanding of the mobility of the grain boundaries. We have recently completed an extensive study of boundary mobility in the absence of crystalline defects. However, boundary motion can be driven by a difference in the defect energy density on the two sides of the boundary. This is relevant both to the metallurgical phenomena of recrystallization and also to the evolution of microstructures in a radiation environment. In the latter case, displacement cascades can produce large point defect densities that can be locally inhomogeneous and so cause boundary motion. The goal of this project is to perform the first evaluation of the mobility of grain boundaries driven by a difference in point defect densities across the boundary. This is directly relevant to grain boundary motion due to radiation damage. It also addresses a long-standing question as to whether grain boundary mobilities associated with curvature-driven growth are the same as the mobilities in defect-driven growth such as in recrystallization.

Summary of Accomplishments

This study has looked at the influence on grain boundary motion of the interaction of a high concentration of vacancies in the vicinity of the grain boundary. The current study is only qualitative. A more quantitative analysis was not possible within the parameters of this project. The results indicate that the influence of vacancies on boundary motion depends on the relative mobility of the vacancies and the grain boundary. In the limit that the boundary mobility dominates, there appears to be a short-ranged bias for motion that sweeps up the vacancies. However, if the boundary then fluctuates away from the vacancies, its subsequent motion appears random. In the limit that the vacancy mobility dominates, the vacancies are absorbed by the boundary when they impinge upon, but do not appear to induce significant boundary motion. Note that the two boundaries in the current study were chosen for their relatively high mobility, so the latter scenario is probably the more common. It was also noted that the absorption of vacancies made only modest changes in the boundary energy and did not appear to change the boundary mobility. This is consistent with the prevailing view that grain boundaries provide ideal sources/sinks for vacancies.

The present work suggests that, for the previous simulation studies that reported boundary motion due to the presence of displacement cascades, the vacancies produced in the cascades are not the primary cause of the motion. This suggests future studies of the influence of self-interstitials on boundary motion. Another area of future research suggested by this study is the temperature dependence of grain boundary mobility. In this study, deviations from the generally assumed Arrhenius temperature dependence were observed. It would be important to understand the factors that control the temperature dependence of mobility.

Significance

This work will expand the fundamental understanding of factors that influence grain boundary motion and, therefore, grain growth. Sandia's success relies on being at the forefront of materials characterization and development. The current work will advance the fundamental understanding of the mechanistic processes that control the evolution of microstructure especially both for standard processing, i.e., recrystallization, and for radiation environments.

Hyperspectral Flow Cytometer

149204
Year 1 of 1
Principal Investigator: M. B. Sinclair

Project Purpose

Hyperspectral imaging has established itself as an enabling tool in biological research. The ability to simultaneously measure the emission from multiple fluorescent species allows one to simultaneously monitor multiple biological processes or structures. In addition, the effects of unwanted artifacts such as autofluorescence or crosstalk can be eliminated with hyperspectral data. We have recently developed and demonstrated a hyperspectral confocal microscope that is capable of rapidly acquiring hyperspectral images with submicron spatial resolution. We will employ the lessons learned from the construction of the microscope to develop a hyperspectral imaging flow cytometer that will achieve many of the same benefits as are achieved with the microscope. The instrument will utilize an excitation laser that is rapidly scanned in the direction perpendicular to the flow direction in a flow cell. Thus, the motion of biological cells through the flow cell, coupled with the laser scanning will allow for 2D scanning of the cells. The collected fluorescent light will be dispersed in a prism spectrometer and recorded by a fast CCD (charge-coupled device) detector. The instrument will be configured to provide variable resolution images and will also be capable of operating in a non-imaging mode where a single spectrum will be obtained as the cell transits the focal volume. It is anticipated that, like the hyperspectral microscope, this instrument will have a significant impact on multiple areas of interest for Sandia such as algal biofuels.

Summary of Accomplishments

During this FY, we performed extensive literature searches and internet searches to verify the uniqueness of the proposed approach. We did not find any designs that were similar to the one proposed here. We have performed calculations to determine the appropriate range of microfluidic flow rates and laser scan speeds required for the cytometer. We determined a range of parameters for which the hyperspectral confocal microscope can be reconfigured to provide proof of concept for the cytometer. We obtained square-channel capillary tubing and fabricated a simple flow cell that is compatible with optical imaging. We have assembled a pressure-driven flow system capable of producing flow velocities in the imaging cell that are compatible with the imaging system. We have begun integration of the flow system with the hyperspectral imaging system.

Significance

If successful, this new instrument would be ideal for fast characterization of algae and could be used to optimize their characteristics for biofuel production.

Managing Shared Memory Data Distribution in Hybrid HPC Applications

149571
Year 1 of 1
Principal Investigator: K. Pedretti

Project Purpose

Sandia and other national laboratories have invested heavily in message passing applications for distributed-memory parallel computers. In the past, these computers have contained a single processor core, or a small handful of cores per compute node. In this environment, Sandia and others have found the “message passing everywhere” model to be the most effective means of programming these machines, both in terms of performance and programmer effort. Today, the ongoing movement in the computing industry to many-core computing, with compute nodes containing tens to hundreds of cores, is forcing application developers to again reexamine shared memory programming models for intra-node use coupled with message passing for inter-node communication. There are several ongoing efforts within Sandia, such as the Trilinos Mantevo project, that are exploring such hybrid models. One of the critical issues discovered by these efforts is the importance of good intra-node data distribution, so that cores access nearby memory as much as possible. The tools for accomplishing this are currently primitive, ad-hoc, non-portable, incomplete, and, in general, not well understood. This project will explore and invent new options for managing intra-node data distribution for commonly used shared-memory programming models. The overall goal will be to devise a set of standard application interfaces for managing data distribution (placement, migration, and interrogation). One promising approach is to leverage the object-oriented abstractions provided by the Trilinos framework to expose the new capabilities, making them automatically available to a large set of existing applications. We will also pursue operating-system-level mechanisms for automatic data migration and load balancing, based on virtual memory techniques and performance counter data. If successful, the results of this project will enhance our understanding of the issues surrounding intra-node data distribution and provide tools for effectively managing it.

Summary of Accomplishments

In this project we examined several existing techniques for managing data distribution in a multicore NUMA (Non-Uniform Memory Access) environment, the basis for the upcoming “Cielo” capability supercomputer. As scientific applications are becoming increasingly hybrid, incorporating threaded programming models within nodes, support for data distribution becomes a limit on intra-node scalability. We demonstrated the static nature of current techniques, which require time-consuming code modifications or user intervention. On our 24-core, 2-socket, 4-NUMA domain test system, performance differences of up to 5× were observed between the default operating system data placement policy and optimized policies, such as “migrate on next touch.” We utilized existing profiling tools to visualize application data access patterns, enabling a more complete understanding of our application domain. To address the limitations observed, we have begun to develop a new approach that monitors application behavior at runtime, using performance counters and memory management information, to dynamically migrate memory pages without user intervention.

Significance

Heterogeneous many-core processors with deep memory hierarchies and intra-node nonuniform memory properties are expected to be a pervasive component of exa-scale computers, which are anticipated to appear in the 2018 time frame. This project is focused on creating key enabling technologies for managing intra-node data distribution on these systems, which will be critical for achieving high performance. All mission areas that require exa-scale computing could benefit from this work.

Biotechnology Development for Biomedical Applications

149665
Year 1 of 1
Principal Investigator: S. A. Casalnuovo

Project Purpose

We propose a four-component technical project that applies Sandia's scientific and engineering expertise to specific problems at the forefront of cancer research.

- Computational Biology: The enzyme L-asparaginase (L-ASN) is used to attack asparagine-deficient cancer cells. However, L-ASN also consumes glutamine, causing serious side effects. We will apply Sandia developments in molecular modeling to design stable enzyme mutations with improved selectivity for asparagine over other amino acids resulting in improved cancer chemotherapy.
- High-Performance Prosthetic Limbs: Linking man and machine by making electrical connections to the peripheral nervous system could yield tremendous benefits for advanced prosthetics. Physically interfacing growing nerve tissue with engineered electronics with adequate longevity, biocompatibility, and functionality has proven to be the core underlying challenge. We will develop new regenerative nerve interface electrodes that are materially and structurally compliant, incorporate nanoparticle-doped polymer systems, and are inspired by micro-neurosurgical practice, therefore overcoming current limitations.
- Biodetection: Monitoring for rare circulating tumor cells (CTCs) in blood is one of the most promising options to identify metastatic processes. Microfluidic chips are a promising solution to this "needle in a haystack" technical challenge. Sandia will apply its microfluidic chip expertise to improve the efficiency of CTC capture and to integrate a biochemical analysis capability to evaluate therapy options.
- Bioinformatics: The most often used visualization of "-omic" data is the clustered heat map (CHM) but, due to the vast increase in the amount of experimental data available, the computational times necessary for statistical calculation of CHMs has become limiting. We will explore novel parallel statistics algorithms to dramatically speed up the analysis of large arrays of biological data, leading to more interactive ways to extract information from these data sets, potentially inspiring new approaches for data analysis, and improving our capabilities for systems-level analysis necessary for improving the efficacy of personalized therapies.

Summary of Accomplishments

- Computational Biology: We have performed the first nanosecond time-scale simulations of the full L-ASN2 tetramer. We have developed preliminary hypotheses for mutations that will increase L-ASN2 selectivity as well as structural insight into tetramer stability. Key mutation sites were identified based on residues with high probability for contacting the unwanted glutamine, but not the required asparagine substrate. Additional mutation sites have been identified on a flexible surface loop that forms the active site upon substrate binding.
- High-Performance Prosthetic Limbs: Our work suggests that polymer systems can be made conductive by adding multi-walled carbon nanotube (MWCNT) fillers, but that it is important to control the structure and distribution of these particles to achieve useful, consistent and predictable levels of conductivity. Our data suggests that conductive composites will act primarily as conductors with modest capacitance, providing

encouragement for the viability of this approach. We have also shown that electrospinning can be used with very different polymer systems to create MWCNT-filled structures, and that changes to process parameters can control the geometry of electrospun films.

- Biodetection: We have demonstrated the capture of LNCaP human prostate cancer cells using a novel microfluidic device. The detection of protein markers for LNCaP cells has been demonstrated with fluorescence techniques. We are developing equivalent catalytic electrochemical techniques but further development is required before this approach can be reliably used.
- Bioinformatics: We have developed a set of routines for generating both simple and composite clustered heat maps for a variety of input data. We have demonstrated the functionality of this toolbox by clustering protein kinases based on ligand binding affinities.

Significance

The capabilities developed in this project will support biological weapons detection and biological warfare nonproliferation efforts of DoD, DHS, and the intelligence community. They will also support warfighter protection and rehabilitation efforts.

Advanced Atom Chips with Two Metal Layers

149939
Year 1 of 1
Principal Investigator: M. G. Blain

Project Purpose

We propose a multi-metal layer atom chip for advanced position control of an ultracold ensemble of trapped atoms. Atom chips are an intriguing system for precision metrology and quantum information devices. These devices combine ultracold atoms—well known for pristine quantum control—with the precision of microfabrication techniques. Using the magnetic fields generated by current-carrying wires microfabricated upon the substrate, atoms can be confined via the Zeeman effect. This allows magnetic guides for matter wave interferometers and atom conveyors for controllably positioning atoms near microfabricated structures and optical resonators. An attractive prospect for atom chips is the possibility of constructing more complex potentials using complicated conductor patterns, and the precise spatial and temporal control of the resulting magnetic potentials. However, modern atom chips are single layer or ad-hoc multilayer devices, which limit the flexibility and repeatability of the design. In our approach, we will use a true multilayer metal atom chip to demonstrate a crossed-wire conductor pattern that traps and controllably transports atoms across the chip surface to a target of interest.

Summary of Accomplishments

We have initiated the construction of more complex atom chips to realize more precise spatial and temporal control of the resulting magnetic potentials, and hence the spatial positioning of individual atoms. Most modern atom chips are single level or ad-hoc, macroscopic multilevel conductor devices that limit the flexibility and repeatability of the design. In this work, we have defined a true multilayer metal microfabrication process to build an atom chip capable of demonstrating a crossed-wire conductor pattern that traps and controllably transports atoms across the chip surface to a target of interest. Demonstration of this device, which is still being fabricated, will be a first of its kind. We have a developed the multilevel conductor microfabrication process, completed the device design and layout, and initiated fabrication of a crossed-wire atom chip for advanced position control of an ultracold ensemble of trapped atoms. Unique to the fabrication process is the replacement of plasma deposited silicon dioxide (SiO_2) as the inter-metal dielectric with sputter-deposited aluminum nitride (AlN), a high thermal conductivity dielectric material. As the thermal conductivity of AlN is two orders of magnitude greater than SiO_2, the use of AlN should allow currents on the order of several amps to be sustained by the conducting wires. Using the results of Biot-Savart law modeling to compute the magnetic field generated by a steady current through the wires, we have designed an atom chip that allows atoms to be confined via the Zeeman effect. The magnetic guides designed here serve as an atom conveyor to controllably position atoms near microfabricated optical cavities. We have also demonstrated the integration an array of surface microcavities on the surface of the atom chip, each of which can serve as one half of an optical cavity.

Significance

Microdevice scale integration of optical cavities with atom chips will enable new capabilities for those quantum information processing techniques (for example both quantum sensing and quantum computing) that require the interconversion of information between photons and atoms. Such capabilities have the potential to dramatically improve the efficiency of quantum information processing, capabilities of which are relevant to Sandia's missions. Understanding and realizing the potential and impact of photon-matter interconversion on quantum computing and quantum sensing has impact on multiple national security missions of DOE and federal agencies such as the National Security Agency, the Intelligence Advanced Research Projects Activity, and the Defense Advanced Research Projects Agency.

Statistical Measures for Change Detection

150122
Year 1 of 1
Principal Investigator: K. M. Simonson

Project Purpose

This project will develop and study statistical measures for change in images collected using Synthetic Aperture Radar (SAR) sensors. Standard measures for change in complex imagery, now in widespread use in the SAR community, include the coherency factor and the change in image magnitude. These measures can each be computed on a pixel-by-pixel basis over registered images collected during two different revisits to a single scene. The resulting change maps highlight scene elements whose complex signature (magnitude and/or phase) differs from one revisit to the next.

While coherency and magnitude change maps provide much valuable information, the statistical properties of the associated measures make them prone to artifacts from a variety of noise sources. In particular, the sample coherency factor is highly variable when the underlying coherency is low, and magnitude change is extremely sensitive to small changes in the flight path of the moving platform on which the radar is mounted.

The goal of this project is to develop and test two-visit and multivisit SAR change measures that are sensitive enough to highlight real scene change, while maintaining a high level of robustness to the types of system changes (noise, flight path, small registration errors) that are inherent in SAR collections. The performance of all proposed measures will be quantified over a large collection of exercise and real-world data from various Sandia radar systems.

The development of new statistical change measures will help Sandia to maintain its position as a technical leader in radar sensing and processing applications throughout the intelligence, surveillance, and reconnaissance community.

Summary of Accomplishments

We defined three new measures for SAR change detection, and compared their mathematical properties to those of existing measures found in the literature or applied in practice. The new measures are all designed to gauge change in the sample coherence function for repeat-pass SAR operations. The statistical distribution of the sample coherence function has several undesirable features, most particularly a variance that increases as the mean decreases. To enable robust inference, the new measures all involve transformation of the raw sample coherence values to a different domain in which the types of changes sought are more readily distinguishable from noise-induced patterns. The first metric, referred to as the “Z-transformed change product” employs a normalizing transformation that is commonly applied in the (real) correlation domain, but which has also been shown to provide a good approximation for the (complex) coherence function. Use of this function enables construction of a test statistic for coherence change, whose distribution is approximately standard Gaussian under the null hypothesis of no change. The second measure, a “normalized coherence difference” utilizes a heuristically selected sigmoid function to provide robustness to noise at the low and high ends of the coherence scale, and helps to reduces the visual clutter present in many SAR change maps. And the final measure, called the “statistically normalized change product” uses pixelwise mean and variance estimates for coherence, computed over a sequence of complex SAR images, to detect departures from typical patterns of change in a scene that is regularly revisited. SAR data from a wide range of sources were employed in developing the new measures, and demonstrating their performance in relevant mission scenarios.

Significance

Sandia and DOE are established leaders in the use of SAR sensors for national security missions, with expertise in designing and building sensor systems, and developing near-real-time algorithms for image processing and exploitation. The work proposed here will benefit existing and future systems, developed for a range of military sponsors, and will help Sandia to advance our reputation for excellence in the development and implementation of state-of-the-art radar processing algorithms.

Information Sharing with Information Assurance through Cryptographic Obfuscation

150275
Year 1 of 1
Principal Investigator: J. Mayo

Project Purpose

The goal of this research was to investigate new potential solutions for secure information sharing — enabled by program obfuscation and other cryptographic techniques — that would have strong benefits for national security. We focused on assured sharing scenarios with a two-way privacy objective, for data searches that do not reveal unnecessary information to their requestors and also do not make query details visible to data stewards.

Summary of Accomplishments

We identified relevant contributing approaches from existing work, conceptualized several candidate solutions adapted from these approaches, and made preliminary assessments of their functionality and security attributes. The candidate solutions were found to have different and complementary tradeoffs.

Significance

This work not only offers preliminary guidance on potential solutions, but also confirms the value of further research in this area and establishes some vocabulary and reasoning for such investigations. The work helps to establish Sandia's role in information sharing research related to national security. Strong interest in this area is evident from a range of potential agencies in the intelligence community, DoD, DHS, law enforcement, and industry.

Preliminary Work Toward Developing Efficient Thermal Neutron Detection Using Gd Conversion Layers

150636
Year 1 of 1
Principal Investigator: M. P. Siegal

Project Purpose

Novel thermal-neutron-detection technologies with high efficiency are needed. The detection of special-nuclear-material (SNM) is of critical importance for national security and specifically nonproliferation. Many forms of SNM emit gamma-rays and neutrons. Characteristic gamma-rays from SNM are usually of moderate energy and easily shielded. In contrast, neutrons emitted from SNM are more penetrating and are therefore an important observable. He-3 gas-filled tubes with polyethylene moderators are ubiquitous for thermal-neutron-detection because of their high efficiency and low sensitivity to gamma radiation. Due to a recent increase in demand for He-3 and its very limited production, the remaining domestic supply is currently being rationed.

We propose to develop a thermal-neutron-detector that exploits the high-thermal neutron capture cross-section of gadolinium (Gd) instead of He-3. The very high cross section of Gd means that ~ 20-µm thick coatings can be used for efficient neutron absorption, which is necessary for the reaction products to escape the active medium. Gd emits both gamma rays and energetic “conversion” electrons following neutron absorption. The emitted electrons have energies ranging from 10s–100s keV. The measured electron signal produced from such a detector will be directly proportional to the incident neutron flux.

This work will develop protocols necessary to reduce the residual stress associated with the physical deposition of Gd so that films with thicknesses greater than a few micrometers can be stable without peeling from the substrate, and will perform preliminary measurements on the detection of gamma radiation from neutron capture using thin Gd foils. Detecting the number of gamma rays emitted at 79 keV and 181 keV will determine the appropriate Gd thickness. Together, these tasks will demonstrate the ability to coat thick Gd films on a substrate surface and to develop the ability to measure energetic electrons.

Summary of Accomplishments

This project had two major milestones and achieved both of them.

First, Gd has never been used to detect conversion electrons from thermal neutron capture. Therefore, this initial project was designed to reduce the technical risks for such development. The critical factor is the ultimate Gd film thickness required for this — approximately 20 microns. The physical deposition of any film results in significant residual stress, which as thickness increases beyond a certain limit, causes the films to spall or peel from a substrate. Our goal was to make this stress negligible by controlling the kinetic energy of the depositing Gd species during sputter deposition. During the course of experimentation, we also learned that the Gd films rapidly oxidized in air upon removal from the deposition chamber, causing the stress to slowly relieve itself over a period of days and resulting in “splotchy” films that easily flaked from the Si substrate. The problem was resolved by depositing a thin 50-nm layer of Nd-doped Al onto the Gd surface before air exposure. This prevented unwanted oxidation and enabled stable measurements of the residual film stress. We quickly learned how to grow negligible stress films and produced a stable 20 micron thick Gd film directly on 2-inch diameter Si(100) without the use of adhesion layers. The method developed resulted in an invention disclosure.

Second, we demonstrated the detection of gamma rays associated with the release of conversion electrons via thermal neutron capture in Gd foils. Unfortunately, gamma rays are ubiquitous, and can be easily shielded from detection. However, this demonstration shows the feasibility of using Gd for neutron detection. Follow-up work will focus on developing the capability to detect the associated conversion electrons, which do not exist in the background and will eliminate false positives.

Significance

This work confirms that gamma ray detection of neutron capture is difficult to isolate from the background and that detection of conversion electrons will lead to easier interpretation and the elimination of false positives. Nevertheless, detection of specific gamma rays above background are related to specific conversion electrons. Future work will focus on developing such detection.

Thermal neutron detection is required for a range of national security and nonproliferation missions. DOE's Radiation Sensors and Sources Roadmap lists large-area thermal neutron sensors as both high priority and impact. Such neutron detectors may also benefit other NNSA organizations that conduct nonproliferation, treaty compliance, and verification missions. The DHS Domestic Nuclear Detection Office also specifically calls out a need for thermal neutron detectors that do not use He-3.

Securing Application Software on Untrusted Hosts

150637
Year 1 of 1
Principal Investigator: R. C. Armstrong

Project Purpose

Authentication is fundamental to allowing electronic access to computer networks, and yet devices such as SecureID™ are computers themselves and subject to similar vulnerabilities. Current digital authentication techniques for users and devices in computer networks assume that the underlying hardware and software operates with full integrity. However, modern systems are too complex to sufficiently analyze, making the task of discovering well-crafted exploits an exercise in luck. We need ways to execute our authentication algorithms effectively without worrying about the integrity of the system in which they are embedded.

A methodology that would permit the secure authentication in the presumed presence of unknownable malefactors would be an advantage. Such a system would have to be insusceptible to reverse engineering, tampering, and hijacking and provide a method for disabling the device from a distance that would render it inoperable forever after.

The device resulting from this project will meet these requirements, authenticating a user in the standard way by using private/public key pairs and doing so by signing challenges sent through a network. The difference here is that the user's private key, along with the code necessary to sign challenges, would be embedded in a code seal cryptographically obfuscated state machine. This will effectively make the private key stored in the device inaccessible, even to an intruder with total control over the device. Because this machine requires a sequenced instruction key from an off-device networked "oracle" held by the certifying authority, the machine operates only at the sole discretion of that authority. Without this instruction key the code seal machine is nonfunctional and can be disabled. In combination, this arrangement allows the authentication function to be carried out securely even in the presence of malware.

Summary of Accomplishments

While code seal is fully functional for compiling a state machine, the current implementation cannot use C code. Current plans call for implementing a C-code to code-seal compiler later this year and our completed work consists of a platform for the code seal engine. We have created an authentication device from an off-the-shelf small computer called a Gumstix™ that has the form factor of a stick of gum (actually about half that size). We have used Bluetooth connectivity as well as USB to authenticate with a proximate (in test ~ 30 ft) host or local desktop, with authentication to remote hosts using an existing secure shell authentication agent protocol. Biometric authentication using a thumbprint device has been incorporated to ensure that the user is with the device.

We currently have everything necessary to implement the code seal authentication described above except for the code seal compiler anticipated later this year. At this point the integrity of the authentication relies on physical security rather than the cryptographic authentication provided by code seal, but will be ready for fully obfuscated authentication when the new code seal compiler comes online. Exploratory work has also been done to provide the same functionality on a cell phone (where code seal would be necessary to ensure integrity).

Significance

Cybersecurity generally, and authentication in particular, is an abiding concern for DOE and DOE missions and is a required part of its infrastructure. More secure and more convenient ways to meet that concern contribute to the success of that mission.

Hardware Based Authentication Approach

150969
Year 1 of 1
Principal Investigator: J. A. Romero

Project Purpose

The ability to authenticate the source and integrity of data is critical to the monitoring and inspection of special nuclear materials, including hardware related to weapons production. Current methods rely on electronic encryption/authentication codes housed in monitoring devices. This always invites the question of implementation and protection of authentication information in an electronic component necessitating electromagnetic interference shielding, possibly an on-board power source to maintain the information in memory. The use of valuable computational resources also is required to deal with these protocols ultimately detracting from the limited total capacity of the monitoring device for data collection or logging operations. A passive method which does not rely on on-board electronics to provide the authentication capability automatically becomes attractive.

Fiberoptics has opened an area enabling information to be transferred using light as a carrier. Due to the non-charged nature of light, external magnetic and electrical fields have little effect. This property also makes it difficult to "read" information impressed on it using non-contact remote methods. The communication industry has incorporated discrete optical devices into a single fiber by introducing calculated changes in the refractive index and spacing of these changes, within the fiber. This enables manipulation of the reflectance and transmission character of the incoming light. The ability to manipulate the fiber properties in this manner is key to this project. We will explore the potential to manipulate the output spectrum and intensity of an input light source. This randomization could produce unique-signature authenticating devices with the potential to authenticate data. An external light source projected through the fiber with a spectrometer at the exit would "read" the unique signature. No internal power or computational resources would be required.

Summary of Accomplishments

We have shown that an optical fiber's spectral transmission properties can be modified. The main focus involved the use of photonic bandgap (PBG) fibers having an honeycomb structure of hollow channels through which the light propagates. This is vastly different from conventional solid core optical fibers. By depositing materials of varied refractive index along the walls of the 3- to 9-micron diameter channels, we achieved a modification of the spectral transmission properties. Atomic layer deposition (ALD) was the enabling technology. This technique has never been explored in this application and has opened a vast array of other potential applications in the area of optics, sensors, and bioactive materials. The uniqueness of the combination of ALD and PBG fibers has been the basis for submission of an invention disclosure.

Significance

By modifying the spectral transmission properties of the fiber, a first step has been taken toward producing a passive means to authenticate components or other assets in the safeguards community. This work ties to DOE's missions of reducing the global threat of nuclear terrorism and proliferation of weapons of mass destruction by providing a new safeguards tool for protection of vital assets.

As noted, the use of ALD and PBG fibers has not been explored in the literature. This now becomes a very promising area of research for applications in other technology areas. Coatings sensitive to environmental stimuli could be placed in the PBG fiber which, when exposed to a relevant environmental event, would produce a detectable response. The fibers are on the order of 125 microns in diameter, which allows their integration into components of small form factor. Other coatings exhibiting catalytic properties may also produce a unique detectable effect. Bioactive coatings similarly could produce a response that could be observed optically when exposed to relevant biological materials (for example, biothreat agents).

Uncertainty Quantification and Validation of Combined Hydrological and Macroeconomic Analyses

150971
Year 1 of 1
Principal Investigator: T. J. Brown

Project Purpose

The scientific community does not have a clear understanding of the impacts of changes in global climate on natural and man-made systems. Without analogous historical conditions, modeling provides the best way to experiment and learn about these interacting systems. There are a multiple modeling efforts underway to better understand and quantify the uncertainty in the expected global and regional climate conditions over the next 50–100 years. There are models being designed to better understand impacts of climate changes on natural systems (hydrologic). One of the research gaps that needs to be closed is demonstrating that the models and analysis approaches are valid — that we understand the problems well enough to pose solutions that are robust despite the uncertainty in the climate and regional hydrologic conditions over the next 50 — 100 years. This project will develop a generic conceptual model of the physical and logical relationships between climate, hydrologic, and economic systems to identify characteristics of valid approaches for regional analyses and identify validation tests that will build confidence in the model's ability to simulate the dynamics of large changes in water supply, water demand, and socio-economic conditions. Part of the validation design is identifying key uncertainties.

Summary of Accomplishments

In this conceptual model validation step, we developed an analysis methodology that will integrate validation into the modeling design and analysis steps. We identified model elements that are essential to identifying and understanding of the risk to national security. The next generation of risk assessment models must represent global stresses, population vulnerability to those stresses, and the uncertainty in population responses and outcomes that could have a significant impact on US national security. Dependencies between electric power, water supply, and temperature need to be represented in the next generation of climate risk models. The dynamics between surface water temperature and generator operations should be evaluated to improve quantification of the potential economic consequences of increased temperatures in countries with environmental constraints on cooling water discharge. The models and analyses need to include the policy and controls that might be used to reduce the risks.

We also identified tests that are needed to validate the models including evaluation of key assumptions about the next generation of electric power generation, electric power demand, and climate stress impacts on operational capacities. Future climate risk models should add a test at each time step to verify that the modeled changes in economic activity do not significantly alter carbon dioxide emissions and to check for internal consistency between the global climate model and the consequence models. The models also need to be expanded to evaluate key assumptions regarding the ability of global agriculture and mining to offset projected changes in US production due to reduced water availability.

Significance

This effort builds confidence in the foundational capabilities Sandia is developing for DOE Office of Science efforts, including the NNSA climate impact effort. Our intelligence community, DHS, and defense agencies are concerned about the impacts of climate change and will need demonstrated risk assessment capabilities for threats including climate change.

A Polarization Independent Silicon Photonic Transceiver

151171
Year 1 of 1
Principal Investigator: A. L. Lentine

Project Purpose

Moore's law scaling of microprocessor technology development dictates that within the next 10 years power consumption in large-scale computers will be dominated by their electrical interconnects. One technology that has emerged as a potential solution to this bottleneck is silicon photonics. Recently, we have demonstrated the world's lowest power silicon modulators at only 3 fJ/bit. These modulators also address the bandwidth limitations of traditional electrical and parallel optic communication approaches. However, these devices exhibit a severe polarization dependence that is incompatible with standard single mode fibers (e.g., SMF-28) used for optical communications. To use this device, special polarization-maintaining fibers need to be used, which adds to the cost and fabrication complexity of the complete solution. Here, we propose an integrated polarization diversity approach to demonstrate a silicon photonic transceiver that will be compatible with standard single mode fibers, and that avoids the use of special polarization maintaining fibers.

Summary of Accomplishments

We designed a planar silicon photonic polarization splitter/rotator which is the key component in a polarization-independent optical transceiver. The device is compatible with Sandia's existing silicon photonics process and allows planar edge attachment of the fibers; that will ease the insertion of the device into new silicon photonics applications.

Simulations have been performed by our collaborator at the Massachusetts Institute of Technology that calculate the loss of each polarization as a function of the length of both the splitter and rotator. The splitter length can be from 50–100 μm long with losses from 1%–2% for both the transverse magnetic (TM) and transverse electric (TE) polarization. The TM arm of the splitter is followed by a polarization rotator that converts the TM polarization to TE polarization. While modulators can be designed for TM polarization, they work best in TE polarization. The conversion from the TM to the TE mode by the polarization rotator shows a loss of about 2% at 100 μm length, and less than 1% at 150 μm. Thus, the key metric of polarization dependent loss (PDL) can be theoretically less than 0.1 dB for a combined polarization splitter and rotator device.

We also investigated an out-of-plane polarization splitter/rotator that converts both incident fiber polarizations from a near-surface normal fiber directly to TE polarization in two outgoing planar waveguides. This device is also compatible with our silicon photonics process. Other groups have achieved a PDL of 0.66 dB. However, this device will require some additional packaging development to attach the out-of-plane fibers, unlike our simulated planar design.

Significance

A complete silicon photonics platform that is complementary metal oxide semiconductor–compatible represents a new capability that will have significant benefits across nearly all DOE and DoD mission areas. From high-speed, low-power communications in high-performance and embedded computers, to radar, satellite and wireless communications applications, a complete silicon photonics platform will prove to have wide-ranging impact. The application impact extends across the DOE spectrum from scientific discovery and innovation to nuclear security and American competitiveness. Silicon photonics is very likely to transform the computing and communications industries over the next decade along with critical military and nuclear security applications.

Conceptual Model Development for Energy Security Assessment of Liquid Fuel Disruptions

151173
Year 1 of 1
Principal Investigator: E. D. Vugrin

Project Purpose

Energy security is a national priority, as energy systems are frequently necessary for the operation of other national critical infrastructure (CI) sectors. The nation needs to protect these systems against physical and cyber threats and to develop rapid, efficient recovery strategies that restore energy systems following disruptive events. The first step in securing the energy sector is the development of formal methods for energy security assessment. These methods should 1) be systems based, and 2) integrate protection and recovery processes. A systems-based methodology that represents cross-sector dependencies on civilian CI will capture cascading impacts and enable the identification of unseen vulnerabilities. Integration of protection and recovery concepts will add a dynamic component to traditional security assessment methods, enabling systems owners to compare the relative benefits of protection vs. resilience investments.

The purpose of this project is to research and develop a conceptual model representing military mission dependencies on liquid, petroleum-based fuels and interconnectivity of elements of military missions. This model will be suitable for use in the development of energy security assessments of military missions relative to petroleum fuel supply disruptions. Furthermore, it will provide a foundational approach for future development of more general energy security assessment methods. Successful completion will advance the current state of both vulnerability assessment (VA) and resilience science. Developmental efforts to integrate resilience with protection will add a new dynamic aspect to traditional vulnerability assessment methods. Researching dependencies on civilian CI will enable development of novel design basis threats, leading to more comprehensive consequence evaluation.

This approach will be more complex than existing VA methods. Developing formal descriptions of mission dependencies and interactions will be a key challenge. Resilience evaluation of systems with cross-sector dependencies is a known challenge in resilience analysis. The benefit will be a more comprehensive evaluation methodology, improving energy security.

Summary of Accomplishments

Primary project accomplishments include the following:

- We developed a conceptual connectivity model that represents mission dependencies on petroleum fuels. This model includes identification of mission connections between five basic US Air Force missions, mission dependencies on civilian and military infrastructure, mission dependencies on two types of fuel, and initial development of temporal considerations that determine the resilience of mission to fuel disruptions.
- We developed an inferential approach for identifying pipelines servicing Air Force bases in order to overcome data gaps.
- We defined a data schema for associating military missions, their functional elements, and the locations (e.g., buildings) housing these functional elements, which could be populated and implemented to meet conceptual connectivity model requirements.

- We applied this model to Andrews Air Force Base (AFB) and created a fault tree analysis of for the flight mission at Andrews AFB.

Significance

Completion of this project represents an initial step towards the development of more comprehensive vulnerability and energy security assessments. The systems-based conceptual model permits more comprehensive accounting of consequences that can cascade across mission. Additionally, this modeling approach enables the identification of system vulnerabilities (and dependencies on civilian infrastructures) that may have been previously unrecognized. Furthermore, this type of broader, comprehensive analysis approach will hopefully better prepare emergency planners for potential system disruptions.

The lessons learned on this project that relate to overcoming data gaps, developing system models of missions, and recognizing civilian dependencies will benefit the US Army Energy Security Program, the Defense Critical Infrastructure Program, US Air Force Installations and Energy, and other similar programs.

Novel Detection Methods for Radiation-Induced Electron-Hole Pairs

151175
Year 1 of 1
Principal Investigator: M. Cich

Project Purpose

Radiation detectors have long sought to improve performance by engineering material properties and detector geometry to improve the collection of carriers generated during the stopping of high-energy particles in the detector volume. The spectroscopic information about the incoming radiation energy is contained in the number of carriers collected per particle of radiation, so current detector materials required both high stopping power for the incident radiation and excellent carrier transport. We propose, in this project, to investigate new sensing mechanisms that can detect the radiation-induced carriers immediately after generation, without requiring the transport and collection of these carriers.

A number of candidate solid-state radiation detector materials offer clear improvements over commonly used germanium and silicon detectors. These advantages include higher resolution, higher sensitivity, smaller detector volumes, and uncooled operation. Unfortunately, bringing the electrical performance of these candidate materials to the level of single-crystal germanium, which has had decades of extensive development, is a barrier that may be insurmountable. However, there are other means of detecting the carrier pulse associated with the radiation-matter interaction. For instance, the generated carriers can result in a transient change in the complex refractive index. The material development then only has to optimize optical performance, which may be more forgiving of material defects than electrical performance. Alternatively, the use of radio-frequency (RF)/ microwave signals to measure the transient changes in local dielectric properties offers another frequency band in which the radiation-induced signal can be detected without the background associated with the essentially DC-coupled standard charge signal. We propose simulations of optical and RF/microwave methods for transient charge detection, focusing on determining which materials properties are most critical for optimizing response.

Summary of Accomplishments

We have conducted a preliminary study of three concepts for radiation detection, based on optical ring resonators, electron paramagnetic resonance (EPR), and RF probing of dielectric properties.

Our investigation into resonant photonic integrated circuits brought forth some interesting possibilities. A very large response is possible within a carrier excitation level consistent with energetic alphas. Many rings can be packed close together and multiplexed to form a pixilated sensor. Thanks to the use of these rings in high-speed optical integrated circuits, they are well adapted to fast readout. They may find a niche in measurement of high radiation fluxes.

Standard EPR is not sensitive enough to be used for radiation detection. Using optical detection, this sensitivity can be improved. However, optical readout methods are limited to the performance level of scintillators if the signal arises from the microwave-induced change in recombination probability of the excited state. Therefore, it would make more sense to improve scintillator materials instead of developing a new technique, unless there were a very clear means to extract either direction information or particle discrimination using optically detected magnetic resonance and a particular sensing material. We did not find obvious opportunities in this direction. Recent literature suggested that excited states can be studied with very high sensitivity using coherent anti-Stokes Raman scattering. There would be a significant amount of work needed to find the optimum detector material — it would need to have a radiation-generated radical with a large Raman cross-section. Given the probability that a known scintillator material may work in this application, a coherent anti-Stokes Raman scattering survey of those materials would be a valuable next step as a feasibility study. Finally, our look at RF stripline circuits revealed some possibilities. Detecting loss tangent changes was found to be more feasible than dielectric changes and was most practical in the 10–30 GHz frequency range.

Significance

Improvements in nuclear detection methods are relevant to a range of national security missions. The Department of Homeland Security will benefit from new capabilities of portal monitors. This project also ties closely with the nonproliferation and verification missions of DOE/NNSA by offering new options for identification of nuclear materials by spectroscopy and low-power, easily used detectors.

Optimal, Automated Threat Detection and Localization in a Cluttered Radiation Background

151176
Year 1 of 1
Principal Investigator: N. R. Hilton

Project Purpose

Processing the vast amount of radiation detection data generated during a threat search with an imaging detector is a challenge, yet quick detection and accurate location of radiological and nuclear (rad/nuc) threats are critical to US safety and security. Standard image reconstruction and analysis methods have limited ability to automatically find weak radiation sources, and they yield high false-positive detection rates because of the highly cluttered background-radiation environment. Interestingly, the field of nuclear medicine has the identical task, and recent work at the University of Arizona (U of A) has significantly advanced the state of the art in this field.

The purpose of this collaborative project between Sandia and U of A is to adapt these nuclear-medicine methods to the task of standoff rad/nuc detection, in order to solve the performance and operational problems currently plaguing this national security application. These new nuclear-medicine methods make a clear distinction between 1) image-processing methods that process reconstructed images that are easier for humans to read, and 2) the signal-detection methods we propose that are tailored in fashion that allows computers to perform specific detection and estimation tasks. This work will create a link between radiation-detection experts in two mostly isolated areas of research and development (i.e., nuclear medicine and national security), with the hope that it will lead to subsequent hardware-based demonstrations of this approach.

Summary of Accomplishments

Our proposed approach was to optimally and automatically extract the locations and energy spectra of non-background radiation sources from raw detection data. Each anomalous source could then be automatically classified as threatening or benign using spectroscopic analysis tools customized from the Sandia-developed Gamma Detector Response and Analysis Software. We can also apply this methodology to guide the detection hardware design.

We created simulation tools to study a large-area coded-aperture gamma-ray imaging system that views (while moving) random scenes of urban buildings comprised of materials with random background radiation emission characteristics. A target point source of varying activity can be randomly placed within a background scene. Our simulation tool then computes the imaging system's detector responses. To detect and locate any targets, we processed these raw data in two different ways and compared each method's performance. One method applies a scanning linear estimator (SLE), and the other uses maximum likelihood reconstruction to form images to which a threshold criterion is applied to perform the detection and localization tasks. The SLE uses statistical properties of the raw detection data, which are obtained by simulating several hundred scenes. With a real imaging system, these same properties would be obtained from observations of a similarly wide variety of locations in a city; however, no direct measurement of any specific location is needed for our method to yield the same desired performance results in that scenario.

With these simulation tools, we have demonstrated the relative performance advantage of our proposed methods for detecting and locating radiation sources hidden within a cluttered radiation background. The first simulations used monochromatic radiation for both the source and background. To these software tools, we then added the ability to simulate and process realistic spectroscopic information about both target and background sources of radiation. Results of this additional work are pending.

Significance

This project advances the state of the art in rad/nuc detection and characterization, which is directly relevant to several DOE, DHS, Defense Threat Reduction Agency (DTRA), and other national security missions. DOE and DHS DNDO (Defense Nuclear Detection Office) are two primary examples of organizations with declared interest in improving standoff radiation detection capabilities. Using what we have learned and the tools we have created, we anticipate continuing this scientific collaboration by responding to applicable proposal requests from these and other research sponsors.

The Effect of Chrome Adhesion Layer on Quartz Resonator Aging

151221
Year 1 of 1
Principal Investigator: K. O. Wessendorf

Project Purpose

Sandia uses quartz resonators for all our war reserve (WR) and joint test assembly applications. Some applications like the W76 and the possible W88 life extension program require a very stable frequency source with excellent aging (low drift) characteristics. These parts are manufactured by one of our qualified vendors outside Sandia. Over the years, Sandia and the vendor have seen aging variations that have not been explained by the typical mechanisms known in the industry. After some research in a life extension project, a small sample of parts led us to believe that chrome migration and subsequent oxidation might possibly explain the variability we observe. This project would allow us to test and analyze a group of resonators with known differentiating metallization, and via accelerated aging, determine the true cause of this variability. In this project, we propose to design and manufacture a set of quartz resonators with a wide range of metallization thickness ratios between the chrome and gold that will allow us to examine both the cause of this aging and which plating thickness ratios provide the best aging performance while not degrading other key characteristics.

Summary of Accomplishments

We aged three groups of resonators that differed only in the thickness of the chrome adhesion layer. The manufacturer Statek Corp. used three thicknesses considered thin, nominal and thick which were 100, 250 and 450 Å thick, respectively. We aged approximately 40 resonators for each group for 16 days at 105 °C and took data at 70 °C, which is the turnover temperature of the resonators. The data is showing different overall aging responses between all the groups with the nominal chrome layer showing the best aging and minimum frequency change, of all the groups. An analysis of the surfaces of a sampling of resonators showing best, average, and worst performance has been performed and the data is being analyzed.

Significance

This work relates to the Sandia war reserve projects and DOE national security/nuclear security missions. This work will assist frequency device engineering and science so that Sandia can provide higher quality components for demanding frequency control applications.

Unpublished Summaries

For information on the following FY 2010 LDRD projects, please contact the LDRD Office:

Laboratory Directed Research & Development
Sandia National Laboratories
Albuquerque, NM 87185-0123

Project Number	Title
130703	Assessment of Software Streaming Technology
130711	Information Systems Analysis using Agent Collectives
130716	Miniaturized Integrated RF Systems
130796	Nanomaterials for Surety Application
130806	Material Development for Radiation Hardness
141599	Local Space Environmental Sensing Suite
141600	Localized Ion Radiation Effects
141605	Packaged Integrated Thin Sensor
141608	Self-Consuming Structural Composites
141683	Advanced Gas Transfer Systems Technology
141690	Nanoparticle Based Filler for Neutron Generator Epoxies
142540	Surety Portal
149281	Hybrid EEG / tDCS Devices
149401	Active Radiation Detection
149567	Automated Malware Analysis
149630	Exploration of Cloud Computing
150772	Advanced Analytics for NW Supply Chain Assessments
151170	A Model-Based Approach for Detection and Avoidance of Subversion in System Development Tool Chains

Appendix A: FY 2010 Awards and Recognition

Award Description	LDRD Contribution
R&D100 Award: *R&D Magazine*: Accoustic wave Biosensor	Project 93617, "Shear Horizontal Surface Acoustic Wave Microsensors for Class A Viral and Bacterial Detection."
R&D100 Award: *R&D Magazine*: Multifunctional Optical Coatings	Project 130741, "Nanomanufacturing: Nano-Structured Materials Made Layer-by-Layer," and others.
HENAAC™ Award for Professional Achievement: *Carlos Gutierrez*	Project 117837, "Studies of the Viscoelastic Properties of Water Confined Between Surfaces of Specified Chemical Nature," and others.
Asian American Engineer of the Year: *Clifford Ho*	Project 93556, "Joint Physical and Numerical Modeling of Water Distribution Networks."
Fellow of the American Association for the Advancement of Science: *Dave Haaland*	Project 67081, "3D Optical Sectioning with a New Hyperspectral Deconvolution Fluorescence Imaging System," and others.
IEEE Fellow: *Christine Coverdale*	Project 105985, "Evaluation of New Testbeds for Hostile Environment Testing of Micromachines, Optoelectronics, and Electronics."
IEEE Fellow: *Paul Dodd*	Project 105726, "Radiation Hardened Components for Space Qualified Point-of-Load Power Conversion."
Materials Research Society Fellow: *Neville Moody*	Project 105805, "Nanomechanics of Films on Compliant Substrates to Enable New Flexible MEMS and NEMS Devices," and others.
American Society of Mechanical Engineers Fellow: *Wei-Yang Lu*	Project 126615, "Size Effects in Continuum Modeling."
American Society of Mechanical Engineers Fellow: *Leslie Phinney*	Project 67067 "Noncontact Surface Thermometry for Microsystems,"and Project 79773, "Atomic-Scale Modeling of Phonon-Mediated Thermal Transport in Microsystems."
Materials Research Society Graduate Student Award: *Carlee Ashley*	Project 141704, "Nature Versus Nurture in Cellular Behavior and Disease."
Outstanding Graduate student 2010 - The University of New Mexico Chemical and Nuclear Engineering department: *Carlee Ashley*	Project 141704, "Nature Versus Nurture in Cellular Behavior and Disease."
Brindley Lecture Award - Clay Minerals Societ: *Randy Cygan*	Project 149205, "Natural Materials for Carbon Capture."
Plenary Lecture: 14th US-Japan Seminar on Dielectric and Piezoelectric Materials: *Geoff Brennecka*	Project 142543, "Enabling Self-Powered Ferroelectric Nano-Sensors: Fundamental Science of Interfacial Effects Under Extreme Conditions."
Best Paper Award - The Minerals, Metals and Materials Society 2010	Project 131303, "Reimagining Liquid Transportation Fuels: Sunshine to Petrol."
Best Paper Award - Nuclear Weapons Engineering Analysis Conference	Project 117853, "Novel Foam Encapsulation Materials and Processes."
Outstanding Paper Award - IEEE 2009 Electronic Components and Technology	Project 117847, "3D Integration Technology for Highly Secure, Mixed Signal, Reconfigurable Systems."

Appendix B: FY 2010 Project Performance Measures

Measure	Number of FY 2010 Projects
Refereed Publications	**206**
Other Communications	**575**
Technical Advances	**123***
Patent Applications	**40***
Post-Doctoral Researchers	**83**
New Staff Hired from Post-Doctoral Researchers	**18**
Awards	**27**

*CY2009

Appendix C: FY 2010 Mission Technology Areas

Benefiting Mission Area	Number of FY 2010 LDRD Projects
DOE/Nuclear Security	**201**
DOE/Energy Security	**162**
DOE/Scientific Discovery and Innovation	**237**
DOE/Environmental Responsibility	**34**
Homeland Security	**169**
Department of Defense	**186**
Other Federal Agencies	**117**
Industry	**53**