OAK RIDGE
NATIONAL LABORATORY
MANAGED BY UT-BATTELLE
FOR THE DEPARTMENT OF ENERGY

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Laboratory Directed Research and Development Program

FY 2009 Annual Report

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Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2009 ANNUAL REPORT

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INTRODUCTION

The Laboratory Directed Research and Development (LDRD) program at Oak Ridge National Laboratory (ORNL) reports its status to the U.S. Department of Energy (DOE) in March of each year. The program operates under the authority of DOE Order 413.2B, "Laboratory Directed Research and Development" (April 19, 2006), which establishes DOE's requirements for the program while providing the Laboratory Director broad flexibility for program implementation. LDRD funds are obtained through a charge to all Laboratory programs.

This report includes summaries all ORNL LDRD research activities supported during FY 2009. The associated *FY 2009 ORNL LDRD Self-Assessment* (ORNL/PPA-2010/2) provides financial data and an internal evaluation of the program's management process.

ORNL is a DOE multiprogram science, technology, and energy laboratory with distinctive capabilities in materials science and engineering, neutron science and technology, energy production and end-use technologies, biological and environmental science, and scientific computing. With these capabilities ORNL conducts basic and applied research and development (R&D) to support DOE's overarching mission to advance the national, economic, and energy security of the United States and promote scientific and technological innovation in support of that mission. As a national resource, the Laboratory also applies its capabilities and skills to specific needs of other federal agencies and customers through the DOE Work for Others (WFO) program. Information about the Laboratory and its programs is available on the Internet at <http:// www.ornl.gov/>.

LDRD is a relatively small but vital DOE program that allows ORNL, as well as other DOE laboratories, to select a limited number of R&D projects for the purpose of

- maintaining the scientific and technical vitality of the Laboratory,
- enhancing the Laboratory's ability to address future DOE missions,
- fostering creativity and stimulating exploration of forefront science and technology,
- serving as a proving ground for new research, and
- supporting high-risk, potentially high-value R&D.

Through LDRD the Laboratory is able to improve its distinctive capabilities and enhance its ability to conduct cutting-edge R&D for its DOE and WFO sponsors.

To meet the LDRD objectives and fulfill the particular needs of the Laboratory, ORNL has established a program with two components: the Director's R&D Fund and the Seed Money Fund. As outlined in Table 1, these two funds are complementary. The Director's R&D Fund develops new capabilities in support of the Laboratory initiatives, while the Seed Money Fund is open to all innovative ideas that have the potential for enhancing the Laboratory's core scientific and technical competencies. Provision for multiple routes of access to ORNL LDRD funds maximizes the likelihood that novel ideas with scientific and technological merit will be recognized and supported.

Table 1. ORNL LDRD Program

	Director's R&D Fund	Seed Money Fund
Purpose	Address research priorities of the Laboratory initiatives	Enhance Laboratory's core scientific and technical disciplines
Reviewers	Initiative Review Committees (IRCs) composed of senior technical managers and subject matter experts	Proposal Review Committee (PRC) composed of scientific and technical staff representing the research divisions assisted by 2–3 technical reviewers for each proposal
Review process	Preliminary and full proposal review, including a presentation to the IRC, and an annual review of progress	Full proposal review including a presentation to the PRC; review of progress if funding is awarded in two phases
Review cycle	Annual	Monthly
Project budget	Typically ~$600,000	<$190,000
Project duration	24–36 months	12–18 months
LDRD outlay	~80% of program	~20% of program

Director's R&D Fund

The Director's R&D Fund is the strategic component of the ORNL LDRD program and the key tool for addressing the R&D needs of the Laboratory initiatives. The initiatives, which are the focus of the Laboratory Agenda, are the critical areas on which the Laboratory must concentrate if it is to be prepared to meet future DOE and national requirements for science and technology.

The success of an initiative depends to a large extent on the Laboratory's ability to identify and nurture cutting-edge science and technology on which enduring capabilities can be built. To do this, ORNL uses the resources of the Director's R&D Fund to encourage the research staff to submit ideas aimed at addressing initiative-specific research goals. Each spring, the Deputy Director for Science and Technology issues a call for proposals. The call emphasizes specific research priorities selected by management as being critical to accomplishing the Laboratory's initiatives.

The initiatives and research priority areas for FY 2009 were as follows:

- *Science for Extreme Environment: Advanced Materials.* Through this initiative ORNL is positioning itself as a world leader in understanding and controlling interfacial physical and chemical phenomena in complex systems of relevance to energy. During the year, the Laboratory invested $5.21M to 20 LDRD and Strategic hire projects, among others, to study how chemical information and interactions encoded into materials through synthesis drives their assembly, nanoscale structure, and function; develop a method for producing submicron, attoliter-scale aqueous droplets on-demand at the intersection of nanochannels; gain deeper understanding of the failure of conventional first-principles local density approximation (LDA) density functional theory (DFT) methods to predict the energetics and other properties of wide classes of materials in which strong electron-electron correlations play an essential role; gain fundamental understanding of the atomic-nanoscale processes that result in passivation or degradation of structural metals in contact with high-temperature reactive gas mixtures; gain better understanding of energy transformation pathways; gain insights in electrochemical energy storage with supercapacitors; synthesize soft materials that have an unprecedented level of architectural control from the molecular to mesoscale; create novel polymer

brushes derived from poly(cyclohexadiene), including poly(cyclohexadiene sulfonate), poly(phenylene), and poly(phenylene sulfonate); gain molecular-level understanding of the design principles of the assembly of an artificial photosynthetic unit; and design and construct reaction centers that are efficient photocatalysts for CO_2 reduction employing visible light.

- *Neutron Sciences.* In support of our objective to make ORNL the world's foremost center for neutron sciences, LDRD is being used to integrate neutron scattering into the research programs at the Laboratory and to develop new instrumentation. During the year, $3.4 million of LDRD supported 17 projects. LDRD investments were made to advance Spallation Neutron Source (SNS) capabilities in protein crystallography; enable neutron analysis on the structure and function of novel proteins at atomic levels; develop bio-inspired material for solar, hydrogen, bioenergy, and nuclear energy; use neutron scattering techniques in the analysis of the structure, function, and dynamics of biological materials; use neutron solution scattering and reflectometry to model and understand the structural changes associated with virus assembly, assault, and infection at cell membranes; reduce risk of cavitation damage and improve target lifetime; develop high-pressure and high-temperature capabilities at SNS; develop a technique of inelastic neutron scattering to study magnetic excitations and relaxation for nano-engineered materials; gain fundamental understanding of the structure in metallic glasses and how the structure features evolve during phase transformation and mechanical deformation; and study the fluid-surface interactions and the molecular mobility of CO_2 and methane (CH_4) in coals, shales, and sandstones at temperatures and pressures similar to natural underground conditions.
- *Ultrascale Computing.* The intent of this initiative is to establish ORNL as a world leader in computing and computational sciences to deliver new insights and to achieve breakthroughs with broad impact for U.S. scientific leadership. Toward this goal, the Laboratory invested $4.45 million during FY 2009 to support 17 projects to advance a next-generation, high-performance computing (HPC), nuclear reactor transport solver; develop HPC applications in biological research; develop a culture-based social network analysis and evaluation system; develop multiscale computational tools to investigate and optimize key variables of supercapacitors; develop scalable strategies for dealing with failures at the application and middleware level for HPC; develop next-generation multiphysics computational fluid dynamics solvers; develop an ultrascale computer tool for integrated simulation of multi-physics phenomena in nuclear fuel elements; develop knowledge discovery and cohesive decision-making capabilities for multi-modal data analytics in biomedical applications; develop computational capability for the design of complex materials; investigate the cost (hardware and operational burden) and effectiveness of fault tolerance in quantum computer; develop algorithms to overcome the scalability barriers blocking existing implementations of climate simulation models; assess biofuels scenarios to evaluate feedbacks between land use of bioenergy crop production, hydrological cycle, ocean thermohaline circulation, and climate using the Community Climate System Model; and develop highly scalable scientific software for the latency-tolerant, multi-paradigm environment for next-generation HPC.
- *Systems Biology.* Through this initiative we seek to use systems biology to provide a scientific basis for sustainable solutions to the development and use of energy and the management of carbon and water cycles. Understanding these cycles, what drives them, and how they can be managed will provide a scientific basis for dealing with the changes our society faces during this century and beyond. During FY 2009, LDRD investments totaling $3.5 million were made to support 13 projects. LDRD investments were made to provide insights into the impacts of global warming to species composition and shifts in community-level changes; study microbial metabolic synergies and specialized syntrophic relationships responsible for numerous environmental processes; develop novel biocatalysts amenable to genetic engineering; create easy and intuitive access to the annotation process for a wide experimental community; design advanced experimental systems to evaluate and understand responses of terrestrial ecosystems and their components; study how changes in root

exudate alter the function of associated soil microbial community; develop computer simulation methods directed toward understanding the dynamical origin of the glass transition in proteins and its relation to salvation; and develop a microfluidic platform for site-specific capture of individual bacteria, cultivation.

- *Advanced Energy Systems*. The intent of this initiative is to stimulate the development of new technologies that have the potential to supply, distribute, and use energy with high efficiency, at low cost, and with low environmental risk. Toward this goal, the Laboratory invested $4.58 million in FY 2009 to support 13 projects in a wide range of energy technologies, including fuel reprocessing separations, nanocomposites for advanced thermoelectrics, and advanced fuel cell electrolytes, to develop a method for increasing the efficiency of light-emitting diodes; develop advanced models of internal combustion of alternative fuels; apply radiochemistry to nuclear forensics; develop technology for efficient power transfer to electric vehicles; develop technology to improve the efficiency of internal combustion engines; develop methods for americium removal from spent nuclear fuel; develop an understanding of critical pieces of information for advanced high-temperature reactor design; automate freeform construction technologies and materials; and develop advanced Cermet waste form concepts for the optimal storage of high-level wastes.
- *Emerging S&T for Sustainable Bioenergy.* The intent of this initiative is to focus, integrate, and strengthen ORNL's comprehensive bioenergy-relevant research capabilities, including geospatial science and technology, to support the Nation's creation of a sustainable bioenergy generation and delivery infrastructure. Toward this goal, the Laboratory invested $1.53 million during FY 2009 to support five projects to develop an architecture to promote scientific collaboration and citizen science; define conditions that promote long-term economic viability of bioenergy feedstock production while protecting biodiversity; model and optimize the biofuel supply chain; and develop a bioenergy implementation strategy that addresses environmental, economic, and climate concerns while meeting energy demand.
- *Understanding Climate Change Impact: Energy, Carbon, and Water.* The intent of this initiative is to develop reliable integrated end-to-end climate prediction and assessment capabilities and to develop unique competencies in climate change, climate impacts science, computational science, observational capabilities, national and homeland security, environmental science, energy usage and production, carbon management, and geospatial science and technology. Toward this goal, the Laboratory invested $1.5 million during FY 2009 to support four projects to develop a new capability in coupled climate-carbon modeling; use climate-system modeling to hindcast the historical eruptions (Mt. Pinatubo); develop new methodologies to assess the predictive skills of climate model outputs and downscaling approaches and reduce the uncertainties; and estimate the impacts of relatively severe rates and levels of climate change on major regions of the world and regions of the United States.
- *National Security S&T.* The intent of this initiative is to make ORNL a desired provider of innovative technical solutions to compelling national problems that materially improve global, national, and homeland security. In support of this goal, six LDRD projects were funded for $1.3 million to develop advanced radiation sensors and systems; improve communication security and perform complex calculations using quantum physics; develop a navigation system that will perform in GPS-denied environments; and develop technology to improve the cyber security capability of the nation's energy delivery system.

To select the best and most strategic of the submitted ideas, the Deputy Director establishes a committee for each initiative to review the new proposals and associated ongoing projects. The committees are staffed by senior technical managers and subject matter experts, including external members.

Proposals to the Director's R&D Fund undergo two rounds of review. In the first round, the committees evaluate preliminary proposals and select the most promising for development into full proposals. In the second round, the committees review the new proposals and ongoing projects that are requesting second- or third-year funding. After the reviews are completed, the committees provide funding recommendations to the Deputy Director for Science and Technology, who develops an overall funding strategy and presents it for approval to the Leadership Team, ORNL's executive committee headed by the Laboratory Director. All projects selected for funding must also receive concurrence from DOE.

In FY 2009, $33 million was allocated to the ORNL LDRD program to support 159 projects, 74 of which were new starts (Table 2). About 90% of the fund's annual allocation is awarded to projects at the beginning of the fiscal year. The remainder, about 10%, is held in reserve primarily to support research projects of new R&D staff members being recruited to address strategic Laboratory needs. The levels of investment in each initiative are summarized in Fig. 1.

Table 2. ORNL LDRD by fund

	Director's R&D Fund	Seed Money Fund
Costs	$26,977 million	$4,718 million
Number of projects	102	57
Number of new starts	48	26
Continuing (second year of funding)	54	31
Average total project budget (1–3 years)	$601,167	$143,980
Average project duration	24 months	16 months

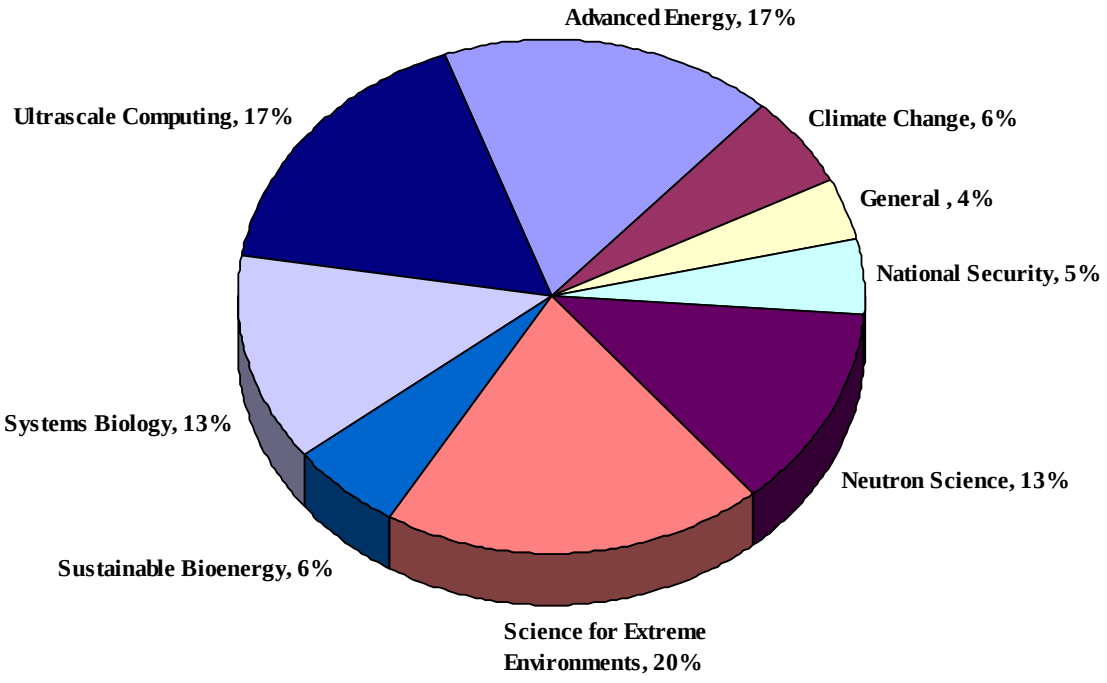

Fig. 1. Level of Director's R&D Fund investment in the Laboratory initiatives for FY 2009.

Seed Money Fund

The Seed Money Fund complements the Director's R&D Fund by providing a source of funds for innovative ideas that have the potential of enhancing the Laboratory's core scientific and technical competencies. It also provides a path for funding new approaches that fall within the distinctive capabilities of ORNL but outside the more focused research priorities of the major Laboratory initiatives. Successful Seed Money Fund projects are expected to generate new DOE programmatic or WFO sponsorship at the Laboratory.

Proposals for Seed Money Fund support are accepted directly from the Laboratory's scientific and technical staff (with management concurrence) at any time of the year. Those requesting more than $28,000 ($190,000 is the maximum) are reviewed by the Proposal Review Committee (PRC), which consists of scientific and technical staff members representing each of the Laboratory's research divisions and a member of the Office of Institutional Planning, who chairs the committee. To assist the committee, each proposal is also peer reviewed by two or three Laboratory staff members selected by the chair. Proposals requesting $28,000 or less are reviewed by the chair normally with the assistance of a technical reviewer. All Seed Money Fund proposals receiving a favorable recommendation are forwarded to the Deputy Director for Science and Technology for approval and require DOE concurrence.

In FY 2009, $5.03 million of the LDRD program was apportioned to the Seed Money Fund to support 57 projects, 25 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

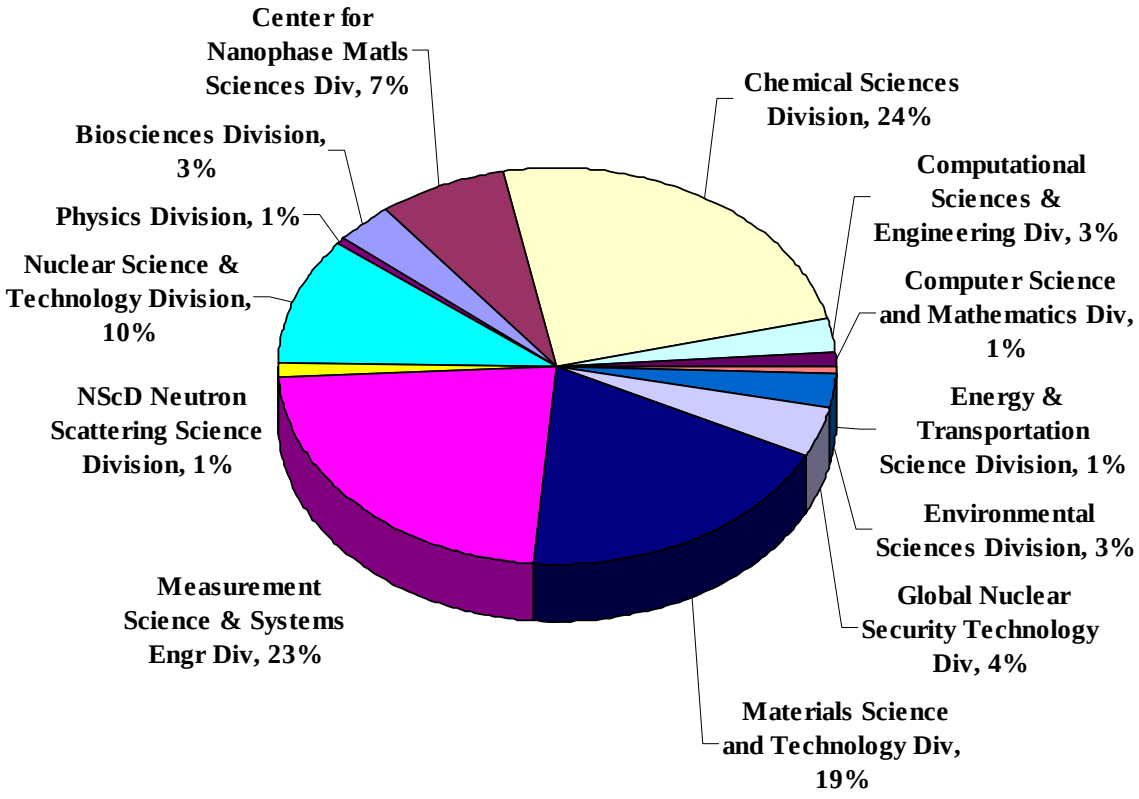

Fig. 2. Distribution of Seed Money Fund by research division for FY 2009.

Report Organization

This report, which provides a summary of all projects that were active during FY 2009, is divided into ten sections: one for each of the eight Laboratory Initiatives discussed above, a General category of projects funded through the Director's R&D Fund by the Deputy Director for Science and Technology, and the Seed Money Fund. This section is further categorized by the research division of the principal investigator. The summaries are arranged by project number, and each summary contains (1) a project description, (2) a discussion of the project's relevance to the mission, and (3) results and accomplishments through the end of FY 2009. Publications resulting from the project are also listed.

Summaries of Projects Supported Through the Director's R&D Fund

SCIENCE FOR EXTREME ENVIRONMENT: ADVANCED MATERIALS

00027

Fundamental Mechanisms of Self-Assembly of Ordered Nanostructures in Heterogeneous Ceramic Materials

G. Malcolm Stocks, Amit Goyal, Jianxin Zhong, and Yanfei Gao

Project Description

Successful fabrication of ordered arrays of nanostructures of one multicomponent ceramic material embedded in another multicomponent ceramic matrix provides enormous application opportunities in high temperature superconductors, multiferroics, and many other materials systems with high potential for technological applications. Motivated from the recent demonstration of nanoscale self-assembly of $BaZrO_3$ nanodots in a $YBa_2Cu_3O_{7-\delta}$ superconducting ceramic thin film using pulsed laser deposition, this project examines the simultaneous phase separation and ordering (SPSO) of embedded nanostructures in heterogeneous ceramic materials, via synergistic efforts in fundamental theoretical formulations, simulations, and experiments. The project scope includes the development of a continuum-based, nonequilibrium thermodynamics model as well as atomistic models to study the growth kinetics, complemented by experimental fabrication and validation of novel self-assembled nanostructures. The outcome of this research provides guidance in the development of material selection and controllable nanostructural evolution for fabrication of novel materials.

Mission Relevance

This project is directly relevant to DOE Office of Basic Energy Sciences programs in high-temperature superconductivity, advanced nanostructured materials, computational science, and material theory. At ORNL this work is particularly relevant to stated goals of the Center for Nanophase Materials Sciences and the Leadership Computing Facility. For nonsuperconductivity applications, we can directly extend our work to incorporation of oxide nanodots/nanorods within a ceramic matrix for energy applications such as energy-efficient solid-state lighting and photovoltaic cells, which are of great interest to the DOE Offices of Science and Energy Efficiency Renewable Energy, as well as the Department of Defense, National Science Foundation, and many high-technology companies.

Results and Accomplishments

In this project, the key accomplishments to date are that (1) the mechanism of simultaneous phase separation and strain ordering (SPSO) resulting in self-assembly of $BaZrO_3$ (BZO) nanodots within $YBa_2Cu_3O_{7-\delta}$ (YBCO) was understood and theoretically modeled; (2) via control of strain, it was shown experimentally that the self-assembly could be altered or modified to result in alignment of nanodots in different directions; (3) using this theoretical understanding and via the experimental control of strain, optimal arrangements of insulating nanodots within the YBCO matrix was demonstrated to result in very high performance superconducting films, with excellent flux-pinning in high, applied magnetic fields.

Synergistic experimental and theoretical efforts established that the nanoscale BZO patterns form to minimize the combined free energy of mixing, phase boundary, and elastic interaction, which originates from the lattice mismatch. A phase-field model was developed to study the kinetics of this ordering process. While the vertical ordering is governed by the strain-mediated surface nucleation mechanism, the long-range lateral ordering is primarily determined by lattice symmetry and elastic anisotropy. A kinetic mechanism map has been constructed that illustrates the competition between deposition rate and surface diffusion on the SPSO process. Ordered nanocomposites of $BaTiO_3$–$CoFe_2O_4$ mixtures were also fabricated using pulsed laser ablation. Composites of 4 vol%–35 vol% $CoFe_2O_4$ in $BaTiO_3$were fabricated. Domain switching mechanisms have also been studied in line with the recent experimental work on the composite film of $BaTiO_3$–$CoFe_2O_4$ as part of this project. We have fabricated phase separated cap buffer layers comprised of MgO in $LaMnO_3$ using self-assembly. Such phase-separated buffer layers provide an alternate way to induce defects into heteroepitaixally grown superconducting layers on the phase separated layer. Antiphase boundaries nucleate at the interfaces of MgO and $LaMnO_3$. A three-dimensional (3D), single-crystal oxide nanofence comprised of single-crystal MgO nanowire units was synthesized via epitaxial growth on single crystal (100) $SrTiO_3$ substrates. Such single-crystal nanofences offer a single crystal 3D template for epitaxial growth of 3D electronic, magnetic, and electromagnetic devices. Finally, we have fabricated self-assembled, ferromagnetic, cobalt nanostructures (from nanodots to nanowires) within epitaxial, insulating yttria-stabilized zirconia (YSZ) thin-films grown epitaxially on Si (100) surfaces using pulsed layer deposition. The dimensions and spacing of the self-assembled Co nanostructures demonstrate the possibility for ultrahigh density data storage of ~1 Tbit/in.^{2} for the next generation of storage media.

Publications

Gao, Y.-F., J. Y. Meng, A. Goyal, and G. M. Stocks. 2008. "Spatial ordering and anisotropy in surface stress domains and nanostructural evolution." *JOM* **60,** 5458.

Shin, J., A. Goyal, K. More, and S. H. Wee. 2008. "Fabrication of epitaxial γ-Al_3O_3 and spinel $NiAl_2O_3$ films on $SrTiO_3$ by pulsed laser ablation." *J. Crys. Growth* **311**(1), 210–213.

Shin, J., A. Goyal, S. Jesse, and D. H. Kim. 2009. "Single-crystal-like, c-axis oriented $BaTiO_3$ thin films with high-performance on flexible metal templates for ferroelectric applications." *Appl. Phys. Lett.* **94**(25), 252903.

Shin, J., A. Goyal, and S. H. Wee. 2009. "Growth of epitaxial γ-Al_2O_3 films on rigid single-crystal ceramic substrates and flexible, single-crystal-like metallic substrates by pulsed laser deposition." *Thin Solid Films* **517**(19), 5710–5714.

Wee, S. H., A. Goyal, Y. L. Zuev, and C. Cantoni. 2008. "High performance superconducting wires in high applied magnetic fields via nanoscale defect engineering." *Supercond. Sci. Technol.* **21,** 092001.

Wee, S., A. Goyal, Y. Zuev, and C. Cantoni. 2008. "Superconducting wire with record performance in high applied magnetic fields via nanoscale defect engineering." *Supercond. Sci. Technol.* **21,** 092001.

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Wee, S. H., A. Goyal, K. More, and E. Specht. 2009. "A three-dimensional, biaxially textured oxide nanofence composed of MgO single crystal nanobelt segments." *Nanotechnology* **20,** 215608.

Wee, S. H., A. Goyal, and Y. L. Zuev. 2009. "Growth of thick $BaZrO_3$-doped $YBa_2Cu_3O_x$ films with high critical currents in high applied magnetic field." *IEEE Trans. Supercon.* **19,** 3266.

Wee, S. H., J. Shin, C. Cantoni, H. M. Meyer, S. Cook, Y. L. Zuev, E. Specht, X. M. Xiong, M. P. Paranthaman, V. Selvamanikcam, and A. Goyal. 2009. "Phase-separated, epitaxial, nanostructured $LaMnO_3$+MgO composite cap layer films for propagation of pinning defects in $YBa_2Cu_3O_{7\delta}$ coated conductors." *Appl. Phys. Exp.* **2**(6), 063008.

00031

Energy Flow and Conversion on the Molecular Level: A View at Molecular Photoelectromechanical Machines

Sergei V. Kalinin, Gilbert M. Brown, Ilia N. Ivanov, and Stephen Jesse

Project Description

The convolution of societal, economic, and political factors in the last several years has propelled global warming to the forefront of public awareness, stimulating the search for renewable green energy sources and efficient energy utilization. Organic molecular systems suggest a possible solution, instigating a massive effort to develop novel materials and device structures for organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). Very often, these systems demonstrate extremely high (50–90%) quantum yields in molecular form, which drops to 1–5% in device structures.

The crucial task in maximizing the efficiency of molecular systems is developing the capability to measure, on the nanometer and ultimately molecular levels, the individual processes involved in energy conversion, including (1) photon absorption and exciton formation, (2) exciton diffusion and separation, and (3) charge transport and effects of molecular organization surrounding medium and substrate on these processes. This project has the objective of separating these systems into individual functional components assembled in two-dimensional molecular layers that are amenable to scanning probe imaging and spectroscopic measurements. In this way the individual processes involved in solar energy conversion can be addressed separately. Observing and understanding these steps will allow materials with increased efficiencies and extended lifetimes to be designed for OPV and OLED systems. This project will establish the foundation for the new area of molecular electromechanical machines (i.e., a means for actuation and manipulation on the molecular level).

Mission Relevance

Understanding fundamental mechanisms of energy conversion between light, electrical, and chemical in organic and bio-inspired systems is one of the highest priorities for the DOE Office of Basic Energy Sciences (DOE BES). Optimization of energy efficiency in OPV and OLED devices is a priority for the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE). This project directly addresses these missions by (1) creating the model systems that allow nanometer- and molecular-scale studies of energy conversion phenomena in molecular systems and assemblies, (2) studying their self-assembly as a route for self-repairing devices, and (3) studying electroluminescent and photovoltaic phenomena on the nanoscale in both molecular systems (DOE BES) and realistic multicomponent devices (DOE EERE). Beyond DOE, this project is directly relevant to the mission of the Defense Advanced Research Projects Agency (i.e., artificial vision, molecular optoelectronics, molecular electromechanical machines) and optical data storage. The electrical scanning probe microscope (SPM) in a liquid environment and shielded probes developed here are an enabling component for probing cellular and biomolecular systems, relevant to the National Institutes of Health.

Results and Accomplishments

The primary FY 2009 effort focused on the (1) development and optimization of the single molecule band excitation molecular unfolding microscopy in liquid environment with electrical and mechanical actuation and (2) noncontact electromechanical detection in liquids. The band excitation–based SPM has demonstrated its unique potential for ambient and UHV imaging of energy dissipation and dynamic phenomena on solid surfaces. However, its implementation in liquids was severely constrained by the hydrodynamic damping of the cantilever that limits sensitivity (e.g., the width of the resonance peak in

liquid is ~10–20 larger than in air, and ~1000 than in vacuum) and detection limit. Second, the use of electromechanical detection (required to probe molecular redox process) is limited by the onset of electrochemical reactions in aqueous environments. In the course of the project, we have (1) demonstrated the possibility for dual-frequency electromechanical detection and established veracity of obtained data using model ferroelectric and "hard" biological systems, (2) established an approach to differential double-layer mediated response and intrinsic molecular properties taking into account variability in elastic properties, and (3) successfully performed elasticity and dissipation imaging on a single molecule during unfolding experiment. The project has resulted in two publications (another two in preparation), and three invited talks at international conferences. The framework developed for imaging in aqueous environments can now be transferred to nonaqueous electrolytes. Brian Rodriguez, a postdoc supported by this project, has become a faculty member at UC Dublin, Ireland (following a Humboldt fellowship at MPI Halle).

Publication

Rodriguez, B. J., S. Jesse, K. Seal, A. P. Baddorf, S. Habelitz, and S.V. Kalinin. 2009. "Intermittent-contact mode piezoresponse force microscopy in liquid environment." *Nanotechnology* **20**, 195701.

00032

Nanostructured Thermoelectrics for Power Generation: Smaller Is Cooler

Rongying Jin, Ho Nyung Lee, Sheng Dai, Gyula Eres, and Brian C. Sales

Project Description

This project focuses on synthesizing novel thermoelectric materials (cobalt-based layered oxides) with two-dimensional (2D) and one-dimensional (1D) nanostructures, and developing state-of-the-art techniques to measure their thermopower and thermal and electrical conductivities so that the efficiency of these nanostructured materials can be accurately determined. The results include (1) detailed studies of thermoelectric, structural, and magnetic properties of bulk Na_xCoO_2 and $Ca_3Co_4O_9$, which serve as reference and foundation for comparison with their counter nano forms; (2) systematic investigations of thermoelectric properties of $Bi_2Sr_2Co_2O_9$ epitaxial thin films that show the power factor can be enhanced more than double of that obtained from bulk single crystals; and (3) development of measurement capabilities, allowing us to measure three thermoelectric quantities of individual nanorods Bi_2S_3.

Mission Relevance

The proposed capability for thermoelectric property measurements on 1D and 2D nanomaterials will serve basic research needs for nanoscience and nanotechnology development, particularly for power generation. This research will benefit the Solar Energy Utilization and Energy Efficiency program of the DOE Office of Basic Energy Sciences and the FreedomCAR and Vehicle Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy. This project will also benefit programs of other federal agencies, such as the Direct Thermal to Electric Conversion Program of the Defense Advanced Research Projects Agency and Power and Propulsion programs of the National Aeronautics and Space Administration.

Results and Accomplishments

For this project, significant progress was made during FY 2007 and FY 2008 (see project summaries in previous reports). Due to preparation of EFRC proposals in FY 2008 that involved in all principal investigators, we requested a postponement to wrap up this project in FY 2009. Since we observed an extremely interesting correlation between electrical conductivity and thermopower in high-quality $Bi_2Sr_2Co_2O_9$ epitaxial thin films, we attempted to further investigate the ion-size effect on their thermoelectric performance through the chemical substitution. Unfortunately, the replacement of either strontium by calcium or bismuth by lead degrades electrical conduction due to poor crystallinity. Although the manuscript is still in preparation, our work on thermoelectrics is recognized by researchers in the field as evidenced by the invited talk by the PI at the 2009 Spring Meeting of the Materials Research Society. In addition, progress has been made in writing articles, reporting thermoelectric properties obtained from $Na_{0.8}CoO_2$, $Ca_3Co_4O_9$, and $Bi_2Sr_2Co_2O_9$ single crystals.

00041

Smart Materials Toward a New Paradigm of Super-Efficient Separations Using Only Energy Input: Conformational Switching Based on Magnetic Nanoparticles

Bruce A. Moyer, Peter V. Bonnesen, Radu Custelcean, Lætitia H. Delmau, Adam J. Rondinone, Frederick V. Sloop, Jr., Volker S. Urban, and Jonathan Woodward

Project Description

This work was aimed ultimately at establishing a new class of molecular switches based on the hypothesis of magnetically induced conformational change. This concept can in principle provide a dramatic increase in the efficiency of separations, a critical energy-technology area. If extractants could be switched "on and off" using only energy input vs. chemically based cycling, binding-release cycles would be so efficient that huge concentration factors would be achievable in small equipment with no secondary waste. That is just what is needed for transforming chemical separations in the nuclear fuel cycle and in many other applications. Specifically, we aimed to tether a selective metal ion receptor between an anchor substrate and a magnetic nanoparticle (NP) such that the stretching effect caused by the force acting upon the NP in a magnetic field leads to an unfavorable conformational change in the receptor, resulting in the release of its bound metal ion. Receptors such as crown ethers and calixarenes, for example, are excellent candidates for such systems. For simple initial prototype systems, we employed $CoFe_2O_4$ NPs tethered to polyethylene glycol (PEG) chains, which were then additionally anchored to a flat silica-coated silicon wafer. The synthesized layered materials were characterized by SEM, TEM, X-ray reflectometry, FTIR reflectance-absorption spectrometry, ellipsometry, and tracer distribution measurements.

Mission Relevance

This work will potentially benefit the DOE Office of Basic Energy Science (DOE BES) program; however, spin-offs can be expected in separations, decontamination, environmental cleanup, and detection, benefiting programs in the DOE Office of Nuclear Energy, Office of Environmental Management, and National Nuclear Security Administration. Other likely beneficiaries of this technology are the Defense Advanced Research Projects Agency and the Strategic Environmental Research and Development program (both of the Department of Defense) and theDepartment of Homeland Security, particularly in developing technologies for radionuclide decontamination or detection. Follow-on proposals were submitted to the BES Advanced Nuclear Energy Systems program in FY 2007 and to the

DOE BES Single-Investigator/Small-Group Research program in FY 2009. Although these proposals received positive reviews, neither was funded. However, we consider the concept and results viable for further funding attempts when opportunities arise.

Results and Accomplishments

We have (1) successfully prepared cobalt ferrite nanoparticles of 15 ± 2 nm diameter from sol-gel condensation reactions as well as 30 nm ± 10 nm diameter ones via an aqueous hydrothermal route and modified the surfaces with a reactive layer of isocyanate-terminated propylsilane groups; (2) coated silicon wafers with amine-terminated PEG molecules; (3) demonstrated the attachment of the NPs to the PEG-coated silicon wafers; and (4) initiated experiments to demonstrate magnetic response of the attached NP layers. Batches of 6 nm cobalt ferrite NPs were prepared; these were covalently coated with reactive isocyanate groups for further derivatization. Larger, monodispersed 15 nm NPs were prepared by successive growth layers upon the unfunctionalized 6 nm seeds. Still-larger 30 nm diameter NPs were synthesized by hydrothermal treatment of colloidal metal hydroxides, but this method yielded a wider size distribution (±10 nm diameter) and were not attached to PEG-coated silicon wafers. Transmission electron microscopy with elemental analysis showed well-dispersed NPs with clear indication of silicon on the NP surfaces. Silicon wafers with a SiO_2 polished coating on one side were employed as substrates for surface modification, resulting in attachment of the NPs to surface-bound PEG. Wafers were first functionalized with Si-$(CH_2)_n$-NCO (n = 3 or 10) moieties through Si-O-Si linkages with standard silane coupling chemistry. X-ray reflectometry detected the organic silane monolayer. Attachment of PEG was achieved by soaking the coated wafers in a solution containing mono-protected diamino PEG under dry conditions. Ellipsometry (VASE) indicated PEG layers of 1.5–2.3 nm thickness, in agreement with X-ray reflectometry results. The reactive NPs described above were tethered to the amine-terminated PEG layer on the wafers by soaking the wafers in a dilute dispersion of the NPs in chloroform, either with or without the presence of a magnetic field. Application of the magnetic field was observed to give denser surface coverage of the NPs. VASE indicated the presence of the NPs on the surface of the wafer to give a NP layer of thickness 14 nm; a void volume of 79% was consistent with the electron microscopy, showing separated rafts of close-packed NPs. X-ray reflectometry with and without applied magnetic field showed a clear magnetically induced structural change in the NP layer. Attempts to employ FTIR spectroscopy and tracer-distribution studies were not successful due to lack of sensitivity. Overall, results paved the way for future efforts, especially in establishing successful methodology for preparation of surface-tethered NPs and for layer characterization with good evidence for magnetic response. Future efforts will focus on further preparations and characterization of flat-layer systems but also preparation of NP layers on large-surface area materials such as porous silica chromatography beads and the inner walls of capillary electrophoresis columns. Magnetism experiments will also seek to go to the next step to magnetically induce structural changes in NP layers that lead to changes in chemical reactivity, especially switching type phenomena.

00045

Molecular Fragment Databases for De Novo Structure-Based Design

Benjamin P. Hay

Project Description

The objective of this project is to create a series of novel molecular-fragment libraries for use in computer-aided molecular design (CAMD) applications. These libraries, which will contain atomic coordinates and structural descriptors for tens of thousands of unique organic scaffolds, provide building

blocks for constructing molecules on the computer using de novo structure-based design techniques. The process of generating the molecular-fragment libraries will be automated through the development of library-building software. This tool will operate by functionalizing an existing hydrocarbon library with synthetically attractive terminal groups such as ethers, amines, and amides. The utility of each new library will be verified through trial runs with the in-house CAMD tool *HostDesigner*. Methodology resulting from this study has a broad potential application. CAMD provides a rational approach to identify molecular architectures for radionuclide receptors used in nuclear separations (advanced nuclear energy systems), highly specific receptors for detection and analysis of chemical and biological agents (national security, medicine), model systems to study enzyme function (catalysis), and molecular components that self-assemble to form functional materials (solid state lighting, solar energy, nanoscale materials).

Mission Relevance

The deliberate design of molecules and materials with desired physical and chemical properties is a current challenge that cuts across scientific disciplines. This project develops new CAMD capabilities to address this challenge. DOE Office of Science Basic Research Needs workshop reports, generated in support of recent initiatives, document pervasive opportunities for CAMD application. Examples include the design of actinide sequestering agents (Advanced Nuclear Energy Systems), molecular configurations for electric field enhancement (Solid-State Lighting), light absorbers, photovoltaics, and photoelectrodes (Solar Energy), and components for self-assembled nanostructured materials (Nanoscience Research). Results from this project have potential application in any research program that entails design of organic compounds and materials. Given that such activities occur in many research programs, there is broad potential for benefit to other federal agencies. Examples would be the design of molecular-scale machines (National Science Foundation), magnetic resonance imaging agents (National Institutes of Health), and components for nanoscale computer processors (Defense Advanced Research Projects Agency).

Results and Accomplishments

A set of library-building codes, *makelinks* consisting of 15,327 lines of Fortran, has been extensively tested, and production versions have been completed. Performance has been validated by comparing the output for specific test hydrocarbons against data generated systematically by hand and against output from conformational searches performed with commercial modeling software, PCModel. Starting from the original HostDesigner hydrocarbon library, containing 8,265 fragments, *makelinks* has been used to create 11 large libraries containing hydrocarbon fragments terminated with one or two functional groups. Fragment libraries that have been completed and tested to ensure that they are compatible with the HostDesigner code include (first functional group, second functional group, number of new fragments): (1) ether oxygen, none, 32,950; (2) ether oxygen, ether oxygen, 33,051; (3) secondary amine nitrogen, none, 62,472; (4) secondary amine nitrogen, secondary amine nitrogen, 99,661; (5) secondary amine nitrogen, tertiary amine nitrogen, 199,172; (6) tertiary amine nitrogen, none, 61,183; (7) tertiary amine nitrogen, tertiary amine nitrogen, 110,752; (8) N-terminal amide, none, 86,061; (9) N-terminal amide, N-terminal amide, 114,557; (10) C-terminal amide, none, 77,560; and (11) C-terminal amide, C-terminal amide, 80,734.

An additional utility code, *splice*, was created to combine these large libraries. This code was used to unite the initial hydrocarbon library with the 11 new ones, yielding a master library containing a total of 996,418 fragments. Tests have confirmed that this master library functions correctly with HostDesigner, yielding the ability to explore a much richer region of structure space during the design process.

00050

Structure of Fluids Confined in Nanoporous Materials Using Neutron Scattering

Gernot Rother and Ariel Chialvo

Project Description

Confinement of fluids in porous materials plays an important role in many natural and technical systems, for instance carbon sequestration in rock formations, component separation, and hydrogen storage for fuel cells. The properties of fluids confined in spaces of nanoscopic size often deviate significantly from bulk, which is due to sorption and finite size effects. Neutron scattering techniques are perfectly suited for the study of sorption effects, which allow for the first time the measurement of the mean density and volume fraction of the sorption phase. We study the properties of the sorption phase of pure fluids systematically for different fluid–matrix combinations and different conditions of pressure and temperature. For confined fluids, Small Angle Neutron Scattering (SANS) is used, which allows to measure structural properties of pore fluids exhibited in the nanometer range. To separate confinement effects from interface effects, we also study fluid–solid interactions at flat interfaces using Neutron Reflectivity. Experimental work is complemented by classical molecular modeling to give detailed insight into the origins of the complex sorption patterns found in many systems with emphasis on high-density depletion effects.

Mission Relevance

Research on fluid–solid interactions under controlled conditions of pressure and temperature is central to two Energy Frontier Research Centers (EFRC) proposals that recently were awarded funding. In the ORNL-led FIRST center, the structure and dynamics of fluid–solid interfaces with relevance for various energy applications will be studied by a range of experimental and computational methods. This LDRD provided some key results that were used in the FIRST proposal to justify our approach of combining neutron scattering (SANS and NR) with molecular modeling. In the LBL-led Center for Nanoscale Control of Geologic CO_2, we will apply SANS techniques to the study of CO_2 and CO_2+water mixtures confined in nanoporous minerals. Both EFRCs have received initial funding for 5 years and will start in August this year.

Results and Accomplishments

During FY 2009 two SANS experiments were conducted on sulfur hexafluoride confined in silica aerogel. The data analysis is currently under way. From analysis of the temperature scans at low fluid densities, it was found that the neutron transmission is not only a function of the mean fluid density in the sample but also depended on the temperature of the sample. This finding could be due to a significant densification of the sorption phase upon cooling. This behavior leads to an increased scattering contrast, and thus to increased small angle scattering and reduced neutron transmission. The influence of temperature on the properties of the sorption phase formed by confined fluids is largely unknown. We conclude from our data that the determination of the pore fluid density though the Lambert-Beer law is not always applicable. It is, however, possible to measure the pore fluid density or the related quantity of excess adsorption separately without ambiguities. Our approach to this task is twofold: We are setting up a volumetric sorption apparatus for measurements at high pressures and moderate temperatures. This apparatus has been built and tested with supercritical SF_6. Temperature can be varied in the range of 30–80ºC with ±0.1ºC stability. The volumetric measurements with bulk SF_6 gave experimental reproducibility in the range of about 0.5% in the region of low and high densities, while the error in the critical region can increase to about 2–4%. These values compare favorably to reported accuracies for

comparable instruments. Our setup permits combined volumetric/gravimetric measurements, which will be particularly useful for the studies of fluid mixtures.

Mirek Gruszkiewicz is exploring the use of the vibrating tube densimeter for the measurement of pore fluids. Both methods will also be suitable for future studies of fluid mixtures. Analysis and publication of the SANS data will use these excess adsorption data.

Ariel Chialvo has developed a model to qualitatively describe high-density depletion phenomena. Future classical molecular dynamics simulation work by Ariel Chialvo will refine this model and study the effect in nano-porous environments.

The work on metamorphosed rocks and rock weathering was continued with a number of SANS and USANS experiments. The obtained data provide detailed insight into the respective mechanisms on the nanometer length scale. Experiments with contrast-matching H_2O/D_2O mixtures probed the connectivity of the pore networks. Future experiments will study pure fluids and fluid mixtures in synthetic and natural rocks.

Publications

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05034

Single Molecular Imaging and Spectroscopy of Adsorbed Molecules

Minghu Pan, Stephen Jesse, Petro Maksymovych, Vincent Meunier, and J. F. Wendelken

Project Description

We have been implementing a new, ORNL-designed, scanning tunneling microscope (STM) based on the designs of our collaborators but with significant improvements in both the hardware and software. A key aspect of this project is the intimate and demonstrated coupling between experiment and theory. Our

theoretical effort will allow us not only to use the STM images to determine bonding site and configuration but also will guide the interpretation of inelastic signal strengths as a function of bonding configuration and tip position over the molecule. We will use this new capability to explore the dependence of vibrational modes, strength, energy, and lifetime (energy transfer) of adsorbed molecules bound to different substrates. In addition, the instrument will be utilized to examine with atomic resolution the vibrational (or bosonic) coupling in high-temperature superconductors.

Mission Relevance

The project is relevant to the DOE Office of Basic Energy Sciences program. The promise of nanotechnology will be realized only through continued advancement and utilization of techniques capable of imaging materials properties on the nanoscale. Our goal in this project is to push the theme of imaging functionality at the nanoscale to the limit of single-atom or molecular imaging and spectroscopy. What we can see, we can then control, and engineer the chemistry, energy flow, light absorption, mechanical response, electronic states, spin, and transport. This new instrument coupled closely with theory and modeling can be a kingpin for bringing the ORNL Center for Nanophase Materials Sciences (CNMS) into the forefront of nanoscale functional imaging and thus contribute to the future expansion of the CNMS.

Results and Accomplishments

We designed, constructed, and tested a new variable-temperature STM in 2008. This STM has the capability not only to image with atomic resolution but also to simultaneously record the electronic and vibrational spectra at temperatures ranging from 8 K to room temperature with highly stable temperature control. In 2009 we made improvements to the variable temperature performance of the STM developed in the first year and then performed low temperature experiments on the Au(111) surface. The single crystalline Au(111) samples were prepared by cycles of sputtering with argon at 1 keV (5×10^{-6} mbar, I = 2 mA) and annealing at 850 K. Constant current imaging, differential conductance spectra have been obtained. Inelastic electron tunneling (IET) spectra were taken by measuring the second derivation of the tunneling current using the lock-in technique with a modulation voltage of 8 mV for d^2I/dV^2 spectroscopy. In constant-current imaging, conventional atomic resolution images of Au(111) were obtained, which are characterized by a geometric effect resulting from partial dislocations that separate fcc from hexagonal close-packed (hcp) stacking in the well-known herringbone reconstruction. IET spectroscopy at low temperatures was then used to investigate vibrations of Au(111). For Au(111) the energy range of phonon modes extends from 0 to 18 meV. The vibrational spectrum taken on Au(111) shows point symmetric maxima centered at an energy of around ±10 meV with a full width at half maximum (FWHM) of 12 meV. The peaks are well within the energy range of phonons on the Au(111) surface integrated over the entire Brillouin zone. The low-energy peaks near 10 meV on Au(111) are attributed to phonons at surfaces. A future investigation enabled by this project will be the study of phonon excitation on the reconstructed Au(111) surface by spatially mapping the second derivation of the tunneling current at a given sample voltage across step edges and topological defects.

Publications

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05054

Bandgap Narrowing of Oxide Semiconductors Using Noncompensated *n-p* Codoping for Enhanced Solar Energy Utilization

Zhenyu Zhang, Gyula Eres, M. Parans Paranthaman, Baohua Gu, and Wenguang Zhu

Project Description

Bandgap narrowing of oxide semiconductors has been recognized as the main avenue for enhancing their performance in photoelectrochemical solar energy conversion. This initiative is centered on a conceptual breakthrough, termed noncompensated n-p codoping, for controlled reduction of the bandgap of TiO_2 and ZnO for a wide variety of catalytic and optical applications. Rather than doping an element individually by trial-and-error, this novel concept embodies two essential ingredients: an *n-p* pair is kinetically and energetically easier to be doped into the host, and the noncompensated nature of the dopant pair creates an extra band in the gap region, effectively narrowing the bandgap. The validity of the concept is supported by preliminary first-principles calculations. Systematic modeling will be carried out to determine the optimal synthesis conditions for efficient codoping, to establish the quantitative dependence of the bandgap narrowing on the codopant concentration, and to investigate the catalytic properties of the new class of materials. Critical materials synthesis using two distinctly different methods with unique advantages will be performed to firmly establish the principle of noncompensated *n-p* codoping in host materials. Complimentary characterization techniques will be used to systematically study the correlations between the chemical composition and optical and photochemical properties, as well as the energy conversion efficiency and chemical stability of the new materials. This project represents an important step toward developing a strong ORNL program for solar energy conversion based on integrating advanced materials synthesis capabilities and fundamental understanding of materials properties for high efficiency solar energy utilization, guided by predictive theoretical modeling and simulations.

Mission Relevance

This work is directly relevant to DOE's research portfolio in basic science. It is particularly relevant to DOE initiatives in materials science and fundamental research for alternative sustainable energy.

Results and Accomplishments

The results can be summarized as follows. On the theory side, we used different schemes of first-principles density functional theory (local density approximation plus onsite Coulomb repulsion, and hybrid approaches) to establish the dependence of the band gap narrowing of TiO_2 on the different combinations of the *n-p* codopants. We predicted that the codoping of chromium and nitrogen will have substantially enhanced thermodynamic and kinetic soluability to be substitutionally doped in TiO_2. We found that TiO_2 codoped with Cr-N pairs exhibit a novel "half semiconducting" feature, potentially offering new research opportunities for developing new materials for spintronics. We extended the noncompensated *n-p* codoping concept to other systems, including diluted magnetic semiconductors.

On the experimental side, we used wet chemistry synthesis approaches to fabricate a variety of TiO_2 nanoparticles, all in anatase phase, but either pure, or doped with chromium or nitrogen, or codoped with Cr-N pairs. We characterized the nanoparticles using a line of spectroscopic and structural techniques, including optical absorption, Raman scattering, X-ray photoelectron spectroscopy, scanning tunning spectroscopy, and electron paramagnetic resonance, and confirmed many of the salient features predicted in the theory part. We used a complementary growth technique of pulsed laser deposition to fabricate anatase-phase thin films with different dopant combinations and densities, and confirmed many of the

structural and spectroscopic properties as observed from the wet-chemistry samples. We obtained preliminary results indicating substantially enhanced efficiencies for water splitting on the surfaces of the Cr-N codoped TiO_2 nanoparticles under light irradiation in the visible region.

Publications

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05061

Nanostructured Mesoporous Photocatalysts for CO_2 Reduction

A. C. Buchanan III, Michelle Kidder, Gilbert Brown, Reza Dabestani, and Edward Hagaman

Project Description

Photoreduction of CO_2 by visible light is one the most challenging processes in solar energy-to-fuel conversion. The goal of this project is to design and construct organized assemblies of metal reaction centers in mesoporous silica scaffolds that will serve as efficient photocatalysts for CO_2 reduction employing visible light. Two distinct oxo-bridged metal reaction centers will be covalently grafted to the pore surface of SBA-15 mesoporous silica. The two metal centers will be designed such that, upon irradiation with visible light, a metal-to-metal charge transfer (MMCT) band can be excited resulting in electron transfer and generation of a metal center in an oxidation state capable of CO_2 reduction. The flexibility in selection of metals and oxidation states, diverse synthetic strategies for tethering metal centers to the surface, control over metal ratios and grafting densities, and the ability to tune interfacial properties such as polarity through further chemical modification provides great opportunity for the design of efficient new photocatalysts for CO_2 reduction. These materials will be characterized by an array of techniques including X-ray diffraction, BET analysis, NMR and FTIR spectroscopies, and ICP elemental analysis. The photochemical properties of these materials and the details of the MMCT step will be examined by steady-state and time-resolved optical spectroscopic techniques. Finally, we will examine the photocatalytic reduction of CO_2 with these designed catalysts to determine conversion efficiencies and product selectivities.

Mission Relevance

Carbon dioxide utilization for the production of fuels such as methane and methanol, fuel and chemical feedstock precursors such as CO, and other value-added chemicals remains a major scientific challenge and opportunity. The DOE has major programs focusing on carbon dioxide capture, storage, and conversion (Fossil Energy), as well as the use of solar energy for production of electricity (Basic Energy

Sciences, Energy Efficiency and Renewable Energy) and fuels (Basic Energy Sciences). Hence, this project which aims to design and produce new nanostructured photocatalysts for the conversion of carbon dioxide into fuels using visible light has direct relevance to these DOE program goals. In addition, DOE-Basic Energy Sciences has a significant programmatic mission for fundamental research resulting in the design of novel catalysts for energy applications, and this project is directly relevant to that mission. Proposals to DOE/BES and DARPA were submitted, but not selected, and the search for follow-on funding continues.

Results and Accomplishments

Research focused on the synthesis and characterization of M(IV)-O-Sn(II) [M = Ti, Zr, Hf] hetero-bimetallic catalysts tethered to the pore surface of SBA-15 mesoporous silica. Detailed studies of the Ti(IV)-O-Sn(II) system revealed several methodologies for successfully introducing the titanium and tin sites providing control over site densities and Ti:Sn ratios on the SBA-15. We also examined the use of a Ti-O-Ti dimer organometallic precursor to prepare Ti(IV)-O-Sn(II) grafted catalysts and probe the significance of titanium site isolation on MMCT formation and catalytic activity. XANES and solid state ^{119}Sn NMR spectroscopies have provided insights into the titanium and tin bonding environment on the surface. The catalytic materials were characterized by elemental analysis, FTIR, and nitrogen physisorption measurements. We found that the photocatalysts maintain their mesoscopic order with high surface areas and large pore diameters. Diffuse reflectance UV-Vis spectroscopy of the SBA-15 attached Ti-O-Sn catalysts showed extended optical absorption to about 450 nm in the visible region. This is characteristic of the desired MMCT process {Ti(IV)-O-Sn(II) → Ti(III)-O-Sn(III)}, and the MMCT band intensity is dependent on the Ti:Sn ratio. The M(IV)-O-Sn(II) [M = Ti, Zr, Hf] catalysts were found to be active for the photocatalytic reduction of CO_2. In the case of titanium, CO was the sole reaction product. In the case of zirconium and hafnium, methane was also observed as a significant product. This research provides compelling evidence that nanostructured mesoporous silica-confined, oxo-bridged heterobimetallic catalysts can serve as photocatalysts for CO_2 conversion.

Publications

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05079

Supra-macromolecular Assembly of Artificial Photoconversion Units

Hugh O'Neill, Kunlun Hong, and William Heller

Project Description

The goal of this project is to gain a molecular level understanding of the design principles that support and promote the assembly of an artificial photosynthetic unit for the conversion of light into electric or chemical energy. A synthetic system is sought that is capable of self-assembly into a biomimetic membrane structure and is able to incorporate functional catalytic units within a supra-macromolecular structure. Synthetic electroactive block co-polymers can provide a biomimetic environment and self-assemble into nanostructures with tunable phase morphology. Their functionality can be widely varied

through choice of monomers and polymerization reactions (e.g., incorporation of binding sites for chromophores and catalysts). We propose to use photosynthetic proteins to understand the fundamental principles of synthetic architectures suitable for solar energy applications. This will lead to an in-depth understanding of the weak intermolecular forces that govern supramolecular assembly and result in a block co-polymer system that can perform in a manner analogous to the natural photosynthetic membrane. This project brings together ORNL's recognized expertise in photosynthesis, polymer synthesis and neutron science. In addition, our collaboration with the Georgia Tech team (part of the AtlantICC Alliance; http://www.atlanticcalliance.org/index.html) who have expertise in organic photovoltaics, will further strengthen our ability to attract future funding in this area.

Mission Relevance

This project primarily deals with the control of molecular processes at interfaces. It is focused on bioinspired molecular assemblies, novel nanoscale and self-assembled materials, self-repairing conversion materials and solar fuel concepts. The successful pursuit of this project will contribute to the long-term strength and research objectives of the laboratory. At the end of this work we will have an in-depth understanding of the design principles required for the development of a membrane system for artificial photoconversion applications. As this project primarily deals with the control of molecular processes at interfaces, it addresses the solar energy research component of the Advanced Materials Initiative. It will position this team to solicit funding through the Basic Energy Sciences Solar Energy Initiative and Materials Science and Engineering Division. In addition, the complementary nature of the skill sets of the team members and the tool-kit of experimental techniques developed during the project will also grow other programs related to bioinspired materials research.

Results and Accomplishments

Manuscripts on the solution structure of LHC II in detergent solution and the effect of detergents on its stability have been completed and submitted for peer review. Work has commenced on the development of synthetic analogues of LHC II using recombinant DNA techniques. The lhcb1, lhcb2, and lhcb3 subunits have been cloned, expressed, and purified. In addition, a truncated peptide with the amino acid sequence of helix 1 of lhcb1 has also been expressed and purified. These constructs are being investigated for their ability to bind and orient chlorophyll in synthetic membranes. Polyethylene oxide (PEO)–polypropylene oxide (PPO) triblock copolymers that differ in molecular mass and also the ratio of hydrophobic to hydrophilic masses are being used to investigate the interaction of LHC II with synthetic polymers as well as the protein's ability to modulate the phase behavior of the block copolymers.

Amphiphilic electroactive diblock copolymers composed of polythiophene and PEO blocks (PEO-b-P3HT) of different lengths have been synthesized. The spectroscopic properties of the PEO-b-P3HT block copolymers have been investigated using fluorescence spectroscopy. In addition, their photocatalytic properties have been investigated to test their ability to support photodependent hydrogen production.

Publications

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05090

Synthesis, Assembly, and Nanoscale Characterization of Confined, Conjugated, and Charged Polymers for Advanced Energy Systems

Jimmy Mays, John Ankner, Philip Britt, Mark Dadmun, Kunlun Hong, and Mike Kilbey

Project Description

Conjugated polymers hold the key to future fundamental advances in science and technology. A major barrier that hinders the application of conjugated polymers for energy conversions has been a lack of understanding how conjugation affects structure and properties, which springs directly from a lack of well-defined materials. The objectives of this project are to develop the chemistry necessary for creating tethered, interfacial layers of poly(para-phenylene) (PPP) and their derivatives on solid substrates and to study how the self-organization, confinement of these polymers impact their nanoscale structure and properties. The surface-tethered layers will be created by functionalized polycyclohexadiene (PCHD) chains with complementary functionality on the substrate. Then they will be converted to PPP brushes by aromatization. Doping of PPP brushes will yield highly ordered arrays of conducting polymer chains. These materials will be the first well-defined conjugated polymer brushes, and the study of their structure and properties will provide unique insight into the impact of nanoscale confinement on their properties. The proposed work will focus mainly on synthesis of these novel materials, structural characterization via neutron reflectometry/scanning probe microscopy, and conductance measurements. Efforts to study the electrochemical behavior of the systems will also be advanced.

Mission Relevance

This project is relevant to programs at DOE, the Department of Defense (DOD), and the Department of Homeland Security (DHS). We are creating novel polymer brushes derived from poly(cyclohexadiene), including poly(cyclohexadiene sulfonate), poly(phenylene), and poly(phenylene sulfonate), where we will have control over the polymer molecular weight, microstructure, grafting density, and substrate, and will develop fundamental understanding of the correlation between the structure of the polymer chains and the structure and properties of the polymer brushes. This foundation will then be utilized to develop future research projects focused on charged or conducting polymer brushes with specific properties (e.g., photovoltaic, proton conducting) of interest to DOE, DOD, and DHS. The Army Research Office Broad Agency Announcements indicate that conjugated polymers are of interest to several programs. One is Dr. Michael Gerhold's program on optoelectronics, where novel optoelectronic materials are sought. The other is the Polymer Chemistry program of Dr. Douglas Kiserow, which describes an interest in such materials for a range of applications.

Results and Accomplishments

We have synthesized the first high molecular weight poly(p-phenylene) brushes of tunable thickness by reaction of end-functionalized poly(cyclohexadiene) chains with –OH groups on surfaces, followed by aromatization. Brushes have been made by reaction of the end-functionalized PCHD in solution with the substrate and by spin coating. Spin coating gives thicker and more uniform brushes. PCHD brushes may be completely aromatized resulting in a small decrease in thickness and small increase in roughness. The dry PCHD brushes and the PPP brushes have been characterized by a combination of ellipsometry, FTIR

and UV-Vis spectroscopy, and AFM. Brushes up to about 30 nm in thickness have been achieved. Neutron reflectivity has been used to characterize the thickness and roughness of solvated PCHD brushes in various solvents. The brushes swell strongly in chloroform (a thermodynamically good solvent) and shrink in tetrahydrofuran (a near theta solvent), as expected. Initial attempts to measure conductivity of the PCHD, PPP, and doped PPP brushes using a conventional 4-point probe show no differences in conductivity. We are currently carrying out measurements with a micro 4-point probe specifically designed for use with nanometer thick films. Comparison with PPP materials made using the same synthetic strategy but not tethered to substrates will be carried out in order to determine the effect of surface confinement and orientation on the electrical properties of these materials. Analysis of the electrical properties of the isolated sulfonated poly(p-phenylene) domains could provide an intriguing method to monitor the effect of nanoconfinement on the properties of these unique systems.

05195

Controlled Hierarchical Self-Assembly of Robust Organic Architectures

Benjamin P. Hay, Radu Custelcean, and Nathan C. Duncan

Project Description

The power to predict and control the assembly of matter at the molecular level is the key to unprecedented control over many intriguing and useful material properties. Although design concepts for the structure-directed self-assembly of soft materials have emerged from advances in supramolecular chemistry and crystal engineering, general methods for implementing these concepts do not exist. Moreover, materials self-assembled from organic building blocks are often fragile and intolerant to extreme conditions. This project addresses these limitations by utilizing a computer-aided design approach for molecular building blocks that are structurally encoded to create targeted assemblies of predictable architecture and dimensions, and validating the approach by producing robust crystalline materials via dynamic covalent chemistry (DCC). The design strategy entails a novel hierarchical approach involving (1) DCC self-assembly of nanoscale polyhedra and (2) using these polyhedra as nodes for the DCC self-assembly of crystalline networks. Successful accomplishment of this project will represent a fundamental breakthrough in the design and synthesis of advanced functional materials for energy applications, providing a rational approach to a new class of well-characterized three-dimensional organic materials with unprecedented chemical and thermal properties.

Mission Relevance

This research presents a new paradigm in the synthesis of soft materials, coupling computational insight with dynamic covalent chemistry to achieve an unprecedented level of architectural control from the molecular to mesoscale. The results will provide proof of principle for the existence of a rational route to a novel class of robust, crystalline organic materials with deliberately tailored structures and properties, laying the foundation for understanding the relationship between structure and function, and ultimately enabling the design and control of matter needed to develop inexpensive and plentiful sources of energy. Thus, the research proposed herein is expected to benefit initiatives of the DOE Office of Basic Energy Sciences where functional organic materials play a role, such as catalysis, energy storage, CO_2 sequestration, solid-state lighting, and solar energy utilization.

Results and Accomplishments

Research has concentrated on the forming organic crystals using reversible imine formation as the coupling reaction. This involves the reversible coupling of carbonyl compounds (aldehydes or ketones) with amines. The strategy is to use carbonyl compounds either as vertices for tetrahedral building blocks or as nodes for frameworks. Both tri- and tetra-carbonyl substituted molecules were identified as synthetic targets. Initial efforts focused on the preparation of these molecules.

To date three tetracarbonyl nodes and one tricarbonyl vertex have been prepared and purified in gram quantities. Synthesis of a second tricarbonyl vertex is being pursued at UT-Knoxville (Prof. M. D. Best, JDRD, "Synthesis and Assembly of Geometrically Defined Building Blocks for Dynamic Covalent Synthesis of Robust Higher Order Frameworks").

Computer-aided design runs using in-house HostDesigner software identified diamine molecules that offer the correct structural characteristics to direct the formation of the desired assemblies. Candidates identified by HostDesigner were evaluated with the MM3 model, after validating performance against a large amount of imine crystal structure data. In the case of crystalline frameworks, novel algorithms were derived and coded to generate powder diffraction patterns for comparison with experimental data. Initial attempts to combine carbonyl and amine building blocks have thus far resulted in formation of amorphous, polymeric materials. Systematic studies are under way to identify general reaction conditions (solvent, added water, pH, temperature, and time) that promote formation of the desired imine-based crystalline frameworks and/or tetrahedral assemblies.

05236

Understanding Interfacial Electrochemical Phenomena in Advanced Energy Storage Capacitors Using Spectroscopy and Modeling

Kevin L. Shuford, Gilbert M. Brown, Sheng Dai, and R. W. Shaw

Project Description

During this one-year project, we investigated a quantitative assessment of ion transport above surfaces, which ultimately will lead to tailored electrode materials that will permit transitional improvements in electrical energy storage capacitors. We investigated planar carbon materials as the baseline case before examining carbon films with highly controlled pore characteristics that have been proposed as the electrode material for advanced capacitors. We examined the interaction of neutral and ionic dyes above glass and carbon films using fluorescence emission. We studied synthetic techniques to prepare mesoporous carbon films using templating techniques. Our effort also included modeling and simulation of transport dynamics to determine how ions diffuse into and out of mesoporous carbon, as well as establish how the interfacial pore structure mediates charging events in electric double layers.

Mission Relevance

Effective utilization of electricity generation from alternative energy sources is critically dependent on the development of cost effective and efficient electrical energy storage systems. A thorough knowledge of electrode double layer charging effects and alteration of the oxidation state of molecules bound in surface pores will result in improvements in the energy storage capacity of electrochemical capacitors. Currently the primary challenge to understanding electrochemical energy storage with supercapacitors resides in the mediating effects due to electrode pores and the transport of electrolyte ions into and out of those pores.

Our results will ultimately lead to vastly improved materials and designs for electrical energy storage devices.

This early effort was important in helping us prepare a successful proposal to DOE Office of Basic Energy Science under the Energy Frontier Research Center competition. We declined to apply for renewal of the project since it successfully led to follow-on funding. Our work is continuing through our participation in the "FIRST Center: Fluid Interactions, Reactions, Structures, and Transport" project.

Results and Accomplishments

Nonporous carbon films with thicknesses ranging from 20 nm to 100 nm were synthesized on quartz cover glass slides by pyrolysis of a thin, spin-coated photoresist film. In bulk measurements, the addition of a surfactant to the photoresist resulted in a porous carbon material.

We used two optical techniques—fluorescence lifetime determination and fluorescence correlation spectroscopy—to investigate the characteristics of neutral and ionic emissive dyes near surfaces. Ultrafast pulsed laser excitation in a total internal reflection excitation geometry was employed for the former measurements, and continuous wave argon ion laser excitation was used in an epi-illumination geometry for the latter. Both of these methods probe near-surface molecules in a roughly <1 μm layer and discriminate against those in the bulk solution. This allows for investigation of lifetime alterations and changes in diffusional coefficients mediated by proximity to the surface. We measured the fluorescence lifetime of nile red (a neutral dye molecule) in acetonitrile solvent, both immediately above a carbon surface and in bulk solution, and found 4.9 ns and 4.5 ns decay constants, respectively; this indicates that the excited state lifetime is indeed affected by a proximal carbon surface. Molecular diffusional effects were gauged using fluorescence correlation spectroscopy where we observed preliminary three-dimensional diffusion times of 188 μs for nile red above glass and 135 μs for the same dye above a carbon film. Adsorption/desorption processes on the glass surface may be responsible for the longer characteristic diffusion time.

The preliminary modeling effort consisted of exploring the validity of macroscopic electrodiffusion theories for spatially confined systems. In addition, we have begun using electronic structure calculations to define parameters for model potentials that will be used in future molecular dynamics simulations.

05285

Mapping Energy Transformations Pathways and Dissipation on the Nanoscale

Sergei V. Kalinin, Stephen Jesse, and Albina Borisevich

Project Description

The convolution of societal, economic, and political factors in the last several years has propelled global warming to the forefront of public awareness, stimulating the search for renewable green energy sources and efficient energy utilization. The key to fundamental understanding of energy conversion phenomena, and hence to the optimization of materials performance and efficiency, lies in the nanoscale probing of energy transformation pathways in real materials. The structural and electronic aspects of defect structures in solids can now be addressed in exquisite detail by electron microscopy and spectroscopy. Similarly, techniques such as scanning tunneling microscopy have brought about the capability to study dynamics and chemistry, including vibrational transitions and photochemical processes, on the single

molecule level. What has been missing to date is the capability to probe energy transformation pathways and dynamic processes in solids on the mesoscopic level of 1–100 nm. This project aims to understand the atomistic origins of energy transformation and dissipation in systems at the level of a single atomically defined defect. This goal is being achieved using systems with engineered defect structures combined with scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) capabilities perfected at ORNL and recently developed scanning probe microscopy (SPM) methods that can address energy dissipation on a single defect level. Ferroic systems with reversible local dynamics will be used as prototypes for more complex electrochemical and mechanical processes. The success of this project will for the first time allow linking the defect functionality in energy conversion processes or phase transformations to its atomistic structure, opening a pathway for the fundamental understanding of structure-property relationship on the single defect level.

Mission Relevance

The role energy and energy technology play in maintaining the environment, homeland security, and economic growth has risen to the top of the public agenda. This energy challenge has strongly affected the political and scientific landscape in the United States and the world by defining new priorities for basic, applied, and industrial research. In-depth understanding of energy conversion and dissipation is required before the groundbreaking solutions for the energy problems facing us in 21st century are found. Recent trends in DOE clearly emphasize the growing role of (1) fundamental research in resolving energy problems and (2) the role of advanced instrumentation in this research, as reflected in recent BESAC Grand Challenge documents. This project aims to achieve as understanding of energy transformation mechanisms, fluctuations, dissipation, and information transfer on the nanoscale in model ferroic systems as the ultimate goal of energy-related fundamental research.

Results and Accomplishments

The central concept in this project is relating the energy transformation pathways on a single defect level to their atomistic structure using ferroic systems as models with nondisruptive and locally reversible transformations. We identified ferroelastic domain walls and bicrystal interfaces as defect structures that are (1) universally present in real materials, (2) well-defined on mesoscopic and atomic levels, (3) can be studied both by SPM (switching dynamics) and STEM (atomic and electronic structure), and (4) can be integrated with theory (mesoscopic phase-field models), providing a comprehensive understanding of energy transformation-structure relationships on the atomic level. The *in-line* band excitation SPM and spectroscopic modes of piezoresponse force microscopy have been developed into user-friendly data acquisition and data analysis tools and are now incorporated on five ambient and one ultrahigh voltage platforms in the Center for Nanophase Materials Sciences, as well as on an additional data analysis station. The switching behavior at grain boundaries and ferroelastic domain walls was probed, and results were found to be in an excellent agreement with mesoscopic phase field modeling. Thus, we have for the first time demonstrated that bias-induced phase transitions can be studied quantitatively on level of a single atomically defined defect, and corresponding mesoscopic mechanisms can be elucidated. Furthermore, we have explored the set of neural network–based models for classification and analysis of the STEM and SPM data and have developed (1) interpretation for EELS images, (2) atom shape analysis for STEM, and (3) demonstrated direct mapping of Ising model parameters in polycrystalline capacitors. While the developments of methods for direct defect identification is in progress, the feasibility of the concept has been demonstrated.

Publications

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05309

Interfacial Reactions of Metal-Fluid Systems at Extreme Conditions

David R. Cole, Michael Brady, James Keiser, Ariel Chialvo, Gernot Rother, David Wesolowski, Lawrence Anovitz, Karren More, Harry Meyer, and Mostafa Fayek

Project Description

In order to achieve a fundamental understanding of the atomic-scale processes governing the interaction of reactive fluids, metal alloys and reaction products under extreme conditions, we propose to investigate fluid and solid interfacial structures, speciation and dynamics at the atomic to macroscopic scales. We will specifically study the high-temperature (700–800°C) oxidation of a model Fe-Cr alloys in the presence of water vapor to demonstrate the capability to study interfacial reactions under such extreme conditions. *Ex-situ* studies will include neutron scattering (small angle, reflectometry, diffraction, inelastic), infrared spectroscopy and secondary ion mass spectrometric investigations of corroded samples exposed to $H_2{}^{16}O$, $H_2{}^{18}O$ and D_2O in order to track hydrogen through the system and to differentiate between O_2, H_2, H^+, OH^- and H_2O attack. We propose to develop unique *in situ* neutron sample environments and to conduct proof-of-principle neutron reflectometry and scattering experiments that will reveal hydrogen speciation and distribution during active oxidation reactions. These studies will be complemented by detailed electron microscopy imaging of select samples. Coupling these approaches with molecular dynamics simulations will enable the development of new conceptual and computational models for metal oxidation in water-rich environments at extreme temperatures, and sets the stage for targeting follow-on proposal calls from the DOE Offices of Basic Energy Sciences (BES), Fossil Energy, and Energy Efficiency and Renewable Energy.

Mission Relevance

The anticipated results of this project and future applications of new methodologies are directly relevant to high-temperature oxidizing environments containing water vapor ubiquitous in energy production. Virtually all combustion environments (gas turbines, reciprocating engines, fossil-fired plants etc.) contain water vapor. New research capabilities at ORNL provided by this effort will form the basis for

targeting future funding opportunities related to the declared DOE BES grand research challenges, especially in the fields of interfaces and extreme environments as identified in the Basic Research Needs (BRN) workshop reports. In particular, the BRN report on Materials Under Extreme Environments specifically identifies that fundamental understanding of the atomic-nanoscale processes resulting in either passivation or degradation of structural metals in contact with high-temperature reactive gas mixtures is critically needed for ultrasupercritical steam electrical power generation facilities, biofuels combustion and solid oxide fuel cell utilization.

Results and Accomplishments

The year one efforts were focused on preparing materials for ex-situ neutron scattering, Fourier transform infrared spectroscopy (FTIR), and secondary ion mass spectrometric (SIMS) investigations. The alloys were oxidized from 700–800°C for times ranging from 1 to 144 h in dry air, dry air with 10% H_2O, and dry air with 10% D_2O. The XRD, SEM, and TEM studies indicated qualitatively similar oxide scale microstructures in the protective Cr_2O_3 regime in both dry air and in the presence of H_2O or D_2O. We completed an exploratory study of possible nanostructural changes incurred by wet and dry oxidation at 800°C in ferritic 444 and austenitic 347 stainless steel foil samples by conventional and ultra-high-resolution small-angle neutron scattering. An increase in the small-angle scattering was observed on oxidation of both 444 and 347 material, on the order of 2–10 fold depending on the extent of oxidation. This scattering increase may reflect pore formation within the oxide or underlying alloy.

We have performed classical equilibrium molecular dynamics simulation of ("frozen composition") high temperature (800°C) air in contact with a Fe-20Cr bcc substrate to analyze the poorly understood behavior of this solid/fluid interface at extreme conditions. The significant emerging picture from this simulation is the dramatic density and composition inhomogeneities of the interfacial region.

Analysis of the surface of oxidized steel samples was carried out using FTIR. The data for Fe-20Cr thus appear to be consistent with the presence of a water or hydroxyl-bearing species at the surface of the oxide, but the broad nature of the peaks suggests several bonding environments.

05342

New Density Functionals for Ab Initio Calculations Derived from Many-Body Theory

Fernando A. Reboredo, Markus Kent Eisenbach, Paul R. Nicholson, Don M. Stocks, and George Malcolm

Project Description

One of the major stumbling blocks in theoretical condensed matter physics and materials science is the failure of conventional first-principles local density approximation (LDA) density functional theory (DFT) methods to predict the energetics and other properties of wide classes of materials in which strong electron-electron correlations play an essential role. While DFT is, in principle, an exact theory, approximated exchange correlation functionals fail to describe structural defects and other properties of these materials. We are attacking this problem performing accurate quantum Monte Carlo (QMC) calculations of an interacting electron gas subject to a central impurity potential. This system closely relates to an atom in a real material while retaining a simplicity that is amenable to highly accurate solution under a wide range of conditions.

Mission Relevance

The goal of the project is to obtain basic information of the inhomogeneous electron gas that will allow solving the main obstacle that prevents ab initio calculations based on DFT to be used successfully to understand a wide range of materials relevant to DOE's mission and goals. In particular, the information we expect to obtain will be crucial to understand strongly correlated materials in general and transition metal oxides, rare earth magnets, and actinide-bearing reactor core materials with obvious applications to solar energy, nuclear energy, and hard magnets, to cite but three.

Results and Accomplishments

We have obtained a proof of principle that the proposed calculations can be performed in a spherical jellium system as initially proposed. Specifically, we have already tested and compared computer programs that can perform calculations both at the mean field and at the many-body level in small systems. Already in these tested systems we have found states in which many-body effects play an important role, which are difficult or impossible to obtain with standard mean field approaches.

We have improved a method to obtain the ground state wave-function of a many-body electron system to be used as a trial wave-function in QMC calculations. We have validated the method by comparing it with accurate configuration interaction calculations in carbon and oxygen. These atomic systems have the same spherical symmetry of the model impurity system.

The next step is to perform large and high quality calculations in the model suitable for publication. We have also formulated a new approximation of DFT, and we are developing the tools to compare it with many-body results.

Publication

Reboredo, Fernando A. 2009. "Systematic reduction of sign errors in many-body problems: Generalization of self-healing diffusion Monte Carlo to excited states." *Phys. Rev. B* **80,** 125110.

05373

Investigating the Role of Physical Interactions and Block Sequence Tailoring on Macromolecular Self-Assembly Through Micellar Systems

S. Michael Kilbey II

Project Description

In this project the role of sequence tailoring and reversible physical interactions on the self-assembly of polymer micelles in aqueous solutions is being studied. A new modular approach for creating centro-symmetric three-armed stars is being developed and used to create star-like polymers that change their configuration in response to external stimuli. The flexibility enabled through the modular approach is key, allowing diverse sets of materials to be easily created from a library of constituents. By controlling the composition and sequence of the constituents, the structure, dynamics and response of the star copolymers can be tailored. In addition to complete and rigorous characterization of the novel materials synthesized, the structure and dynamics of the self-assembled micelles will be examined using dynamic and static light scattering. This project is transformative in that by tailoring sequence and composition, we

are able to isolate the role of molecular-level design on self-assembly, nanoscale structure, and dynamics, paving the way for designed materials for a variety of applications.

Mission Relevance

A grand challenge in materials science and chemistry to understand how the chemical information and interactions encoded into materials through synthesis drives their assembly, nanoscale structure and function. The knowledge gained from this fundamental research program will significantly contribute to our understanding of soft matter (polymers), providing crucial information into how to design novel materials with specific properties and structure, ultimately enabling breakthroughs in next-generation materials and devices, including materials for solar energy conversion, fuel cells, and battery technologies. This work is also enabling for processing via self-assembly, which capitalizes on free energy gradients and weak interactions. As a result, this research aligns with programs of the DOE Office of Basic Energy Sciences, particularly in materials and chemical sciences, and it may, by paving the way for understanding structure-function relationships in bio-inspired systems, benefit agencies having missions in advanced materials for sensors, security and defense (e.g., Defense Advanced Research Projects Agency, Defense Threat Reduction Agency), as well as in biomaterials and therapeutics for improved human health.

Results and Accomplishments

Efforts since the inception of the project in July have focused on (1) synthesis of constituent "arms" of the stars and their characterization, (2) preparation of the central linking core necessary for realizing the novel three-arm star-block copolymers, and (3) demonstration of the modular approach through sequential linking reactions. A library of end-functionalized polymers and block copolymers have been synthesized and characterized. The ability to specifically link these polymers to complementary reactive groups using orthogonal approaches has been verified using "clickable" base layers grafted to surfaces. By virtue of the polymers losing translational freedom, these surface modifications facilitate characterization. The approach developed during the first year to create the central core needed for the modular approach to construction of the star-like copolymers was successfully revised to overcome issues of cross-reactivity. A considerable amount of effort was expended to optimize reaction conditions for linking end-functional polymers to the central core and to characterize the efficacy of the orthogonal reaction(s). Findings to date suggest that the orthogonal reactions are not as robust for polymer systems as they are for small(er) molecules. Nevertheless, it appears that this novel synthetic approach for making complex copolymers has advantages for integrating dissimilar materials, thereby enhancing Laboratory capabilities for creating tailored polymeric materials. These studies will ultimately enable insights into how chemical information and interactions integrated into the molecular assembly affect nanoscale structure and dynamics.

Publication

Hinestrosa, J. P., B. S. Lokitz, J. M. Messman, and S. M. Kilbey. 2008. "Well-defined base layers for clicking polymer brushes." *Proc. Amer. Chem. Soc. Div. Poly. Chem. (POLY Preprints)* **49**(1).

05374

Materials Behavior Underlying the Electrochemical Performance of Advanced Batteries

Sheng Dai, Nancy Dudney, Karren More, Ed Hagaman, Bob Shaw, De-en Jiang, Andrew Payzant, Claus Daniel, and Edgar Lara-Curzio

Project Description

This work undertakes two research thrusts aimed at developing underlying knowledge of basic materials behavior that governs lithium battery electrochemical performance and lifetime. Specific objectives include (1) dynamic characterization of the initial development of the solid electrolyte interphase (SEI) in terms of morphology and molecular composition at a heretofore unattained level of resolution, thus demonstrating the ability to fundamentally relate these characteristics to energetics and kinetic factors, and (2) development of an understanding of the evolution of stress states and mechanical behavior of electrodes and the SEI in order to directly connect structure and materials processing routes to the factors that make major contributions to a lithium battery's durability (lifetime) and safety. To accomplish these goals, it will be necessary to (1) tailor advanced, *in situ* characterization tools for effective use with battery material systems that utilize ORNL's world-class capabilities in electron microscopy, molecular spectroscopies (e.g., nuclear magnetic resonance, electron spin resonance, vibrational spectroscopies), X-ray diffraction, and mechanical behavior; (2) establish the necessary suite of instruments to conduct standard electrochemical characterization of battery cells (or half cells) in order to relate *in situ* microscopy, molecular spectroscopies, X-ray, and mechanical observations and measurements to macroscopic current-voltage performance; and (3) develop processing routes to synthesize model systems that facilitate analysis of the results in terms of thermodynamic, kinetic, and stress factors.

Mission Relevance

It is readily apparent that efficient, affordable electrical energy storage is the key to meeting the challenges of future energy security and climate change in the transportation and stationary and portable power generation sectors (http://www.sc.doe.gov/ bes/reports/files/EES_rpt.pdf). It is also clear that, particularly for transportation, an enormous improvement in battery performance is needed to displace fossil-based fuels for everyday needs. The technical challenges to reach the necessary level of ultimate performance of electrical energy storage devices (batteries and supercapacitors) are daunting; none are more so than the need for materials (both electrodes and electrolytes) that exhibit long-term stability at high rates of charge transfer under both oxidizing and reducing conditions. The needed advances will require basic and applied research in materials science and electrochemistry as well as extended materials and systems development and testing. In this project ORNL will undertake initial steps to grow a robust program of research devoted to materials for future electrical energy storage devices by focusing on a few key processes that underlie the electrochemical performance of advanced lithium batteries.

Results and Accomplishments

Installation of Hummingbird in situ *TEM system.* Initial testing of the liquid flow cell holder, which was made for the Hitachi HF3300 transmission electron microscopy/scanning transmission electron microscopy (TEM/STEM) instrument by Hummingbird Scientific, has been conducted. For these initial assessments, the liquid cell was filled with a dilute saline solution plus 20% platinum-based catalyst supported on carbon. These tests were designed to evaluate two primary features of the liquid cell: (1) the thickness of the liquid gap as well as the ability of the cell to hold a nonflowing liquid and (2) the image resolution in STEM mode. The holder design is based on an initial liquid cell design by ORNL's Niels de Jonge. The cell is composed of two small (2 mm × 3 mm) silicon chips with a thin layer of (electron

transparent) silicon nitride (~50 nm) on the opposing surfaces. A small region on the back side of the silicon chips is etched away to the silicon nitride layer, forming a "window" for transmission of the electron beam and imaging of the solid material(s) held within the liquid-filled gap.

For the initial tests conducted in FY 2009, 20% Pt/C was dispersed in a dilute saline solution (provides a conductive liquid). A 2 μL droplet was applied to the "top" silicon nitride surface (across window), and the "bottom" chip was placed on the surface. To create a somewhat reliable gap thickness and to protect the windows from any sharp edges of the solid material that could cause the windows to break, small latex spheres (~5 μm diameter) were applied to the edges of the silicon nitride surface of the top window. Once the liquid-filled cell was secured in place at the tip of the holder, the holder was inserted into the column of the Hitachi HF3300 TEM/STEM. In this initial test, a <3 nm resolution was demonstrated for the catalysts.

As a result of these initial tests, several critical follow-on tasks were established and are currently in progress:

- A new "collaborator" for chip/window design and manufacturer has been identified to produce thinner Si_3N_4 windows, smaller window sizes, and proper electrical contacts for the battery cell. Both ORNL and Hummingbird are working with this new company to design the improved chips such that reproducible and reliable chip/windows are available for these experiments.
- Once a final chip/window design has been accepted, the electrical contacting for rapid charge-discharge cycling of the *in situ* electrochemical cell will be established, tested, and validated.
- A low-temperature heater will be an added capability.

In addition, a new Weinberg Fellow, Ray Unocic, will be joining the Microscopy Group in mid-August and will be devoted to this task nearly 100%.

Battery testing facility. The battery test lab is currently operational and is equipped with instruments for assembling and characterizing energy storage devices such as batteries, specifically lithium ion batteries, and capacitors. A fully functional glovebox is available that permits assembly of energy storage devices under inert atmospheres. An automatic crimper is located inside the glovebox and enables users to bring custom electrodes and electrolytes from their laboratories to use in the assembly of novel and unique coin cells. The coin cells can then be removed from the glovebox and characterized in ambient conditions. The automatic crimper provides reproducible coin cell assembly conditions and eliminates variations in individual coin cells that complicate analysis. A coin cell disassembling tool is available that allows users to disassemble their coin cells after characterization and use while keeping the integrity of the electrodes intact. Consequently, the electrodes can be interrogated after undergoing repeated cycling, which is important for durability and lifetime studies. Two primary instruments are presently in use to characterize coin cells: the Maccor battery test system and the Solartron analytical system. The Maccor system is a fully automated, programmable battery test system with multiple, independent test channels that can be utilized simultaneously to examine multiple energy storage devices. The Maccor system operates in a variety of voltage and current ranges up to 10 V and 5 A. It is capable of measuring charge and discharge properties as well as making impedance measurements. The Solartron analytical system is a cell test system with multiple independent channels capable of a variety of electrochemical measurements. Thus, the battery test lab offers users a suite of instruments specifically designed to quickly construct and characterize batteries and capacitors.

Our computational modeling focuses on understanding the properties of novel electrochemical window electrolytes. The operation of lithium-ion batteries depends on the high electrochemical window of the nonaqueous electrolyte. Electrolytes commonly used in commercially available lithium-ion batteries include ethylene carbonate and propylene carbonate, which have a voltage window of less than 5 V. To

achieve higher voltages and hence high energy density, new electrolytes must be discovered. Sulfones represent a type of electrolyte with a voltage window higher than 5 V. To further improve upon the sulfones, which showed wide electrochemical stability windows in excess of 5.0 V vs. Li/Li^+, we used quantum mechanical calculations to explore how substitution by fluorine affects the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (the HOMO-LUMO gap), which is related to the reduction-oxidation properties of the electrolyte. We found that substituting the three hydrogen atoms on one methyl group of methoxyethylmethyl sulfone (MEMS) with fluorine increases the HOMO-LUMO gap from 6.4 eV to 7.0 eV, which indicates better resistance to redox chemistry, hence desirable. However, we found that replacing all the hydrogen atoms in the molecule with fluorine actually decreases the HOMO-LUMO gap to 5.8 eV, which is undesirable. These computational results indicate a delicate control of the electrolyte property by substitution and offer a useful guide for directing our synthesis effort towards the right target.

In the next year, we plan to study more sulfone molecules together with the substitution effect. Besides the HOMO-LUMO gap, we also will examine the electron affinity and ionization potential, another measure of redox properties. By relating the calculated properties with the measured electrochemical windows for the sulfone electrolytes, we hope to establish a structure-property relationship that would allow us to predict new electrolytes with high electrochemical windows for lithium-ion batteries.

Program Development Accomplishments

The work on *in situ* TEM and other characterization tools for SEI layers was incorporated into two DOE Office of Basic Energy Sciences proposals: SISGR, led by Chengdu Liang, and EFRC, led by David Wesolowski. The *in situ* TEM component played a key role in the success of these proposals.

05375

Attoliter Droplets on Demand in Nanochannels: New Opportunities for Investigating Chemical Reactivity and Catalysis in Nanoscale Reactors

Seung-Yong Jung, Scott Retterer, and Charles Patrick Collier

Project Description

We propose a new method for producing sub-micron, *attoliter-scale* (10^{-17} L) aqueous droplets on demand at the intersection of nanochannels. At the intersection of two apposed aqueous channels with an immiscible oil channel, two submicron, oil-dispersed aqueous droplets containing different reactants can be forced to collide with each other and fuse, completely mixing their interior contents by diffusion in less than a millisecond. This can be used to produce monodisperse reaction vessels two orders of magnitude or smaller in volume than in current state-of-the-art microfluidic devices, while satisfying the constraints of perfect sealing and passivation against nonspecific adsorption of large macromolecules like proteins at the droplet periphery. The resulting surface-to-volume (S/V) ratios of droplets at this scale will be in excess of 10^6, which may open up new areas of research across several fronts, in particular the study of catalysis and reaction dynamics of transient chemical and biochemical intermediates in confined environments. As a proof-of-principle demonstration of the method, we will measure single-enzyme kinetics in the nanoreactors with a well-defined time zero for initiating the reaction, and with sub-millisecond temporal resolution.

Mission Relevance

The ability to probe reaction dynamics of highly reactive, transient chemical, biochemical and electrochemical species in confined environments with unprecedented temporal resolution will provide important new capabilities vital to next generation DOE missions. Results from this work will add to our fundamental understanding of catalysis, chemical synthesis, and energy in nanoscale confined systems, and thus may be directly applicable to targeted DOE initiatives such as advanced materials, advanced energy systems and systems biology. In addition, practical technological advances, such as in sensors and detection technology resulting from this research may be exploited for cross-cutting programs such as national security.

Results and Accomplishments

The deliverables for the first year of funding as stated in the original proposal were the design and fabrication of the nanochannel crossbar chips, and the demonstration of control of droplet formation and injection in the central oil channel. The first deliverable, design and fabrication of nanochannel crossbar devices, has been completely met. For the second deliverable, proof-of-principle demonstrations of droplet formation through micromachined membranes emulating the nanochannel openings into a main carrier channel have been performed. These experiments were carried out to investigate the roles played by the shapes of nanochannel openings for forming ultrasmall droplets, in addition to channel diameter, as well as the effects of the wetting properties of the interface on droplet formation. We determined that shear-induced redistribution of surfactant at the oil-water interface during droplet formation at a microfabricated T-junction results in loss of passivation of the interface against nonspecific adsorption and inactivation of enzymes as a function of decreasing droplet size. This can be monitored and controlled in the current device design using bright field images of micron-scale droplets forming and detaching from channel outlet pores. We expect that the stresses acting at the droplet interface and the surfactant dynamics should scale for submicron-size droplets. Finally, capillary wetting and filling of nanochannels by aqueous solutions containing fluorescent dye have been demonstrated.

Publication

Liu, Y., S. Y. Jung, and C. P. Collier. 2009. "Shear-driven redistribution of surfactant affects enzyme activity in well-mixed femtoliter droplets." *Analytical Chemistry* **81,** 4922–4928.

05571

Membrane-Based Energy Efficient Integrated Separation Processes and Systems for the Production of Biofuels

Ramesh R. Bhave

Project Description

The research will focus on the development of novel membrane-based, energy-efficient, integrated separation processes and systems for the production of biofuels using domestic renewable alternatives such as microalgae. The economics of biofuels production is currently not cost competitive with fossil fuels. Our research efforts will evaluate commercially available membranes and ORNL-related membrane products to develop new approaches for selective, efficient, and cost-effective separations. The role of adsorption and fouling on dewatering efficiency will be investigated, and methodologies to optimize performance will include disruptive techniques and membrane functionalization. We will investigate membrane-based separations for biomass concentration/dewatering using representative microalgal

strains such as *Nannochloropsis* cultivated in-house under well-controlled conditions. We plan to perform a preliminary evaluation of novel membrane-based processes to remove alcohol, water, and residual catalyst removal post alkali-catalyzed transesterification to improve quality and purity. The potential annual energy savings are estimated to be at least $2 million for large-scale biofuels production systems.

Mission Relevance

Separations is one of the key focus areas of the DOE Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program (DOE EERE/ITP). New research initiatives in biomass processing using membranes can deliver improved energy savings and reduce water use critically important to improve the energy efficiency of industrial processes. We anticipate significant benefits to DOE EERE/ITP as a result of this research focusing on development of novel approaches in separation and purification to improve process and energy efficiency. Membrane-based research in biofuels processing which aims to improve process efficiency and water recovery would be beneficial to the Environmental Protection Agency as it would reduce waste treatment costs and also improve air quality. The use of renewable resources such as microalgae for producing alternative fuels such as biodiesel using membrane-based separation processes would be of interest to the Department of Agriculture (USDA) and the Department of Defense (DOD). USDA is actively pursuing research to develop alternatives to fossil fuels, and DOD supports research in algal biodiesel.

Results and Accomplishments

Several experimental units were designed and fabricated to perform membrane evaluations. A number of algal strains were characterized for flux and separation performance. Batch quantities of *Nannochloropsis* cultures ranging from 10 to 25 L were cultivated. Several enhancements to the cultivation techniques were incorporated, which include porous membrane tubes for more efficient gas diffusion and mixing, pH control, and controlled flow of CO_2/air mixture. For the dewatering of algal biomass, several polymer and inorganic microporous membranes were evaluated, including membranes fabricated at ORNL. We have established the optimal pore characteristics for maximizing separation and filtration performance. Initial results show flux with inorganic microporous membranes to be several-fold larger than polymer membranes. Backpulsing was found to be critical in maintaining high flux along with relatively high shear in the feed channel. Microalgal adsorption reduced flux. Adsorption was stronger on membranes made of hydrophilic materials than on those made of hydrophobic materials, requiring more aggressive cleaning strategies.

05574

Understanding Microstructure-Mechanics Relationships of Advanced Structural Materials Using High-Performance Computational Modeling and *In Situ* Time-Resolved Neutron Diffraction

Wei Zhang

Project Description

Property degradation of welds in advanced materials severely limits realization of the energy benefits of these materials at extreme service environments. The fundamental understanding of weld residual stresses, microstructure, and properties is critical for enabling the safe, efficient, and reliable operation of welded structures. Progress towards amelioration of weld property degradation has been slow due to the occurrence of complex welding phenomena with different physics, length, and time scales whose

synergistic effects on weld failure remain unclear. This project aims at developing a unique capability to enable a fundamental understanding of weld microstructure-mechanics relationships by utilizing *in situ* neutron diffraction and advanced high-performance weld modeling. The neutron diffraction will provide time-resolved spatial mapping of microstructure and stress during testing in extreme conditions emulating those experienced in harsh service environment. The measured data will be used to validate advanced weld models. In particular, this approach of combining the advanced neutron diffraction experiment and the weld models will be applied to study the high-temperature performance of high-strength steel welds fabricated using friction stir welding (FSW), a newly developed advanced solid-state welding process.

Mission Relevance

New knowledge and capabilities derived from this project will provide an improved understanding of weld microstructure-mechanics relationships and the ability to understand failure in the welds of advanced materials such as high-temperature, high-strength alloys. The use of advanced neutron diffraction and high performance computing–based weld models is a compelling example of the unique strength of national laboratories to address the significant problem of weld property degradation. Such knowledge is relevant to specific programs, including DOE Nuclear Energy (e.g., next-generation reactors), Fossil Energy, and Energy Efficiency and Renewable Energy (e.g., computational manufacturing initiative); the Department of Transportation's Alternative Fuels Transportation Infrastructure program; and the Nuclear Regulatory Commission's Nuclear Reactor Safety Research program.

Results and Accomplishments

The outstanding weld mechanical properties of FSW, along with improved safety and low environmental impact, have made it an enabling technology for construction and repairing of structures used in next-generation energy production and conservation systems. To tailor the FSW microstructure and properties based on scientific principles, a critical prerequisite is knowledge of the thermal and mechanical history experienced by the material during welding. In the present work, a next-generation model of FSW based on fully coupled thermal-material-flow transient simulation is developed to overcome the limitations of current-generation quasi-steady-state models. A key feature of this advanced next-generation FSW model is the use of dynamic mesh, which combines the benefits of both Lagrangian and Eulerian formulations. In other words, the tool motion is accurately captured with the Lagrangian movement of the elements, while at the same time the Eulerian formulation permits the material to flow through the mesh, maintaining good mesh quality. The material constitutive behavior is treated with the model based on Zener-Hollomon parameters, and the values of material constants were determined from the experimental data of compression tests at various temperatures and strain rates by Professor Choo's group at the University of Tennessee. A good agreement between the calculated and measured temperature profiles was achieved, indicating the validity of the transient model. The model is useful for designing the pin tool and process parameters to tailor the weld microstructure and properties based on scientific principles. Efforts on developing advanced weld models on scientific high-performance computing architectures are under way in collaboration with the ORNL Center for Computational Sciences.

NEUTRON SCIENCES

00015

A Robust Polymer Scaffold System for Bio-inspired Membranes

John F. Ankner

Project Description

The objective of this project is to develop expertise in the preparation of, and investigation using neutron scattering of, soft material scaffolds that can be used to create bio-inspired membranes. Interfaces play a key role in biological processes, and many biological molecules function at interfaces and in confined environments. Therefore, developing robust platforms that can be used to examine structure-property-function relationships of biomolecules attached to and penetrating into interfaces is crucial to ORNL taking a leadership role in bridging biology and biological processes to the development of next-generation materials, devices, and processes.

Results and Accomplishments

During FY 2009, the project's final year, refinement of polymer synthesis, deposition, and surface functionalization and characterization was achieved. This was accomplished by utilizing the controlled free-radical polymerization technique known as reversible addition fragmentation chain transfer (RAFT) polymerization to synthesize well-defined block copolymers. The first block is comprised of poly(glycidyl methacrylate), which serves as an anchor block by covalently attaching to surface hydroxyls, while the second block consists of the reactive monomer vinyl dimethylazlactone (VDMA), which allows for facile surface functionalization. This approach provides control of both molecular weight (through the RAFT polymerization) and tethering density. We have successfully functionalized surface-bound PVDMA brushes (e.g., *N*-*N* bis(carboxy methyl)-lysine-hydrate and stimuli-responsive carboxylic acids) and are preparing to perform model protein binding studies. The modified surfaces have been characterized utilizing ellipsometry, GeATR-FTIR spectroscopy, and atomic force microscopy. In addition, several of the modified surfaces have been characterized on the Liquids Reflectometer at the Spallation Neutron Source in both solid and liquid cells in order to observe *in situ* structural changes induced at the polymer–solution interface. Currently, we have measured the PVDMA brushes, hydrolyzed PVDMA brushes, and *N*-*N* bis(carboxy methyl)-lysine-hydrate functionalized PVDMA brushes in air and various dueterated solvents. Efforts to extract information on conformational changes of the brushes under a variety of solvent conditions continue.

Other research areas impacted by this project include contributions to the development of a controlled surface grafting research platform, improved liquids sample environment cell, the Liquids Reflectometer's wet chemistry laboratory, the Liquids Reflectometer's hardware settings (slit positions and shielding placement), and data analysis (frame overlap mirror). With these competencies in place, and with instrument and accelerator improvements, significant strides in neutron reflectivity measurements to support measurements of polymers at the liquid–solid interface should be achieved.

Program Development Accomplishments

Our activities have led to the development of the infrastructure and preliminary data needed to seek external funding to continue this project.

Publications

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00022

High-Throughput Neutron Crystallography for Macromolecular Structure, Function, and Design

Dean Myles, Hugh O'Neill, and Edward Snell

Project Description

This proposal aimed to address the last remaining challenge and bottleneck in neutron protein crystallography—the rational growth of single crystals of soluble and membrane-bound proteins that are suitable for neutron analysis. Traditional screening methods are inefficient, slow, and labor intensive, often with lag times of 2–4 years before successful structure determination. We used high throughput, robotic protein crystallization screening techniques to allow multiple parameters to be rapidly and systematically screened and evaluated, enabling dozens of proteins to be assayed against thousands of variables at the same time. Working with colleagues at the Hauptman-Woodward Medical Research Institute (HWMRI), we planned to tackle at least 30 different protein systems, including cellular, signaling, and membrane-bound proteins and enzymes of interest in medical, pharmaceutical, industrial, bio-defense, and bio-energy research. At time of this report, this number has risen to 53 proteins. Patterns and shifts in H_2O/D_2O solubility behavior have been identified that are becoming predictive. Analysis tools have been developed. Six projects are developed to the point of neutron analysis. Seven projects have provided novel crystallization conditions that are being developed using conventional X-ray analysis. The demonstrated success of this rational approach will deliver significant rewards to ORNL, making the unique capabilities of the MaNDi, TOPAZ, and IMAGINE instruments accessible and available to thousands of structural molecular biologists.

Results and Accomplishments

Structural biology provides understanding of the structure and function of protein systems at the molecular level. Because of its clarity and precision in defining protein structure, X-ray protein

crystallography is the method of choice for *de novo* protein structure determination at near atomic resolution. However, the positions of hydrogen atoms, which are of fundamental importance in enzyme mechanism, protein-substrate interactions, and protein-protein recognition, cannot be seen at all in the vast majority (>99%) of these structures. In contrast, the atomic positions of hydrogen—and especially the deuterium isotope—can be readily determined in neutron protein structures. There is now tremendous opportunity to build a world-class user support and research program in neutron protein crystallography at ORNL that will provide ORNL with a strategic lead and unique signature in structural biology.

A practical limitation of neutron diffraction is the need for crystals that are typically >1000 times larger than for X-ray analysis. This is the single biggest challenge and bottleneck in neutron crystallography, recognized by our potential users and funding agencies alike. This project is meeting the challenge by adapting and harnessing high-throughput, robotic protein crystallization screening techniques to develop rational, automatic approaches for optimization and growth of large neutron–sized crystals. We note and stress that while *ab intio* crystallization is the bottleneck for *all* structural biology, the neutron work proposed here starts from the tremendous advantage of having known X-ray crystal conditions and structures. The risks are therefore low, and success rates for optimization are proving to be high. This success will have high visibility and radical impact in our user community, greatly extending the number, range, and complexity of neutron-based structure analyses accessible to the MaNDi and TOPAZ instruments at the Spallation Neutron Source, and will deliver unique strategic capability at ORNL.

Working with Dr. E. Snell of HWMRI, we adapted screening protocols developed for *ab initio* protein crystallization to systematically map and explore the multi-dimensional protein solubility and crystallization behavior that will favor large crystal growth. Robotic technology for liquid dispensing, coupled with experiment design, response surface mapping, and automated image analysis, provides a platform for volume optimization of many samples simultaneously. In this method, the macromolecule and the biochemical crystallization cocktail are mixed under oil in 1536 well plates. Each 1536 well is imaged after loading and then at 1 day, 1 week, 2 week, and 4 week intervals. The images are stored and available for viewing as soon as they are acquired. Every system is duplicated so that single failure of any item does not stop the process. Success is easily measured, as crystal dimensions and their volumes are quantitative metrics and will enable a rational statistical analysis of the results, allow global trends to be identified, and enable the multi-dimensional crystallization phase space of every protein to be mapped. This knowledge is then used to guide our scale-up work at ORNL. For neutron diffraction, improving the signal-to-noise ratio by perdeuteration (replacing hydrogen with deuterium atoms) can dramatically decrease the volume of sample needed for successful data collection. However, the subtle differences in fixed-point properties of D_2O and H_2O affect protein solubility, intermolecular interactions, and association between H/D macromolecules in small but significant ways. The same robotic systems used for optimizing sample volume were used to understand the shift in crystallization/optimization in deuterium-based solutions.

We have developed this work in two phases: the first to develop protocols, and the second to apply them to proteins of biological interest. Specifically, in Phase 1, we survey well-behaved and well-known protein systems to determine if we can generalize the critical biochemical parameters required to seamlessly transition from H_2O to D_2O based solutions. This knowledge enabled volume optimization to be carried out with minimal sampling. In Phase 2, demonstration projects were selected to provide paradigm models for key classes of enzymes and proteins involved in health, medicine, bio-catalysis, and processing, including for DOE's biofuels, hydrogen production, and solar initiatives, as well of proteins of key fundamental and biomedical importance. The improved crystallization and neutron analysis of any one of these systems would be a significant achievement in itself, not only providing new and enhanced structural information but elucidating the mechanism and understanding of action.

Task 1, Pilot phase. We analyzed crystallization conditions for 53 different proteins. Proteins were selected from functional classes of proteins, targeting proteins where the X-ray structures are known, that are amenable to neutron diffraction, that crystallize with ease, and where the neutron structure would be of interest in understanding aspects of biological role and function. Some proteins are commercially available. Others have been cloned, expressed, and deuterium labeled under this project in the Bio-Deuteration Laboratory at ORNL. All proteins—commercial and custom synthesized H and D labeled samples—were resuspended in appropriate crystallization buffers, repurified by column chromatography, and analyzed by SDS PAGE before shipping to HHMRI. Each target protein is screened against 1536 unique crystallization trials, and digital images showing the outcomes are archived for analysis. The effects of additives, co-factors, pH, pD, concentration, temperature, D_2O, perdeuteration, precipitants, and multiple other parameters are being screened and evaluated.

Task 2. All results on all proteins are being used to populate a database that will help identify positive trends and enable a designed approach to volume optimization for subsequent samples in the pipeline. Analysis programs have been developed at HWRI to score and map the crystallization results in a graphical representation of crystallization "chemical space" and "parameter space," which enables correlated variables to be recognized, distinguished, and grouped as distinct color-coded patterns.

Task 3. Work on a number of Phase 2 projects is under way. The protocols and crystallization rules learned in Task 1 are guiding the application and development to targets of high value and interest to ORNL researchers. Conditions have been optimized for predictable growth of large neutron–sized crystals of several proteins (proteinase K, D-rubredoxin, papain, Hubiquitin and D-ubiquitin, beta-lactoglobulin). Novel crystallization conditions have been established for other Phase 2 proteins of specific programmatic interest to research programs at ORNL (Cellobiohydrolase I , *Aequorea victoria* GFP, OmcA), and to our collaborators at partner institutes (HDAC, Arginase,`Cytochrome 553). Work on others is in progress, and the likelihood of success seems high.

Program Development Accomplishments

This program has been a success, demonstrating that access to technologies for high-throughput crystallization will equip and enable multiple research groups at ORNL and in the broader user community to engage in neutron research, building strategic capability not only in the neutron sciences but translating this more widely into broad programmatic activities across the Laboratory and beyond. In addition to employing a talented post-masters biochemical researcher and a postdoctoral crystallographer, we have engaged and trained four graduate and three undergraduate students in these projects. First results were disseminated in posters and invited talks at national and international science meetings in 2007, 2008, and 2009. A long-term funding strategy is being elaborated that will win support from the National Center for Research Resources at the National Institutes of Health (NIH) for the support and development of a P41 biotechnology center to support the growth and development of neutron structural biology, and neutron protein crystallography in particular, with the NIH. This project will provide us with the necessary experience and preliminary results that will make that bid a success.

Publications

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00023

Magnetic Structure Under Simultaneous High Temperature and Ultrahigh Pressure Conditions

Chris A. Tulk, Antonio Moreira Dos Santos, Jamie Molaison, Bryan Chakoumakos, Juske Horita, and Dave Cole

Project Description

This project is aimed at expanding the range of phase space that could be investigated with neutron diffraction by using current SNAP-instrument pressure cell equipment and developing heating capabilities that enable simultaneous generation of high temperature and high pressure. This would require first designing a system that is compatible with our high pressure equipment, procuring it and assembling the components for testing. The high pressure, high temperature system has been constructed and tested to temperatures approaching 1000 K. Several samples have been run at the High-Flux Isotope Reactor (HFIR) instrument over the past year using this equipment to study the onset of a pressure-induced ferromagnetic phase of cobalt oxide. This work is complemented by high-energy X-ray scattering studies and maximum entropy analysis, where we were able to show the tetragonal lattice distortion and the transfer of electronic charge into the *ab*-plane. Additional experiments were performed by the postdoctoral fellow working on this project on semi-conductor clathrate crystals at high pressure. These samples were observed to undergo a series of transformations as the pressure is increased to above 22 GPa, and analysis of these structures is under way. In addition, we have identified benefits of cooling the Paris-Edinburgh cell and have designed, constructed, and tested a cryogenic cooling system for the Paris-Edinburgh cell. Furthermore, six presentations of this work have been given at international conferences, and five manuscripts are being prepared.

Mission Relevance

This project explores the behavior of magnetic materials at high pressures by neutron diffraction, so it naturally falls under one of the major research areas of ORNL, namely neutron science. This also fits the broader mission of DOE to operate world-class neutron scattering facilities in this country and the Materials Science and Technology program within the DOE Office of Basic Energy Sciences. This project has its focus on providing a fundamental understanding of the magnetic properties of materials under extreme conditions, and we fully expect these results to be relevant to understanding complex magnetic interaction in applied systems. More specifically, the high pressure sample environments developed for this project provide unprecedented pressure ranges for doing neutron diffraction in the United States. Not only does this project provide the basis for postdoctoral research, but it also will provide tools that benefit the Spallation Neutron Source (SNS) and HFIR user facilities.

Results and Accomplishments

High pressure magnetic systems scientific overview. During the past year work has continued well with activities on a number of fronts. We have continued to investigate the magnetic properties of

cobalt oxide with increasing pressure. Cobalt monoxide orders antiferromagnetically at 290 K with a tetragonal distortion. More interestingly, the magnetic spin is not oriented along the tetragonal unique axis but at an angle of about 27° (and at 8° from the (111) plane) corresponding approximately to the [113] direction. This exceptional occurrence is likely due to a competition of effects between the Jahn-Teller distortions of the high spin d_7 ion with the spin orbit coupling resulting from its unquenched angular momentum. While some explanations were suggested for such a unique feature, such as multiple k-vector (later disproved), asymmetric cation-cation superexchange, and noncollinear alignment of the spin and orbital angular momentum, experimental evidence for the cause is still lacking.

Experiments conducted as part of this project have included the study of the onset of magnetization as both temperature and pressure are increased, thus mapping the Neal transition, as well as extensive and complementary high energy X-ray scattering studies and Maximum Entropy Methods (MEM) analysis that have illustrated the pressure-induced tetrahedral lattice distortion. These results were obtained from four experiments on the wide-angle neutron diffractometer (WAND) at HFIR, from two experiments on the H-E beamline at sector 1 at the Advanced Photon Source (APS) at Argonne National Laboratory, and from a trip to a laboratory at the National Research Council of Canada to learn the MEM data analysis techniques. This work is now being written for publication.

Semiconductor clathrate materials, the $Ba_8Ga_{16}Ge_{30}$ and the $Sr_8Ga_{16}Ge_{30}$ systems. Semiconductor clathrate systems are structurally analogous to the water hydrate systems and form a possible thermoelectric compound. These semiconductor clathrates are compounds consisting of an open-framework lattice of mainly silicon, germanium, and gallium, containing a second large cation (alkali or alkali-earth) trapped in its cages. The vibrational freedom that the guest atoms experience allows such materials to behave like "phonon glasses" and usually show promising thermoelectric properties. In this work, *in situ* high pressure powder diffraction was performed in two germanium clathrates: $AE_8Ga_{16}Ge_{30}$, where AE = Sr, Ba. The pressure was applied to the samples by means of a diamond anvil cell (DAC) up to 25 GPa, and powder diffraction data was collected in a high energy (100 KeV) synchrotron beam line allowing data collection over a wide q range [0.2–50 $Å^{-1}$]. Both structures were analyzed as a function of pressure, particularly with respect to the influence of the charge transfer of the guest atoms to the host lattice during compression and phase transformation.

The data will be the subject of two papers, one detailing the high pressure isostructural and bonding transformations in the crystalline forms, and the other detailing the structure of the high pressure structural forms. Further experiments are planned on the SNAP neutron instrument this fall/winter.

Other systems. (1) Mg(OH) with Juske, isotopical effects of D and H substitution on sample compressibility of bucite. Two experiments have been carried out at the WAND instrument at HFIR over the pressure range from ambient conditions up to 8 GPa. This work is in collaboration with researchers from Chemical Sciences Division, and a manuscript is in preparation. (2) $Ba_4Nb_2O_9$, a system possibly applicable for dielectrics, shows a yet-to-be-described supercell structure. A proper structural description of this supercell is to be found. Samples of this material have been synthesized in collaboration with the High Temperature Materials Laboratory (Claudia Rawn) and are now being studied by means of X-ray and neutron powder diffraction. It is planned that TEM work will be performed to confirm at the local level the results obtained from diffraction. (3) MnAs is a material with a known potential for a magneticaloric effect that can be enhanced by the application of pressure. Structural studies on the hexagonal-orthorhombic phase transitions of this system under applied magnetic field were perform at HFIR in collaboration with Sergio Game from the University of Campinas, Brazil. Structural studies of the onset of magnetization under pressure on SNAP are

planned for the next year. (4) We are currently hosting a guest from the University of Porto who is performing studies on $Ln_5(Si_{1-x}Ge_x)_4$ (Ln = Gd, Tb, Ho). This system is well known for first-order structural transitions that can be induced both by magnetic field and applied pressure. The nature of these transitions will be studied by means of X-ray and neutron scattering.

Technology development activities resulting directly from this project (sample heating, and cooling in the Paris-Edinburgh [P-E] high pressure cell) are given below.

Heating system for the Paris-Edinburgh cell. The design of the graphite furnace assembly was completed along with the design of the pyrophyllite gasket assembly. Tests of the assembled system have been conducted up to 280 W, the maximum rated capacity of the electrical fuses in the cables from the power supply to the pressure cell. At these power levels temperatures approaching 1000 K have been possible. After several such tests, including tests under hydraulic load, it became clear that the details of the heat treatment process of the gasket material are critical for pressure performance of the system. As such, a comprehensive evaluation of heat treatment process and high pressure performance was made. Several different samples of pryophyllite were heat treated at increasing temperature (500 to 1200 K) to obtain the optimal performance within the P-E cell. Initial diffraction measurements were conducted on the WAND at HFIR. The angular dispersive nature of the WAND required that the incident beam pass through the gasket material holding the sample between the anvils. It became clear that the graphite furnace heating technique is best suited to the pulsed, time-of-flight neutron diffraction at the SNS, where the incident beam can pass through the anvils and scatter at a narrow and fixed 2 theta range centered at 90°. The first high-pressure/variable temperature experiments on the SNAP are planned for the winter and summer SNS run cycle.

A cooling system for the Paris-Edinburgh cell. Over the past year we have decided that there is substantial benefit to be gained from cooling the sample below ambient temperature. To that end, we constructed and tested a cooling stage for the Paris-Edinburgh cell (the postdoctoral fellow hired by this project worked with SNS sample environment persons and contributed technical expertise for this project). This cooling system operates by first pre-cooling the P-E cell using liquid nitrogen flowing through a channel in copper clamps mounted directly on the cell assembly (the P-E cell weighs roughly 35 kg). A secondary cooling system then cools the cell further using a closed-cycle helium refrigerator, which is thermally coupled directly to the anvils of the P-E cell. This system has been designed, constructed, and tested offline in the laboratory, and initial tests have been conducted in a neutron beam at the HFIR facility and most recently at the SNAP instrument. Temperatures below 100 K are reached within 2 h using only the liquid nitrogen precooling system; at that point the liquid nitrogen system is shut off and the closed-cycle refrigerator takes the cell and sample to lower temperature. A base temperature of 26 K has been attained with one day of cooling.

Publications

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00019

Probing Molecular Interaction Between Microbial-Cell Protein and Mineral Surfaces with Neutrons

Liyuan Liang, Baohua Gu, John Ankner, Dean Myles, Wei Wang, and Alex Johs

Project Description

The purpose of the project is to investigate interactions between microbial-cell proteins and mineral surfaces, which are critical to understanding the electron transfer mechanisms and microbial ecosystem reactions/responses in subsurface environments. We hypothesize that direct contact between microbial-cell proteins and mineral surfaces is necessary for electron transfer along a respiratory chain to iron oxide minerals. We use neutron reflectometry and small angle X-ray scattering in combination with aqueous chemical and surface analytical techniques to study the effects of surface charge, chemical affinity, and specific interactions on binding between mineral functional groups and cell proteins. Iron oxide nanoparticles, hematite thin films and the decaheme cytochrome OmcA derived from the outer membrane of *Shewanella oneidensis* MR-1 are used as a model system for the study.

Mission Relevance

This project is relevant to the Genomic Science Program (GSP) and the Environmental Remediation Sciences Program (ERSP) of the DOE Office of Biological and Environmental Research. Understanding the process of electron transfer and mineral respiration is directly contributing to the GSP. Microbial and mineral interaction has profound implication to bioremediation and therefore is relevant to the DOE ERSP. This project is also beneficial to several National Science Foundation (NSF) and National Institutes of Health (NIH) programs, including NSF programs on Cellular Systems and the Interagency Opportunities in Multi-Scale Modeling in Biomedical, Biological, and Behavioral Systems, and NIH programs on Research on Microbial Biofilms and Quantitative Approaches to the Analysis of Complex Biological Systems.

Results and Accomplishments

The third year effort focused on (1) small-angle X-ray scattering (SAXS) experiments to study the solution structure of the multiheme cytochrome OmcA and (2) data processing and preparation of a manuscript, which was submitted to *Biophysical Journal* for publication.

The structure outer membrane cytochrome OmcA from *Shewanella oneidensis* MR-1 was characterized by SAXS and its interaction with hematite by neutron reflectometry (NR). SAXS results showed that OmcA is a monomer that adopts a flat ellipsoidal shape with a dimension of $3.4 \times 9.0 \times 6.5$ nm^3. Changes in redox state affect OmcA conformation. In addition, OmcA interacts with small organic ligands known to act as electron shuttle molecules, such as flavin mononucleotide (FMN), resulting in the formation of high-molecular-weight assemblies. Our model system developed in this project was successfully applied to show that OmcA forms a well-defined monomolecular layer on hematite surfaces. This allows OmcA to preferentially interact with hematite in a conformation that maximizes its contact area with the mineral

surface. The results provide experimental and quantitative evidence that OmcA specifically interacts with hematite and small organic molecules to facilitate electron transfer to minerals.

The success of this project has been communicated to our sponsors in the DOE Office of Biological and Environmental Research (DOE BER), and the core program at ORNL funded by the Environmental Remediation Sciences Program will fully utilize the neutron capabilities. Recent data in the literature suggests that outer membrane cytochromes may also be involved in the reduction of Hg(II) species by dissimilatory metal-reducing bacteria. Thus, this work is particularly relevant to the DOE BER Science Focus Area (SFA) on Hg(II) transformations in environments. The expertise developed in this project has been folded into the ORNL SFA.

Publications

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Wang, Wei, Liyuan Liang, Alexander Johs, and Baohua Gu. 2008. "Controlled synthesis, manipulation of surface hydrophobicity, and self-assembly of hematite nanocrystals." 18th Annual V.M. Goldschmidt Conference (Goldschmidt 2008), Vancouver, Canada.

05004

Neutron Scattering Study of Magnetic and Spin Dynamic Behavior in Amine-Stabilized Transition Metal and Transition Metal Oxide Nanoparticles

Andrew D. Christianson, Sheila N. Baker, William T. Heller, Mark D. Lumsden, Stephen E. Nagler, and Brian C. Sales

Project Description

We propose to study amine-stabilized transition metal based nanoparticles for novel, size-dependent magnetic effects and spin dynamics. An integral part of the proposed research is to develop synthetic protocols for magnetic nanoparticles amenable to the requirements of inelastic neutron scattering experiments. The primary means of doing this is to deuterate the ligands of amine-stabilized magnetic nanoparticles. One sufficient quantities of nanoparticles are synthesized neutron scattering experiments will be used to elucidate the fundamental magnetic behavior. Metallic nanoparticles are very active fields of research in the basic and applied sciences. These materials are being intensively studied for a wide

variety of applications including catalysis and advanced functional materials. The physical constraints resulting from the size of such systems have produced new behaviors, some of which have the potential to be of industrial interest. ORNL is well positioned to take a leadership role in the study of nanoscale magnetism due to the combination of world class materials synthesis and neutron scattering instrumentation.

Mission Relevance

Nanoscale science has been called out in numerous reports as a fundamental technological challenge that, when solved, will lead to profound advances in the current state of the art in many areas such as drug delivery, pollution control, magnetic data storage, energy efficiency. These reports discuss at great lengths the potential future applications as well as areas where very little is known about the fundamental behavior at the nanoscale. Of particular interested for this project is the fundamental behavior of magnetic nanoparticles. Given the potential of functional magnetic nanoparticles to contribute to some of the important problems facing society, a fundamental understanding of the basic physical properties is critical. As such, the fundamental research into nanoscale magnetism falls into the purview of DOE. Consequently, proposed research will provide key additional knowledge physical behavior of magnetic nanoparticles and as such has direct relevance to the mission of the Division of Materials Sciences and Engineering in the DOE Office of Basic Energy Sciences.

Results and Accomplishments

In the project's first year, we successfully synthesized MnO magnetic nanoparticles with both hydrogenated and deuterated capping ligands. In the second year of the project, the synthetic protocol was developed further to minimize the use of high-cost deuterated 1-octadecanol. The nanoparticles size and composition were characterized using scanning transmission electron microscopy, X-ray diffraction measurements, and magnetization measurements. These particles were then used for subsequent neutron scattering measurements as follows: In the first year of the project, we successfully performed neutron diffraction experiments on 8 nm samples of MnO. The effects of nanoscale confinement were clearly observed; both the structural and magnetic peaks are broadened compared with the bulk. The temperature dependence of the magnetic peak indicates that the antiferromagnetic transition is suppressed to 113 K. To explore the differences in the magnetic behavior of bulk vs. nano MnO in greater detail, we performed polarized neutron diffraction experiments to explicitly separate the magnetic diffuse scattering and compare this with that observed in the bulk. The general conclusion from this work is that the diffuse magnetic scattering is a much more substantial part of the overall magnetic scattering for the nanoparticles than in the bulk. No additional neutron depolarization as a function of temperature (2–300 K) was observed, suggesting that a ferromagnetic component to the magnetism does not develops as a function of temperature in contrast to claims in the literature based upon bulk measurements.

Publication

Sun, Q.-C., X. S. Xu, J. L. Musfeldt, R. Tenne, A. Zak, S. Baker, and A.D. Christianson. 2009. "Dynamical charge and structural strain in MoS_2 and MnO nanoparticles." American Physical Society National Meeting, March, Pittsburg, Pa.

05028

Rotating Solid Target Design Development for the Spallation Neutron Source

Thomas J. McManamy, Roy K. Crawford, Phillip D. Ferguson, F. Gallmeier, James Janney, and Mark J. Rennich

Project Description

A rotating solid target could provide a simple, robust, highly flexible, and long lifetime alternative for the second Spallation Neutron Source (SNS) target station. A rotating target is also insensitive to the selection of long pulse (~1 ms) or short pulse (~1 μs) operation. Even slow rotation (a few hertz) greatly reduces the average power density and radiation damage. As a result, the cooling requirements are relaxed and target lifetimes are greatly increased (years) compared to fixed targets. Notably, the reduced cooling fraction in a tungsten assembly increases neutron production and efficient coupling to the moderators can be achieved using smaller beam spots. Implementation of a rotating target requires the development of a practical mechanical design including dynamic water seals, effective cooling, maintenance handling methods, and optimizing the source geometry to fit the desired suite of neutron instruments. This effort includes the following tasks: (1) neutronic and mechanical evaluation and optimization of major design options, including wing or slab moderator neutronic performance, horizontal or vertical axis mechanical evaluation for a range of disk radii from 0.25 to 1 m, and radiation damage and heat loads estimates as a function of disk radius; (2) design optimization for a selected axis and moderator configuration, including target and moderator mechanical layout and neutronic performance optimization, target structural and thermo-hydraulic preliminary design, and concept development for remote handling; (3) concept development for target bearing and sealing methods; and (4) mockup of design solutions for key technical problems.

Mission Relevance

This project will benefit the DOE Office of Basic Energy Sciences, which is interested in building a second target station at SNS. There is a risk that cavitation damage with a target like the presently used mercury target may restrict the allowable beam power for reasonable target lifetimes at the second target station without development of a gas mitigation scheme. Having in hand a design solution for the target may help expedite approval of the second target station. In addition to design simplicity, long lifetimes, and higher reliability, the solid rotating target may also offer significant advantages in improved neutronic performance. Without a conceptual design, it is unlikely that the rotating target concept would be considered mature enough to support such a major funding decision.

Results and Accomplishments

The 3 MW design completed in 2008 looked promising. It included a drive unit module approximately 4 m above the target designed to be independently replaced hands-on. Development of reliable seals and bearing was identified as a key technical problem, and a full-scale drive module was selected for mockup testing. To fit within budget the target and shaft were not included, but the 2500 lb weight was simulated by a spring-actuated pre-load mechanism. State-of-the-art commercial graphite–on–silicon carbide rotating water seals were used. Deep groove ball bearings were selected for the thrust and radial bearings. Graphite packing rings were used for the gas seal on the shaft to prevent leakage of the helium around the target and shaft to the region above the shielding. Fabrication went well, and the unit was run for slightly over 1000 h at 30 rpm with the water lines pressured but with only a low flow rate. There were no significant problems, and the water seals showed no evidence of leakage. In general, the fabrication and the testing were very successful. The fabrication experience also gave a better understanding of the

tolerances that could be maintained for reasonable cost. The European Spallation Source teams at Bilbao, who became interested in this work, entered into collaboration with SNS and have fabricated a 4 m shaft and dummy target based on this design. The assembly will be tested with the drive module by SNS in 2010. They are also proposing to fabricate a target to study the water flow, which could be tested with the drive module.

Publications

Janney, J., T. McManamy, M. Rennich, and F. Gallmeier. 2009. "Thermal stress analysis of a 3 MW rotating solid target." *Proceedings of 9th International Topical Meeting on Nuclear Research Applications and Utilization of Accelerators,* Vienna.

McManamy, T., M. Rennich, J. Janney, and P. Ferguson. 2009. "3 MW solid rotating target design." Proceedings of the 9th International Workshop on Spallation Materials Technology, in *Journal of Nuclear Materials* (October).

00529

Pushing the Limits: High Impact Neutron Protein Crystallography

Leighton Coates and Dean Myles

Project Description

Our objective is to enable neutron analysis on the structure and function of two novel proteins at atomic levels of detail, each of which will push neutron protein crystallography into new areas. Neutron protein crystallography produced several high impact scientific publications in the 1990s, exciting the biological community about the possibilities of using neutron science. Although there has been a steady trickle of neutron structures since the advent of neutron crystallography, the number of proteins studied by neutron diffraction remains low. The development and publication of high impact projects utilizing neutron protein crystallography to address new sorts of biological questions will be a key asset to stimulate and build the biological user community for the single crystal diffactometers that will operate at the Spallation Neutron Source and the High-Flux Isotope Reactor. The study of complex proteins using neutron science offers novel applications for neutron protein crystallography, which can provide answers to key biological questions that cannot be answered even with near-atomic-resolution X-ray structures.

Mission Relevance

At the start of the project, only nine unique proteins, whose atomic coordinates are deposited in the protein data bank, had been studied to high resolution using neutron diffraction. These proteins share a number of similarities; they are all stable proteins that diffract X-rays to well beyond atomic resolution (1.2 Å) and have been studied for many years. Many of the nine proteins studied are available for purchase from all major suppliers of biochemical reagents. Studies on these types of proteins, while providing interesting science, will never yield the high impact results or publications necessary to stimulate wider interest in neutron protein crystallography and recent developments in it. The chances of obtaining peer-reviewed funding to work on proteins of this type are minimal at best. Most peer-reviewed research in the structural biology area is conducted on proteins overexpressed within a host system. Understanding membrane protein structure and function remains an outstanding grand challenge in biology, and its strategic and fundamental importance in human health, medicine, agriculture, and bioenergy cannot be overstated.

Results and Accomplishments

We identified β-lactamase as an important protein for neutron studies. β-Lactamase is a protein that can break down several antibiotics, enabling the development of bacterial antibiotic resistance. Bacterial resistance to β-lactam antibiotics is a serious problem limiting current clinical therapy. A neutron structure could enable a better understanding of how Toho-1 β-lactamase breaks down many current antibiotics. Toho-1 β-lactamase is an extended-spectrum β-lactamase that has acquired efficient activity not only to penicillins but also to cephalosporins, including the expanded-spectrum cephalosporins. This work marks the first successful study of a β-lactamase using neutron diffraction.

We were able to utilize lab facilities at the ORNL Center for Structural Molecular Biology to grow very large protein crystals suitable for neutron diffraction studies (6 mm^3) and successfully collected a complete neutron diffraction data set to 2.1 Å at the LADI III instrument at the Institut Laue-Langevin (ILL) in Grenoble, France. Unfortunately, there is only a single operating neutron instrument in the United States that can collect data on our crystals; as this instrument is heavily oversubscribed, it was necessary to travel to the ILL for data collection.

Refinement of the data is near completion (R_{factor}, 23.38%; R_{free}, 25.37%), and a manuscript has been submitted to *Journal of Molecular Biology* for publication. This marks the starting point of several possible studies probing the development of more potent antibiotic compounds and the catalytic mechanism by which the enzyme operates. In further experiments we aim to study the binding of next-generation antibiotics using the TOPAZ and IMAGINE diffractometers, both at ORNL, as soon as they become available. These diffractometers should be able to handle unit cell axes up to around 100 Å on each axis. For axes above 100 Å, MaNDI will be the most suitable diffraction instrument.

05045

Neutron Structural Virology

Flora Meilleur, William Heller, and Dean Myles

Project Description

Arthropod borne viruses (Arboviruses) are major sources of human disease. Their natural vector is blood-sucking insects. They cause some of the most devastating infectious diseases known to human and veterinary medicine, including yellow fever, dengue fever, and West Nile fever. Collectively, arboviruses are second only to malaria as a threat to global health. Arboviruses share certain properties of structure and function, suggesting that information gained about any one of these viral agents may be applicable to other members of this virus family that includes human and animal pathogens. Sindbis virus is prototypic. Its structure comprises two nested icosahedral shells that sandwich a lipid membrane bi-layer and protect a single-stranded RNA core. Cellular interaction and infection involves dramatic structural reorganization of the virus. Our objective is to model and understand the structural changes that are associated with virus assembly, attachment and infection at cell membranes using neutron solution scattering and reflectometry. A detailed understanding of the mechanism by which these structurally unique groups of infectious agents gain entry to cells is essential for the successful pursuit of pharmaceutical development of antiviral compounds that block the infection process to treat and prevent infection by the members of this viral family.

Mission Relvance

Arboviruses are major sources of human disease. Collectively, arboviruses are second only to malaria as a threat to global health. Worldwide, approximately 2.5 billion people are at risk of contracting this disease annually. Despite the enormous economic and medical impact of these agents, very few effective vaccines exist for their control. Therefore, this work will be of strong interest to the biomedical community, showcase the capabilities of the Spallation Neutron Source (SNS) and the High-Flux Isotope Reactor (HFIR), and generate interest in neutron techniques among biomedical researchers in a manner that will drive cross-cutting science and expand the user community of these facilities. This work will also benefit agencies that are concerned with human health and veterinary medicine, such as the Department of Agriculture and the National Institutes of Health.

Results and Accomplishments

Our ultimate goal is to investigate the structures of viruses grown from two different sources (baby hamster kidney and chicken cells) at pH 7.2 and 6.4 in order to track the virus structural changes in response pH reduction. All the data are collected on the BIO-SANS (CG3) beamline of the HFIR. Specifically in FY 2009, the low pH contrast series were measured and analyzed using the strategy employed for the data collected at neutral pH in FY 2008. All the data sets collected since the start of the project have been analyzed using model dependent and model independent methods. In the model independent method, Guinier approximation is used to determine the radius of gyration, R_g, of the virus particle. The model-dependent analysis using multiple concentric shells of different scattering length density and radius suggests that four shells are needed to fit the data satisfactorily. The analyses are being finalized for publication.

These small-angle neutron scattering experiments show that structural data of infectious or functional entities of large size and complexity can be collected using the neutron scattering instruments at ORNL and interpreted. This is critical as it illustrates the unique potential of neutron techniques for studying native virus particles, which will help attract the virology community to conduct structural studies on the SNS/HFIR instrument suite.

Publication

He, L., A. Piper, F. Meilleur, D. A. Myles, R. Hernandez, D. T. Brown, and W. T. Heller. In press. "The structure of Sindbis virus produced from vertebrate and invertabrate hosts determined by small angle neutron scattering." *Journal of Virology.*

05088

Inelastic Neutron-Scattering from Magnetic Heterostructures

Randy Fishman, Lee Robertson, Mark Lumsden, and Jian Shen

Project Description

Inelastic neutron scattering is the world's most powerful tool to study the magnetic dynamics of solids. But only with the recent development of improved neutron optics and more powerful neutron sources such as the Spallation Neutron Source (SNS) has it become feasible to study the magnetic dynamics at interfaces and in confined geometries. We propose to develop the technique of inelastic neutron scattering from magnetic heterostructures consisting of alternating magnetic and nonmagnetic layers. To demonstrate the feasibility of this technique, we shall study Dy/Y and Ho/Y multilayers, which were

chosen for the close lattice matches and the large dysprosium and holmium moments. Molecular-beam epitaxy will be used to fabricate heterostructures by repeating bilayers with roughly 45 Å of dysprosium or holmium and 30 Å of yttrium. Magnetic characterization will be performed using the magnetism reflectometer at the SNS and inelastic measurements will be performed at the High-Flux Isotope Reactor (HFIR). Simultaneously, we will develop the theory of inelastic neutron scattering from magnetic heterostructures by using a coupled Green's function technique.

Mission Relevance

The development of an inelastic neutron-scattering technique for the study of magnetic herterostructures will have wide-ranging implications for a variety of materials of technological and scientific interest. This new technique will enhance the potential applications of the SNS and HFIR, both of which are central to the DOE mission.

Results and Accomplishments

The synthesis group of Jian Shen was unable to produce high-quality samples of Dy/Y multilayers. As a result, the funding for this project was severely cut in FY 2009, with funds to support a theory postdoctoral researcher and little else.

Despite this setback, we acquired high-quality Dy/Y samples from the group of Gary Mankey at the MINT center in Alabama. Some of Mankey's materials costs were paid from the LDRD fund. The first samples arrived at ORNL in the summer of 2009. Elastic neutron-scattering measurements confirmed the high quality of those samples. By stacking several multilayer samples on top of each other, inelastic measurements were able to obtain significant cross sections. While the inelastic results are promising, we are waiting for more samples from Mankey before beginning our analysis of these inelastic measurements in earnest.

In our modeling efforts, we have tested a new Green's function approach for the spin-wave dynamics on a generalized Villain model. That approach yields both the spin-wave frequencies and intensities. This work appeared in *Journal of Physics: Condensed Matter.*

We have also used a spin-wave analysis to study the magnetic instabilities in aluminum-doped $CuFeO_2$. The aluminum-doped material $CuFe_{1-x}Al_xO_2$ ($x > 0.016$) exhibits a noncollinear and multiferroic magnetic ground state, which we have studied using Monte-Carlo simulations. The results of that work appeared in two papers: one in *Physical Review B* and another in *Physical Review Letters.*

More recently, we have studied the source of the net chirality observed in Dy/Y multilayers. Our results indicate that there are two mechanisms at work. First is the elastic torsion produced by a chiral deformation at the interface. Second are steps at the Dy-Y interface which can produce a net chirality of the dysprosium helix. The second mechanism may dominate after field cooling, explaining why the net chirality observed in Dy/Y multilayers can change sign. Control of chirality would have technological ramifications that are wide ranging. This work has been submitted to *Physical Review Letters.*

We are currently preparing a manuscript on the change in spin-wave dynamics from bulk dysprosium to the Dy/Y multilayer geometry. Discrete excitations that appear in an isolated dysprosium layer follow the bulk-like dispersion when dysprosium layers are coupled by an RKKY interaction through the yttrium spacer. This work will be submitted to *Physical Review B*.

Publications

Fishman, R.S., F. Ye, J. A. Fernandez-Baca, J. T. Haraldsen, and T. Kimura. 2008. "The Importance of stacking to the collinear magnetic phases of the frustrated antiferromagnet $CuFeO_2$." *Physical Review B, Rapid Communications* **78,** 140407.

Haraldsen, J. T., and R. S. Fishman. 2009. "Spin rotation technique for non-collinear magnetic systems: Application to the generalized Villain model." *Journal of Physics: Condensed Matter* **21,** 216001.

Haraldsen, J. T., M. Swanson, G. Alvarez, and R. S. Fishman. 2009. "Spin-wave instabilities and non-collinear magnetic phases of a geometrically frustrated triangular-lattice antiferromagnet." *Physical Review Letters* **102,** 237204.

Swanson, M., J. T. Haraldsen, and R. S. Fishman. 2009. "Critical anisotropies of a geometrically frustrated triangular-lattice antiferromagnet." *Physical Review B* **79,** 184413.

05125

An Experimental, Theoretical, and Molecular Modeling Approach to Characterizing the Structure and Dynamics of Charged PAMAM Dendrimers in Solution

Wei-Ren Chen, Gregory S. Smith, Kenneth W. Herwig, Kunlun Hong, William A. Goddard, Yi Liu, Yun Liu, and Lionel Porcar

Project Description

Poly(amidoamine) dendrimers (PAMAM) with ethylenediamine (EDA) cores and amino groups are synthetic, nano-scale macromolecules with promising potential for use in biomedical applications. While a number of studies have focused on the structure of dendrimers in solution, several questions pertaining to aqueous PAMAM solutions remain unanswered. A combined experimental, theoretical, and molecular modeling study is conducted to understand how charge and counterion condensation affect the single-molecule structure, the interaction potential between PAMAM dendrimers, and relevant dynamic processes. The dynamic behavior of interest includes backfolding and confined water migration relevant at the single molecule level as well as the self-diffusion of dendrimers in concentrated solutions where inter-dendrimer interactions play a dominant role. Specially tailored dendrimers with molecular architectures selectively highlighted by hydrogen isotopic labeling will be synthesized and utilized for small-angle neutron scattering (SANS), neutron spin-echo (NSE) spectroscopy, and neutron backscattering spectroscopy measurements. A theoretical description of the effective interaction will be used to model the neutron scattering results. Significantly, we will carry out multi-scale simulations of a dendrimer in solution to elucidate structural and dynamical details not accessible experimentally. This work will reveal fundamental scientific behavior critical for assessing the therapeutic potential of dendrimers.

Mission Relevance

The focus of this project is on understanding the rich phase behaviors of PAMAM dendrimers, a novel macromolecule possessing both polymeric and colloidal structural natures, via a synergetic approach combining neutron scattering, molecular dynamics simulations, and material synthesis. The overarching goal of our work is consistent with the mission of the DOE Office of Basic Energy Sciences.

Results and Accomplishments

In our experimental study, a SANS technique is used to explore the various structural aspects of the PAMAM dendrimer solutions at their charged states. We developed a mean-field model for the SANS coherent scattering cross section I(Q). Based on the results of our data analysis, we first found that the inter-dendrimer interaction is greatly influenced by their polymer-colloid structural duality. Second, an unexpected generational dependence of the counterion association is revealed, which is attributed to the backfolding of the dendrimer molecule. A SANS-contrast variation method was employed to quantitatively evaluate the volume of the intra-molecular cavity of the PAMAM dendrimer in terms of the associated water molecules number. Moreover, we found that upon increasing the dendrimer concentration in aqueous solutions, the molecular size, parameterized by radius of gyration RG, is found to remain nearly invariant, an observation manifesting its colloidal structural nature. However, a significant transition in the intra-molecular density profile is found. We also observed a strong conformational dependence on the counterion valency. Last, a quasi-elastic neutron scattering experiment also revealed the dynamical aspect of the pH responsiveness of the dendrimer.

Based on the new force field for the charged PAMAM dendrimer, in which all the constituent atoms of dendrimer, water, and counterions are incorporated explicitly, that was developed during the first year of this project, a collective intra-dendrimer motion observed by NSE was analyzed at the atomistic level. Our results suggest the strong correlation of the coordinated segmental motion of dendrimer and its molecular protonation.

Publications

Chen, Wei-Ren, et al. 2007. "Study the counterion effect on the structural properties of charged G4 PAMMA dendrimer aqueous solutions by small angle neutron scattering." *Macromolecules* **40,** 5857.

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Chen, Wei-Ren, et al. 2008. "Assess the intra-molecular cavity in PAMAM dendrimers by small angle neutron scattering." *Macromolecules* **41,** 8916.

Chen, Wei-Ren, et al. 2009. "Counterion association and structural conformation change of charged PAMAM dendrimer in aqueous solutions revealed by small angle neutron scattering." *Macromolecular Symposia* **279,** 65.

Chen, Wei-Ren, et al. 2010. "Intra-molecular structural change of PAMAM dendrimers in aqueous solutions revealed by small angle neutron scattering." *Journal of Physical Chemistry B* **114,** 1751.

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Liu, Yun, et al. 2010. "Formation of the dynamic clusters in concentrated lysozyme protein solutions." *Journal of Physical Chemistry Letters* **1,** 126.

05225

Dynamically Polarized Samples for Studying Biological and Soft Condensed Matters

J. K. Zhao, Neil Demarse, Joshua Pierce, Leighton Coates, Stephen Nagler, Christina Hoffmann, Wai Tung Hal Lee, Don Crabb, and Joseph D. Ng

Project Description

The project aims at developing a scientific method for studying biomolecules and other condensed matters using polarized neutron scattering from Dynamically Polarized Samples (DPS). Hydrogen is the most abundant element in biomolecules. Unfortunately, its incoherent scattering is often the biggest source of scattering background. The DPS technique is a way to both drastically reduce this background and increase the coherent signal without expensive and difficult deuteration. Initially using lysozyme, we plan to develop and study biochemical methods of introducing polarizing agents into protein crystals without damaging them for DPS diffraction experiments. After achieving hydrogen polarization and conducting diffraction studies, we will investigate proteins with high impact potentials, such as GAPDH. GAPDH is a DNA binding protein that is implicated in cancer drug resistance. We propose to investigate its structure and functional mechanism using DPS. In addition, we propose to study methods that would take advantage of the future 30 tesla ZEEMANS facility in a way that might revolutionize neutron protein crystallography. We plan to carry out a proof-of-concept experiment on a simple model system to selectively polarize crystallographically nonequivalent protons in high field. This would allow site-specific studies of complex molecules by neutron scattering similar to X-ray "anomalous diffraction".

Results and Accomplishments

The project has successfully accomplished all three planned goals in the first year of its funding: we have started the dynamic polarization process on protein crystals, started the introduction and screening of the polarization agents into protein crystals, and have preliminarily selected a system for the study of crystallographically non-equivalent protons using DNP. In addition, we have followed through the hiring plan and brought Dr. Neil Demarse on board in spring 2009.

Introduction and screening of polarization agents into lysozyme protein crystals. The first task is to introduce polarization agents into protein crystals without damaging the proteins. We used lysozyme as our test protein and the chemical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as the polarization agent. TEMPO is relatively easy to handle. In addition, it has the advantage that some forms of TEMPO derivative can be used as spin labels. Namely, it can be attached to specific sites on proteins and protein crystals, thereby creating a separate reference phase in crystallography. We introduced TEMPO into lysozyme crystal in two separate ways. The first is to co-crystallize TEMPO with lysozyme. The second method is to soak lysozyme crystals in buffer containing TEMPO. The lysozyme crystals were then screened with X-ray diffraction for possible structure distortions to the lysozyme protein and to access changes in crystal quality.

Lysozyme crystals were crystallized with and without TEMPO. The crystals were grown in buffers containing 5% NaCl, 50 m*M* sodium acetate, and 5 m*M* of TEMPO. These crystals were then studied by X-ray diffraction at Toledo University at room temperature. The structure was solved by molecular replacement with MOLREP (Vagin, Teplyakov, *J. Appl. Cryst.*, 1997) using a previously solved crystal structure of lysozyme collected at room temperature (Protein Data Bank Code: 1AZF). A visual inspection of the crystal packing using the program O (Jones, Zou, Cowan, *Acta Crystallogr A*, 1991) displayed a periodic, ordered and symmetrical arrangement of the asymmetric unit. Refinement and model building using REFMAC (Murshudov, Vagin, Dodson, *Acta Crystallogr D*, 1997) and O yielded a

final structure to 2.0 Å resolution with an R factor of 22.2 % (Rfree = 24.1). The crystals belonged to the $P4_32_12$ spacegroup with cell dimensions a = 79.2 Å, b = 79.2 Å, and c = 38.0 Å. The root mean standard deviation (RMSD) between the lysozyme structures with and without TEMPO was calculated to be 0.17 Å, indicating that there is no significant difference in their tertiary structures. *Therefore, we believe that the TEMPO polarizing agents introduced into the lysozyme crystal did not alter the protein structure or its conformation.*

Detailed examination of the electron density map revealed several regions of positive-electron density on the surface of lysozyme. After a thorough analysis of the electron density maps of other lysozyme structures from the Protein Data Bank, we concluded that these regions do not correspond to densities in lysozyme structures. It's likely that they are from water molecules on the protein surface. However, these electron densities were much greater than that of a typical water molecule and their distances to the nearest neighboring atoms were shorter than that of a hydrogen bond. Therefore, that it is also likely that these regions correspond to poorly ordered TEMPO molecules on the protein surface, or protein regions oxidized by TEMPO. The TEMPO used in these experiments is not specific in interacting with amino acids. However, under the low pH (4.8) condition that the samples are in, TEMPO may act as oxidants and interact with the protein. We are looking at the nearest contact atoms of these regions, which might give us further information on these positive density regions.

The possibility that these positive electron densities come from TEMPO is an encouraging sign for employing spin labels. We have recently obtained 4-(2-iodoacetamido)-TEMPO, which can bind to cysteine residues on protein surface. Our plan is to use the 4-(2-iodoacetamido)-TEMPO with GAPDH crystals. GAPDH is a protein that is deeply implicated in drug resistance in cancer cells. Detailed understanding of the GAPDH protein will have real life clinical impacts. The GAPDH with spin labels will be studied with synchrotron radiation at the Advanced Photo Source in August this year. In the mean time, we have performed a polarization experiment using the 4-(2-iodoacetamido)-TEMPO and the GAPDH protein in solution and test the feasibility of this TEMPO derivative as a polarizing agent (see next section). In addition, we are also evaluating other TEMPO derivatives (3-(5-fluoro-2,4-dinitroanilino)-PROXYL) that can bind to surface lysine and arginine residues.

Lysozyme crystals soaked in solution containing TEMPO were also characterized using X-ray diffraction. The experiment was carried out at the Medical University of South Carolina. The crystals were soaked in solutions containing 3 m*M* TEMPO prior to X-ray diffraction. The X-ray data were refined to 2.1 Å resolution. The yielded electron density map is similar to that of the co-crystallized protein studied above, indicating that the two methods of protein crystal preparation result in no significant differences.

Start dynamic polarization of protein crystals. Lysozyme crystals co-crystallized with TEMPO were polarized at the University of Virginia Dynamic Polarizing Facility. The dynamic polarizing facility consists of a 5 Tesla solenoid magnet and a 1 K refrigerator. The microwave that is required for inducing the coupling between the electron spins of the paramagnetic centers and the nuclear spins of the hydrogen is provided by an EIO klystron tube. The TEMPO concentration in the sample is about 10^{19} cm^{-3} paramagnetic centers in the lysozyme crystal. These initial polarization experiments focused on whether the protein crystal would polarize at all. With further optimization (polarizing agent doping, and better running condition of the polarization equipment), we believe it will be possible to achieve much higher proton polarization.

In addition to polarizing protein crystals, we were able to test the feasibility of using the spin label 4-(2-iodoacetamido)-TEMPO as a polarizing agent. We were able to achieve about -45% protonpolarization after about one hour.

Select system for proof-of-concept studies on crystallographically nonequivalent protons with different chemical shifts. At this point, we believe that proteins with spin labels will offer the best system for studying crystallographically nonequivalent protons. Hydrogens around these spin labels can be targeted by NMR signals for selective polarization and depolarization. Inorganic systems such as hydrogen bonded ferro- or antiferroelectric materials in the KDP family, or small organic molecules such as benzene will still be evaluated.

Program Development Accomplishments

Our polarization result was presented at the International conference on Neutron Scattering in May 2009. We are collaborating with Dr. Basim of the Medical University of South Carolina and have submitted a preliminary research proposal DOE Office of Science's "Experimental Program to Stimulate Competitive Research (EPSCoR); Building EPSCoR-State/National Laboratory" program in June 2009.

Publications

Pierce, Josh, Don Crabb, and J. K. Zhao. 2009. "Dynamically polarized sample for neutron scattering at the Spallation Neutron Source." *Proceedings of the 18th International Symposium on Spin Physics. Charlottesville, Va., 2008. AIP Conference Proceedings* **1149,** 872–875.

Pierce, J., D. G. Crabb, S. Tomanicek, N. Demarse, J. Maxwell, J. Mulholland, and J. K. Zhao. In press. "Dynamically polarized sample at the Spallation Neutron Source." *Journal of Physics: Conference Series*.

05140

Mapping the Protein Structure-Function-Dynamics Landscape

Pratul K. Agarwal

Project Description

This project will dramatically impact and extend the use of neutron scattering techniques in the structure-function-dynamics analysis of biological materials by developing experimental, analytical, and computational techniques that exploit residue-specific H/D-labeling techniques to systematically target, highlight, and distinguish the dynamics of individual H-labeled residues in otherwise functional deuterated protein systems. We will develop and apply these capabilities in model systems and demonstrate their combination and use in neutron spectroscopy, neutron crystallography, and molecular dynamics (MD) simulation. As a test system, we will use a small 53-residue protein rubredoxin from *Pyrococcus furiosus* (RdPf), the most thermostable protein characterized to date. Specifically, we will (1) develop protocols for expression and production of site-specific H/D-labeled RdPf, (2) explore the residue specific temperature dependence of protein dynamics using neutron spectroscopy, (3) determine neutron crystallographic structures at identical temperatures to locate and model H-labeled residues, and (4) analyze this information with respect to high-performance MD simulations. Once developed, we will apply these techniques to analyze the specific structure-function-dynamics of the medically important enzyme DHFR, which is a major target for drug design.

Mission Relevance

This project will dramatically impact and extend the use of neutron scattering techniques in the structure-function-dynamics analysis of biological materials by developing experimental, analytical, and computational techniques that exploit residue-specific H/D-labeling techniques to systematically target, highlight, and distinguish the dynamics of individual H-labeled residues in otherwise functional deuterated protein systems. This program will deliver new scientific capabilities and results of particular interest to the National Institutes of Health, the National Science Foundation, and DOE programs in biomedicine, bioengineering and biotechnology, specifically for biomedical, pharmaceutical, and bio-inspired design, and will greatly extend the capabilities of the Spallation Neutron Source and the High-Flux Isotope Reactor and the user base in the biosciences.

Results and Accomplishments

This ongoing project is investigating the interconnection between protein structure, dynamics, and function using a multi-disciplinary approach. Rubredoxin from *Pyrococcus furiosus* (RdPf) has been labeled and studied under different solvents (H_2O and D_2O), using neutron scattering and computational modeling. In particular, the following neutron studies have been performed:

- *Specific labeling of Rubredoxin methyl groups with hydrogen remainder deuterated.* We measured (on Basis) this sample and a fully deuterated sample. The analysis of this data is in progress.
- *Measured protonated Rubredoxin, hydrated at 0.2 and 0.37 with D_2O.* We measured deuterated Rubredoxin hydrated with H_2O at the same hydration levels. The goal of the experiment is to resolve a long-standing debate in the community of the role of solvent in triggering or enabling the local dynamics of a protein. Clearly, at low Q it is apparent that the water dynamics initiates at a lower T than the protein.

Additionally, computational modeling of thermophilic and mesophilic Rubredoxin is allowing interpretation of the neutron data. The following results indicate new insight into Rubredoxin. Continuing work is planned to investigate the enzyme dihydrofolate reductase for the interplay between structure, dynamics, and function. In particular, the role of solvent in driving the enzyme motions and therefore the enzyme activity is being analyzed.

Publications

Ramanathan, A., and P. K. Agarwal. 2009. "Computational identification of slow conformational fluctuations in proteins." *J. Phys. Chem. B* **113**(52), 16669–16680 (featured on the cover).

Ramanathan, A., P. K. Agarwal, M. G. Kurnikova, and C. J. Langmead. In press. "An online approach for mining collective behaviors from molecular dynamics simulations." *J. Comp. Bio.* **17**.

05227

Fundamental Neutron Scattering Studies of the Molecular Mobility and Interactions Between Natural Porous Media and Greenhouse Gases for Efficient Geological Carbon Storage and Enhanced Coal Bed Recovery

Yuri B. Melnichenko, G. Cheng, E. Mamontov, G. D. Wignall, M. Mastalerz, J. Rupp, A. Radinski, and R. Sakurovs

Project Description

Carbon dioxide emissions from anthropogenic sources are frequently directly linked to the rising level of atmospheric CO_2 and to global warming. Carbon capture and sequestration in geological formations is a proposed measure for arresting the rising concentration of atmospheric carbon dioxide. Saline aquifers, depleted oil and gas reservoirs, and unmineable coal seams are top contenders for geological storage, based on their estimated storage capacity, geographical extent, and geological and engineering considerations. However, the lack of knowledge about molecular mobility under confinement and about molecule–surface interactions between greenhouse gases and natural porous media results in generally unpredictable sorption kinetics and total sorption capacity for injected fluids and, therefore, constitutes barriers to the deployment of this technology. To circumvent these barriers, we recently performed proof-of-principle experiments and demonstrated the exceptional potential of conventional and ultrahigh-resolution small-angle neutron scattering (SANS/USANS) to provide unique, pore-size-specific insights into the mechanisms of CO_2 sorption in coals and to characterize the density and volume of the sorbed CO_2, factors that are key to determining efficacy of potential sequestration reservoirs. Here we propose to conduct systematic fundamental studies of the fluid–surface interactions; modification of the structure; and the molecular mobility of CO_2 and CH_4 in coals, shales, and sandstones at temperatures and pressures similar to natural underground conditions. ORNL has extensive experience and expertise in applying SANS and quasi-elastic neutron scattering (QENS) techniques to investigate the phase behavior and dynamics of bulk and confined fluids in artificial porous materials as well as in coals at elevated pressure. These capabilities will be extended to the evaluation of adsorption and diffusion of greenhouse gases (CO_2, CH_4, and their mixtures) in other natural porous materials (sandstones and organic-rich shales) of interest for carbon capture applications and enhanced by employing the new state-of-the-art SANS and QENS instrumentation that is available at the the High-Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS).

Mission Relevance

This research is relevant to the Core Research Activities in Geosciences research (Chemical Sciences, Geosciences, and Biosciences Division) and Neutron and X-ray Scattering (Materials Sciences and Engineering Division) within the DOE Office of Basic Energy Sciences. It supports the President's clean coal initiative "to advance technologies that can help meet the nation's growing demand for electricity while simultaneously providing a secure and low-cost energy source and protecting the environment." The practical implications of this work may also be of great value to select projects within the Office of Fossil Energy's carbon sequestration research portfolio. This study will help us understand the reasons for variable CO_2 injectivity at different storage sites observed during the field tests. The ability to predict the effectiveness of CO_2 sequestration is important for economically viable sequestration practice, which may contribute to the reduction of greenhouse emissions and thus improve environmental quality in the United States and elsewhere.

Results and Accomplishments

Two coal samples were obtained from a seam (Tanquary site) into which CO_2 had been injected during a field-scale operation in Illinois as a part of the DOE-sponsored Illinois Basin Partnership. SANS/USANS experiments with these samples saturated with CO_2 and methane over a range of pressures and temperatures were conducted. The results will help us understand field phenomena observed during CO_2 injection. Samples of shales with high organic matter content and relatively low organic matter content but high carbonate content were obtained from the New Albany Shale horizon, a formation of interest for CO_2 sequestration target. SANS/USANS experiments with these samples saturated with CO_2 over a wide range of pressures were completed. The results will help us understand how coals with different lithologies respond to CO_2 exposure. A collection of various coals (20 samples) was obtained from R. Sakurovs. This unique selection has representatives of virtually all common bituminous coals from different countries including Australia, United States, Poland, and New Zeeland. All coals from this collection were extensively characterized by a range of analytical techniques. The ultimate goal is to find a relationship between the coal structure depicted from the SANS/USANS patterns, and their petrochemical composition inferred from the data of analytical analyses. Two coals from this selection, saturated with CO_2 and helium, have been studied using SANS/USANS to verify the influence of porosity and maceral composition on the matrix stability and adsorption capability.

A custom-made automated pressure control system (APCS) was obtained from Porous Materials, Inc. A design of new pressure cells with extended Q-range (Qmax ~ 1 $Å^{-1}$) was developed and a prototype was built in July 2009. After testing of the prototype is complete, a suite of four cells will be built and used simultaneously in a tandem with the APCS. This mode of operation will dramatically increase speed and quality of the data collection using HFIR GP-SANS. In addition, use of new cells will allow for exploring the accessibility of small pores with dimensions below 20 Å to CO_2 and methane molecules. This range of pore sizes was not previously accessible due to limitations of the existing high-pressure cell with Qmax ~ 0.2 $Å^{-1}$.

SANS/USANS experiments were conducted using CO_2 and CD_4 saturated silica xerogels of three different porosities as well as carbon aerogel. The xerogel samples were synthesized in Hokkaido University (courtesy of Dr. H. Mayama). Carbon aerogel samples were obtained from Oscellus, Inc. and shaped into disks and cylinders, suitable for SANS/USANS and QENS experiments, respectively. These porous matrices were chosen as model systems representing major structural features of sandstones and coals. SANS/USANS experiments with two CO_2 saturated aerogels and xerogels have been conducted, the data reduced and analyzed. The analysis of the remaining data is in progress.

SANS/USANS characterization of the structure of four coals, two shales, and one sandstone is complete, the analysis of the remaining data is in progress. The first high-pressure QENS experiment on the BASIS instrument at SNS was conducted in June 2009. The data on diffusion and residence time of CD_4 molecules in carbon aerogel were obtained and analysed. The data analysis will be performed in conjunction with the available SANS data on the methane adsorption in carbon aerogels. A QENS experiment covering an extended range of pressures is scheduled in September 2009.

Publications

Melnichenko, Y. B., and G. D. Wignall. 2009. "Density and volume fraction of supercritical CO_2 in pores of native and oxidized aerogels." *Int. J. Thermophysics* **30,** 1578.

Melnichenko, Y. B., A. P. Radlinski, M. Mastalerz, G. Cheng, and J. Rupp. 2009. "Application of neutron scattering techniques (SANS and USANS) for studying CO_2 sorption in the coal at high pressure conditions." *Int. J. of Coal Geology* **77,** 69–79.

Radliński, A. P., T. L. Busbridge, E. MacA. Gray, T. P. Blach, G. Cheng, Y. B. Melnichenko, D. J. Cookson, M. Mastalerz, and J. Esterle. 2009. "Dynamic micro-mapping of CO_2 sorption in coal." *Langmuir* **25,** 2385–2389.

05246

Neutron Scattering and Osmotic Stress to Study Intrinsically Disordered Proteins

Christopher Stanley, Erica Rowe, Hugh O'Neill, and Valerie Berthelier

Project Description

Proper protein function relies on interactions that create correctly folded and assembled structures while still maintaining the flexibility required for their activity. Intrinsically disordered proteins (IDPs) are a special class that best exemplifies the need for structural flexibility. These proteins possess either an unstructured domain or are fully disordered until recognizing a target molecule, upon which a synergistic effect from folding and binding occurs. Exactly how this mechanism imparts specificity in IDPs is poorly understood and structural characterization remains difficult since they are not amenable to crystallization. We propose using small-angle neutron scattering (SANS) combined with osmotic stress to directly investigate the link between structure and thermodynamics for IDP conformational changes and interactions. The osmotic stress created by an added osmolyte modulates biomolecular transitions and thereby allows the associated hydration and energetics to be probed. The advantage of SANS is that the structure in solution is directly measured. It is expected that this research will provide unique insight into the mechanism of IDP function while simultaneously making advances in the use of neutron scattering for the study of biological systems through the combination with osmotic stress.

Mission Relevance

This research project takes particular advantage of the unique neutron facilities and supporting laboratories at ORNL. We are using the BioSANS instrument at the High-Flux Isotope Reactor (HFIR). For future SANS experiments, we will carry out deuterated protein expression in the Bio-deuteration Facility at the Center for Structural and Molecular Biology (CSMB). Also, we are working with Kunlun Hong in the Center for Nanophase and Materials Science (CNMS) for deuterated polymer synthesis to be used for neutron experiments. We also strive for educational outreach and have an undergraduate research student, Laura Grese, from the University of Tennessee, Knoxville, assisting us on the project. Overall, this research fosters collaborations and should assist in positioning ORNL at the forefront of neutron scattering applications in biological and biomedical research.

For the long-term development of this research project, we have identified a funding opportunity from a National Institutes of Health (NIH) R01/R21 grant.

Results and Accomplishments

The major scientific accomplishments of the research project to date have been (1) the development of our combined SANS and osmotic stress approach for studying protein hydration, conformation, and protein-protein interactions; (2) the preparation of our two IDP fragments of CREB binding protein (CBP) along with full-length CBP; and (3) the performance of SANS measurements on the BioSANS instrument to investigate the structure of CBP fragments.

We performed SANS experiments on hexokinase (HK) to investigate protein hydration by solute molecules, called osmolytes, and the interactions responsible for HK dimer formation. We were awarded three days of beamtime on BioSANS (IPTS-1282) for this study with the experiments conducted in January 2009. HK preferential hydration follows the osmolyte series: triethylene glycol (TEG) < betaine < poly(ethylene glycol) of molecular weight 400 (PEG 400), where steric exclusion is the predominate effect for PEG 400. This part of our research project has been very important and informative since we will apply our combined SANS and osmotic stress approach to study IDP conformational flexibility, transitions, and interactions.

A key step of the project is to produce the full protein CBP as well as two of its IDP fragments in order to acquire structural information via various biophysical techniques including SANS. As of today, the optimal steps for CBP expression and purification have been determined, and initial characterization using light scattering, circular dichroism and fluorescence spectroscopy has been performed. We were awarded three days of beamtime on BioSANS (IPTS-1809) for our first CBP studies conducted in October 2009, and data analysis is under way.

Publications

Stanley, C.B., H. M. O'Neill, E. L. Rowe, and V. M. Berthelier. 2009. "SANS and osmotic stress to investigate protein preferential hydration and association." International Conference on Neutron Scattering, May, Knoxville, Tenn.

Stanley, C.B., H. M. O'Neill, E. L. Rowe, and V. M. Berthelier. 2009. "Protein hydration and association studied by small-angle neutron scattering." Comparative and Experimental Medicine and Public Health Research Symposium, June 15, Knoxville, Tenn. (award for best oral presentation).

05272

A Study of Real-Space Neutron Scattering Methods

J. Lee Robertson

Project Description

We propose a coordinated study of neutron scattering techniques that employs spin-echo encoding of the scattering angle to relax the requirement for tight collimation when accessing extremely small wavevectors Q. One technique in particular, spin-echo resolved grazing incidence scattering (SERGIS), offers a unique capability for studying disordered materials with two-dimensional structures. Our goals are to (1) develop a theoretical framework to analyze the observed correlation functions, which are represented in real space, from selected systems with tunable structural properties in order to explore the full capability of this novel technique; (2) develop a completely new data analysis p for obtaining the pertinent structural parameters from the SERGIS measurements; and (3) establish the foundation for building a fully optimized world-leading neutron scattering instrument. We will apply Monte Carlo and Brownian dynamics simulations not only to achieve a unified basis for interpreting the measurements but also to gauge the integrity of our experimental and theoretical approaches. The unique contribution of this research, we believe, lies in establishing a physics-based capability that combines theory, experiment, and modeling to provide an unbiased data interpretation protocol that is essential for utilizing this novel real-space scattering technique.

Mission Relevance

The focus of this project is placed on understanding the scientific merits of this new real-space neutron scattering technique in structural characterization of soft matter systems via a synergetic approach combining statistical mechanics with Monte Carlo (MC) and molecular dynamics (MD) simulations. The overarching goal of our work is consistent with the mission of the DOE Office of Basic Energy Sciences, which provides world-class scientific user facilities and fosters and supports the discovery, dissemination, and integration of results in the areas of the fundamental research in the natural sciences and engineering.

Results and Accomplishments

The first objective of this project is aimed at establishing a link between the measured spatial correlation functions and the physical quantities of interacting systems. It is well known that a fundamental understanding of phase behavior in colloidal states is a major challenge of contemporary statistical physics. In this context, model colloidal suspensions, such as poly(methyl methacrylate) (PMMA) colloids, have provided experimental realizations of phase manipulation that have been investigated using a variety of techniques such as dynamic light scattering and confocal microscopy. Recently, it has been revealed that the addition of nonadsorbing polymers to sterically stabilized colloidal dispersions induces an additional short-range attraction, due to the entropic effect, to the existing hard spheres' repulsive interaction. Extensive computational studies, kinetic theories such as mode-coupling theory, and light scattering experiments have been carried out to understand the new phase phenomenon generated by this additional feature. However, a general understanding of the circumstances under which additives affect the phase transition is still lacking.

Unlike the traditional elastic neutron scattering technique, the new scattering method measures the Fourier transform of the scattering cross section and results in spatial information that is presented in real space as the spatial correlation function. During the last year, we have developed systematic data analysis protocols via the integral equation and computational approaches, respectively, to interpret the scattering data that will be provided by spin echo small-angle neutron scattering (SESANS). Our findings clearly manifest the uniqueness of SESANS to study the structure and interaction mechanism of materials. An extension of our theoretical analysis is expected to render a precious opportunity to unveil the interplay between molecular interactions and the phase behavior of materials, which governs the future development of materials science and industrial applications.

To analyze the liquid or solution systems in this project, we are developing an appropriate simulation algorithm to compute the isotropic pair distribution function, which is needed for more complex problems in our future SERGIS measurements. This algorithm is new, and its accuracy was first tested with one-component hard sphere liquids of diameter $\sigma (= 2R)$. It is also being extended to study liquids of nonspherical objects, mixtures, two-dimensional fluids, and a united-atom model for polymeric materials with monomer units being coarse-grained into spheres.

Program Development Accomplishments

Our current work allows us to lay the solid physics ground and develop the required analysis tools for future SESANS and SERGIS measurements. These preliminary studies are suitable for the submission of DOE and National Science Foundation proposals to advance the current search to the next level. The progress of this project will certainly greatly facilitate the design and construction of novel real-space neutron scattering spectrometers at the Spallation Neutron Source and the High-Flux Isotope Reactor.

Publication

Shew, Chwen-Yang, and Wei-Ren Chen. 2010. "A Monte Carlo algorithm for computing SESANS correlation functions in real space: Hard sphere liquids." *Journal of Chemical Physics* **132,** 044906.

05306

Structure and Structure Evolution in Amorphous Materials—Fundamental Understanding of Materials Behaviors Far from Equilibrium

X.-L. Wang, A. D. Stoica, K. Littrell, and J. R. Morris

Project Description

The structure-property relationship is the cornerstone of materials science and engineering. Understanding a material's structure and how it changes at different length scales is of paramount importance in materials design. Under extreme environments, materials are often thrown into a nonequilibrium state, whose behaviors cannot be understood with a simple extension of existing theories. Indeed, materials behavior far from equilibrium is one of the five scientific grand challenges identified by DOE. This project is intended to demonstrate ORNL's ability to address fundamental questions in materials far from equilibrium using ORNL state-of-the-art characterization tools and computing facilities. The material of choice is metallic glass. Neutron scattering will be used as a primary tool to gain fundamental understanding of the structure of metallic glasses at multi-length scales and, more importantly, how the structure features at different length scales evolve during phase transformation and mechanical deformation. The ability to conduct simultaneous measurements of diffraction and small-angle scattering in a complex sample environment represents a significant experimental challenge. Successful completion of this project will showcase the new instruments and scientific opportunities at the Spallation Neutron Source (SNS) and the High-Flux Isotope Reactor (HFIR) and strengthen ORNL's position in future funding calls.

Mission Relevance

Materials behavior far from equilibrium has been identified by the DOE Office of Basic Energy Sciences (DOE BES) as one of the five grand challenges that must be tackled "to address the DOE missions in energy efficiency, renewable energy resources, improved use of fissile fuels, safe and public acceptable nuclear energy, future energy sources, and reduced environmental impacts of energy production and use." Unlike what happens under small perturbations, far-from-equilibrium behavior is not a simple extension of equilibrium state. Instead, it corresponds to qualitatively different types of behavior and response; in some cases, the materials have quite distinct properties (desirable or not) from their equilibrium behavior. To date, the microscopic origin of far-from-equilibrium behavior still remains a largely unchartered territory. In particular, experimental studies of far-from-equilibrium behavior have been plagued by the lack of research tools for *in situ* investigation of the dynamical process that characterizes the nonequilibrium transient behaviors. The advances in characterization tools such as the SNS are expected to break the *in situ* characterization barrier. In particular, by combining time-dependent diffraction and small-angle scattering, it will be possible to examine structural evolution simultaneously at different length scales, providing key information on the interaction of these scales. This project is designed to showcase how instruments at the SNS can help advance our understanding of materials behavior far from equilibrium and hence contribute to the design and development of new materials for energy applications.

Results and Accomplishments

We worked on two model systems including Zr- and Ca-based metallic glasses to study their mechanical deformation and nanoscale crystallization behaviors. We have carried out *in situ* small-angle neutron scattering (SANS) experiments at HFIR and simultaneous diffraction and small-angle X-ray scattering (SAXS) experiments at the European Synchrotron Radiation Facility (ESRF), for a series of samples under tension and compression and/or also at elevated temperatures. Both SANS and SAXS data for

Ca-glasses indicated significant changes upon annealing, and visible interference peaks. Detailed analyses of these *in situ* experimental data, coupled with advances in simulations, will yield significant insights into deformation and crystallization behaviors in metallic glasses. In addition, a new analysis method has been developed to separate the diffraction patterns of a crystalline phase from the glass matrix in case of partial crystallization. Further, we examined the short-range order or cluster structure in Zr-Cu glasses, which provided experimental evidence of a close correlation between the coordination number of unlike bonds and the liquid stability. Theoretically, the initial emphasis has been on implementing molecular simulations that may be compared with experiments. This work will soon be extended to examine the dynamic structure factor. Thermodynamic behavior has been observed through cooling simulations from high temperatures, for three Zr-Cu glasses. Simulations showed three regimes: the conventional "high temperature" liquid behavior, the low temperature "frozen-in" glass behavior, and a large transition regime.

Publications

Ma, D., et al. 2009. "Efficient local atomic packing in metallic glasses and its correlation with glass-forming ability." *Phys. Rev. B* **80,** 014202.

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05567

Protein Dynamics: Neutron Scattering Methodological Development

Jeremy C. Smith

Project Description

Motions in proteins play a key role in their function. The research here will provide a framework for understanding correlated dynamics in proteins by integrating computer simulation with experiments on the next-generation Spallation Neutron Source (SNS) at ORNL. Computational methods will be developed for obtaining simplified descriptions of protein dynamics from computer simulation that are suitable for direct interpretation of dynamic neutron scattering experiments with special reference to the investigation of the dynamics of correlated inter- and intramolecular motions in protein crystals and the pressure dependence of protein dynamics.

Mission Relevance

Recent DOE press releases, reports, R&D, and budget priorities indicate that this project is well-aligned with DOE's neutron scattering research focus for the next five years. The present project will begin to address the roadblocks in improvement of our understanding of the use of computer simulation in the analysis of neutron scattering with computer simulation.

Results and Accomplishments

In the first year significant progress has been made in understanding the origin of the temperature dependence of elastic incoherent neutron scattering from globular proteins. The subdiffusive behavior of atoms in proteins, as detected by the elastic incoherent structure factor, was characterized theoretically. Trap models, involving a random walk with a distribution of waiting times, cannot account for the subdiffusion, which was found rather to arise from the fractal-like structure of the accessible configuration space. The role of methyl groups in the onset of low-temperature anharmonic dynamics as

detected by elastic incoherent neutron scattering in a crystalline protein at low temperature was investigated using atomistic molecular dynamics simulation. The incoherent scattering glass transition in proteins was further investigated using the instantaneous normal mode method. Those characteristics of the negative modes were determined that correlate with the dynamical (or glass) transition behavior of the protein, as manifested as an increase in the gradient with *T* of the average atomic mean-square displacement derived from neutron scattering at ~220 K. Examination of the form of negative instantaneous normal modes was shown to furnish a physical picture of local diffusive dynamics accompanying the protein glass transition.

Publications

Krishnan, M., V. Kurkal-Siebert, and J. C. Smith. 2008. "Methyl group dynamics and the onset of anharmonicity in myoglobin." *Journal of Physical Chemistry B* **112**(17), 5522–33.

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Neusius, T., I. M. Sokolov, and J. C. Smith. In press. "Subdiffusion in time-averaged, confined random walks." *Physical Review E.*

Schulz, R., M. Krishnan, I. Daidone, and J. C. Smith. 2009. "Instantaneous normal modes and the protein glass transition." *Biophysical Journal* **96**(2), 476–84.

ULTRASCALE COMPUTING

00014

An Evolutionary Framework for Porting Applications to Petascale Platforms

Kalyan S. Perumalla, Vladimir Protopopescu, Sudip Seal, Jeffrey Vetter, and Srikanth Yoginath

Project Description

This project investigates a fundamentally new approach to petascale computing that addresses the severe synchronization overheads inherently associated with large numbers of processors. Inherent tight coupling among processors is relaxed by incrementally and semitransparently enabling speculative computing using novel synchronization mechanisms such as reverse computation. The envisioned framework attempts to move beyond traditional checkpointing-based approaches to newer directions in reversible computing, thereby freeing applications from tight global coupling. This framework enables easy porting of existing message passing model (MPI)-based applications and moving them in a backward-compatible, evolutionary fashion to petascale computing platforms, without having to restructure existing codes. The overall effort offers significant benefits along multiple directions, including new scientific techniques such as reverse computation–based relaxed parallel execution, new petascale extensions to existing message passing standards, and least-effort paradigms to porting existing applications for potentially significant productivity and efficiency improvements.

Mission Relevance

The project will benefit supercomputing applications, such as large-scale scientific computing/simulations that are critical to DOE and other agencies. It is intended to improve the utilization of high-performance computing platforms and also facilitate gains in productivity by reducing model redevelopment and/or porting efforts for execution on larger numbers of processors. In addition to DOE, the technology developed as part of this project could potentially be applied to scalable scientific computing efforts in other agencies, such as the Defense Advanced Research Projects Agency's High Productivity Computing Systems (HPCS) program.

Results and Accomplishments

We have accomplished the most significant goal of the project, namely that of clearly demonstrating that our new asynchronous speculative execution technology can deliver dramatically better parallel performance in stark contrast to the inefficiencies of time-stepped scientific codes when executed on very large number of processors. Specifically, in simulation benchmarks (radio wave propagation and synthetic benchmarks) time-stepped execution on 10,000 or more processors, asynchronous execution was convincingly shown to relieve the severe synchronization overheads incurred by traditional barrier-based approaches. In fact, while the traditional execution begins to exhibit slowdowns around 8192 processors, our asynchronous execution continues to scale well beyond 16,384 processors. In

addition to demonstrating the performance potential in the new execution methodology, we have also examined issues in applying it to complex codes. We have developed the design for a backward compatible framework with a subset of the MPI interface extended to support asynchronous, speculative execution. We have also demonstrated the significance of performance gains of reverse computation vs. checkpointing in reversing basic linear algebra services (BLAS), especially due to caching effects. We have also studied the fundamental aspects of reversibility in various scientific simulations, including molecular dynamics and electromagnetism. We have uncovered new fundamental modeling aspects that underlie reversibility of models.

Interesting relationships have been obtained between the trace size of simulation and entropy of the simulated phenomenon. These findings have strong bearing on the use of asynchronous speculative execution methods for porting applications to petascale platforms.

Publications

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Seal, S. K., and K. S. Perumalla. 2009. "Scalable parallel execution of an event-based radio signal propagation model for cluttered 3D terrains." *Proceedings of International Conference on Parallel Processing.*

Yoginath, S. B., and K. S. Perumalla. 2008. "Parallel vehicular traffic simulation using reverse computation-based optimistic execution." *Proceedings of the International Workshop on Principles of Advanced and Distributed Simulation.*

Yoginath, S. B., and K. S. Perumalla. 2009. "Reversible discrete event formulation and optimistic execution of vehicular traffic models." *International Journal of Simulation and Process Modeling.*

00016

Development of a Global Advanced Nuclear Fuel Rod Model

Srdjan Simunovic, Larry J. Ott, Phani K. Nukala, Kevin T. Clarno, Charles F. Weber, Theodore M. Besmann, and Sarma B. Gorti

Project Description

Advanced nuclear fuel is the primary technology required for the realization of new nuclear reactor technologies, including transmutation fuel designed to consume spent fuel and nuclear weapons material. Central to the development of advanced nuclear fuels with enhanced reliability and accident performance, extended burnup, ease of fabrication, capability to contain significant fractions of minor actinides, and reprocessing is the need to develop a fundamental understanding of the materials involved. The objective of the research is to develop the computational framework needed for fine-scale simulation of nuclear fuel, thereby incorporating the relevant multi-physics and chemistry occurring within a fuel pellet/rod during operational conditions. Such a computational framework is capable of simulating a large-scale, fully three-dimensional model of nuclear fuel elements to the desired resolution dictated by underlying fuel physics/chemistry. The developed model provides interfaces and mechanisms for coupling reactor fluid thermodynamics, thermo-mechanics, neutronics, fuel chemistry, chemical species transport, and more detailed multiscale physics models. Due to the physical complexity of the problem and the need for high spatial and temporal resolution of the model, scalable computing algorithms that target relevant phenomena at appropriate scales are necessary. The nuclear fuel modeling computational framework is implemented on the ORNL leadership computing systems.

Mission Relevance

Comprehensive, fully three-dimensional computer models of a nuclear fuel rod do not exist. Current "legacy" fuel performance tools are entirely empirical; hence they are not predictive for processes outside existing design space and databases. Execution of this program was therefore a groundbreaking work in the area of fuel performance modeling. This work is directly relevant to the DOE Nuclear Energy Program, specifically for the development and modeling of advanced reactor fuel systems. The development strategy was to build on ORNL's existing capabilities in fuel performance modeling and to leverage advanced computing tools developed under the DOE projects Scientific Discovery Through Advanced Computing, and Advanced Simulation and Computing. The detailed multi-scale model of the nuclear fuel rod provides the framework for incorporating atomistic and electronic fuel models funded by the DOE Office of Basic Energy Sciences.

Results and Accomplishments

The prototype integral fuel performance code was built by combining components from existing nuclear fuel modeling codes, new fuel chemistry models, and Finite Element Method (FEM) based solvers with proven parallel computational performance. The project was started during the second half of FY 2007, so that the research and development plan was adjusted from its original two fiscal year schedule, to the two year duration across three fiscal years, 2007–2009. During the FY 2007, we developed a nuclear fuel model that combined neutronics, thermal, and mechanical solvers. Neutronics solver was implemented as an internal heat source for the thermal solver and the effect of fluid flow was modeled as a convection boundary condition. All the material properties and heat sources were assumed constant. During FY 2008 we have developed separate computational modules for neutronics, isotope composition, chemistry and material properties that allow for modeling of nonlinear variation of properties based on temperature, material composition, power generation history, etc. During FY 2009 we have implemented material models for porous plasticity, material swelling, and nonlinear thermal and mechanics modules for transient and nonlinear simulations. The transport simulations were not considered due to the lack of

information about the physical transport parameters for fission products in the fuel. Development of a new chemistry module has been initiated in collaboration with the Royal Military College in Canada. The new chemistry module employs advanced algorithms for acceleration of thermo-chemical equilibrium calculations and will eventually replace the current, commercially based chemistry solver.

Publications

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05038

Preparing for New Programming Languages for Ultrascale Applications

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Project Description

The languages developed under the High-Productivity Computing Systems (HPCS) program (Chapel, Fortress, and X10) offer a significant number of new features aimed at improving the productivity of scientific application developers and users. Traditional programming approaches (sequential language + message passing library + thread library) will face increasing challenges to scale to petaflop and exaflop performance levels, as well as scaling of the codes themselves. The HPCS languages currently offer the best path to provide computational scientists with qualitatively new tools which have the potential to scale to meet the challenges of the coming decade. However, these languages are significantly different from the traditional approach to parallel programming and developers will require help and guidance to rapidly and effectively adapt their applications to fully realize the capabilities of coming systems. The objective of this project is to develop local expertise in these new languages in the context of applications of strategic interest to ORNL and DOE and to interact with the language developers to ensure the best possible support for these applications. This work will give ORNL applications and facilities a strong strategic advantage in bringing these new programming environments into production when they reach the appropriate level of maturity.

Mission Relevance

This work is focused on developing expertise and experience with next-generation parallel programming environments for coming petaflop and exaflop computer systems. These environments are central to computational science and other simulation applications of interest to the DOE, the Defense Advanced Research Projects Agency, and other Department of Defense agencies. The target applications are directly related to key DOE mission areas: computational chemistry and materials, fusion modeling, climate modeling, and nuclear energy. There are direct ties to planned DOE programs such as the Fusion

Simulation Project; the Nuclear Energy Advanced Modeling and Simulation program; and Simulation and Modeling at the Exascale for Energy, Ecological Sustainability, and Global Security.

Results and Accomplishments

During FY 2009, we continued to interact with the vendor language development teams on both the features and expressiveness of the languages. We continued to use the MADNESS Tree Walking application as a primary motivator for our work, delving deeper into the issues associated with efficient runtime implementations capable of supporting similar applications with irregular parallelism requiring dynamic load balancing. During the course of the year, an opportunity emerged for a spin-off activity involving the introduction of asynchronous method invocation into the Unified Parallel C (UPC) programming language. UPC is part of the Partitioned Global Address Space (PGAS) family of languages considered by many to be transitional between sequential languages (C, Fortran, etc.) and the more sophisticated HPCS languages (Chapel, Fortress, X10). Asynchronous remote methods are one of the fundamental features that the HPCS languages have included from the start, while the PGAS languages do not provide such concepts. We consider asynchronous methods to be one of the programming concepts that make the HPCS language both more effective in expressing extreme scales of parallelism, and one of the key challenges to bringing new users into this next generation programming paradigm. The introduction of asynchronous remote methods into the PGAS languages may provide an effective bridge to help educate developers in this new approach. Additional work was focused on the language interoperability question, driven by the AORSA (fusion) application and its effective use of established numerical libraries to obtain high levels of scalability.

Publication

Shet, Aniruddha G., V. Tipparaju, and Robert J. Harrison. 2009. "Asynchronous programming in UPC: A case study and potential for improvement." In *1st Workshop on Asynchrony in the PGAS Programming Model (APGAS),* collocated with the 23rd International Conference on Supercomputing (ICS) 2009, June 8, Yorktown Heights, N.Y.

05040

A Petascale Parallel Programming Environment for Scientific Software

Edoardo Aprà, Robert J. Harrison, William A. Shelton, and Vinod Tipparaju

Project Description

Next-generation computers composed of 100,000+ processors, multiple cores-per-node, and complex memory hierarchies (e.g., the CRAY petaflop computer installed at ORNL in 2008) present formidable challenges to the development of highly scalable scientific software. These challenges, pervasive in all computational scientific disciplines (energy, climate, etc.), require the development of novel software tools capable of exploiting the aggregate hardware resources of petascale computers. Our solution to these problems is a latency-tolerant, multi-paradigm environment that insulates the developer of scientific codes from the intricacies of hybrid software (i.e., that effectively treat multithreads and distributed network resources). This represents a significant advance over the current state of the art, which mostly uses message passage interface (MPI) constructs. We aim to reach maximum computational efficiency by developing a parallel execution environment based on the Global Arrays toolkits and built directly on top of the fastest communication protocol available. Other significant outcomes will be the development of in-house expertise in the low-level capabilities of the petascale hardware, and a much reduced and fully

understood software stack. We will work with Cray and ORNL's Center for Computational Sciences staff to integrate this software and its requirements into the Cray development and deployment test suites in order to ensure productive use as soon as the hardware becomes available. These tools will be tested by applying them to the NWChem and MADNESS.

Mission Relevance

Our project will have a significant impact on the larger software effort that aims to provide computationally efficient software tools for petascale infrastructure (DOE, National Science Foundation, and Defense Advanced Research Projects Agency all have activities in this direction). While the roadmaps of several current DOE energy-related initiatives (e.g., Global Nuclear Energy Partnership, solar energy) contain a significant simulation component, none of the major DOE Office of Science chemistry and material science simulation codes can yet run reliably and efficiently on the Cray XT4. This is despite significant effort being made by various groups to address software and system issues. We have identified the major causes of this problem as being an overly complex and poorly understood software and lack of in-house control over the critical software components. Our proposed activities address these issues by developing a smaller software stack that is fully controlled and understood, and by working to eliminate problems very early in the product life cycle.

Results and Accomplishments

A major second-year achievement was the demonstration of the parallel efficiency of NWChem at very large scale (more than 100,000 processors) on the Cray XT5. This was achieved both by modifying and tuning the parallelization approach in NWChem and by using a new implementation of the ARMCI library. Coupled Cluster was the theoretical method implemented in NWChem that has shown this large-scale performance.

Recently hired Vinod Tipparaju accomplished the task of delivering a new implementation of ARMCI for the Cray XT platform; this has allowed us to overcome both performance and stability issues. Thanks to these advances, NWChem can now perform near the peak performances expected on Cray XT computers. As a result of this work, we submitted a paper, titled "Liquid Water: Obtaining the Right Answer for the Right Reasons," that has been selected as 2009 Gordon Bell award finalist after having reached the outstanding floating-point performance of 1.09 petaFlops using 186,000 Cray XT5 processors.

Vinod Tipparaju has been involved in the Remote Memory Access (RMA) working group of the MPI-3 Forum (and he has attended quite a few of the 2008/2009 MPI3 Forum meetings). His work has resulted in drafting a new proposal, "MPI-3 RMA: A flexible, high-performance RMA interface for MPI-3."

Edoardo Aprà reported some of the LDRD accomplishments in an invited presentation, titled "Computational Chemistry at the Petascale: Are We There Yet?," at the SciDAC 2009 Conference in San Diego on June 3-6, 2009.

Publications

Aprà, E., R. J. Harrison, W. A. de Jong, A. P. Rendell, V. Tipparaju, and S. S. Xantheas, 2009. "Liquid water: Obtaining the right answer for the right reasons." *SC '09: Proceedings of the 2009 ACM/IEEE Conference on Supercomputing*, Portland, Oreg.

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05043

Global Climate Feedbacks and the Development of Biofuel Climate Scenarios

John B. Drake

Project Description

The attraction of developing renewable energy sources is that biomass production removes as much CO_2 from the atmosphere as the biorefinery and subsequent fuel use emits. The carbon neutral aspect, though attractive, must be considered carefully in the context of land-use change and possible effects on climate and the environment. This project will test the hypothesis that significant feedbacks between the land use of bioenergy crop production, the hydrological cycle, the ocean thermohaline circulation, and climate exist and are a key element of climate change in the next century. We will test this hypothesis by developing a biofuels scenario and simulating the climate under this ORNL-defined biofuels scenario. Our methodology uses the Community Climate System Model (CCMS) to simulate an ORNL-defined biofuels scenario and to elucidate and quantify new feedbacks in the climate system. The novelty of our method will be in the use of a very high resolution land model in conjunction with the coupled climate system model. This is required for two reasons. First, to capture the land use changes that may be predicted as a result of increased biofuel production and consequent destruction of ecosystems, and second, to represent the multiscale heterogeneous forcing of the climate system by hydrological, biogeochemical, and energy fluxes from the land. Development of the ability to define and evaluate our own scenarios in this important area of climate science will position ORNL as the leading DOE laboratory in climate science and central to plans for climate modeling initiatives.

Mission Relevance

The growing importance of climate change in the DOE research portfolio should lead to new opportunities for climate simulations that target energy supply and carbon mitigation scenarios. The Climate Change Research Division of the DOE Office of Biological and Environment Research (DOE BER) program has as part of its mission to determine the safe levels of atmospheric CO_2 and to improve climate models by making them more comprehensive and reliable. The activities of this project are relevant to these DOE missions in several ways: (1) by implementing a highly resolved land model into a coupled climate system simulation; (2) by developing datasets, methodologies, and conceptual framework to define the land use change associated with increased biomass production; (3) by discovering climate feedbacks associated with biofuel energy strategies; and (4) by assessing the level of impact that biofuels could have on the global carbon budget and temperature and precipitation patterns of future climates.

Results and Accomplishments

The first year milestones have been met with a definition of a climate change scenario. This ORNL scenario for bioenergy branches from the SRES A1FI scenario, and we have analyzed the climate simulation results of the base case recently run on the Leadership Computing Facility of the National Center for Computational Sciences. The biofuels extension of this fossil energy dominated scenario assumes that cropland is allocated first to meet population demands for food and, as a result, the biofuels are grown in the left over and marginal land. This scenario has been vetted with several groups including a team from Brazil.

The maps of crop allocation and bioenergy land usage based on clustering algorithms have been mapped to a 4 km land-use grid. We are finalizing these maps that form the basis of the boundary condition data set that will be used to force the climate model. A few additional variables that indicate length of growing

season and more information about the physical climate variables have been added to the clustering in order to gain more realistic coverage of agricultural crops. The clustering technique is being used for these plant functional types as well as biofuel crops under changing climatic conditions.

A revision of the A1FI population scenario has also been suggested and calculated. The standard scenario shows too rapid a decrease in population after 2050, given national and international projections. The model configuration with high-resolution land components never quite materialized. We finished the river directions at 1km. The land use change masks for different crops were computed in the GIS environment, but have not yet been transferred to the gridded maps for CCSM inputs. There was not a good reason to do this until the crop plant functional types were in place and this has only recently been done in the Community Land Model. Still we do not have reliable physiological parameters for switch grass. The effort in this regard has been shifted under the new proposal (see below) to work with George Hurt at University of Maryland who is responsible for doing the crop–PFT harmonization for the AR5 scenarios of the Intergovernmental Panel on Climate Change. We learned enough to understand the enormity of the task and to engage expertise external to the lab.

Program Development Accomplishments

Follow on funding has been secured fro the DOE OBER in the form of a project call "Integrated Earth System Modeling." This project is in collaboration with Dr. Jae Edmonds (Pacific Northwest National Laboratory) who uses integrated assessment techniques to define climate change scenarios, something lacking in our project. John Drake has transferred principal investigator responsibilities for the new project to Peter Thornton. Collaborators in the USDA Forest Service are also now extending the techniques developed here to address trees and forest ecosystems under future climate change. Funding for this project has also been arranged between Forrest Hoffman and Bill Hargrove.

Conclusions

The research plan is now focusing on 4 km instead of 1 km horizontal land use resolution. This will match complementary work with downscaling climate model results that we are doing jointly with the Civil and Environmental Engineering Department at the University of Tennessee and that has been submitted as a JDRD project in collaboration with another ORNL LDRD project on decadal climate prediction. The comparison of river hydrographs and hydrology from the two approaches will be a value added with little or no revision to this project's research plan.

05046

Overcoming the Barrier to Ultrascale Climate Simulation

R. K. Archibald, J. B. Drake, K. J. Evans, D. B. Kothe, J. B. White III, and P. H. Worley

Project Description

Climate simulation will not grow to the ultrascale without new algorithms to overcome the scalability barriers blocking existing implementations. Until recently, climate simulations concentrated on the question of whether the climate is changing. The emphasis is now shifting to impact assessments, mitigation and adaptation strategies, and regional details. Such studies will require significant increases in spatial resolution and model complexity while maintaining adequate throughput. The barrier to progress is the resulting decrease in time step without increasing single-process performance. In an attempt to overcome this time barrier, we will implement and test fully implicit, parallel-in-time, and multi-resolution methods. We will use standard tests defined for numerical climate simulations and benchmark

solutions to the shallow-water equations on a sphere. We will then be poised to incorporate the best algorithms in full climate models, thus lifting climate simulation to the ultrascale, and clearing the way for new predictive skill in climate simulation.

Mission Relevance

This project could revolutionize the scalability of climate simulation, enabling breakthrough scientific progress within the DOE Office of Biological and Environmental Research, Climate Change Prediction Program (CCPP). Because CCPP funds modeling efforts jointly with the National Science Foundation, that agency's climate science stands to gain from this project as well. The various modeling efforts among U.S. agencies regularly share ideas and implementations, so improved algorithms would be of equal interest to the modeling programs within the National Aeronautics and Space Administration and the National Oceanic and Atmospheric Administration. The methods we propose to develop hold great promise for climate simulation, but they are also applicable to other areas within the DOE Office of Science, particularly those that target the ultrascale computing, such as the Advanced Scientific Computing Research program. The applied mathematics program of the DOE Mathematical, Information, and Computational Sciences Division is similarly a natural beneficiary of the numerical algorithms to be developed by this project.

Results and Accomplishments

In the second year of this project we accomplished the following. We extended our analysis of our fully implicit implementation of the global shallow-water equations using the High Order Method Modeling Environment with the Trilinos solver framework. We compared existing fully explicit leapfrog and semi-implicit methods with our fully implicit time integration. We demonstrated implicit time steps 30 to 60 times larger than the gravity-wave stability limit and 6 to 20 times larger than the advective-scale stability limit without loss of accuracy. We completed a separate implementation of the shallow-water equations on the cubed sphere using multi-wavelet discontinuous Galerkin with exact-linear-part (ELP) time integration, and we compared it to discontinuous Galerkin with total-variation-diminishing Runge-Kutta time integration. ELP allowed a sixty-fold increase in time step for the linear standard test case and a ten-fold increase in time step for nonlinear test cases. In our analysis of the "parareal" parallel-in-time method, we experimentally confirmed the theoretical result that the method is unstable for advection-dominated problems, like the shallow-water equations. We were able to implement a high-order (6th) single-step explicit method for the linear test case, along with a locally implicit second-order single-step method for the nonlinear test case. These implementations use finite differences for the spatial derivatives, with added stability coming from minimizing the norm of the mass and differential operators given extra points in the stencil. The method allows time steps near the theoretical stability limit, and steps may be combined to reduce parallel-communication calls.

Publications

Archibald, R.K., K. J. Evans, J. B. Drake, and J. B. White III. 2009. "Time acceleration methods for advection on the cubed sphere." *Proceedings of the 9th International Conference onComputational Science,* 253–262.

Archibald, R. K., K. J. Evans, J. B. Drake, and J. B. White III. Accepted. "Multiwavelet discontinuous Galerkin accelerated EPL method for the shallow water equations on the cubed sphere." *Monthly Weather Review.*

Evans, K. J., D. W. Rouson, A. G. Salinger, M. A. Taylor, W. Weijer, and J. B. White III. 2009. "A scalable and adaptable solution framework within components of the Community Climate System Model." *Proceedings of the 9th International Conference on Computational Science,* 332–341.

Evans, K. J., M. A. Taylor, and J. B. Drake. In press. "Accuracy analysis of a spectral-element atmospheric model using a fully implicit solution framework." *Monthly Weather Review.*

05047

Cost and Effectiveness of Fault Tolerance in Quantum Computing

Ryan Bennink, Jim Kohl, Doug Lepro, and Dude Neergaard

Project Description

Quantum computing (QC) is a future technology that has the potential to radically alter the computing landscape by making feasible certain kinds of important, but currently intractable, computations. The true potential of QC will depend critically on the effectiveness and cost (hardware and operational burden) of methods to overcome the ubiquitous imperfections in real devices and environments. Such methods call for a large amount of physical redundancy, making QC far too large to be simulated using known methods. We are developing a groundbreaking simulator of quantum computers that have a large fault-tolerant redundancy. This simulator will lead to pioneering studies that go beyond existing studies of error codes and generic estimates of critical error thresholds in several ways: (1) by predicting the start-to-finish performance of "killer app" quantum algorithms in realistic settings, (2) by determining trade-offs between cost and performance, and (3) by identifying performance barriers and possible solutions. The knowledge to be gained from such numerical studies is essential for the development of robust quantum algorithms and architectures.

Mission Relevance

QC has been identified as a national research priority and a strategic priority for ORNL. It is of great interest to military and intelligence communities around the world because of its potential to render current encryption technologies insecure and to solve certain intractable computational problems. U.S. agencies including DARPA, IARPA, ARO, NRO, DTO, and NSA currently fund research on quantum computing. The development of better QC simulation methods and tools at ORNL generally strengthens ORNL's position as a leader in high-performance computing and helps establish ORNL as a "go-to" player in QC research and development. Already, this project has led to ORNL becoming one of three national laboratories chosen to participate in a new IARPA program in QC, bringing ~$640K/year to ORNL for an anticipated 5 years.

Results and Accomplishments

The second year of this project had three major thrusts: (1) development of a prototype simulator in Matlab; (2) conversion of the prototype to efficient C++ code; and (3) explicit codification of Shor's quantum factoring algorithm as a case study for simulation. The first two thrusts built upon the major accomplishment of the first year, namely, the development of a multi-faceted algorithm for substantially reducing the memory and computational steps needed to simulate a fault-tolerant quantum computer on a conventional (non-quantum) computer.

A prototype simulator using the custom algorithm was developed and verified. The prototype was written in object-oriented Matlab, and consists of a core simulation engine plus support classes implementing quantum bits, quantum bit operations, quantum error correction protocols, and quantum registers with multiple layers of error coding. While the prototype demonstrates the cost-saving benefits of the algorithm (for instance, the ability to track the state of 63 physical quantum bits, containing 10^{19} possible states), the slowness of Matlab's object system makes the prototype too slow for simulating QCs of interesting sizes.

The original C and XML framework was evolved into a fast object-based C++ framework based on the Matlab prototype simulator. Besides the development of classes for the quantum elements listed above, a sophisticated `ComplexArray` class was developed to efficiently store and manipulate the sparse, large-

dimensional tensor data describing the state of a quantum computer. Features of this class include the ability to perform complicated tensor products, dimension swapping, and permutations.

Finally, a C++ program that outputs Shor's algorithm on n bits ($n \leq 254$) as an explicit quantum circuit was produced. While high-level descriptions of Shor's algorithm are common, explicit circuits are not. The circuit generator we developed includes recent algorithmic improvements from the literature and provides test cases for studying the viability of useful quantum computations in the presence of error.

Publication

Neergaard, M., J. Kohl, D. Lepro, and R. Bennink. 2008. "Simulating fault-tolerant quantum computers." Quantum Computing and Algorithms Program Review, August, Atlanta.

05095

A Knowledge Discovery Framework for America's Transportation System

Budhendra Bhaduri, Cheng Liu, James Nutaro, Oscar Franzese, Xiaohui Cui, Amy Wolfe, and Stanton Hadley

Project Description

America's ground transportation system has helped ensure economic prosperity and high quality of life through efficient movement of people and freight. It is also one of the primary forces behind the two major global crises of today's world—namely, energy scarcity and climate change. To reduce U.S. oil dependence, environmental impacts, and congestion, a number of alternative energy supply, distribution, and end-use transportation systems, technologies, and policies are being explored. However, it is still unclear when and in what precise combination these sources and technologies will emerge as successful and sustainable solutions. Ideally, future plausible development and implementation strategies for alternative energy resources and technologies will secure and support a societal system in which energy, environment, and mobility interests are simultaneously optimized. Given the intertwined nature of such a system across wide geographic scales, assessing the effectiveness of possible planning strategies and discovering their unanticipated consequences require data collection, modeling, and simulation at the finest data, process, and societal response levels *coupled* with the system's behavior over large spatial and temporal scales. The primary goal of the project is to design, develop, and test a simulation-based knowledge discovery framework that enables scenario-based analysis leading to identification and visualization of the consequences of alternative energy usage scenarios.

Mission Relevance

There is increasing realization that a transition from the current petroleum-dependant society in the United States to one driven by alternative energy sources is the desirable solution for a sustainable future. Historically due to the availability of space and cheap petroleum, energy has not been a primary consideration in land transportation planning, which is a dominant source of energy consumption and hence dependency. Previous research have investigated, from purely analytical techniques to simulations capturing micro-behavior, questions and scenarios regarding the relationships among energy, emissions, air quality, and transportation. Primary limitations of past attempts have been availability of high resolution input data, useful "energy and behavior focused" models, validation data, and adequate computational capability. Progress has largely been limited by computational challenges (accommodating the required high resolution along spatial, temporal and behavioral dimensions). This research will

directly address the laboratory's mission areas of energy and computing. ORNL, with nationally recognized experience and expertise in geospatial data sciences, high performance discrete event simulations, transportation planning, and energy technology development, is critically positioned to develop this capability. Moreover, such a capability will position ORNL as the leader in developing next-generation high performance computing driven simulations to address the critical needs of not only the Departments of Transportation Energy, but other federal agencies with a need to design, test, evaluate, and implement future policies.

Results and Accomplishments

Using Knox County, Tennessee, as a test area, a scenario of new energy technology was described with the market adoption of Plug-in Hybrid Vehicles (PHEV). We developed a modeling approach based on an individual consumer choice model that includes various socioeconomic variables defining sets of static and dynamic input to the model. Particular consideration was given to national data availability and scalability. This modeling and simulation capability allows national simulation of technology penetrations and their impact on climate (CO_2 emission) and electric energy infrastructures. In this spatially explicit model, we developed a novel concept of simulating social diffusion of technology adoption using spatial proximity as one of the driving functions. A simple assumption was made that increasing exposure and awareness of new technology (alternative cars) with and without communication with spatial neighbors (for residents) and colleagues (at work) may provide a positive and a negative impact on potential adaptors. Thus the simulation includes a flexible way to stipulate a distance threshold which increases or decreases the likelihood of an individual adoption choice. The geographic scalability essentially describes the spatial extent of a particular phenomenon, in this case, the activities of a county's population, which in turn defines the volume and complexity of the data included in the simulation. For addressing issues related to daily personal surface transportation (excluding freight) and energy demand and usage, and related emissions, an reasonable argument can be made that routine activities of a county's population is primarily restricted to that county and its surrounding counties. Such activities include commute to work, schools, and other trips for services and recreational needs. The national (tract-to-tract) worker commute data was analyzed to create a database that describes the percentage of worker population of any county whose commute footprint is restricted within that county and the surrounding counties. In the context of scalable simulation, estimating the number of entities (such as worker population) needed to be simulated and the spatial extent for which detailed infrastructure data (roads, points of origin, and destination) needed to be acquired for the simulation provides a very valuable capability. Results from the simulation of Knox County, based on a 10% increase in first year PHEV adoption, shows that targeted adoption for families with annual income of $60K and higher could impact 30% more vehicle miles traveled.

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05109

Joining Ultrascale Computing and Neutron Scattering Studies to Enable Revolutionary New Materials Development

Thomas A. Maier, Gonzalo Alvarez, Jeremy Meredith, Michael S. Summers, and Thomas C. Schulthess

Project Description

The goal of our combined modeling/simulation and characterization project is to develop a capability for the deliberate design of complex materials with applications in the energy sector. Our immediate aim is to develop simulation tools with predictive power that will enable computation of emergent properties of strongly correlated electron materials. Additionally, we propose to perform neutron scattering characterization experiments along with the simulations in order to verify predictions, validate the models, and further refine properties. On the computing side, we will focus our efforts on the development of algorithms and computer codes that make effective use of ultrascale computing infrastructure, which will be needed to perform simulations that can predict physical properties of realistic, materials-specific models. The aim of the neutron scattering measurements will be to test, confirm, or reject the hypotheses made with the simulations, and, if necessary, in an iterative process improve the models and computational predictions. As proof of principle, we will study cuprate high-transition-temperature (high-Tc) superconductors, focusing on the pairing mechanism, where we have high hopes in solving one of the most important problems at the forefront of condensed matter science. The tools and procedures we develop in this project will be applicable to a range of new materials systems that will be part of the solutions to the energy challenge.

Mission Relevance

This project is relevant to several DOE initiatives. It is consistent with the vision for computational science beyond the petaflop limit that is being discussed at the highest levels of DOE. Specifically, the DOE Office of Science, Advanced Scientific Computing Research, Mathematical, Information, and Computational Sciences program will greatly benefit from the computational capability developed in this project. The new tools will also be beneficial to the Center for Nanophase Material Sciences (CNMS) by providing a new capability that will enable growth of its user community, an important goal of the CNMS. The project is also in line with DOE's basic research needs for superconductivity. In a recent report, it was stated that "bridging the gaps in practical superconductor performance requires not only empirical exploration of new materials and the factors affecting their performance but also a fundamental understanding of the microscopic origins of superconducting behavior." In addition, this project will help establish ORNL as a leader in the use of neutron scattering in nanoscience and technology, fulfilling an expectation of DOE.

Results and Accomplishments

Our work in FY 2008 and FY 2009 was focused on extending, optimizing, and accelerating the DCA++ code that implements a dynamic cluster approximation for models of correlated electron systems. Our scientific/technical accomplishments during this period can be summarized as follows: (1) We completely rewrote the DCA++ code base using generic programming techniques that build on the model of the C++ Standard Template Library. (2) We extended the scope of the DCA++ code to cover models with disorder in the interaction strength and local chemical potentials. (3) We developed a hybrid parallel programming model for the DCA++ code that naturally scales to O(100,000) cores when applied to disordered Hubbard models. (4) We increased the speed of the calculations by running the QMC parts of the code in single precision without significant reduction in accuracy. (5) We demonstrated weak scaling of the DCA++

code to up to 150,000 cores on Jaguar with a sustained performance that achieves over 1 PFlop/s. (6) We accelerated the DCA++ code using GPUs resulting in significant speedups of up to 19 times faster while retaining the accuracy required for scientifically meaningful results. (7) We implemented a Lanczos based exact diagonalization solver to replace the QMC solver for models with complex interactions. (8) We co-developed and implemented a new "sub-matrix" update algorithm that further speeds up the QMC parts of the simulation. (9) We have started to implement a new and superior continuous time auxiliary field QMC algorithm to replace the current Hirsch-Fye QMC algorithm. (10) We have extended the scope of the DCA++ application to treat models of composite multi-layer systems.

These advances have allowed us to perform highly efficient simulations of Hubbard models. A simulation of disorder and inhomogeneity effects in cuprate high-temperature superconductors was the first computation to achieve petascale sustained performance (1.3 petaflop/s) for which the 2008 ACM Gordon Bell prize was awarded.

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05237

Data Analytics for Medicine Using Semi-Supervised Learning (DAMSEL)

Barbara G. Beckerman, Robert M. Patton, Christopher Symons, April D. McMillan, Shaun S. Gleason, Ryan A. Kerekes, Vincent Paquit, and Robert M. Nishikawa

Project Description

Presently, knowledge discovery and cohesive decision-making capabilities for biomedical applications are hampered by significant gaps in technology for multi-modal data analytics. We are developing a semi-supervised learning environment that incorporates disparate medical text and images in order to provide a computational framework for data analytics to overcome the gaps. For our framework, called Data Analytics for Medicine using SEmi-supervised Learning (DAMSEL), we are (1) developing an analytical, automated learning framework and tools for processing multi-modality medical data (text and images) for the purpose of data mining and assessment; (2) improving performance, portability, and scalability of this computational framework by leveraging available intelligent software and hardware computing resources and adding functionality to the system; and (3) validating the performance of the system on medical data

in terms of both knowledge accuracy and overall system responsiveness and usefulness. These aims will be accomplished in the context of two biomedical applications: breast cancer (mammography—imaging, pathologies, text reports) and traumatic brain injury (TBI) (using Joint Theater Trauma Registries [JTTR], imaging, and related TBI source data).

Mission Relevance

DAMSEL will facilitate the development of more powerful analytical tools by leveraging all of the data in a more effective manner than present approaches permit. These technologies are at the forefront of systems medicine application development and require computationally intensive environments for processing. Potential sponsors include the National Institutes of Health (NIH) and the Department of Defense (DOD), who have open program announcements and planned initiatives in these areas. For example, NIH's funding opportunity PAR-07-034, will support research in tools for data acquisition, archiving, querying, retrieval, visualization, integration and management; platform-independent translational tools for data exchange and for promoting interoperability; and analytical and statistical tools for interpretation of large data sets. This project is also consistent with such DOE programs as Mathematical, Information, and Computational Sciences, KJ.01.00.00.0; Computer Science, KJ.01.01.02.0; and Computational Partnerships, KJ.01.01.03.0. Other DOE programs that will benefit include National Security, intelligence, and biosurveillance applications.

Results and Accomplishments

The project created a multi-modal learning framework and tools for the analysis of mammography images and reports. We developed a semi-supervised machine learning framework that integrates the text and image modalities by transforming an image feature vector produced through image processing to a lower dimensional space that is smooth with respect to the cancer-specific image similarities described in the radiological reports. The framework requires that the text processing identify a feature space that reflects cancer-specific judgments, and that the image processing identify an overspecified set of initial image features.

The text analysis work produced the following key new capabilities: (1) a genetic-algorithm-based approach to identifying reports of abnormalities; (2) a genetic-algorithm-based approach to identifying key phrase patterns in the language used for the mammography domain; (3) a classifier for mammography documents; and (4) a temporal analysis approach for examining and finding key phrase patterns that behave as precursors to a future event in mammography patients. The key-phrase patterns represent a highly effective set of features for creating cancer-related dichotomies in the data, and support the discovery of a valuable image-processing manifold through the framework.

The image-processing portion of the project developed techniques for high performance mammogram analysis, providing the ability to extract image features describing biological tissue abnormalities. The following techniques were implemented for multi-core processing: fractal encoding, fractal encoding segmentation, histogram analysis, region growing/snakes, wavelet-based multi-resolution segmentation, watershed, and pattern analysis. The image features support the framework's need for a large set of potentially relevant observables that are combined with the text analysis in the machine-learning environment.

Publications

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05240

A Hybrid Continuous/Discontinuous Galerkin Formulation for Next-Generation Multiphysics Computational Fluid Dynamics Solvers

Judith Hill, Sreekanth Pannala, William Shelton, and Kwai Wong

Project Description

We are developing advanced mathematical methods for addressing fuel rod failure, a critical component of nuclear energy production that is critical for achieving true energy independence. Vortex-induced flexure of the closely packed fuel rods, rod-coolant heat transfer, and resulting collisions can lead to extensive damage of the rods. Modeling these phenomena requires a multi-domain, multi-physics simulation approach that addresses the interactions between the fluid flow and the solid mechanics.

Our approach is to develop a hybrid continuous/discontinuous Galerkin (CG/DG) method that provides a self-consistent, seamless multi-domain description. Traditional numerical approaches, such as finite difference and finite volume (FV, p=0 DG) methods are not amenable to geometrically complex hybrid meshes or to problems with disparate spatial and temporal scales. The methods often sacrifice numerical accuracy for ease of implementation and, consequently, violate fundamental physical principles such as conservation laws. Our hybrid method, coupled with optimization principles that address the multi-domain aspects of these problems, addresses the deficiencies of existing techniques. This effort will initiate a new programmatic direction in advanced fluid simulation methods based on DG. Overall, this effort will give ORNL a unique multi-physics computational fluid dynamics capability in sync with hardware and experimental capabilities, and establish the Laboratory as leader in this class of algorithmic development.

Mission Relevance

The development of a CG/DG method will provide a unique self-consistent approach capable of addressing complex geometries and disparate spatial and temporal scales. Combining the CG/DG method and DOE leadership-class computers will make it possible to perform unprecedented three-dimensional multi-domain, multi-physics simulations capable of delivering breakthrough science. To demonstrate the effectiveness of our numerical approach, simulations will be performed on nuclear reactor fuel rod bundles where the physical and algorithmic challenges in this class of complex problems include simulation of heat transfer and fluid-structure interactions as well as addressing the complex geometries and disparate spatial and temporal scales.

Given the rich mathematics associated with the CG/DG formalism, this project provides a path for programmatic direction in applied math to easily explore new numerical methods (for the DOE Office of Advanced Scientific Computing Research). The simulation challenges of the reactor core problem are ubiquitous in many engineering problems of interest to DOE (fusion, climate, industrial technologies, energy efficiency, biology) and its program offices (EERE, FE, BES, HENP, etc.)

Results and Accomplishments

Traditional numerical methods for simulating multi-physics and multi-domain interactions, ubiquitous among science and engineering applications, rely on either Dirichlet-Neumann Robin-Robin, or mortar methods. These two methods are a weak, often one-way, coupling between the physical domains. As an alternative, we have developed a new general method for multi-physics, multi-domain coupling that benefits from the formalism of adjoint-based optimization methods. Two advantages of this approach are that (1) the adjoint-based optimization approach formalizes prior *ad hoc* attempts to match the scalar or vector fields at the boundary, and (2) this approach admits *different* numerical discretizations, such as finite elements or finite differences, in each physical domain, enabling a wide range of applications to make use of this technique.

To date, this project has made significant contributions towards developing a new efficient and robust methodology for multi-physics and multi-domain coupling. In particular, we have proposed a new general optimization-based approach where we minimize the difference between scalar and vector fields at the domain interfaces subject to constraining physics in each domain. Thus far, we have demonstrated the above formulation for several increasingly difficult problems with good accuracy, including steady-state and transient thermal coupling and steady-state and transient conjugate heat transfer. We have demonstrated a robust and accurate method for coupling different numerical discretizations (arbitrary-order discontinuous Galerkin and continuous Galerkin) in different domains and are currently comparing this technique with existing methods.

05243

MPI-3: Programming Model Support for Ultrascale Computer Systems

Richard L. Graham, Edo Apra, Richard Barrett, Thomas Naughton, and Chao Wang

Project Description

Upcoming generations of ultrascale computer systems promise an unprecedented level of computational capabilities and hand-in-hand provide a challenge to use these systems effectively. Hardware technology challenges are driving these systems to be many-core and multi-core systems with immense component counts, and simulation codes, middleware, and system-level software need to be able to run in the face of

errors. We propose to work with the application developer aiming to run on these systems to develop scalable strategies for dealing with such failure at the application and middleware level. We will investigate how to partition the solution between these two levels in the context of the ubiquitous communication standard, the Message Passing Interface (MPI) standard, and present proposed changes to this standard to the MPI Forum for inclusion in the MPI-3.0 standard. We will look at solutions that aim to avoid failures and at scalable mechanisms to recover once such failures have occurred.

Mission Relevance

DOE makes large investments in such areas as climate change, energy science and technology, and material science, with simulation playing an important role in the discovery process. To meet the simulation needs, DOE develops increasingly powerful and complex computer systems. This project aims to provide a solution to one of the pressing issues facing those trying to use these increasingly complex systems—harnessing the full potential of these systems in the face of component failures. With MPI being the ubiquitous parallel communications and process control library used by scientific simulation codes, providing fault tolerance in support of MPI is a key step in developing fault-tolerant applications. By adding fault-tolerant capabilities to the MPI 3.0 standard, adding uncoordinated checkpoint/restart capabilities, and demonstrating the utility of this approach in a small number of scientific simulation codes, we will provide a foundation for developing fault-tolerant simulation codes that will benefit from the enormous potential these emerging platforms provide.

Results and Accomplishments

As part of the first year's work, changes to MPI semantics have been defined. The primary semantic change being introduced is the ability of all MPI communicators to shrink when processor recovery takes place, including the predefined communicator MPI_COMM_WORLD, with a focus on scalable support. Users define the recovery policies. Clarification for the behavior after failure of several existing MPI functions (MPI_Abort(), MPI_Comm_size(), MPI_Comm_rank()) has been added.

A full set of new MPI Application Programming Interface changes to support recovery from process failure has been defined. These include functions to set MPI communicator recovery policy, routines to invoke process recovery, and routines for aiding restarted processes to rejoin existing communicators. A primary guiding principle has been to maintain backwards compatibility with the existing MPI standard, in the sense that applications that do not require support for fault tolerance need not be changed to continue and function correctly with the addition of support for fault tolerance to the standard. In addition, users have some control over the performance penalties paid for the fault-tolerance support. This primarily affects the use of collective communications, and the recovery mode (local or global) chosen for each communicator.

Work on a first prototype implementation of the support for fault tolerance within the MPI standard has begun, with the initial focus being failure detection and recovery at the run-time level.

05259

Computer Design and Predictive Simulation of High-Capacity, Cyclable, and Versatile Nanoporous Supercapacitors for Energy Storage Applications

Vincent Meunier, Robert Harrison, William Shelton, and Bobby Sumpter

Project Description

We proposed to develop multiscale computational tools to investigate and optimize key variables of supercapacitors based on nano-porous carbon materials. There is a projected doubling of world energy consumption within the next decades and a desperate need for low-emission sources of energy. However, the use of electricity generated from renewable sources requires efficient electrical energy storage. A particularly promising technology is carbon supercapacitors, which have higher power density than batteries and have higher energy density than conventional dielectric capacitors due to the large surface area provided by the nanometer-sized pores. The capacitance of a supercapacitor depends on complex phenomena occurring in the pores, the effective dielectric constant of the electrolyte, and the thickness of the double layer formed at the interface. Experimental measurements are hard to perform and difficult to interpret, especially at the nanoscale. Optimization of these key variables requires a fundamental understanding that can only be obtained through detailed scalable first principles calculations combined with mesoscale and microscale simulation tools. As part of this project, we will further improve the scaling of our first principles methods along with the heat (micro), mass (micro) and ionic (meso) transport codes. These types of simulations require computational resources that can only be provided by the NCCS. This work will uniquely position ORNL as the lead institution in simulation of energy storage materials.

Mission Relevance

The research and development of this project will have immediate impact into the prime mission of DOE. It fits exceptionally well into the new DOE Energy Frontier Research Centers and additionally should be of considerable interest to the DOE Office of Energy Efficiency and Renewable Energy. The fundamental aspects of charge storage, motion, solvation and desolvation have large ramifications to biology because ion channels are quite important in nearly all types of life forms. As such we expect considerable interest from the National Institutes of Health and the Environmental Protection Agency. Efficient energy storage is also of importance to the Global Nuclear Energy Partnership (GNEP). In addition, the potential use of supercapacitors for portable power systems crosscuts the continued and high priority interest of the department of defense.

Results and Accomplishments

First, we developed an understanding of the role of pore size and shape on the processes relevant to adsorption and energy storage. Our work towards that objective has been to provide a quantum mechanical based model that accurately describes the behavior of capacitive energy stored for the entire range of pore size (from subnanometer to microscopic). Devising such model was made possible by large-scale calculations performed on the NCCS computational resources (especially Blue Gene P). Remarkably, our model has already been accepted as the state-of-the-art description of carbon based supercapacitors One appealing feature of our approach is that it can be applied to any pore size but also to any type of electrolyte. Its predictive power had been used to devise a new type of capacitors (exhoedral capacitor).

Second, we proposed to model the dynamics of the solvation/desolvation processes. This work is still under way, but much progress has been done already. We identified realistic atomistic models to be used as template materials for dynamics and proceeded with initial large-timescale molecular dynamics runs on a number of them. We have also initiated collaboration with Prof. Rui Qao from Clemson University through the Higher Education Research Experiences program to supplement our portfolio in that area.

Third, we proposed to explore the role of pore chemistry beyond carbon nanopores, including affects of chemical functionalization and other types of elements for the porous materials, including oxides. This topic is relevant to the effect of pseudo-capacitance, where fast and reversible redox reaction occur at the interface. This is a very interesting topic that has only been studied experimentally in the past few years but to which very little theoretical work has been devoted. We have made significant progress in this area, hinging on our team's expertise in chemistry in nano-confined systems. We have provided the first systematic study of carbon nanostructure functionalization though single atom doping (substitution) for all the relevant atomic species such as B, N, O, F, Si, P, S, Se. We also collaborated with various international groups to corroborate our findings with their experimental findings, leading to a number of high-impact publications in international journals. In addition, we have continued to work on the materials aspect of the supercapacitor science, focusing on the promising graphitic nanoribbons materials (GNRs) (for which we collaborated with the group of Millie Dressehaus at Massachusetts Institute of Technology in a *Science* publication) and on the intriguing metal-oxide nanotube.

Publications

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05274

Inferring and Predicting the Social Dynamics of Groups via Psycho-Textual and Communications Flow Analysis

Jack Schryver, Edmon Begoli, Yu Jiao, and Tracy Warren

Project Description

The goal of this project is to develop a new capability in social network analysis using electronic communications data that can be analyzed with text analysis techniques. We extend traditional social networking analysis by including deep-dive analysis of message contents to obtain inferences of group processes. We consider group formation, recruitment, coalition, threat, conflict and schism. Important indicators such as in-group bias and out-group antipathy are rarely coded explicitly in text. Instead, they are embedded in connotative/affective meanings. Semantic analysis has generally focused on denotative meaning, creating a huge potential for knowledge discovery. Most related research is in the field of sentiment analysis–detection of positive/negative orientations toward a predetermined subject. Our work departs from previous work in three main directions. First, we perform a more fine-grained analysis, narrowing the focus from document to sentence level and from pure sentiment to 22 affective states. Second, we integrate common sense affective knowledge. Third, we link affect with entities identified in documents for deeper understanding of affective meaning. This capability will be an indispensible aid for improving our nation's ability to protect itself from terrorism, and has the potential to reshape the way information about individual interactions is stored and analyzed.

Mission Relevance

This research extends ORNL's Knowledge Discovery mission objective. In addition, this research is directly aligned with the mission of the Intelligence Advanced Research Projects Activity (IARPA), the Intelligence Community (IC), and the Department of Homeland Security (DHS). These agencies need innovative and reliable tools to help them analyze the deep contents of massive quantities of electronic messaging data (e-mail, text chat, blogs, and transcribed talk). This research will help establish a capability that is essential for long-term human factors analysis and intelligence analysis (DHS), social-network analysis (IC), and computational and psycholinguistics (IARPA). With internationally recognized experience and expertise in knowledge discovery and data mining, high performance computing, human factors, social networking technology and geospatial sciences, ORNL is strategically positioned to develop this capability.

Results and Accomplishments

The research accomplishments are (1) development of algorithms to extract affective relationships from text and (2) implementation in a software prototype that accepts unstructured text as input. To develop an

affect lexicon, seed lists for several affect categories were manually constructed. PageRank was adapted to regulate the flow of affective meaning from seed words to other terms. A sentence-level algorithm propagates affective meaning from tokens to extracted entities. This algorithm evaluates affective relationships between entities. For example, "John loves Mary" describes a "liking" relationship. A graph algorithm called Random Walk with Restart is applied to subgraphs containing terms that connect entity pairs, and the output ranks represent the affective relationships. The Java prototype includes an automated search interface for multiple document retrieval. When a single document is loaded, it highlights affect terms in a scrolling window; affect intensities are plotted as a word series. A pruned graph of the document is displayed, which users can further prune by selecting affects and entities. The prototype integrates open source code to perform entity extraction, part-of-speech tagging and other natural language programming tasks. Accomplishments in program development are preliminary because scientific and technical achievements were emphasized during the first year. We have held discussions with DHS Human Factors Division, Heather McCallum-Bayliss, Incisive Analysis Program Manager at IARPA; Rebecca Goolsby, Office of Naval Research; and Alenka Brown-VanHoozer, DoD-CIO/ASD-NII. As these discussions go forward, our objective is to identify relevant BAAs scheduled for release in the coming year, or prepare unsolicited proposals.

05282

High-Throughput Computational Screening Approach for Systems Medicine

Pratul K. Agarwal

Project Description

High performance computing (HPC) continues to revolutionize biology. Computational thinking and techniques will have a significant impact on future biological research as it is substantially reducing the time between data acquisition and knowledge discovery. Human health, in particular, is poised to benefit considerably from the impact of computational modeling and simulations. The search for new medicines is based on the identification of potential drug candidates that bind to and change the activity of disease targets (proteins). Traditionally, this search has centered upon the active site of an enzyme or binding site of a receptor. Recently, we have demonstrated that protein sites on the surface (*allosteric sites*) are capable of altering protein activity in much the same way as traditional drug agents in the buried active site. However, due to the size of the energy space of the protein as well as the chemical space of the compounds, screening presents a challenging problem.

Here, we propose a joint effort between the computational and structural biologists and medicinal and computational drug design chemists to develop new high-throughput methods for approaching rational drug design and drug discovery. HPC will be used to predict the location of allosteric sites in protein targets and to simulate the interaction between drug-like small molecules and target sites. *In silico*–based screening of drug candidates will lead to a considerable cost and time saving for the expensive wet-lab screening and, therefore, accelerate critical steps in systems medicine.

Mission Relevance

Computational biology is an important component of Genomic Science Program of the DOE Office of Biological and Environmental Research (DOE BER). The proposed research will allow development of HPC tools and software for characterization of biomolecular-biomolecular interactions, which is an important component of Genomic Science Program goals. The fundamental understanding of the

biological processes occurring at the molecular level in the living cell, as enabled by the proposed research, has fundamental implication in energy and environmental research. Proposed work is relevant to the DOE Office of Advanced Scientific Computing Research as well as to DOE BER. The proposed research for development of tools and software for systems medicine is relevant to human health. Therefore, it is relevant to mission of the National Institute of General Medical Sciences (in NIH). The outcome of the proposed research would lower the time and cost for discovery of new medicine, thereby promoting human health.

Results and Accomplishments

We have successfully identified allosteric sites for two medically important target enzymes. The enzyme dihydrofolate reductase (DHFR) is an anticancer target, while the enzyme beta-ketoacyl-acyl carrier protein reductase (FabG) has important implications in antibacterial activity. DHFR is a classic drug target and a widely studied enzyme both theoretically and experimentally. FabG reduces the beta-ketoacyl-acyl carrier protein to a beta hydroxy intermediate in the fatty acid synthesis system. Our methodology for the identification of the allosteric sites is based on modeling the rate-limiting reactivity catalyzed by these enzymes. In both enzymes the rate-limiting step is the hydride transfer from cofactor nicotinamide adenosine dinucleotide. The identification of the allosteric sites was based on modeling the reaction coupled protein vibrational modes. A high-throughput docking infrastructure has been developed for determining the best binding pose of the ligands with the enzyme targets given the receptor binding (allosteric) sites. In the first phase of this project, a test compound library constituting 1010 compounds was docked on the set on the allosteric sites. Based on the free energy of binding and the corresponding scores, the top compounds and best poses of the ligands on the allosteric sites were identified. The infrastructure is currently deployed on ORNL's Jaguar supercomputer, and in the second phase of this project we are interacting with the structural biologists and computational chemists at St. Jude's Medical Research Center to screen the two enzyme targets against a library of 500,000 medically relevant compounds.

Publications

Ramanathan, A., and P. K. Agarwal. 2009. "Computational identification of slow conformational fluctuations in proteins." *J. Phys. Chem. B* **113**:16669–16680 (featured on the cover).

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05294

Denovo: The Next-Generation HPC Solver for Multiscale Nuclear Energy Transport

Kevin T. Clarno, Thomas M. Evans, Gokhan Yesilyurt, Mark L. Williams, and John A. Turner

Project Description

Nuclear technology now permeates virtually all aspects of the American economy and is a necessary part of any U.S. energy security strategy. Predictive nuclear energy simulations will involve the modeling of the many physical phenomena that are inherently coupled, including Boltzmann radiation transport, and will require tremendous computational resources. Experience in many fields has demonstrated that in coupled-physics calculations, a three-dimensional Boltzmann transport solver requires most of the computational resources because of its seven-dimensional phase space. We will extend an existing production-quality parallel transport solver to develop a first-of-a-kind capability that creates a

mathematically consistent two-level approach to addressing the significant multiscale (in phase space) challenge associated with predictive simulation of novel reactor concepts. Through hierarchical domain decomposition in full phase space, we will amortize the inherent spatial sweep scaling limitation of traditional transport solvers to fully utilize the multicore architectures in present and future leadership-class computing platforms. We will advance the next-generation high-performance computing (HPC) nuclear reactor transport solver to establish ORNL as the sole source for massively parallel multiscale neutronics codes by incorporating a scalable algorithm that provides a consistent multilevel approach to the multiscale problem in a coupled-physics environment.

Mission Relevance

The Nuclear Energy Advanced Modeling and Simulation (NEAMS) program within the DOE Office of Nuclear Energy (DOE NE) is evolving into an application-oriented software development program that will establish several nuclear reactor and fuel, separations and safeguards, and waste repository simulation code teams. The completion of this project in 2011 will demonstrate the highly scalable integrated solver capability of Denovo for massively parallel multiscale nuclear energy radiation transport solvers. The benefits of parallel multiscale Boltzmann transport solvers extend well beyond the present focus of the Nuclear Energy Advanced Modeling and Simulation (NEAMS). Nuclear nonproliferation, security, and safeguards in the National Nuclear Security Administration and the Department of Homeland Security under programs related to special nuclear material production and protection and radiological dispersion devices require high-fidelity transport solvers with tremendous computational requirements. Advanced DOE NE reactors, fuel fabrication facilities, and separations facilities will require extensive analyses of potential criticality excursions to demonstrate the safe operation and material accountability, some of which are coupled-physics challenges such as fissile material in solution within a separations facility.

Results and Accomplishments

This project has exceeded several exceptional technical achievements and is on track to meet all of the goals of the Revised Research Plan. Through the LDRD funding, the Denovo transport code has been enhanced to include an eigenvalue solver, which is required for nuclear reactor physics, and has efficiently utilized up to 60,000 cores of Jaguar in solving several large-scale demonstration problems. The primary technical achievements in FY 2009 include (1) porting to the Jaguar hardware and demonstrating scalability to 40,000 cores and running problems on 57,600 cores; (2) development of an eigenvalue transport solver for reactor simulation applications; (3) demonstrated fidelity for several target nuclear energy simulations; and (4) establishing the groundwork for further advancements in FY 2010 and FY 2011. We have redesigned the input/output in Denovo and now can achieve >1.6 GB/min on parallel reads involving up to 40,000 cores. We performed weak-scaling studies of the Denovo KBA sweep algorithm up to 40,000 cores. The time to solution is 38% greater at 40,000 cores due to latencies, but this is acceptable because there are no increases in iteration count as the problem size increases. A solver was implemented in Denovo to compute the eigenvalue/eigenvectors with both a traditional approach, with known performance for a class of problems, and a novel approach that will leverage the massively parallel hardware and will be the subject of a future journal article. The groundwork coding was established in Denovo to compute the macroscopic cross sections and simplify the incorporation of the SCALE nuclear data processing tools.

Publications

Evans, T. M., K. T. Clarno, and J. E. Morel. In press. "A transport acceleration scheme for multigroup discrete ordinates with upscattering," *Nuclear Science and Engineering*.

Evans, T. M., A. Stafford, and K. T. Clarno. In press. "Denovo—A new three-dimensional parallel discrete ordinates code in SCALE." *Nuclear Technology*.

05568

Component Modeling

Gary E. Giles, Jr.

Project Description

Information about this project can be obtained from the principal investigator.

SYSTEMS BIOLOGY

00020

Systemic Approaches in Recombinant *Zymomonas mobilis* to the Regulation of Ethanol Fermentation

Steven D. Brown, Gregory B. Hurst, Dale A. Pelletier, Timothy J. Tschaplinski, Shihui Yang, and Yunfeng Yang

Project Description

Ethanol is currently blended as an oxygenate in transportation fuel. Its expanded use has great potential to reduce fuel imports, to create American jobs, and to improve our nation's energy security. However, there are barriers and challenges to a rapid expansion of cellulosic-ethanol production. Robust process-tolerant and inhibitor-resistant microbes are recognized as key short-term technological goals. We propose to elucidate the molecular basis of process inhibitor tolerance and stress responses in *Zymomonas mobilis* using systems biology tools, the recently completed genome sequence, a recombinant capable of fermenting C-5 and C-6 sugars, an acetate tolerant strain, and physiological studies. Understanding the molecular basis for inhibitor tolerance and stress in a genetically tractable organism will provide rapid and fundamental insight into important fermentation attributes and potential improvements for applied ethanol production. This study will provide baseline data useful for other opportunities involving modeling and simulating microbial systems, be applicable to other stressors, have broader implications to other bioenergy-related microbes, and demonstrate the power of integrating the laboratory's systems biology tools to position the laboratory well for future funding opportunities.

Mission Relevance

The *Z. mobilis* stress responses to be characterized in this project are aligned with key science research milestones outlined in the Biomass to Bioethanol roadmap. Our systems biology approach will delineate important loci, regulators, and key metabolites in stress response and inhibitor tolerance pathways. Thses studies will likely lead identification of useful biomarkers and targets for strain improvement and potentially provide broader insight into other ethanol-producing microorganisms. The proposed study will demonstrate and expand ORNL's expertise in the application of a systems-level approach to the study of *Z. mobilis* that could be readily adapted to other ethanologenic microorganisms of importance to the Genomic Science Program of the DOE Office of Biological and Environmental Research (DOE BER) and to the biomass programs in the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE).

The fundamental and applied outcomes of our research will assist DOE with the goals outlined in the President's Advanced Energy Initiative to help break America's dependence on foreign sources of energy and develop cleaner, cheaper, and more reliable alternative energy sources. We have applied many of the capabilities developed under this project in support of new projects for DOE BER and DOE EERE.

Results and Accomplishments

We have developed and integrated ORNL's systems biology capabilities and our studies have provided fundamental and practical insights into inhibitor tolerance mechanisms for industrial catalyst development. UT-Battelle submitted two patent applications from this project and we have published three papers in top journals such as *Nature Biotechnology*, two more have been submitted, and three are in preparation. The lead-PI was invited to contribute two book chapters and the project supported seven invited talks and seven poster presentations. This project supported training for students (DOE Academies Creating Teacher Scientists 2007 and 2008), technicians, and a postdoctoral fellow. One technician and the postdoc associated with this project won the Biosciences distinguished achievement awards from these studies. This project augmented ORNL's transcriptomics capabilities through the application of high-density microarray, various bioinformatic tools and RNA-seq using next-generation sequencing technologies. We have applied the platform developed through this project in support of other projects such as the DOE BioEnergy Science Center (BESC) transcriptomic studies.

Publications and Patents

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Yang, S., T. J. Tschaplinski, N. L. Engle, S. L. Carroll, S. L. Martin, B. H. Davison, A. V. Palumbo, M. J. Rodriguez, and D. S. Brown. 2009. "Transcriptomic and metabolomic profiling of *Zymomonas mobilis* during aerobic and anaerobic fermentation." *BMC Genomics* **10,** 34. doi:10.1186/1471-2164-10-34 (highly accessed).

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Microorganisms Having Enhanced Tolerance to Inhibitors and Stress. U.S. Provisional Patent Application 61/184,961 (ORNL: 2220.0), June 8, 2009.

00021

Unraveling the Regulatory and Biosynthetic Genes That Control Cellulose Production in the Model Bioenergy Crop *Populus*

Udaya Kalluri, Timothy McKnight, Dale Pelletier, Jennifer Morrell-Falvey, Gregory Hurst, Patricia Lankford, and Sara Jawdy

Project Description

The percentage of usable substrate per unit feedstock biomass is one of the prime factors affecting efficiency of conversion to ethanol. The long-term goal of this project is to unravel novel biosynthetic and regulatory genes that control plant cell wall composition, specifically cellulose, in *Populus*. A twofold approach is proposed towards this goal. Task 1 will develop carbon nanofiber–based transient expression system as a rapid screen to divulge roles of candidate genes in wall biosynthesis. Development of such a system will circumvent the current impediment of long turnaround times in generation of stable transgenic plants for evaluation of gene function in *Populus.* Task 2 will develop and apply protein interaction assays such as chromatin immunoprecipitation and pull-down assays to cell wall biosynthesis studies. Progress made through this project will add new technological and scientific capabilities to

ORNL, which will propel not only the pursuit for a comprehensive understanding of cellulose biosynthetic pathway in bioenergy crops but also the pursuit of plant systems biology–based solutions in support of other DOE missions.

Mission Relevance

A better understanding of the molecular controls on plant cell wall composition will lead to warranted applications towards improving the efficiency of biomass conversion to ethanol. The protocols being developed through this project can find direct applications in the current and future projects sponsored by the DOE Office of Basic Energy Sciences, such as Plant Feedstock Genomics for Bioenergy and large bioenergy research efforts, specifically, the BioEnergy Science Center. Moreover, owing to the potential broad applicability of the approaches developed through this project, we also anticipate future funding opportunities to exist with the DOE Office of Biological and Environmental Research in the Genomic Science Program (Fundamental Science), the Department of Agriculture, and the National Science Foundation (such as NSF Plant Genome Research Program). These approaches will also be relevant to the anticipated DOE large science solicitations in the Genomic Science Program (Bioremediation and Carbon Cycling).

Results and Accomplishments

Results based on carbon nanofiber chip-based single cell assay experiments have resulted in an Invention Disclosure (Kalluri, McKnight and Melechko, Invention 2211, DOE S-115,242, "Platform for Immobilization and Observation of Subcellular Processes," elected to PFTT portfolio of UT-Battelle, LLC). A research article on proteomics methods was prepared, submitted, and published as cover art for a peer-reviewed journal with impact factor 5.5 (see publication listed below). In addition, a research article on the cell-wall imaging method was prepared and submitted to *New Phytologist*. The early results and concepts developed based on the present project have contributed to scale-up efforts totaling ~$2 million per year through the DOE BioEnergy Science Center (BESC). The antibody-based imaging technique and proteomics methods developed have found larger-scale applications under the DOE BioEenergy Science Center project.

Publication

Kalluri, U., G. Hurst, P. Lankford, P. Ranjan, and D. Pelletier. 2009. "Shotgun profiling of *Populus* developing xylem proteome." *Proteomics Journal* **9**(21), 4871–4880.

00040

Electricity and Biohydrogen Production via a Systems-Level Understanding of Microbial Fuel Cells

A. P. Borole

Project Description

Power output from microbial fuel cells (MFCs) is a limiting factor impeding application of these devices for energy production. In the first year, acidophilic MFCs were investigated. Electricity production was demonstrated at low pH, using an H-type MFC. In the second year, a two-pronged approach was taken to improve power density of MFCs. Engineering and biological factors limiting the power density were identified and optimized to improve power densities. Novel enrichment strategies employed in this approach resulted in identification of new exoelectrogenic families.

This project was targeted for development of expertise in two areas: microbial communities/biofilms, and energy production. Electrogenic microbial communities were tracked over time with different carbon sources via 16S r RNA and DGGE analysis. Application of the MFCs to energy production was studied for two industrial processes: biorefinery-based ethanol production and food industry processes. Electricity production with simultaneous removal of biorefinery by-products was demonstrated, enabling water recycle in biorefinery. Electricity production from a milk dairy farm wastewater was also demonstrated. In the third year, electrochemical analysis of the improved MFCs was conducted. The results were published via peer-reviewed publications and patent applications.

Mission Relevance

The project addresses DOE mission to obtain energy independence, while improving environmental quality. The project deals with energy production in the form of electricity and hydrogen from renewable resources such as sugars, organic acids, as well as wastewaters and waste materials. The ability to effectively produce electricity from cheap renewable resources is an important goal for the DOE. Specific programs in DOE likely to benefit from this research are the Fuel Cell and Hydrogen Infrastructure Program (of the DOE Office of Energy Efficiency and Renewable Energy), the Genomic Science Program (of the DOE Office of Biological and Environmental Research), and clean coal technology (of the DOE Office of Fossil Energy). The Environmental Protection Agency will potentially benefit as well. The Department of Defense (DOD) needs remote and portable energy sources to power transmitters, receivers, sensors, monitors, etc. MFCs are very stable, although low-energy, devices that could be used in such applications. This project can potentially help improve power yield from MFCs to enable use in other DOD applications requiring greater energy needs.

Results and Accomplishments

Novel electrode designs for MFCs were created and implemented to demonstrate power densities up to 490 W/m^3. Materials and electron mediator issues associated with operating MFCs at low pH conditions were investigated. Electricity production with *A. cryptum* as a biocatalyst was demonstrated (work published in *Biot. Lett,* 2008).

The overall accomplishments are listed here:

- Designed MFCs with reduced ohmic resistance and compact design to enable enrichment of biofilm-forming exoelectrogenic organisms.
- Developed a novel enrichment strategy to improve selection of electrogenic biocatalytic microbial consortium (patent application submitted).
- Improved anode performance and obtained power densities higher than those reported in literature (>5000 mW/m^2).
- Developed and implemented electrochemical impedance spectroscopy techniques to demonstrate that the anode developed in this study was no longer limiting MFC power production.
- Identified path forward to develop sustainable MFCs using air as the oxidant.
- Obtained proof of principle for application of MFCs in biorefinery.
- Submitted four patent applications to USPTO.
- Published six articles.
- Presented results at more than ten international conferences.

Publications and Patents

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Borole, A. P. *Microbial Fuel Cells for Gas-Phase Reactants.* 2009. Patent Application filed U.S. 12/419,681.
Borole, A. P. *Microbial Fuel Cell Treatment of Ethanol Fermentation Process Water.* 2009. Patent Application Serial No. 12/366713.
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Borole, A. P., and C. Tsouris. *Microbial Fuel Cell Treatment of Fuel Process Wastewater.* 2009. Patent Application Serial No. 12/366709.
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Borole, A. P., C. Y. Hamilton, T. A. Vishnivetskaya, D. Leak, C. Andras, J. Morrell-Falvey, B. H. Davison, and M. Keller. 2009. "Integrating engineering design improvements with exoelectrogen enrichment process to increase power output from microbial fuel cells." *J. Power Sources* **191**(2), 520–527.
Borole, A. P., J. Mielenz, T. A. Vishnivetskaya, and C. Y. Hamilton. 2009. "Controlling accumulation of fermentation inhibitors in biorefinery water recycle using microbial fuel cells." *Biotechnol. Biofuels* **2**(7), on line: http://www.biotechnologyforbiofuels.com/content/2/1/7.
Borole, A. P., D. S. Aaron, C. Tsouris, and C. Y. Hamilton. Accepted. "Understanding long term changes in microbial fuel cells using electrochemical impedance spectroscopy." *Environ. Sci. Technol.*

00043

Microfluidic Platform for Individual Microbe Capture, Cultivation, and Selective Release

Martin Keller, Anthony Palumbo, Jim Elkins, Tim McKnight, Nance Ericson, and Mitch Doktycz

Project Description

The recent application of molecular phylogeny to environmental samples has resulted in the discovery of an abundance of unique and previously unrecognized microorganisms. The vast majority of this microbial diversity has proved refractory to cultivation with traditional methods; thus, little is known of their physiology or capabilities. We are (1) developing a microfluidic platform that will allow the site-specific capture of individual bacteria, cultivation with controlled doubling cycles, and selective release for downstream collection and further analysis; and (2) applying flow cytometry to isolation and subsequent manual cultivation of single cells. The microfluidic platform will incorporate encapsulation of cells in gel microdroplets. This cultivation under low nutrient flux conditions will be followed by further characterization and analysis of microbial microcolonies through "lab-on-a-chip" concepts. The subsequent analysis will include the implementation of multiple displacement amplification (a linear type of DNA amplification) for subsequent analysis by genome sequencing. This approach will ultimately replace the flow cytometry approach, leading to higher throughput and reduced costs. The flow cytometry approach is being further developed by applying the method to anaerobic bacteria. We are exploring methods to handle anaerobic bacteria in the flow cytometry.

Mission Relevance

The ability to grow and study previously uncultured organisms will enhance our understanding of microbial physiology and metabolic adaptation and will provide new sources of microbial metabolites. These capabilities are applicable to DOE programs involved in bioenergy, bioremediation, and carbon sequestration. In all these applications use of novel microorganisms may lead to more efficient processes relevant to DOE missions. For example, DOE is interested in isolation of more efficient bacteria for the degradation of cellulose to sugars and the processing of sugars to alcohol. In addition, these capabilities will have applications to National Institutes of Health (NIH) and potentially the Department of Homeland Security. NIH applications could come from areas such as isolation of novel pathogens and characterization of gut microorganisms.

Results and Accomplishments

During FY 2009 further progress was made towards designing and fabricating microfluidic structures capable of generating alginate microdroplets. A range of solution conditions were assessed, and various droplet generating schemes were evaluated. A publication summarizing these studies was published. The ability to encapsulate bacteria into alginate microdroplets was demonstrated. Cultures were grown and analyzed on-board the microfluidic platform. These bacteria were capable of dividing and various techniques including whole genome amplification were evaluated. Further, appropriate flow control systems were assembled and evaluated.

A complementary approach, using a piezoelectric droplet generator, to producing alginate microdroplets was also investigated. Comparisons with this technology showed no deleterious effects due to the emulsion conditions used on chip. This piezo droplet technology was used for encapsulating and characterizing bacteria isolated from a local field research site.

Publication

Kalyanaraman, M., S. T. Retterer, T. E. McKnight, M. N. Ericson, S. L. Allman, J. G. Elkins, A. V. Palumbo, M. Keller, and M. J. Doktycz. 2009. "Controlled microfluidic production of alginate beads for *in situ* encapsulation of microbes." *1st Annual ORNL Biomedical Science and Engineering: Exploring the Intersections of Interdisciplinary Biomedical Research,* 100–103.

00044

Methodological Development of Computer Simulation in Molecular Biophysics

Jeremy Smith

Project Description

Motions in proteins play a key role in their function. Here we establish a program developing methodological aspects of combining computer simulation with neutron scattering experiments with a view to characterising correlated dynamics in proteins relevant to bioenergy in different functional states and environments. Work is also being performed aimed at understanding the functional mechanisms of cellulase activity.

Mission Relevance

Progress made through this project will place ORNL in an advantageous position to secure funding from anticipated solicitations from the DOE Offices of Basic Energy Sciences and Biological and Environmental Research over the next several years. The results from the project will, moreover, add new technological as well as scientific capabilities to ORNL, which in turn will strengthen ORNL's position as a leader in biophysical bioenergy research.

Results and Accomplishments

Coarse-grained biomolecular simulation with REACH: Realistic Extension Algorithm via Covariance Hessian algorithm was developed and shown to be transferable. The role of water molecules in proton transfer in bacteriorhodopsin was determined. The response of small-scale, methyl rotors to protein-ligand association was determined in a simulation analysis of calmodulin:peptide binding. The folding of membrane-embedded peptides was characterized. Energy triplets for writing epigenetic marks were discovered. A common folding mechanism of a beta-hairpin peptide via nonnative turn formation was revealed by unbiased molecular dynamics simulations. Hydrogen bond–driven loop-closure kinetics in unfolded polypeptide chains was revealed using unbiased classical molecular dynamics simulation.

Publications

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Thukral, L., J. C. Smith, and I. Daidone. In press. "Common folding mechanism of a beta-hairpin peptide via non-native turn formation revealed by unbiased molecular dynamics simulations." *Journal of the American Chemical Society.*

Ulmschneider, J. P., J. C. Smith, A. Killian, and M. B. Ulmschneider. In Press. "Folding of membrane-embedded peptides." *Journal of Chemical Theory and Computation.*

Xu, Q., Y. Chu, H.-B. Guo, J. C. Smith, and H. Guo. In press. "Energy triplets for writing epigenetic marks: Insights from QM/MM free energy simulations of protein lysine methyltransferases." *Chemistry: A European Journal.*

05055

Host Genetic Diversity as a Variable Selection Environment for the Gut Microbiome

Elissa J. Chesler, Anthony V. Palumbo, and Mircea Podar

Project Description

Specific host genetic factors that influence the composition of the gut microbial community and its correlations or causal relationships with chronic diseases are poorly understood. A colony of standard inbred and hybrid mice will be used to study the connection between mammalian genetic variation and gut microbial ecology. Using genomic approaches in both gut microbial communities and the mouse intestine, we will identify variation in gut microbiomes and establish the heritability and pleiotropic effects of genetic variation on interactions of host and normal flora. These studies will lay important foundations for an integrative and interdisciplinary research program that will allow us to map the interface between the mouse genome and the gut microbiome. We will approach this by analyzing the association of the abundance of specific microorganisms with the steady-state abundance of mouse mRNAs. This will allow us to identify networks involving host and microbe for causal studies. The goals of using mouse models are to identify predictive biomarkers and polymorphic loci that determine susceptibility to a number of human diseases that result from the interplay of gut microbes, genetic susceptibility factors, and environmental exposure including celiac disease, irritable bowel syndrome, and Crohn's disease.

Mission Relevance

The techniques developed here in rapid screening of community composition of environmental samples are applicable to DOE programs. Community composition has implications in key mission areas such as biofuels, bioremediation, and carbon sequestration. This project is of interest to the DOE Office of Biological and Environmental Research in studies of biological complexity and health effects of radiation. It is also of tremendous interest to the National Institutes of Health, and there are likely to be calls for proposals in this area over the next few years. There are several human diseases that this work would allow ORNL to address in future proposals. The Environmental Protection Agency has shown an interest in tracking sources of enteric contamination in streams, lakes, and rivers. Thus, there is an interest in studies of domesticated and wild animals as potential sources of contamination to water bodies. The techniques developed in this project will be applicable to this area.

Results and Accomplishments

We have collected samples of intestinal RNA and cecal content DNA from a panel of genetically diverse mice, the Collaborative Cross. Primers have been designed for isolation of rare uncultured microbes using *in situ* hybridization labeling and flow cytometry. Heritability analysis of gut microbial phenotypes was performed in the eight progenitor strains of the Collaborative Cross. Between 7000 and 25,000 sequences were obtained from each intestinal microbe sample. Seventy-seven sequence clusters had significant strain by sex effects on their abundance in the mouse intestine. We found that most of the differentially abundant microbial clusters were elevated in single strain of mouse, though the organism was present in all strains. The sequence clusters were entered into a terrain mapping analysis, which confirmed that gut microbial community composition is a strong classifier of mouse strains. We were also able to demonstrate that overall, there was heritable variation in intestinal expression of metabolizing enzymes and intestinal immune processes. Combinatorial analysis methods were developed for the analysis of gut microbes and their association to intestinal mRNA species at the level of microbial taxa. Using these

applications we have been able to demonstrate that abundance of specific microbes is associated with abundance of specific metabolic process related genes.

Publications

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05133

Carbon Drivers of the Microbe-Switchgrass Rhizosphere Interface

Christopher W. Schadt, Hector F. Castro-Gonzalez, Marie Anne De Graaff, Charles T. Garten III, and Aimee T. Classen

Project Description

Plants allocate a significant proportion of their carbon belowground as roots and root exudates. These often-labile carbon substrates serve as the energy source for complex microbial communities that inhabit the rhizosphere and stimulate ecosystem nutrient processes. In spite of its ecological importance, root exudation is poorly understood, and even less is known about how changes in the amount and type of root exudate might alter the functions of the soil microbial community. Microbial functional group composition in the rhizosphere is likely influenced directly and indirectly by a number of complex factors, including interactions with the dominant plant species as well as interactions with other microorganisms. Studies of the feedbacks between root exudation and microbial community function will enable better understanding of how shifts in plant genetics (e.g., bioenergy crops) may alter soil carbon cycles, crop sustainability, and carbon sequestration. In laboratory and greenhouse studies, we will merge the power of two technologies—^{13}C stable isotope probing (SIP) and DNA analysis—to link root exudate quality and quantity with microbial community structure and function in the rhizosphere using switchgrass as a model system.

Mission Relevance

Understanding of the rhizosphere interface supports DOE objectives in carbon cycling and the role of soils in bioenergy crop sustainability. This project proposes an approach that could be used in several ecosystems by further development of genomic tools for ecosystem research. This will benefit research programs in the DOE Office of Energy Efficiency and Renewable Energy, other federal agencies such as the Environmental Protection Agency and the Department of Agriculture, and state extension progams. Within the DOE Office of Biological and Environmental Research (DOE BER), this project will enhance the goals of the Program for Ecosystem Research (PER) to understand and predict effects of environmental changes associated with energy production on terrestrial ecosystems. PER has encouraged explorations across levels of biological organization and the use of genomics in ecology. This project will also fit goals of the Genomic Science Program of DOE BER to characterize the functional repertoire of microbial communities in natural environments and position ORNL to compete for DOE's planned investment in Genomic Science centers that focus on Carbon Cycling and Climate Change Research.

Results and Accomplishments

We have successfully (1) designed microcosms enabling us to semi-hydroponically grow plants under anexic conditions to collect, and accurately identify root exudates; (2) identified some of the major root exudates derived from the switchgrass cultivar "Alamo" using HPLC and GCMS methods; (3) set up microcosms to identify exudates from three different switchgrass cultivars exhibiting distinct root architectures to look at genotypic variation; (4) designed and initiated labeling of plant material using an airtight, closed circulation CO_2 chamber for producing ^{13}C labeled plant biomass and exudates for soil incubations; (5) conducted soil incubations using synthetic exudate analogs; and (6) developed the initial simple compartment model of microbial community dynamics. During FY 2010 we will finish publications from data collected in previous years and complete follow-on experiments under the new BER SFA funded last year.

Publication

Castro, H. F., A. T. Classen, E. E. Austin, R. J. Norby, and C. W. Schadt. In press. "Soil microbial community responses to multiple climate change drivers." *Applied and Environmental Microbiology*.

05169

Design, Simulate, and Prototype Facilities for Macroscale Experiments of Ecosystem Response to Climate Change

Paul J. Hanson

Project Description

New advanced facilities are urgently needed for rigorous, scientific evaluations of the responses of complex ecosystems to unique climate conditions not observable in current natural settings or through the use of climate gradients. We designed a next-generation, state-of-the-art experimental system needed to evaluate and understand responses of terrestrial ecosystems and their components to simultaneous above- and belowground warming expected for a range of future climate scenarios. We envision a long-term research program using new experimental systems to address uncertainties in process-level responses of microbial, plant, and animal communities in whole, intact ecosystems. The proposed effort included a physical (heat and mass flow) and biological modeling phase to establish performance criteria for the facilities, engineering design studies to optimize specific plans, and the development of physical prototypes to generate proof-of-concept data sets for peer-reviewable summaries of the new methods. The manipulative systems were designed for application to a wide range of important vegetation types.

Mission Relevance

The objective of this project was to design, simulate, and prototype facilities for macro-scale experiments of ecosystem responses to climate change and to evaluate the magnitude of biological responses associated with this new approach. Such facilities are needed because by 2100 future terrestrial environments may be 4 to 8°C warmer than today depending on their location on Earth. An overlooked reality is that mean deep (>1 m) soil temperatures will also warm with climate change. Therefore, we concluded that experimental systems must be improved to provide the best atmospheric and soil conditions appropriate for characterizing terrestrial ecosystem responses to year 2100 scenarios—air and soil warming by as much as 8 to 10°C. To achieve realistic future warming, ideal experimental systems should elevate both air and soil temperatures while retaining diurnal and seasonal patterns of the target ecosystem.

Results and Accomplishments

Several belowground warming systems were conceptualized and modeled with the general-purpose heat conduction code HEATING 7.3 to arrive at a suitable design. The original concept of a deep soil warming system accessed from an excavated trench was plausible, but it proved to be impractical because the deep-horizontal heaters would have had to extend well beyond the edges of the target-treatment soil volume. Infrared heating of the ground surface by itself was also simulated as an alternate design, but it did not achieve the desired temperature differential (ΔT) throughout the soil test volume. The original concept was ultimately replaced by a novel deep-circumferential heating design. Having accomplished the conceptualization and simulation of an optimized experimental design for deep-circumferential soil warming, project personal produced and completed working drawings for the translation of the theoretical concepts into a workable design for prototyping and testing. Final working drawings were completed and made available for physical construction subcontracting on May 1, 2008.

Measured biological responses to warming were initiated prior to the initiation of warming an including: automated CO_2 efflux rates, depth-specific observations of soil gases, pre-treatment and periodic measures of soil carbon levels, mineralized nitrogen or other essential elements, and microbial population changes.

Prototype operation and performance. The prototype heating was initiated at 2:15 PM, January 1, 2009, and continued with only minor interruptions until November 13, 2009. Target air differential temperatures of +4°C for air temperature were achieved immediately. The same target for soil temperatures to depths as low as 2 m below the soil surface were achieved after 14 d. This rate of heat transfer and storage was faster than originally modeled, but suggests that adequate engineering capacities had been built into the prototype.

The new method for achieving below ground warming successfully captured both diurnal and seasonal patterns of temperature increase at multiple soil depths. Using only a two control points (air temperature and a single deep soil reference point), our method is able to reproduce short term and seasonal temperature dynamics that other warming technologies have either ignored or not been able to achieve. Temperatures for all soil depths routinely approached our target differential of +4°C after day-of-year 59 when initial optimization of controls was achieved.

Selected biological responses. Biological data collection activities have been completed, but the full range of biological data collected is still being analyzed at the time of this report. Automated data for soil CO_2 efflux from the forest floor is, however, now provided as an illustration of the biological importance of this new warming technology. Surface soil efflux (often termed soil respiration) is the complex combination of root, mycorrhizal fungi and heterotrophic microbial activities (fungi and bacteria) belowground. We had anticipated a proportionate increase consistent with the ambient temperature response curve with warming, but we found a disproportionate increase significantly above that curve. We believe these data show that our new systems capacity to successfully generate deep soil warming in a logical and energetically correct manner has produce enhanced biological activity in a manner never before measured under manipulated field-experiment conditions. This finding when verified with other biological data being finalized suggests that it will be important for the scientific community to seriously consider using this warming technology to capture appropriate responses of ecological systems to future warming scenarios associated with climate change.

Projected energy needs for routine operation. For heating of the 3 m prototype to +4°C throughout most of 2009 we measured energy use of both the above- and belowground warming system components. Estimates include the period from February 28, 2009, through November 12, 2009. This measurement

period excludes the warm up and debugging period of operation of the prototype that began on January 7, 2009, but it includes soil having water contents at field capacity or above (during rain events), the dry summer periods, and a rewetting period throughout the autumn of 2009. The mean daily rate of energy use was as follows:

Current mean daily rate of energy use of the 3 m prototype (7.1 m^2 of heated area):
Belowground heating = 9.1 kWh d^{-1} or 1.3 kWh d^{-1} m^{-2}
Aboveground heating = 150.0 kWh d^{-1} or 21.1 kWh d^{-1} m^{-2}

This energy expenditure of approximately 4700 kWh per month is equivalent to that used to cool a very large home during the hot summer months.

The current prototype has an air turnover rate of 3.3 times per minute. That level of air turnover may not be essential or desirable to the warming treatments or to the elevation of CO_2 in future studies. Therefore heating requirement calculations are based on an air turnover rate of one exchange per minute. Scaled to one air exchange per minute per square meter of treated surface area heating of new experimental systems is expected to approach the following:

Belowground heating = 0.39 kWh d^{-1} m^{-2}
Aboveground heating = 6.39 kWh d^{-1} m^{-2}

For belowground heating of a 12 m experimental plot, actual measured energy use rates would be similar or even lower due lower heat migration from the plot driven by a reduced soil volume to edge ratio. Belowground heating in an actual experiment would operate all year. We expect lower annual energy use for aboveground warming through optimized enclosure designs (perhaps an automated and removable roof) and efficient yet operationally logical application of the heating treatments. For example, we might decide to forgo heating during the winter months when air temperature fall below -10°C.

Program Development Accomplishments

The improved ecosystem warming approaches develop under this LDRD project have led to a fivefold increase in funding for ORNL's Climate Change Response Science Focus Area (CC Response SFA) activities (an increase from $1 to $5 million per year). The initial LDRD investment of $700K over 2 years is expected to return 90 times this amount over the duration of the newly funded project (up to 3 years of construction and development followed by 10 years of experimental operation). Funding allocated by DOE BER to the CC Response SFA in FY 2010 is $4.5 million. With an anticipated overhead fraction of 41.7% the $0.75M investment in LDRD Project 05169 will be paid off in one year of continued funding with $1.1M to spare.

In addition to the funded CC Response SFA activity, the development of this expertise at ORNL has also lead ORNL to be able to compete with other DOE national laboratories the right to design and operate next generation studies in difficult arctic ecosystems. Those plans are still pending DOE review. Arctic ecosystem projects would also represent multi-million dollar per year efforts for periods lasting 10 years or longer.

05199

Next-Generation Computational System for Biological Annotation

R. W. Cottingham, S. D. Brown, A. A. Gorin, and L. J. Hauser

Project Description

Most of the genome sequences that have been annotated are rapidly becoming outdated because the annotation process is static and cannot easily integrate new types of data, novel algorithms, or emerging biological concepts (e.g., microRNA regulation from "junk" DNA). Fundamentally, the existing annotation systems are capturing only a small fraction of available knowledge both in terms of volume of the linked experimental information and in terms of biological understanding of the targeted organisms.

We propose a next-generation system to address a number of crucial existing bottlenecks. Our primary goal is to create easy and intuitive access to the annotation process for a wide experimental community, so specialists beyond the core annotation team can contribute their expertise and experimental results directly to the system. The proposed system is designed to (1) support complex system biology concepts, (2) allow both manual curation and fully automatic updates, and (3) provide for evolution of new concepts with minimal implementation effort. The developed framework will be applied to construct a working model of Gene Regulatory Networks (GRNs) in *Clostridium thermocellum* that will generate experimentally testable predictions of expression levels of a selected set of genes under specified conditions.

ORNL has been a leading center for genome annotation. This project will develop a prototype system for the future to enhance ORNL's position as a center of excellence in biological annotation and provide a long needed transition toward data management for systems biology.

Mission Relevance

The capabilities developed by this research will be relevant to the Systems Biology Knowledgebase program of the DOE Office of Biological and Environmental Research (DOE BER) and areas of data management and analysis in support of annotation for key DOE BER programs such as Genomic Sciences Systems Biology, the Joint Genome Institute partnership, Bioremediation, Microbial Sequencing, and Genome Annotation that will be critically dependent on appropriate computational capabilities for data management, annotation, and support of experimental direction. The prototype developed in this project will demonstrate a new approach that could be expanded for these programs and the larger research community.

Results and Accomplishments

Starting with available experimental data from *C. thermocellum*, we have evaluated several bioinformatic tools for elucidating gene regulatory networks using data from other sources. And we investigated alternative computer languages for representing biological data that also is machine readable and will readily support data integration.

Biological samples have been collected that will be analyzed using the high-density tiling arrays. The design of the high-density tiling array has just been finalized and the arrays have been ordered. Methods for RNA prep have been developed for RNA-seq.

Elucidating gene regulatory network in *Clostridium thermocellum*

Gauging operon prediction quality. We tested several methods to assess quality of operon predictions by using microarray data, even if only a few are available (for *C. thermocellum* we had 7 arrays), and based on this we demonstrated that DOOR database predictions are the best.

Editing operon predictions. We developed and implemented a methodology for "editing" individual operon predictions based on the available microarray data. For a comparison, we performed editing on *S. oneidensis* and *E. coli*, where there are experimentally confirmed operons and vast amounts of expression array data. Our algorithm made recommendations on changing boundaries of many operons. More changes were suggested for *C. thermocellum* than for either *S. oneidensis* or *E. coli*.

Reconstructing operons from microarray data only (de novo reconstruction). We also attempted to predict operons for all three organisms *de novo*—by using only microarray information. There was good agreement with both the DOOR predictions and with the experimentally verified ones (as judged by EcoCys database).

Predicting gene interaction networks from microarray data. Finally we have attempted to investigate regulons—"long-distance" genome dependencies in all three organisms. For *S. oneidensis* and *E. coli*, we were able to generate graphs of regulons that show many known pathways. With additional microarray data the same approach will yield insights for *C. thermocellum* too. In year 2, we will combine the regulon graph approach with phylogenetic information from promoter regions.

Computational methods for biological data representation

One aspect of our project aims to develop a new approach for representing biological data that takes advantage of capabilities found in recent technical standards such as XML. An approach currently under investigation is a data description language suitable for capturing biological content of the data, the Extensible Markup Language for Biology (XMLB). We will also investigate SBML and next-generation standards such as OWL as data description languages with similar properties that can also provide capabilities to represent semantic meaning and translate more directly into wiki forms.

Develop improved experimental methods

During the initial period, experience was gained in mRNA enrichment for the RNA-seq experiments, and samples have been obtained that will be used for RNA-seq and tiling array studies. Probes have been designed for the tiling arrays, which are being finalized in consultation with the vendor and will then be produced and delivered.

The purified RNA from each sample will be used as the template to generate cDNA copies labeled with Cy3-dUTP for tiling microarray studies. We will use the total RNA prepared for microarray analyses to enrich for mRNA, cDNA generation, and RNA-seq analysis. Dr. Brown is presently collaborating with Dr. Guido Krupp, founder of AmpTec GmbH (Germany) and testing the company's products, those under development and in conjunction with other commercial enzymes and amplification kits. We have obtained encouraging preliminary results using the ExpressArt® technology (AmpTec GmbH) for linear mRNA amplification following the manufacturer's instructions. We have observed approximately one-third of samples consistently contained DNA derived from *C. thermocellum* mRNA in Sanger sequence analysis of clone library data. We did not observe any bias against specific cDNAs in this limited sample set and showed that including an RNase R treatment or mRNA-ONLY treatment (Epicentre Biotechnologies, Madison WI) did not increase the percentage of enriched mRNA. This propriety technology is being improved and tested in Dr. Brown's laboratory, and we plan to incorporate future refinements into our sample preparations. The quality of cDNA generated using the ExpressArt kit will be assessed using an Agilent 2100 bioanalyzer. The cDNA will be further assessed to preliminary Sanger sequencing of small clone libraries before next-generation sequencing analysis. In FY 2010 we will use

analysis of microarray data to select samples for RNA-Seq analysis and plan to utilize two 454 Titanium runs to generate transcript data for expression and regulatory analyses.

Program development

Our strategy of focusing on developing new kinds of annotation based on transcriptomics and developing new methods for structuring a new kind of knowledgebase has already paid off. This two pronged approach provides synergistic opportunities for funding. We have received ARRA funding for Knowledgebase R&D of $3.2M and an additional $0.5M to develop a pilot Knowledgebase for the Bioenergy Research Centers. We are also developing proposals for a transcriptomic approach to improved genome annotation and bioforensics.

05201

Development of Novel Biocatalysts for the Production of Fuels and Chemicals from Synthesis Gas

James G. Elkins, Brian H. Davison, and Yunfeng Yang

Project Description

Bio-synthesis gas (syngas) is an energy-rich feedstock produced from the gasification of lignocellulosic biomass. Biotechnological improvements in syngas utilization have been difficult due to the lack of industrial strains that can be manipulated at the genetic level. To tackle this, we propose to develop novel biocatalysts amenable to genetic engineering. Robust genetic systems in syngas-utilizing strains would allow manipulation of carbon fixation pathways and redirection of carbon flux towards alcohols and potentially other high-value chemicals. For biofuel production, we plan to engineer organisms that are capable of fixing the carbon and energy available from syngas into the 4-carbon alcohol, 1-butanol. Butanol is known to possess advantages over ethanol including a higher energy density and it can be blended directly with gasoline at increased concentrations. Our research plan includes these primary goals: (1) rational engineering of *Rhodospirillum rubrum* to produce butanol, (2) characterization of butanol producing strains of *R. rubrum* using bench-scale fermentation and determination of solvent tolerance and rates of production, and (3) development of genetic tools for other syngas-utilizing Gram-positive microbes. These tasks will be carried out in parallel and then integrated in year two depending on our results.

Mission Relevance

The work proposed here is highly relevant to several current programs and the overall mission of the Biomass Program of the DOE Office of Energy Efficiency and Renewable Energy, which has increased their interest in gasification routes and has funded one demonstration plant for syngas conversion to ethanol which suggests a strong interest in this field. Enabled by the data generated from this work, a full systems biology approach would be proposed for strain optimization which would be of interest to the DOE Office of Biological and Environmental Research (DOE BER). Several potential academic partners have approached us in the broad area of syngas fermentation. These results would allow a joint submission to the university-led DOE BER Genomic Science Program annual call. In addition, this work could also potentially lead to advanced concepts regarding biomass conversion through gasification which could be incorporated into proposals for renewed future funds for the BioEnergy Science Center.

Results and Accomplishments

Several different standard growth conditions have been established for *Rhodospirillum rubrum* ATCC 11170. Growth on 100% CO has been established using RRNCO medium with 0.5 bar overpressure with shaking (250 rpm) at 30°C in the dark. *R. rubrum* was able to grow in the presence of 2% (w/v) 1-butanol, isobutanol, ethanol, and isopropanol. These results suggest that wt *R. rubrum* ATCC 11170 is not highly sensitive to primary and secondary short-chain alcohols but adaptation experiments need to be conducted in order to test the maximum concentrations that the organism could tolerate. For genetic manipulation of *R. rubrum*, a set of broad-host-range cloning vectors based on pBBR1MCS were obtained and tested for replication and stability. The bcd operon from *C. acetobutylicum* was cloned into pBBR1MCS-5 and mobilized into *R. rubrum*. Crossover PCR constructs that will fuse the CO-sensitive promoter elements from *R. rubrum* to the *bcd* operon and the *adhe* allele from *C. acetobutylicum* are in progress. To evaluate recombinant strains of *R. rubrum* producing butanol from syngas, a bioreactor consisting of a 2 L Bioflow 2000 New Brunswick Scientific vessel with full controls is operating exclusively for this project. Initial work under way includes growing *R. rubrum* anaerobically with light. Three replicative plasmids have been evaluated including, pSOS95Del (erythromycin), pHV33 (thiamphenicol), and pIKM1 (erythromycin), all of which have been successfully used for DNA transformation in a variety of clostridial species. Transformation attempts have been made using a sonoporation technique that we have recently established for Gram-positives. However, no transformants were observed for *C. ljungdahlii* and *C. carboxidivorans*. When the plasmids were protected from DNAse activity by methylation of Dam/Dcm or MspI, the results were also negative. This work is ongoing and additional parameters are being systematically tested for establishing a transformation protocol.

05221

A Systems Biology Approach to Study Metabolic and Energetic Interdependencies in the *Ignicoccus–Nanoarchaeum* System

Mircea Podar, Robert Hettich, Martin Keller, Dean Myles, and Jeremy Smith

Project Description

The archaea *Nanoarchaeum equitans* and *Ignicoccus hospitalis* engage in one of the simplest and most efficient symbiotic relationships. However, the mechanisms by which they recognize each other, establish physical cell contact and regulate the flux of metabolites are unknown. We will use this simple system to develop a cross-disciplinary, experimental and computational platform to study cellular and molecular mechanisms that enable interspecific microbial interactions. Based on complete genomic sequences we will conduct gene expression, proteomic and metabolic profiling of the two organisms during different stages of their association. Data will be integrated into a reconstructed model of the intrinsic metabolic fluxes and genetic regulatory processes as well as those triggered by symbiosis. The specificity of the interaction will be dissected using comparative genomics, gene expression and proteomics with Ignicoccus species that are not symbiotic with *N. equitans*. This will allow us to identify candidate genes that mediate cell-cell communication and to study physical interaction processes at membrane level. Structural and molecular dynamics characteristics of selected proteins and protein complexes will be investigated using computational and experimental methods to understand the mechanisms of intercellular interaction. General principles will be derived on interspecific relationships and how they are mediated at genomic level.

Mission Relevance

Few, if any, microbes in the environment live in isolation of each other. Microbial metabolic synergies and specialized syntrophic relationships are responsible for numerous environmental processes of significant importance for the DOE mission including anaerobic methane oxidation, and biotransformation of xenobiotics and heavy metals. Holistic studies of microbial interspecies relationships are still lacking due to difficulties in maintaining symbiotic and syntrophic systems in the laboratory. Our proposed research is aimed at deciphering physiological, molecular, and genomic mechanisms of interaction between two species. By combining an interdisciplinary, systems biology approach to study this system, we will establish a platform to study more complex syntrophic associations and will derive fundamental principles on how microbes interact. This research is of high importance to DOE Genomic Science Program and will be part of future ORNL Science Focus Area research or collaborative university-led Genomic Science solicitations. Integrated systems biology research on syntrophic/symbiotic relationships is also of high relevance to microbial communities of interest to National Science Foundation programs, to the Astrobiology program of the National Aeronautics and Space Administration, and to the Microbiome program of the National Institutes of Health.

Results and Accomplishments

A batch cultivation system was developed for *Ignicoccus* species and for *Ignicoccus–Nanoarchaeum*. We have isolated sufficient high molecular DNA for genomic sequencing from *I. islandicus* and *I. pacificus*. Sequencing will utilize the new 454 FLX Titanium paired end libraries protocol and we estimate to achieve >95% coverage from a single run. We have also developed a quantitative polymerase chain reaction assay for both *I. hospitalis* and *N. equitans* with linear detection sensitivity to ten cells. We have developed FISH probes and a protocol to stain the three *Ignicoccus* species as well as *N. equitans* with specific fluorescent oligonucleotides ADN with antibodies. We have obtained NimbleGen high-density oligonucleotide microarrays for both species. We isolated total RNA, synthesized and labeled cDNAs and hybridized several microarrays. By analyzing the genes that are differentially expressed between the different cultures, a preliminary set of ~300 genes were identified to be up or down regulated in *I. hospitalis* in response to *N. equitans*. We performed several proteomic runs on both the LTQ linear trapping quadrupole mass spectrometer and the high performance hybrid LTQ-Orbitrap mass spectrometer. We obtained semi-quantitative data on a significant fraction of the proteomes of the two organisms, being able to detect 988 *Ignicoccus* proteins (70% of the theoretical proteome) and 414 *N. equitans* proteins (75% of its proteome). By analyzing the proteomic data of *I. hospitalis* grown in the presence or absence of its symbiont we identified several dozen proteins present at significantly different levels. We also identified several putative *I. hospitalis* proteins that may have been transferred to *N. equitans*, including several membrane proteins. The transcriptomic and proteomic data are analyzed in an integrated metabolic fashion. Several key proteins detected have been selected as targets for molecular dynamics simulations to understand their role in the membrane processes at the *Ignicoccus–Nanoarchaeum* interface.

Publications

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Conference on Archaea Ecology, Metabolism & Molecular Biology, July 26–31, Waterville Valley Resort, New Hamphire.

05256

Developing a Systems Biology Approach for Linking Genetic and Environmental Constraints to Primary Productivity in Model and Nonmodel Species

David J. Weston, Yunfeng Yang, Rich Norby, Stan Wullschleger, and Chris Schadt

Project Description

Global warming is expected to drive major shifts in species composition in the coming decades, and these community-level changes will greatly affect many important processes in terrestrial ecosystems. Given the importance of this issue, it is unfortunate that we are still unable to associate specific genetic attributes to the physiological traits that drive subsequent species compositional shifts. Using three plant model species (Arabidopsis, soybean, and poplar), we will use a comparative network approach to identify groups of genes that are conserved among species and that are associated with net CO_2 assimilation and energy absorbance. These conserved genes or gene networks (i.e., modules) will provide a scaffold by which orthologous genes from non-model species can be further evaluated for associations with net CO_2 and energy gain. We will test this approach using switchgrass, an important non-model species that is adapted to a wide range of environments. Cultivars from contrasting habitats will be collected and used to evaluate within-module gene sequences and expression variation to net CO_2 and energy gain under heat stress and recovery conditions. Completion of the proposed work will provide a systematic framework for identifying genetic and environmental constraints on plant productivity in non-model organisms.

Mission Relevance

Our research is relevant to several areas of interest to DOE: bioenergy, carbon cycle science, global climate change, and ecology. This is especially true as it relates to the development of novel approaches that would allow us to conduct functional genomics on non-model organisms. Our challenge is to have a well-developed and tested capability in the next 12 months. If successful, we believe that our efforts will contribute to the strategic goals of the DOE Office of Biological and Environmental Research (DOE BER) through its Genomic Science Program and Climate Change Mitigation and Response Scientific Focus Areas. We expect that our results will feature prominently in an anticipated Genomic Science Center for Carbon Cycling and Biosequestration solicitation and new experimental research being proposed to DOE BER.

Results and Accomplishments

Physiological characterization of temperature effects on photosynthesis was accomplished by creating temperature response curves for Arabidopsis, soybean, and poplar using gas exchange cuvettes coupled with chlorophyll-a fluorescence. This physiological survey demonstrated that soybean exhibits greater rates of photosynthesis under heat than do Arabidopsis and poplar.

To gain insight into the possible biological pathways driving greater thermotolerance in soybean, we used genome-wide gene expression patterns from both RNA-sequencing and microarrays. Our results indicated that soybean had enhanced expression of genes involved in detoxifying reactive oxygen species (ROS) and gene number expansion in the heat shock proteins (specifically, the Hsps17s family). Biochemical

analysis corroborated this systems-level conclusion by revealing enhanced total antioxidant capacity for soybean relative to Arabidopsis and poplar under heat.

Ideas and results from this project resulted in additional accomplishments, including (1) the successful funding of a Joint Directed Research and Development project (PI Aimee Classen, University of Tennessee, Knoxville); (2) the successful funding of a proposal submitted to Feedstocks Genomics, U.S. Department of Agriculture (PI Victyor Buscov, Michigan Technological University); and (3) invited speaking engagements to the University of California, Los Angeles, Medical Genomics group, the University of Missouri Integrative Biology Program, the iPlant consortium, and the 2010 Gordon Research Conference.

05572

Mitigation of Atmospheric CO_2 through Management of Woody Biomass

Anthony W. King and Tristram O. West

Project Description

This project is a scientific assessment of the opportunity for near-term mitigation of atmospheric carbon dioxide (CO_2) concentrations through global management of woody biomass and wood products. Estimates of the global sequestration potential for wood storage are still highly uncertain but are on the order of 10 billion metric tons of carbon per year (10 Gt C/year), exceeding fossil-fuel emissions of 8 Gt C in 2006. If that potential is realized over several decades, woody sequestration is a significant part of any portfolio of greenhouse gas (GHG) mitigation strategies. Using a novel combination of wood harvest statistics, global vegetation models, and full GHG accounting of wood harvest consumption for energy and storage, we will assess the potential of woody biomass sequestration by evaluating (1) the global annual supply of woody biomass over the period 2010–2050 and (2) the best use of that wood with respect to mitigation of atmospheric CO_2, measured in CO_2 equivalents to account for non-CO_2 GHG.

Mission Relevance

A robust, scientifically based assessment of the CO_2 emissions mitigation potential in management and best use of woody biomass is relevant to DOE missions in energy resource analysis and management, environmental quality and science, particularly those of the Office of Biological and Environmental Research (BER) The results of this project will allow for the proper inclusion of woody biosequestration in analyses of fossil-fuel emissions mitigation portfolios to avoid dangerous climate change. It promises to be a strategy with fewer technological hurdles to deployment and minimal negative, if not positive, impacts on environmental quality. It will also strengthen DOE's portfolio of carbon cycle science. Results of this project will benefit the U.S. Department of Agriculture (USDA) Forest Service or any other federal agency involved in evaluation and eventual implementation of strategies to mitigate fossil fuel emissions. It will directly benefit those looking at biosequestration, and indirectly those who are looking at other alternatives by establishing a robust scientific base for woody biosequestration and it role in any mix of strategies.

Results and Accomplishments

We have identified current wood harvest and storage as a proxy for woody sequestration potential constrained, to first approximation, by land availability, forest productivity, cost of extraction, etc. Estimates of current global wood harvest are on order 1–1.5 Gt C per year. Approximately 30% of that

estimate is waste burned or left to decay at harvest. Additional carbon is lost during conversion to wood products, with only 20–25% of delivered wood harvest sequestered in long-lived products or landfills. We estimate accordingly that current global wood product sequestration is on order 0.1–0.2 Gt C per year. Achieving global wood sequestration on order of 10 Gt C per year will require increasing wood storage by a factor of 100. Extremely aggressive forest and wood management will be required to even approach that level of increase. Potentials for woody biosequestration on order 1–2 Gt C per year are perhaps more likely.

ADVANCED ENERGY SYSTEMS

05011

Nanocomposites for Advanced Thermoelectrics

Brian C. Sales, David J. Singh, Hsin Wang, Jane Y. Howe, and Michael A. McGuire

Project Description

Thermoelectric devices can convert heat into useful electricity with no moving parts. Considerable progress has been made in improving the efficiency of these devices over the past 15 years. Recent improvements in thermoelectric efficiency in thin-film superlattice structures appear to be dominated by a reduction in the lattice thermal conductivity due to scattering from nanograins. A very recent study showed, however, that the electronic structure of a good thermoelectric material, PbTe, could also be improved further through the addition of certain chemical dopants such as thallium. We investigated the effects of the introduction of nanograins into bulk samples of good thermoelectric materials and to explored the ability of certain chemical dopants known as "valence skippers" to tune the electronic structure. One goal was to understand how interface scattering between nanoparticles could lower the thermal transport without significantly altering electronic transport. A second goal was to explore the ability of "valence skippers" such as thallium to improve overall thermoelectric efficiency.

Mission Relevance

This project is relevant to DOE's energy mission. Thermoelectric materials can be used to construct all solid-state devices that directly convert heat into electricity with no moving parts. The heat can come from the sun or can be waste heat generated by a variety of sources including power plants, chemical plants, or automobiles. The basic idea is use thermoelectric modules to convert part of the heat back into useful electricity, thereby improving overall energy efficiency. For automobiles, the net result would be to use less gasoline. The main problem with today's thermoelectric materials is poor efficiency. As a result of this project we have developed a much better understanding of scattering at the nanoparticle host interface and how to "tune" the electronic properties of a nanocomposite for optimum thermoelectric performance. Partially as a consequence of this project, we have incorporated a significant thermoelectric effort into a DOE Office of Basic Energy Sciences program to be funded in FY 2011.

Results and Accomplishments

We discovered that silicon or $Si_{0.8}Ge_{0.2}$ melts form a two-phase system with a variety of clathrate phases including $Ba_8Al_{15}Si_{31}$. Synthesis and transport measurements were carried out using silicon or $Si_{0.8}Ge_{0.2}$ as the host phase and $Ba_8Al_{15}Si_{31}$ added to reduce the thermal conductivity. A large number of nano-structuring approaches were explored. Planetary milling of the material for 40 h in a sealed argon-isopropanol environment produced the best nano-phase material as determined by X-ray diffraction and electron microscopy measurements. The resulting powder was compressed into a solid body using a hot-press or a spark-plasma sintering system. About a 20% increase in ZT was achieved relative to material

used by NASA. Recent reports of a 100% improvement in ZT for similar materials were not reproduced to date. To determine the correct size distribution we need to know how much heat is carried by phonons with a given frequency. David Singh has started to develop the computer codes necessary to perform just such a calculation. Singh completed a calculation of the phonon density of states for a $Si_{0.8}Ge_{0.2}$ alloy. A variety of valence-skipper dopants, including thallium and antimony, were added to PbTe in various amounts. We verified a recent report that 2% thallium in PbTe tunes the electronic structure and increases the ZT of p-type PbTe by 100% resulting in ZT ≈ 1.5 at 700 K. We found that small amounts of various impurity phases added to PbTe could significantly reduce the thermal conductivity, but to date we have not succeeded in simultaneously tuning the electronic structure. Phonon and electronic structure calculations were completed by Singh's group on PbTe and several other possible thermoelectric materials.

Publications

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05015

Irradiation of Advanced Light Water Reactor Fuel in the High-Flux Isotope Reactor

Joel McDuffee, Randy Hobbs, Larry Ott, Donald Spellman, Dennis Heatherly, and Ronald Ellis

Project Description

This project developed a new test capability at the High-Flux Isotope Reactor (HFIR) that will allow testing of advanced nuclear fuels under prototypic, light-water reactor (LWR), operating conditions in approximately one-half the time it takes in other research reactors. This capability will be demonstrated by irradiation of test rods that each contain prototypically dimensioned LWR fuel pellets in pins. As part of this work, a test plan was developed, test fixtures and components were designed and fabricated, and safety evaluations were developed. The test configuration will be used to conduct a SiC clad/uranium-fueled experiment in a HFIR Vertical Experiment Facility (VXF) position.

Mission Relevance

This project is focused on advanced fuel/cladding experimental capabilities in HFIR and its capability to duplicate commercial LWR operating conditions. With the resurgence of nuclear power in the world, many years of pent-up fuels testing will now have a facility at which to conduct a complete fuels experimental program, including fuel development, materials development, experiment fabrication, in-reactor testing at LWR conditions, and utilization of ORNL state-of-the-art post-irradiation examination. There is widespread interest in both the commercial and governmental sectors to support development of longer-lived, robust, advanced fuel materials. Westinghouse/CTP, Knolls Atomic Power Laboratory, and the Nuclear Regulatory Commission have all recently inquired about ORNL's capabilities for fuel testing and examination.

Results and Accomplishments

At the end of FY 2009, the ORNL team had (1) completed and approved design drawings, (2) fabricated the assembly basket with a hafnium shield, (3) fabricated seven capsules containing UN fuel pellets inside a SiC clad, and (4) assembled the fabrication notebook for insertion into HFIR.

The team had great difficulty locating a suitable hafnium shield for this work. Despite months of searching, the team could not find a hafnium cylinder of the size and shape required for this experiment. As a last resort, the project purchased hafnium sheet, wrapped it around a steel mandrel, and welded the seam. This was an unexpectedly laborious and expensive process, but it was successfully completed.

The shield was fabricated with a thickness of 0.107 in., which design calculations indicate will lead to linear power generation rates in the hottest of the pins in the middle axial position that will satisfy the UO_2 safety case. The depletion of the hafnium is at a rate that offsets the burnup effects of 3.8 wt% enriched UN fuel (or 4.95 wt% enriched UO_2 fuel), such that the linear heat generation rate of the fuel stays relatively constant, at least over the first few cycles.

Although we were not able to load the fuel capsules into the reactor before the end of the LDRD, Ceramic Tubular Products initiated a Work for Others contract to continue this project. Irradiation is tentatively scheduled to begin in December 2009.

Publications

Ellis, R. J., J. C. Gehin, J. L. McDuffee, and R. W. Hobbs. 2008. "Analysis of a fast spectrum irradiation facility in the high flux isotope reactor." Paper 533 in *Proc. of PHYSOR'08 American Nuclear Society International Conference on the Physics of Reactors, Nuclear Power: A Sustainable Resource,"* Sept. 14–19, Interlaken, Switzerland.

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05057

Automated Freeform Construction Technologies and Materials

François G. Pin, Randall F. Lind, Catherine H. Mattus, John J. Jansen, Dan J. Naus, Jan Kosny, Robert E. Norris, Jr., and Leslie R. Dole

Project Description

Our objective is to investigate and develop the enabling freeform technologies for automated construction of large-scale components and structures, in particular residential and low-rise commercial buildings. The

two key areas are (1) materials selection and emplacement properties, and (2) the processes and devices through which these materials can be precisely deposited using automation. We will first investigate materials that lend themselves to automated freeform construction processes as well as deposition strategies that maximize strength, geometric accuracy, and throughput. In close coordination, we will also investigate deposition devices and processes that can efficiently support the automated layout of these materials. We will consider the paradigms of in-factory automated fabrication of building modules and on-site automated construction processes. The goals and deliverables of the project are to (1) develop and evaluate a suite of materials and associated automation-suitable deposition controls that demonstrate the feasibility of the freeform automated construction concept, and (2) develop enabling science experiments and tests, including a three-dimensional gantry-based proof-of-principle system, to illustrate the enabling deposition processes at a scale relevant to building construction (e.g., 8 ft × 4 ft wall panel/module).

Mission Relevance

Automated freeform construction (AFC) has the potential to directly benefit the DOE Building Technologies Program by producing buildings with better energy efficiency, strength, environmental sustainability, material utilization, higher quality of assembly, and durability, while lowering waste, costs, and building time. Improved energy efficiency, reduced waste, and the ability to incorporate greener, recycled materials in the deposited cementitious mixtures will also lower greenhouse gas emissions. The Department of Defense could benefit from the potential of AFC to produce complex, multilayer, blast-resistant structures in forward areas rapidly and with limited personnel. The Federal Emergency Management Agency could benefit from the potential of AFC to produce structures rapidly for disaster relief, as well as structures that are resistant to extreme weather events. The Defense Advanced Research Projects Agency and the Office of Naval Research are interested in freeforming large-scale components and molds for the casting and tooling industries. The planetary exploration programs of the National Aeronautics and Space Administration have indicated interest in *in situ* automated construction of extraterrestrial structures.

Results and Accomplishments

We completed a coordinated review of the composite cementitious materials and related extrusion technologies suitable for free-forming large-scale structure components, and developed target ranges of rheological and deposition parameters for cementitious materials that would support the concept of multi-purpose, multi-material, multi-layer free-form construction. Nearly a hundred mixtures of cementitious materials were investigated and experimentally evaluated to progressively achieve fast set times, and suitable free-formability (i.e., plastic and cohesive enough for extrusion), gel time, and gel strength (to support next layer). The major result in this materials area is a basic concrete formulation that achieves both excellent extrusion and post-extrusion characteristics. An invention disclosure on this unique free-formable material formulation has been filed. We have also developed a second class of mixtures using greener, recycled, by-product materials as lightweight aggregates to achieve free-formable cementitious mixtures with higher insulating properties. To support quantitative tests of the materials, we have developed a set of basic instruments, including several penetrometers, to evaluate the gel and set strength and time histories over our time scale of interest (from seconds after mixing to a few hours). We have also developed several nozzles and deposition heads and an integrated gantry-based test stand capable of free-forming cementitious materials at a building relevant scale. Experiments and demonstrations of automated deposition of complex three-dimensional geometries and multi-material layers were performed to illustrate some of the novel concepts for rapid construction of building envelope components. FY 2010 funding is expected from the DOE Building Technologies Program for the initial scoping phase to generate an activity roadmap for the development and demonstration of integrated technologies for Building Information Modeling–driven automated freeform construction.

Publication

Mattus, C. H, R. F. Lind, L. R. Dole, F. G. Pin, and D. J. Naus. 2008. *Cementitious Material with Enhanced Free-Formability.* Invention Disclosure ID-2169, No. S-115, 198, Oct. 31.

05075

High-Performance Proton-Conducting Fuel-Cell Electrolytes Based on Task-Specific Protic Ionic Liquids

Sheng Dai, Timothy Armstrong, Gary Baker, Huimin Luo, and Todd Toops

Project Description

The goal of this project is to develop alternative proton-conducting media based on task-specific ionic liquids (TSILs) possessing tunable physicochemical properties toward highly conductive and robust fuel cell proton electrolytes. This project specifically addresses the research needs for the development of advanced hydrogen-based fuel-cell systems by employing novel protic ionic liquids (PILs). Highly conductive PILs are proposed to replace current, conventional polymer electrolytes as advanced proton-conducting media, achieving superior and robust fuel-cell systems. The introduction of novel proton-conducting electrolytes lies at the forefront of fuel-cell technology development. This research will build upon ORNL's extensive and pioneering expertise in development of ionic liquids. This project will allow us to develop the next generation of proton-conducting media that can (1) mitigate the current problems in polymer electrolyte fuel cells (PEMFCs) associated with platinum loss induced by acid dissolution and, more importantly, (2) be interfaced with non-platinum-based electrocatalytic systems, which are incompatible to the current fuel cell systems based on highly acidic polyelectrolytes.

Mission Relevance

To meet the specific 2010 targets of the Hydrogen, Fuel Cells & Infrastructure Technologies programs of the DOE Office of Energy Efficiency and Renewable Energy (EERE), innovative technologies in development of stable and conductive electrolytes for proton conduction under unhumidified conditions are needed. The project has the potential to achieve this goal through the development of novel PILs. This approach, with its emphasis on using novel PILs and inexpensive synthesis methods to produce useful quantities of true "designer proton conductors," is a perfect candidate for new funding under the Hydrogen Initiatives recently announced by DOE EERE and the DOE Office of Basic Energy Sciences. The new PILs that will be synthesized also have great potential for applications in solar cells, batteries, and supercapacitors. The proof of concept demonstrated by this project will place ORNL at the forefront of the field. This program is also expected to attract follow-on funding for fuel-cell and energy-storage developments from the Defense Advanced Research Projects Agency, the National Nuclear Security Administration, and private industries.

Results and Accomplishments

Vaporization enthalpies for two homologous series of ionic liquids (ILs) composed of 1-*n*-alkyl-3-methylimidazolium cations, [Imm1$^+$] (m = 2, 3, 4, 6, 8, or 10), paired with either the bis(trifluoromethanesulfonyl)amide, [Tf_2N^-], or the bis(perfluoroethylsulfonyl)amide anion, [beti$^-$], were determined using a simple, convenient, and highly reproducible thermogravimetric approach, and from these values Hildebrand solubility parameters were estimated. This approach represents the first use of thermogravimetry to determine these vital IL properties and is expected to make a significant impact in the field, particularly in areas related to their use at elevated temperatures such as in fuel cells. Our results

reveal two interesting and unanticipated outcomes: (1) methylation at the C2 position of [Imm1$^+$] affords a significantly higher vaporization enthalpy, and (2) in all cases, the [beti$^-$] anion served to lower the enthalpy of vaporization relative to [Tf_2N^-]. The widespread availability of the apparatus required for these measurements coupled with the ease of automation suggests the broad potential of this methodology for determining this critical parameter in a multitude of ILs.

We reported 16 members of an entirely new class of protic ionic liquids (PILs) derived from integrated neutralization and metathesis of superbase molecules (phosphazenes or guanidines) via a facile one-pot method. These PILs exhibit exceptionally low vapor pressures (even at 150°C), are inert to strong alkali agents (e.g., aqueous KOH), and exhibit the highest thermal stabilities yet observed for any PIL, suggesting wide potential in energy-related applications, including electrochemical capacitors and PEM-type fuel cells. A typical member of this new PIL family, 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-a]pyrimidinium bis(trifluoromethylsulfonyl)imide ([MTBDH][Tf_2N]) exhibited an enthalpy of vaporization, $\Delta_{vap}H$, of 89 kJ mol^{-1} based on the linear (zero-order) evaporative mass losses at several temperatures well below the thermal decomposition temperature T_{dcp} of 379°C. Remarkably, this value is only 15–30% lower than values determined for typical robust *aprotic* ILs using the same isothermogravimetric approach.

We investigated proton diffusion dynamics in the PIL *N,N,N′,N′*-tetramethylguanidinium bis(perfluoroethylsulfonyl)imide ([Me_4guan][Tf_2N]) using quasielastic neutron scattering (QENS) in the temperature range of 30–360 K (melting temperature of this PIL is ~290 K). These studies uncovered four distinct dynamical processes: First, the methyl group rotations exhibit broadly distributed dynamics which, on the nanosecond time scale, become visible above approximately 100 K (process 1). Second, there is a localized process with a characteristic confinement radius of about 1.6 Å, which likely involves protons of the amine groups (process 2). Processes 1 and 2 take place in both solid and liquid phases, even though the methyl group rotations in the liquid phase are likely too fast to be detected in our experiment. Above the melting temperature, there are two additional diffusional processes (3 and 4) contributing to the dynamics of the liquid phase, both appearing to be of translational character. The faster process (4) is best described as spatially restricted translational diffusion with a characteristic confinement radius of about 8 Å. It is likely that the long-range proton transfer in [Me_4guan][Tf_2N] is associated primarily with the unrestricted translational diffusion process, which is characterized by a diffusion coefficient varying from (4–14) × 10^{-11} m^{2}s^{-1} in the temperature range of 320–360 K.

Publications

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05099

Manufacturable Nanotransistors for Advanced Analog Circuits

C. L. Britton

Project Description

For the first time since nanoscale materials took front stage on research agendas around the globe, emerging fabrication technologies may unlock the power of analog nanoelectronics by enabling true integration of novel nanodevices into functional circuits. Silicon nanowire transistors (SiNWTs) offer potentially dramatic performance improvements over complementary metal–oxide–semiconductor (CMOS) devices in terms of gain (or transconductance), power consumption, and charge sensitivity. Further, their size may allow operation in the terahertz (10^{12} Hz) frequency regime, the holy grail of high-bandwidth radio-frequency (RF) communications systems. Unlike single carbon-nanotube devices, which have shown remarkable properties but are difficult to consistently produce, our approach would extend current manufacturing methods using conventional silicon to enable high-volume, high-yield manufacturing, allowing widespread application and commercialization. The proposed work would go beyond the current silicon nanowire art and focus upon the development of self-aligned-gate nanowire electronic structures for practical circuits, and capitalize on our strength in analog electronics. This research will produce an enabling technology for realization of a new class of high-speed, ultra low-power, highly miniaturized integrated circuits well suited for nanoscale sensing applications.

Mission Relevance

Modern CMOS integrated circuits depend on charge as the fundamental state variable where current is the motion of charge and voltage is the storage of charge. Any development that seeks to maximize the ability to sense either current or voltage in a circuit will contribute greatly to the ability to use a given device for analog processing. The proposed nanowire transistors would not just enhance the function, but their charge sensitivity would actually eliminate much circuitry presently required. For example, conventional circuits require that stages of amplification be added to handle very small signals without distortion. The next generation of nanowire devices, if properly designed, should be able to sense and process small input signals *directly* without the need for large amplification and its associated gain drift and temperature sensitivities. Two prime examples are Hall-effect sensors for automotive applications, which now need large amounts of temperature-stable gain, and direct sensing of biochemical interactions for DNA and proteomic arrays. This project applies to several DOE programs, including basic energy sciences, automotive, building sciences, and life sciences.

Results and Accomplishments

This research has enabled the first successful fabrication at ORNL of metal-oxide-semiconductor field-effect (MOSFET) nanotransistors. Activities this fiscal year have focused on the design, process development, in-house fabrication, and characterization of SiNWTs in nanometer length scales (with micrometer-sized features having been produced during the first year of the effort). A principal goal of the design developed here is to allow eventual mass production using conventional materials. Silicon-on-Insulator (SOI) wafers were chosen as the base substrates for prototype structures. Conventional optical lithography provided patterning of the larger structures, such as pads and interconnect traces, while electron-beam lithography (EBL) was used to define the nanometer-scale structures. Combining the two techniques and adding insulator, dopant and metallization steps required considerable process development.

Nanotransistor fabrication. The goals of design and fabrication of silicon nanowire transistors has been completely met, with nanowire lengths and widths ranging from 40 nm to 500 nm (40, 60, 80, 100, and

500 nm), and the thickness determined by the thickness of the Si-layer on the SOI wafer. Patterning the nanowires by EBL was done on a thinned SOI wafer. To thin the SOI wafer we applied a method consisting of first growing thermal SiO_2 on the wafer (i.e., converting a fraction of the Si device layer to SiO_2) and then removing this oxide using a buffered oxide etch (BOE) solution. This process gave better homogeneity across the thinned SOI wafer due to the uniformity of thermally grown oxide.

Nanotransistors characterization. In this work, we demonstrated N-MOS SiNWT fabrication, improved ohmic contact reliability, and improved individual SiNWT performance characteristics. In addition, we used commercially available spin-on-dopants (SOD) consisting of boron at 2×10^{17} ion/cm^{-3} to reduce short channel effects. A three-zone quartz-tube furnace was procured and adapted to enable thermal drive-in of the dopants (~1200°C). These improvements to the infrastructure and processing capabilities will enable further development of more complex active devices.

Representative results of electrical measurements were made. These results are very encouraging, and indicate that we are able to repeatably fabricate nanodevices with the desired characteristics. In particular, significant progress has been made to improve the noise performance for 40 nm SiNWT compared to that of the 200 nm transistors fabricated in the previous fiscal year.

SiNWTs as biosensors open up new opportunities for the chemical and bio-chemical detection by electrical means. The use of SiNEWT transistor gates offers a significant advantage over conventional FETs for sensing. Carrier mobilities in semiconductor nanowires transistors are extremely sensitive to surface charge density due to very high surface-to-volume ratio of the nanowires, which enhances gating local electric fields. Binding of biomolecules onto the nanowire surface leads to depletion or accumulation of carriers across the nanowire, which modulates the SiNWT conductance. We plan to demonstrate the extreme charge sensitivity initially using controlled pH changes in a suitably packaged fluidic nanowire device. Later, we plan to demonstrate immunochemical labeling of the gate structure to probe bioaffinitive events at ultralow concentrations.

05115

Revolutionary Method for Increasing Efficiency of White Light Quantum-Dot Light-Emitting Diodes

Chad Duty, Philip Boudreaux, Adrian Sabau, Gerald E. Jellison, Michael Hu, Steven Walker, and Charlee Bennett

Project Description

The objective of the project is to demonstrate a method for increasing the efficiency of white solid-state lighting (SSL). Covering a light-emitting diode (LED) with quantum dots (QDs) can produce a broad spectrum of white light. However, current techniques for applying QDs to LEDs suffer from a high density of defects and a nonuniform distribution of QDs, which respectively diminish the efficiency and quality of emitted light. ORNL has the unique capability to thermally anneal QD structures at extremely high power densities for very short durations. This process, called pulsed thermal processing (PTP), reduces the number of point defects while maintaining the size and shape of the original QD nanostructure. The proposed research uses PTP to anneal various QD systems on passive and active substrates and measure the resulting increase in photoluminescent efficiency. A multi-scale energy transport model is also being developed to understand the transport of energy within a QD structure and to take advantage of the enhanced properties of such nanostructured materials.

Mission Relevance

LEDs are sturdy, semiconducting wafers that are vibration and shock resistant, exceptionally long lived, and an order of magnitude more efficient than incandescent lighting. Since lighting consumes about 22% of the nation's energy, DOE has established a goal of developing SSL technology that is 50% efficient and can accurately reproduce the solar spectrum by 2025. If this goal were attained, SSL could save the country $30 billion in annual energy costs, or the equivalent of 200 million barrels of oil. DOE recently established the Next Generation Lighting Initiative (NGLI), representing a commitment of $350 million over the next six years with the goals of accelerating the development of white-light SSL and positioning the United States as a global leader in this technology. Specifically, the development of phosphors and conversion materials is considered the second highest priority (out of nine) of DOE's LED Core Technology Research Tasks.

Results and Accomplishments

During the second year of the project, the primary goals were to (1) explore and develop additional sources of high-quality quantum dot materials and (2) demonstrate a dramatic increase in the photoluminescence (PL) intensity resulting from PTP of the QD structure.

We have successfully synthesized red-emitting CdSe/ZnS (core/shell) regular QDs, green-emitting CdTeSe magic-sized QDs, blue-emitting CdS regular QDs, and blue-emitting CdSe magic-sized QDs. The term "magic-sized" relates to the ability of the QDs to emit at specific wavelengths. In addition to testing the relevant optical properties of these QDs (e.g., UV/Vis absorption and PL emission spectra), their performance was also demonstrated in the form of dried solid deposits on glass substrates, which is directly relevant to the solid-state lighting platform using the QDs as the phosphor-conversion layer.

During the first year of the project, we demonstrated an increase in PL intensity of 17% following exposure to PTP for a given sample. In this second year, we have made various improvements to the deposition techniques, the PL measurement system, and the PTP processing technique, which have resulted in almost a fivefold increase (480%) in the efficiency of the quantum dot structure with very little shift (5–10 nm) in the peak emission wavelength.

Work has also continued on the development of a multi-scale energy transport method for the pulsed thermal processing of QD materials. This work has led to follow-on funding of $250K (FY 2009–2010) from the nanomanufacturing effort of the Industrial Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy.

Publication

Sabau, A. S., C. E. Duty, R. D. Ott, and G. E. Jellison. 2008. "Numerical simulation of annealing of CdSe quantum dots for white light LEDs." Modeling of Multi-Scale Phenomena in Materials Processing Symposium, 877.

05179

Unmixed Combustion for High-Efficiency Energy Conversion

Josh A. Pihl, C. Stuart Daw, Veerathu K. Chakravarthy, James C. Conklin, and Ronald L. Graves

Project Description

Fossil fuel combustion accounts for more than 80% of U.S. energy consumption, and a third of that is used by the transportation sector. With conventional transportation engines able to convert less than 40% of their fuel energy to motive power, combustion engine efficiency is one of the leading barriers to reducing U.S. dependence on foreign oil and minimizing greenhouse gas production. A major source of inefficiency in current engines (20–25% of the fuel energy) is the entropy generated in unconstrained combustion. We propose to develop a novel, unmixed-combustion process that will significantly reduce entropy generation by using an oxygen storage medium (OSM) to constrain the combustion reactions. A similar concept, referred to as chemical looping, is already being developed for stationary power generation, but it relies on continuous circulation of OSM particles. To apply this process to transportation engines, we will demonstrate a combustion process (called Staged Combustion with Oxygen Transfer, or SCOT) with a fixed OSM that is cyclically exposed to alternating streams of fuel and air. We plan a combination of laboratory experiments, thermodynamic analysis, and computer modeling that will lead to a demonstration of the efficiency benefits of unmixed combustion.

Mission Relevance

Despite the central role of combustion engines in transportation energy consumption, very little has been done in the last century to change the fundamental nature of the engine itself. Car and truck engines still rely on reacting fuel and air at high temperatures and using the expanding combustion gases to drive a piston. The resulting mechanical work is accomplished at the expense of considerable inefficiencies: 20–25% of the fuel energy is lost due to the entropy generated by unconstrained combustion. With the increasing concern over energy security and carbon dioxide emissions, there is a renewed focus at DOE's Vehicle Technologies Program on improving the fuel efficiency of combustion engines. To support this goal, we are developing a novel unmixed combustion process that will significantly reduce entropy generation by using an OSM to constrain the combustion reactions. We are working with our DOE sponsors to continue these efforts within our portfolio of combustion efficiency projects. SCOT may also be useful for intake charge preheating in homogeneous charge compression ignition (HCCI) engines, a technology of interest to our DOE sponsors.

Results and Accomplishments

A survey of the chemical looping combustion literature led to the identification of three promising OSMs (ceria-zirconia, nickel oxide on zirconia, and manganese oxide on zirconia) which were prepared or procured. Equilibrium solid and gas phase compositions after oxidation and reduction of the OSMs were calculated using thermodynamic database software. We also measured the storage capacities and oxidation/reduction kinetics of these materials. The components of an experimental setup for evaluation and demonstration of OSMs and SCOT operating strategies were procured.

Detailed thermodynamic analyses of various SCOT configurations were performed to determine how best to utilize oxygen-storage mediated combustion to achieve higher efficiencies. The key benefit of SCOT lies in enabling equilibrium isothermal combustion. Equilibrium operation reduces the entropy generated during the combustion reactions, resulting is improved efficiency. For gas phase combustion, equilibrium is achieved at temperatures exceeding 2500 K, well above the melting point of most engineering materials. SCOT enables equilibrium oxidation at much lower temperatures (1000–1600 K). According to our analyses, operating at or closer to equilibrium could generate small efficiency gains over

unconstrained gas phase combustion for at least two oxygen storage materials (ceria and nickel oxide). Operation at these lower temperatures would also reduce heat losses to the ambient, further improving efficiency, and should practically eliminate NOx emissions.

05214

Development of Cermet High-Level Waste Forms

Robert Jubin, Scott Aaron, Emory Collins, David DePaoli, Guillermo DelCul, Kevin Felker, Douglas Kothe, Bradley Patton, Raymond Vedder, Stewart Voit, and Robert Wham

Project Description

The successful re-expansion of nuclear energy is dependent on the development of waste disposal options that minimize use of repository space and maximize efficiency and public safety. Toward this goal, we are developing advanced cermet waste form concepts for the optimal storage of high-level wastes that will be generated in next-generation nuclear fuel cycles. Cermets, which consist of ceramic phases dispersed in continuous metal matrices, provide a unique opportunity to tailor waste forms that take optimal advantage of the properties of both metallic and oxide materials. In this project, we are exploring the development of cermets consisting of ceramic materials that sequester the short-lived, but highly heat generating ^{137}Cs/Ba and ^{90}Sr/Y components of spent fuel along with metal alloys that enable isolation of long-lived fission products such as ^{99}Tc, noble metal components, transition metals, fuel assembly hardware and cladding materials. The proposed waste form will provide significant cost benefit by improving the heat-handling capability of the waste, enabling increased net repository capacity. We are also investigating the benefits of combining these two waste types and processes to produce an optimum waste form with minimized processing costs. The proof of concept is being established through experimentation and preliminary modeling studies to elucidate the long-term performance of such a cermet waste form. Success in this work will develop an important new option for investigation in programs of the Office of Nuclear Energy.

Mission Relevance

There has been a resurgence of interest in the possibility of reprocessing spent fuel in the United States to recover valuable materials and to reduce the load on waste repositories. In the "traditional" glass high-level waste (HLW), most of the residual activity and decay heat generation that occurs in the first 100–300 years arises from the ~30 year half-life ^{137}Cs/Ba and ^{90}Sr/Y components. Waste loading in the remaining HLW can be increased if these components are separated. The proposed work provides a new option for HLW with the benefits of simplified separations technologies and improved waste forms which, in turn, enables overall cost minimization. The proposed cermet waste form will improve the heat transfer characteristics and reduce the centerline temperature of the waste monolith, and allow for increased waste loading compared to a glass. Success in this work will develop an important new option for investigation in programs of the Offices of Nuclear Energy and Environmental Management. The new cermets also have application for advanced radio-isotope source forms of interest to both the Nuclear Regulatory Commission and the Department of Homeland Security.

Results and Accomplishments

During the first year of this project we have made excellent progress on two major thrusts. The first is the development of a cermet waste form, which is comprised of a ceramic phase and a metal phase. A critical demonstration has been the use of only the intrinsic components of the waste from the aqueous separations of the used nuclear fuel (UNF) and from the proposed recovery and recycling of the fuel

zircaloy cladding materials to form the cermet. The second major effort is directed towards the modeling of the resulting cermet materials. We have developed the methods and tools needed to guide the preparation and tailoring of the cermet waste forms and to model the materials to project their performance in terms of thermodynamics and heat transfer. Specifically, we have

- assembled and begun testing experimental equipment for denitration of simulant waste solutions to produce oxide powders, conversion of reducible components to metals, and hot pressing of the mixtures to cermet forms;
- produced the first cermet pellet from the simulated liquid waste from aqueous UNF reprocessing without the use of additives to tailor the ceramic or metal phases
- produced a cermet pellet from the simulated liquid waste from aqueous UNF reprocessing plus the residual simulated waste resulting from the proposed recycle of the UNF zircaloy cladding materials and fuel assembly hardware again without the use of additives to tailor the ceramic or metal phases
- begun characterization of the resulting cermets produced by different methods including scanning electron microscopy, laser flash thermal analysis, and X-ray diffraction;
- created a thermal transport model to predict the heat transfer and temperature profiles within the heterogeneous cermet waste form; and
- begun an investigation of the thermodynamics to determine effects of the in-growth of decay products on the long term performance of the waste form.

Publication

Jubin, R. T., W. S. Aaron, E. D. Collins, V. F. De Almeida, G. D. DelCul, D. W. DePaoli, L. K. Felker, B. D. Patton, D. B. Kothe, and S. L. Voit. 2009. "Development of cermet high-level waste forms." *Proceedings of the Integrated Radioactive Waste Management in Future Fuel Cycles Conference,* Nov. 8–12, Charleston, S.C.

05224

Investigation of Molten Salt Thermal Performance in Pebble Beds Using Unique Heating Techniques

Graydon Yoder, David Holcomb, Roger Kisner, Fred Peretz, Glenn Romanoski, John Wilgen, David Williams, Dane Wilson, Dennis Heatherly, and Craig Bradley

Project Description

This project will design, procure, and assemble a convective FLiNaK molten salt loop to perform thermal testing of molten salts in a heated, packed pebble bed. (The term FLiNaK refers to the ternary eutectic alkaline metal–fluoride–salt mixture LiF-NaF-KF [46.5–11.5–42 mol %].) A unique pebble heating method that will provide an internal pebble heat source utilizing inductive heating technology developed through the ORNL magnetic materials processing program will be incorporated. This heating method will simulate pebble heating much more realistically than techniques used previously. Instrumentation within the pebble bed will allow both thermal and fluid measurements to be performed, which will allow for examination of both heat transfer and pressure drop characteristics in the bed. The facility will also serve as a platform that can be used for other molten salt testing that is critical to developing high-temperature heat transfer systems.

Mission Relevance

The pebble bed-advanced high-temperature reactor (PB-AHTR) is an advanced high-temperature reactor concept. The experiment proposed for this project will provide information critical to this reactor design and, as such, is relevant to DOE Nuclear Energy programs. Additionally, molten salt is being considered as an intermediate heat-transfer fluid for the next-generation nuclear plant (NGNP) gas-cooled reactor design, and this experiment will help characterize the performance of a FLiNaK heat transfer loop. Flouride salts are also potential candidates as heat-transfer fluids in advanced solar power tower systems. The DOE Solar Energies Technologies Program will benefit directly from this project since this experiment is developing the infrastructure and knowledge base required to use these salts. Finally, salt coolants are often cited as potential candidates for fusion reactor coolants, and the loop developed in this project can therefore potentially help the DOE Fusion Energy Program.

Results and Accomplishments

Parametric studies of both the loop and induction heating system were conducted to establish the scale of the experimental test facility. Specifications were developed for the inductive power supply and coil, and the power supply was purchased and delivered at the end of the fiscal year. Parametric studies conducted for the loop resulted in a set of loop operating requirements, including loop flow rate, pebble bed size, power requirements, and piping size, among others. A walk-in hood that will house the loop has been designed, fabricated, and installed in laboratory D-111, Building 5800. The flow tube and pebble material combination (SiC and graphite, respectively) was selected based on the ease of pebble fabrication and potential SiC forms. This combination established the frequency chosen for the inductive power supply. A bolted flange design was proposed to connect the SiC flow tube to the remainder of the loop using a Flexitalic gasket as the seal. Initial material compatibility testing was performed by modifying an existing test apparatus. Samples of the Flexitalic gasket, one pebble, and a piece of the SiC to be used for the flow tube were statically tested for 1 month in a 700^{o}C FLiNaK bath. Some reaction occurred when the samples were first immersed into the bath which has been attributed to moisture within the structure of the Flexitalic gasket. However, when the specimens were removed from the melt, none of the samples showed any significant degradation. Additional testing is under way to confirm long-term compatibility of these materials.

05266

Liquid Membrane Facilitated Solvent Extraction for Americium Separation from Spent Nuclear Fuel

Melanie Moses DeBusk, Laetitia Helene Delmau, Ramesh R. Bhave, Chaitanya Kumar Narula, and Guillermo D. DelCul

Project Description

Our goal is to demonstrate the potential of immobilized liquid membranes (ILMs) with inorganic supports for extracting americium while operating in a crossflow configuration. Known fuel reprocessing protocols can remove uranium and plutonium but do not remove americium preventing the close-packing of waste due to heat load issues. Considering that the current used nuclear fuel quantities nearly match the legal capacity for U.S. geological repository site in terms of heat load generated by americium-241, it is essential that the americium is removed from used fuel. Our proposed work builds upon the information on organic substrate based ILMs that could not be deployed due to their instability in the harsh environment of nuclear fuel waste. Our ILMs will have inorganic supports, designed from ORNL legacy technology, that are robust. Thus, the ILM technology developed in this project will facilitate the long

term storage of the ~59,000 tonnes of waste that grows at 2300 tonnes/year by accomplishing americium removal and alleviating the heat load issues.

Mission Relevance

The project will impact the handling of used nuclear fuel for separation of americium. Removal of americium is an important step in reducing the heat load generated by used fuel, which will increase storage capacity in a geological repository and is also important in fuel recycling for advanced reactors. Separation of americium by this method will be superior to other methods by eliminating equilibrium limitations and reducing waste streams. The results of this project are of great relevance to handling of used nuclear fuel and future nuclear energy production which fall under the mission of the DOE Office of Nuclear Energy.

Results and Accomplishments

Conditions and system testing setup required for successful testing of membranes for uranium transfer from acid to organic solutions have been determined. Multiple membranes with varying pore sizes and materials have been evaluated for transfer efficiency and stability under pressurized conditions. Data obtained from tested membranes has been used to prepare a few final membranes for evaluation. The results of those evaluations will used to establish the optimal membrane for *in situ* oxidation of the americium surrogate (Ce). The system design required for surrogate testing is almost complete. Efforts are also under way to design a multi-membrane holder for assessing the scalability of the separation process. The successful completion of this project will have a big impact on the storage capacity of a geological repository for storage of used nuclear fuel and the use of used nuclear fuel in advanced nuclear reactors for energy production.

Publication

DeBusk, Melanie Moses, et al. 2009. *Supported Liquid Inorganic Membranes for Nuclear Waste Separation.* UT-Battelle, LLC, Invention Disclosure 200902271 (DOE-S-115,309).

05349

Variable Valve Actuation to Enable Highly Efficient Engines

James P. Szybist, James C. Conklin, James E. Parks, Charles E. A. Finney, K. Dean Edwards, Essam A. Ibrahim, and Ronald L. Graves

Project Description

This project aims to increase the efficiency of gasoline engines by using the unique capabilities of variable valve actuation (VVA) technology. Camshaft actuation of gasoline engine valve trains presents limitations to producing higher thermal efficiencies because the valve events that an engine is capable of must provide robust operation over the entire operating range, precluding continuous optimization of valve events. Engine manufacturers have devised and are producing engines with multiple cam profiles and valve phasing capabilities that do provide an improvement, but still generally limit engines to conventional Otto cycle operation. VVA technology allows valve events to be independent of a camshaft profile, so the engine can be operated using the most efficient thermodynamic cycle and combustion strategy at all operating conditions. The efficiency of each cycle depends on the demanded torque or load at a given engine speed. An engine capable of operating in multiple thermodynamic cycles may be able to operate at high engine efficiencies at all points on the speed/load operating map. This study will utilize

engine system modeling and VVA engine experiments to identify and demonstrate efficiency improvements for a range of operating conditions. The feasibility of additional thermal efficiency improvements through exhaust thermal energy recovery with thermoelectric (TE) devices will also be considered. The improved engine efficiencies will be used to predict improvements in vehicle miles-per-gallon.

Mission Relevance

The purpose of this project is to improve the efficiency of internal combustion engines, thereby reducing fuel consumption. Reducing fuel consumption is a high priority for the DOE's Vehicle Technology Program, which is actively funding research efforts in this area. A significant portion of the research in this area is focused on diesel engine platforms. A project akin to this project, investigating the efficiency improvements through the use of alternate thermodynamic cycles enabled by variable valve actuation technology, is not currently in their research. This project does fit their stated goals, and with a renewed interest in gasoline technology over the past several years, the technology and facilities developed by this project will put ORNL in a good position for follow-on funding.

Results and Accomplishments

An engine experiment with full VVA has been installed, commissioned, and is now fully functional at ORNL. The engine is capable of operating under conventional spark-ignition conditions as well as a number of unconventional four-stroke cycles, and preliminary results have demonstrated an efficiency advantage using valve events to control engine load, instead of a throttle which imposes pumping losses.

The thermodynamics of the water injection event for the six-stroke engine cycle were modeled. Results show that injecting hot water into recompressed exhaust gases yields additional extractable power. A prediction of up to an additional 2.5 bar mean effective pressure (MEP) from the steam injection event, which is up to 50% efficiency improvement under some conditions, can be extracted without any additional consumption of fuel. This thermodynamic model resulted in the submission of a patent application and a draft journal article. The six-stroke cycle will be experimentally demonstrated during FY 2010.

A GT-Power engine model was created to simulate the four-stroke engine cycles, including representations of the engine geometry and flow patterns, and utilizing an extensive second law analysis of the engine. Once validation is complete, the model will be used as a predictive tool for spark-ignition and HCCI combustion.

A new experimental platform was commissioned that is capable of measuring the performance of thermoelectric devices as well as other direct thermal energy recovery devices. The experiment is highly instrumented and is able to generate temperature and space velocity conditions relevant to engine exhaust conditions.

05369

Design of Evanescent-Wave Power Transfer for Parked and Moving Hybrid Electric Vehicles

Matthew Scudiere

Project Description

As Hybrid Electric Vehicles become more prevalent, there is a need to transfer the power source from gasoline on the vehicle to electricity from the grid in order to mitigate requirements for onboard storage as well as reduce dependency on oil. Traditional systems for trains and buses rely on physical contact to transfer electrical energy to vehicles in motion. This is not practical for vehicles of the future. Evanescent waves in loosely coupled transformer systems can theoretically provide the mechanism for this power transfer without physical contact over a significant fraction of a meter, eliminating the need for precision alignment between vehicle and power source.

Initial results from an earlier seed money project demonstrated efficiencies around 30% in the laboratory but simulations indicated that efficiencies in the high 90s were possible with proper tuning; however, there were still issues to be resolved before a proof-of-principle experiment could be successfully designed and implemented. To efficiently transfer tens of kilowatts, very large currents and voltages in the low MHz range could be required.

Because of rapid electronic hardware technology improvements, the issue of operating frequency capabilities of available power electronic components must be frequently reviewed. Until recently, highly efficient (96%) solid state power inverters were limited to frequencies less than 1 MHz due to the limitations regarding turn-on/turnoff times during switched mode operation. This limitation positioned the lower efficiency linear mode power frequency converters as the only solid state alternative to the higher frequency magnetrons, with both devices yielding efficiencies of less than 60%. However, recent advancements in semiconductor technology, specifically with regard to silicon-carbide (SiC) material, has shown that high frequency, high power signal generation via switched mode inverters is possible.

As with most development efforts there are tradeoffs that need to be more fully explored. Initial simulations indicate that while the efficiency is rather flat as a function of frequency near the region of interest, the resonance and power transfer are not. The power transferred is mostly regulated by the load impedance, which can span a rather large range. The down side is that the efficiency also varies with load and is reduced as load increases. A simulation at 5 MHz for a 10 V source showed a 1 W transfer with a peak at 95% efficiency for a 250 ohm load. In this and several other test cases the peak load power did not occur at the same conditions as the peak efficiency. Furthermore, skin effects, eddy current losses, and proximity effects, which can increase significantly with frequency, curtail the upper limit of the operating frequency. Also efficiency reduces with increasing distance between the two antennas as the flux coupling becomes weaker. Our task will balance the physics and economics to optimize power transfer.

Simulations indicate that the peak power transfer and efficiency are both higher at higher frequencies, subject to skin effects as well as eddy current and proximity losses, with the power highly peaked at the resonant frequency. But there appears to be a cap above about 10 MHz where radiation losses (transmitted radio waves) predominate. There are a few solid state hybrid power electronic devices today that can handle these frequencies of 1–9 MHz and more are expected to appear on the market soon if they are needed.

This project will expand our understanding of all these issues via analyses, simulations, and laboratory bench top evaluation systems to explore concepts directed toward designing a workable loosely coupled evanescent wave power transfer system, resulting in experimental proof of principle. A determination of the limits of today's technology will also be reported. The object of this research is to develop an understanding that will allow us to provide the technology necessary to design efficient power transfer to electric vehicles. This will be first implemented in a stationary charging system. And from that knowledge, what is required to incorporate it to a moving vehicle, we believe, will become apparent.

Mission Relevance

This initiative seeks to stimulate the development of new research areas that will result in technologies for Advanced Energy Systems that have the potential to supply, distribute and/or utilize energy with high efficiency, at low cost and with low environmental risks. It is our expectation that this will lead to additional Laboratory capabilities that will support the DOE energy mission. This falls under the subtask: Concepts for transferring energy to vehicles with the potential to mitigate the current vehicular requirement for on-board storage of energy.

The first year has been focused on defining operating parameters that are realizable with present-day technology and incorporating those results into a full-scale laboratory demonstration unit that can be used in the second year to (1) verify various configurations, (2) measure effects on other objects in the vicinity of the antenna, and (3) examine various focusing techniques to improve efficiency and power transfer.

Results and Accomplishments

A demonstration unit was designed using analysis and simulations to operate at 20 kHz, which is below its resonant frequency. The analysis considered reduced losses from skin effects, eddy currents, and currents in proximate conductors. The simulations indicated that this operating frequency will improve efficiency at the expense of total power and yet be able to transfer 5 kW. The operating frequency is well below 1 MHz and well within the operating range of various commercial off-the-shelf components. These components were selected to withstand the large voltages and currents in the resonant transmitting antenna, which were predicted by simulations.

A full-scale demonstration unit is complete. This will verify power transfer and efficiencies at various alignments and separations expected in actual deployment. It will also allow us to examine not only stationary systems but also mobile systems.

This demonstration unit will be used to study various switching control algorithms as well as to measure the effects of conducting magnetic and nonmagnetic objects in the vicinity of the emanating fields. The major effect would be the metal in the undercarriage of the vehicle. Cursory tests performed with an earlier antenna indicate that these objects do indeed have an effect but the impact is small. Also various field focusing techniques will be easily testable. Several ideas have been proposed but have yet to be analyzed. And finally, components that have to operate at very large currents and voltages can be evaluated.

Simulations indicate that efficiencies may not be as high as desired in this region and other approaches to producing high power in the range of 70 to 100 kHz may have to be pursued. Earlier testing at ORNL produced efficiencies of over 80% in this higher frequency region, but power levels were limited by the generating electronics. During the second year, testing of this unit will answer many of these questions.

05573

Rapid Radiochemistry Applications in Nuclear Forensics

H. L. Hall, C. W. Alexander, G. D. DelCul, J. R. Garrison, and D. E. Hanson

Project Description

We will develop fundamentally new strategies and scientific approaches for the nuclear forensics field. We will investigate new sample preparation and radiochemical separations methods that have the potential to dramatically shorten the timeframe in which nuclear forensics can provide quantitative data for interpretation, as well as develop concepts for critically needed post-detonation debris surrogates that will enable a broad range of further developmental and programmatic activities. Key thermodynamic parameters needed for gas phase separations will be determined. Additionally, this research will engage and train students and postdoctoral fellows in radiochemistry, nuclear forensics, and nuclear security.

Mission Relevance

Nuclear forensics—the science and tools needed to identify the source of illicit nuclear materials or to reconstruct the source of a nuclear terrorist attack—is currently a nascent field and is part of the federal government's overall mission in securing the common defense. Multiple agencies have mission roles in the nuclear forensics field, including DOE, through the National Nuclear Security Administration (NA-22 and NA-45). Other mission agencies include the Department of Homeland Security (Domestic Nuclear Detection Office) and the Department of Defense (Defense Threat Reduction Agency). Agencies such as the Department of State and the Federal Bureau of Investigation are users of nuclear forensics data as well.

Results and Accomplishments

This project is proceeding along the two tracks envisioned in the original proposal:

1. Improvements in the sample dissolution process and development of a suitable surrogate for nuclear debris, and
2. Assessments of opportunities for significant improvements in the laboratory separations needed to produce samples for measurement.

For part 1, we have developed an agreement with Lawrence Livermore National Laboratory (LLNL) to collaborate with us on this task, which provides us access to existing chemical compositional data on nuclear debris samples from the U.S. weapons program. LLNL is also collaborating with us on defining what sort of debris materials will be most cogent for the nuclear forensics mission.

Existing debris from the U.S. nuclear weapons program is generally in the form of air filters and desert surface materials from test shots fired before the Atmospheric Test Ban Treaty, and recovered subsurface samples from tests following the treaty's entry-into-force. The chemical compositions of these materials, while challenging in their own right, do not adequately represent the mix of materials expected from a terrorist nuclear detonation in an urban environment. As part of our collaboration with LLNL, we will be able to ensure that our surrogate development is well-aligned with the mission requirements of the national forensics program.

Additionally, LLNL has endorsed our concept of developing unclassified surrogates, irradiated in the High-Flux Isotope Reactor, to their sponsors as a means of greatly improving the fidelity of national exercises in the post-detonation nuclear forensics mission.

For part 2, we have elected to focus initially on the gas-phase chemistry rather than the automation of existing methodology, as this has the potential for much greater increases in the speed of analysis. We have initiated a thorough review of the scientific literature for existing work on the applications of thermochromatography to radiochemical separations, and have begun assembling and reviewing this body of work. Most of this work has previously been applied to the separation and detection of short-lived nuclides in accelerator-based new element/new isotope production experiments. Only a few papers have been published on using organometallic species for gas-phase separations (typically actinide beta-diketonate complexes). We are examining this work closely, as this could potentially simplify experimental reduction to practice (i.e., lower column temperatures, avoiding hard-to-handle gases such as fluorine). We have also identified an existing modeling and simulation code developed for predicting the performance of thermochromatography in new element/isotope production experiments, and we expect to start investigating its performance shortly.

Two graduate students at the University of Tennessee have been identified to work on this effort beginning in FY 2010.

EMERGING S&T FOR SUSTAINABLE BIOENERGY

05063

Scale-Dependent Metrics for Bioenergy: Land-Nutrient-Water Interactions Under Future Energy Scenarios

Virginia Dale, Latha Baskaran, Budhendra Bhaduri, Robin Graham, Richard Middleton, Patrick Mulholland, Esther Parish, Alexandre Sorokine, and Amy Wolfe

Project Description

The anticipated vast increase in bioenergy usage and production clearly will have interdependent environmental and socioeconomic impacts. Several technological pathways connect the various biomass sources to diverse forms of bioenergy (fuels, heat, and power). Currently, the complexity and scale dependency of such decisions and their impacts are not understood, defined, or described with adequate clarity to enable policy makers to develop strategies to ensure a sustainable bioenergy future with acceptable environmental and socioeconomic consequences, particularly under a changing climate regime.

This project will develop scientifically rigorous, practically useful, scale-dependent metrics and an approach that will help policy makers understand environmental and socioeconomic consequences of alternative bioenergy regimes and policies. We will use a specific policy goal to develop a spatially explicit conceptual model of the complex interactions that constitute the bioenergy system. Using a stepwise spatial optimization approach, the sensitivity of the economic, social, and environmental constraints in the model will be deployed at two scales of resolution in watersheds in eastern Tennessee within the Tennessee Valley Authority region. This model will provide a foundation for developing scale-dependent metrics to gauge environmental and socioeconomic effects of alternative methods for achieving specific bioenergy goals.

Mission Relevance

This research effort is of direct relevance to the Biomass Program of the DOE Office of Energy Efficiency and Renewable Energy. The Biomass program needs an integrated strategy for bioenergy implementation that allows the agency to address environmental concerns in view of farming practices, energy pressures, economic constraints, and changing climate conditions. The effort is also relevant to the new Carbon Mitigation Science Focus Area in the DOE Office of Biological and Environmental Research, which encompasses not only terrestrial carbon sequestration but also bioenergy. Other federal agencies (e.g., Department of Agriculture, Environmental Protection Agency, National Aeronautics and Space Administration, and Department of Transportation), the private sector (e.g., the Southern Alliance for Clean Energy), and international organizations will be keenly interested in these research results, for they are the implementers and monitors of the sustainable biofuel plan. The Department of Defense also has a strong interest in the next phase of this research, for it is the largest user of biofuels in the United

States and recognizes the opportunities of developing this strategic resource. States, such as Florida, are actively engaged in finding ways to pursue the next steps in implementing biofuel alternatives (personal communication Don McConnell, UT-Battelle).

Results and Accomplishments

This interdisciplinary team all contributed to the development of the conceptual framework by investigating and contributing information about social and behavioral factors and well as ecological conditions. The geospatial information system was created and the Soil and Water Assessment Tool (SWAT) was parameterized and set up to provide results to feed into the optimization model. Strategies for parallelizing SWAT runs and setting up optimization environment were investigated. Our current strategy is to perform paired sub-watershed runs with alternative SWAT simulation parameter sets. We have developed a spatial optimization model (SOM) that optimizes land-use decisions within a watershed. The SOM efficiently distributes where dedicated energy crops should be grown while maximizing profits (or minimizing costs) while maintaining water quality limits (nitrogen, phosphorous and sediment concentrations) and acceptable land-use displacement (e.g., area of forest, cropland, and pastured converted to energy crops). These metrics were selected from the conceptual model to represent sustainability issues and farmer choices. The SOM is parameterized using SWAT; this integration combines the decision-making power of an optimization model (i.e. SOM) with advanced nonlinear watershed simulation tool (i.e., SWAT). We believe that the SOM will make a significant impact on watershed modeling and sustainability research in the near future. The DOE Office of the Biomass Program will be providing support to test the model projections.

Publication

Kline, K. L., and V. H. Dale. 2008. "Biofuels: Effects on land and fire." *Science* **321,** 199–200.
Kline, K. L., V. H. Dale, R. Lee, and P. Leiby. 2009. "In defense of biofuels, done right." *Issues in Science and Technology* **25**(3), 75–84.

05200

Evolution and Optimization of the Biofuel Supply Chain

Michael R. Hilliard, Ingrid K. Busch, Rebecca J. Hartman-Baker, Richard S. Middleton, Ike Patterson, Michael S. Schultze, and Neil Thomas

Project Description

A multidisciplinary team will develop an architecture for modeling the biofuel supply chain in a detailed spatial optimization context. This modeling provides insight into the potential evolution of the biofuel infrastructure. Constructing the architecture is a challenge involving (1) multiple scales of data, (2) integrating diverse infrastructure models, (3) constructing a realistic intermodal transportation model, and (4) approaches to economic modeling. We will demonstrate the architecture initially for the I-81 corridor, a region encapsulating a large potential cellulosic biofuel supply, representative distribution networks, and considerable end user demand. The model will be used to suggest an evolution of infrastructure for the supply chain, including how much, where, and which feedstocks would be produced, where refineries would locate, how ethanol would be blended and stored, and how fuel would be distributed. The potential impact of policies and incentives could be estimated by changes induced in the supply chain.

Mission Relevance

This effort is of direct importance to several federal agencies. DOE's Office of Biomass is well aware of the need to view the production of biofuels at the supply chain level. The Department of Agriculture is partnered with DOE in the Biomass Research and Development Initiative. The Environmental Protection Agency's (EPA) National Fuel Standard Program specifies the minimum volume of renewable fuel that must be sold in the United States. EPA regulations rely heavily on studies of the impact of fuel production and distribution. The Department of Transportation also has a research and development program in biofuels under its Research and Innovative Technology Administration including studies on the impact of biofuel logistics on infrastructure.

Results and Accomplishments

We developed a national database and geographic representation of the major components of the biofuel supply chain: a highway, rail and waterway transportation network, county-level biomass supply curves (tons by price level), potential refinery locations, and distribution centers. Clustering and central feature identification techniques created the potential refineries and distribution centers. Each potential link in the supply chain (field to refinery, refinery to distribution, distribution to demand) was associated with a distance by mode. Ethanol demand scenarios modeled the replacement of 10%, 20%, or 30% of gasoline assuming growth in travel and improved mileage. Version 1.0 of the model minimizes the total annualized cost of supplying the demanded ethanol from the available biomass using integer programming. The model selects the source and quantity for all of the biomass, refinery locations and sizes, volumes sent along each link, and the county-level distribution. A web-based interface displays results including transportation demand by route. Initial testing focused on four states (Pennsylvania, Maryland, Virginia, and West Virginia). This region provides varying density of biomass, all transportation modes, and both rural and urban demand. The four-state problem generates a formulation with 274,991 variables (1395 binary) and 3636 constraints. A serial implementation solved the problem close to optimality within a few minutes but required 24 h to reach proven optimality. A parallel solver implementation on the Jaguar supercomputer using only 128 nodes solved to optimality in about 3 min.

Publication

Hartman-Baker, Rebecca J., Ingrid K. Busch, Michael R. Hilliard, Richard S. Middleton, and Michael S. Schultze. 2009. "Solution of mixed-integer programming problems on the XT5." Cray User Group Conference, May 4–7, Atlanta.

05238

Spatiotemporal Data Mining Framework for Monitoring Biomass at Regional and Global Scales

Ranga Raju Vatsavai, Auroop R. Ganguly, Forrest M. Hoffman, Thomas Paul Karnowski, Christopher T. Symons, and Tristram O. West

Project Description

This project is addressing two key research challenges that are essential to realizing U.S. energy security, a task that has figured prominently in the recent Office of Biomass Program report. These two challenges are (1) a cost-effective solution to continuously monitor biomass and (2) scalable solutions for species-level information extraction from high-resolution images. Conventional techniques are not adequate for continuous biomass monitoring over large geographic regions. Change-detection techniques, such as

differencing, significance testing, and probabilistic approaches are not sufficient for identifying changes in croplands. We are addressing this problem by developing new spatiotemporal data mining (STDM) approaches with specific focus on

- efficiently monitoring croplands based on spectral, phenological, biogeophysical characteristics by reducing false positives (false changes);
- drastically reducing the ground-truth data required to build models;
- easily adapt models to diverse geographic settings with minimal retraining; and
- automatically recognize sub-classes such as crop types or species (e.g., switchgrass, Chinese tallow, rapeseed, corn, wheat, soybean) from aggregate classes, such as agriculture, with minimal additional ground-truth.

We are addressing scalability issues using modern computing infrastructure, especially distributed and cloud computing.

Mission Relevance

With recent government emphasis on biofuel development for reducing dependency on foreign oil and reducing carbon emissions from energy production and consumption (e.g., DOE Office of Energy Efficiency and Renewable Energy's Office of Biomass Programs, Biomass Multi-Year Program Plan), the landscape of the United States and many other countries is going to change dramatically in coming years. However, biomass monitoring (changes over time) over large geographic regions using remote sensing images poses several challenges. The proposed research will develop automated techniques that exploit the subtle multidimensional signals inherent in biomass monitoring through the joint use of coarse-spatial resolution (MODIS) data and moderate- and fine-spatial resolution satellite images to enable the extraction of multi-temporal biomass information, including crop types and their conditions. We expect that the proposed research will be of great interest to the DOE Office of Biomass program and other government agencies such as the Department of Agriculture and the National Aeronautics and Space Administration, who are working on similar programs (e.g., Global Agricultural Monitoring).

Results and Accomplishments

We developed a basic biomass monitoring framework on MODIS 16 day time series data. We automated several tasks to facilitate continuous monitoring of biomass. Some of the preprocessing techniques, especially filtering and cloud contamination reduction, will help us to move from 16 day composites to better temporal resolution, such as 8 day composites. As a step towards automating change detection, we developed a novel clustering technique, which showed better performance than well-known approaches in the literature. This technique is a key component of an automated unsupervised change detection framework. We also developed a time series prediction based change technique, which combines the predictions from multiple time series models to reduce false positives. This approach seems promising, and we are conducting more experiments and evaluating the results. For characterizing changes, we developed several supervised techniques that improve the information resolution by integrating multi-resolution images and combine unlabeled samples to improve accuracy in situations where sufficient ground-truth data cannot be easily obtained. We also developed a novel framework to characterize changes in terms of phonological events such as green-up onset, peak/maturity, and dormancy onset. Such detections allow identification of important cropping patterns (e.g., early plantations, increase or decrease in crop growing season). These results were widely disseminated through publications in leading conferences and presentations at workshops sponsored by DOE and the National Science Foundation.

Publications

Jun, Goo, Ranga Raju Vatsavai, and Joydeep Ghosh. 2009. "Spatially adaptive classification and active learning of multispectral data with Gaussian processes." 4th IEEE ICDM International Workshop on Spatial and Spatiotemporal Data Mining (SSTDM-2009), Dec. 6.

Vatsavai, Ranga Raju. 2009. "BioMon: A Google Earth based continuous biomass monitoring system (demo paper)." *17th ACM SIGSPATIAL International Conference on Advances in Geographic Information Systems* (ACMGIS 2009), ACM Press/DL.

Vatsavai, Ranga Raju. 2009. "Incremental clustering algorithm for earth science data mining." *9th International Conference on Computational Science* (ICCS (2) 2009), 375–384.

Vatsavi, Ranga Raju. 2009. "Phenological event detection from multitemporal image data." 3rd International Workshop on Knowledge Discovery from Sensor Data (SensorKDD-2009), ACM KDD.

Vatsavai, Ranga Raju. 2009. Invited presentation at NSF GSTI workshop, January, Washington, D.C.

Vatsavai, Ranga Raju. 2009. Invited presentation at the USDA/FAS, January, Washington, D.C.

Vatsavai, Ranga Raju. 2009. Invited presentation at DOE-sponsored Land-Use Change and Bioenergy workshop, May, Vonore, Tenn.

Vatsavai, Ranga Raju. 2009. Presented a tutorial on advanced classification at the IGARSS-09 conference.

Vatsavai, Ranga Raju. In press. "A Spatiotemporal data mining framework for biomass monitoring." *38th IEEE Applied Imagery Pattern Recognition Workshop,* IEEE CS Press.

Vatsavai, Ranga Raju, Shashi Shekhar, and Budhendra L. Bhaduri. 2008. "A learning scheme for recognizing sub-classes from model trained on aggregate classes." *Joint IAPR International Workshop on Structural, Syntactic, and Statistical Pattern Recognition* (SSPR/SPR 2008), 967–976.

Vatsavai, Ranga Raju, and Budhendra L. Bhaduri. 2009. "Comparative analysis of classification approaches in remote sensing." IEEE International Geoscience & Remote Sensing Symposium (IGARSS).

05311

Bringing Biodiversity into the Equations Guiding Sustainable Biofuel Production

Henriette I. Jager, Craig Brandt, Latha Baskaran, Rebecca Efroymson, and Peter Schweizer

Project Description

The future of the U.S. biofuel industry depends on public trust that regulatory policies and industry practices will improve energy security without harming the environment. Plans for increasing biofuel production have come under fire because of real and perceived threats to the environment. This project sought to define conditions that promote the long-term economic viability of bioenergy feedstock production while protecting biodiversity. Our research advanced the science needed to quantify changes in biodiversity in response to projected land-use changes associated with expanding production of bioenergy feedstocks.

Our research strategy involved four tasks. First, we consolidated geospatial datasets to describe fish and mussel biodiversity and other landscape variables needed to map current biodiversity for the conterminous United States. Second, we developed spatial models to forecast biodiversity from landscape and climate influences. Third, if we had had continued funding, we would have applied these models to future bioenergy-landscape projections to predict future changes in the biodiversity landscape and its spatial uncertainty. Fourth, we developed methods for spatial valuation of biodiversity to facilitate joint

consideration of ecological and economic objectives. This research would have provided critical missing ecological pieces needed to integrate biodiversity with economic considerations that will ultimately guide policy decisions towards a sustainable future.

Mission Relevance

The DOE Office of Biomass Program (DOE OBP) will fund a distinct aquatic biodiversity modeling effort as a small part of a larger task focused on bioenergy effects on water quality. This effort is focused on the effects of hypoxia on commercially important fishes and other biota (e.g., shrimp) in the Gulf of Mexico.

Results and Accomplishments

We met or exceeded deliverables promised for FY 2009: (1) assembled geographic data required to characterize current land use, crop cover, climate, and hydrology; (2) implemented a watershed model for the Arkansas-White-Red river basin to link crop cover (including dedicated bioenergy crops) to water quality; (3) developed models to predict current fish richness in the Arkansas-White-Red river basin from climate, crop cover, water quality and water quantity; (4) developed an approach to use SWAT-predicted changes in water quality to forecast future fish richness under different bioenergy futures; (5) presented preliminary fish richness modeling results at the International SWAT conference in August; (6) prepared a draft manuscript describing fish richness modeling; (7) implemented methods for using POLYSYS simulations of alternative future bioenergy scenarios as input to SWAT; (8) reviewed literature on valuation methods for biodiversity; (9) obtained license-sales data from state agencies to measure use-value for game fishes; (10) developed an approach for valuing biodiversity of fishes; (11) participated in an ORNL–Environmental Protection Agency workshop and subgroup focused on ecological valuation of bioenergy-related changes; (12) organized the symposia "Reshaping Landscapes: Bioenergy and Biodiversity," and "Bioenergy and Land-use Change" (both proposals were accepted for the April 2010 meeting of the International Association of Landscape Ecologists) and secured DOE OBP funding for the symposia. Despite clear exceedence of planned FY 2009 accomplishments, this project was cancelled after its first year.

Publication

Baskaran, L.M, H. I. Jager, P. E. Schweizer, and R. Srinivasan. 2009. "Use of the SWAT model to evaluate the sustainability of switchgrass production at a national scale." *Proceedings of the 2009 International SWAT Symposium,* August, Boulder, Colo.

05355

Architecture for Advancing Scientific Collaboration and Promoting Citizen Science

Daniel Getman, Aaron T. Myers, Amy N. Rose, Alex Sorokine, and Phil Nugent

Project Description

It is a priority for scientists to communicate the findings of their research and their work as contributions to civilization. Recent evolutions and advancements in geospatial and cyber technologies, combined with a public that is well informed and interested in energy and climate, have cultivated an environment in which scientific research can benefit significantly from the potentially enormous volume of data that can be provided by "citizen scientists" through their offering of Volunteered Geographic Information (VGI).

From crop selection and management to infrastructure assessment, strategic refinery location, and fuel distribution, bioenergy involves a wide range of scientific research specializations and will require data at a variety of spatial and temporal resolutions. VGI can offer both volume and detailed local knowledge needed in spatial modeling and analysis as well as validation and verification of the results of those processes. Leveraging ORNL's leadership role in geographic information science and systems, energy, transportation, and climate change science along with the laboratories' unique resources, we propose to design and develop a collaborative architecture to bridge the temporal and spatial gaps that exist in data available to research efforts in bioenergy and climate through the utilization of VGI.

Mission Relevance

As a leader in research driven by the federal mission involving geographic information science, energy, transportation, and climate, ORNL is in an excellent position to apply its resources and experience to cultivate this untapped data source in support of bioenergy and climate research. Once this initial work is accomplished, it will be readily applied within the areas of energy, environment, homeland and national security, transportation, and climate within ORNL's mission. This key capability can be extended to demonstrate applicability to other federal agencies with regard to climate change science (DOE and National Oceanic and Atmospheric Administration), environmental assessment (Environmental Protection Agency and U.S. Geological Survey), emergency preparedness and response (Departments of Health and Human Services and Homeland Security), critical infrastructure planning and protection (Departments of Energy, Homeland Security, Defense, and Transportation), and threat analysis (Defense Threat Reduction Agency, and Departments of Homeland Security and Defense). Developing methods to reliably acquire VGI and successfully resolving the challenges associated with using it for scientific research will position ORNL as a leader in research supporting the federal missions.

Results and Accomplishments

Because this project bridges VGI and Citizen Science, a thorough review of literature on these topics and a study of currently available VGI sites were undertaken. It is apparent that issues of estimating data accuracy and uncertainty, achieving the volume and level of detail required, and reducing the costs of data collection are critical to successfully implementing a data collection effort. Our work in determining the requirements of a data model for VGI has shown that understanding and justifying assumed accuracy of data collected by volunteers will require detailed information about the volunteers and the circumstances under which the data were collected. Another consideration is the improvement in the level of complexity of spatial information that can be provided by volunteers. These components have been studied, and appropriate fields have been identified and organized into a data model that can be used to augment existing domain-specific data models and will be integrated into the framework. Additionally, we have formulated a number of methods to offer direct measurement of the accuracy of VGI, indirect qualifiers of VGI accuracy, and several methods to potentially improve the accuracy of VGI. These methods have been organized into a series of functional descriptions, several of which will be integrated into the framework. A formal definition of the data collection scenario and strategy for the implementation, including anticipated issues of data accuracy, volume, level of detail, and method of delivery to researchers, has been developed and is ready to be implemented and delivered at the end of this fiscal year. A description of the process will follow the implementation of the data collection effort. A prototype of the framework has been completed and will be used in the implementation of the data collection effort. The source code and the deployed prototype version of this framework, including specialized capabilities and the data model, will be delivered this fiscal year.

UNDERSTANDING CLIMATE CHANGE IMPACT: ENERGY, CARBON, AND WATER

05064

Possible Impacts of Relatively Severe Climate Change

Thomas J. Wilbanks, Auroop Ganguly, Anthony W. King, and Sherry B. Wright

Project Description

Inspired by a presentation by Gary Jacobs to a Biological and Environmental Sciences Division (BESD) off-site in 2007, this project proposed a "proof of principle" analysis of methods for understanding implications of magnitudes of climate change beyond those being considered at that time.

The context of the proposal was that climate change projections and impact assessments in 2007 were related to a future where greenhouse gas (GHG) concentrations would stabilize at a level near 450 ppm, associated with projections of average global warming in a range of 2.5 to 3.0°C. By 2007, with global GHG emissions rising much faster than the projections, this view of the future was beginning to come into question. This project is one of the early attempts to consider more severe climate futures for regions of the United States and the world.

The project focused on three targeted areas of science advancement and two regions, one in the United States and one in the developing world. The targeted areas of regional impact assessment science advancement were (1) considering variance/extremes within scenario projections of average changes, (2) relating climate change projections to socioeconomic scenarios and story lines, and (3) developing and applying visualization approaches for research and communication. The two regions selected for impact assessment were the southeastern United States and northern India.

Mission Relevance

The DOE Office of Science strategic plan calls for predicting and assessing "the effects of climate change based on models of human actions and costs and benefits of alternatives for mitigation and adaptation." A key indicator of success is "progress in delivering improved climate data and models for policymakers to determine safe levels of greenhouse gases." This project specifically benefits this indicator by improving capabilities to determine how relatively severe climate change might relate to judgments about safe levels of greenhouse gases.

Results and Accomplishments

For the visualization science challenge, the project developed an approach to visualizing climate change futures that has become an ORNL signature over the past year and a half (e.g., the CNAS climate change policy exercise in July 2008 and ORNL's support to the Office of the Secretary of Defense in 2009). For the variance/extremes challenge, the project developed innovative approaches to detecting, describing,

and analyzing variance in climate change parameters and extremes within that variance, which—together with a subsequent spinoff LDRD project—became the foundation for a climate change extremes component of the new ORNL Climate Change Science Institute. For the socioeconomic scenarios challenge, the project developed an approach for socioeconomic scenario and story line development, applied in the Northern India case, which is being viewed internationally as a significant advance in the state of science for constructing socioeconomic story lines and scenarios: the first conversion of qualitative story lines into quantitative projections of socioeconomic indicators.

For the regional assessment component, the project developed comprehensive qualitative assessments of climate change implications of the SRES A1fi climate change scenario, determining research priorities (especially for filling data gaps not addressed by climate change scenarios). It also explored two research hypotheses that, if proved, would lead to major open-literature publications: (1) that Himalayan glaciers will disappear during this century, with dramatic impacts on surface water supply in Northern India and (2) that although decadal average precipitation is expected to increase in the southeastern United States, within this average seasonal droughts are projected to increase in frequency and duration. In both cases, currently available scientific data and tools were insufficient to support conclusive proofs, but research continues to fill the gaps.

Publications

Ganguly, A., et al. 2009. "Higher trends but larger uncertainty and geographic variability in 21st century temperature and heat waves." *PNAS* **106,** 15555–15559.

Moss, R., T. Wilbanks, et al. 2009. "A new paradigm for the next generation of climate change scenarios." *Nature.*

05212

Uncertainty Assessment and Reduction for Climate Extremes and Climate Change Impacts

Auroop R. Ganguly, Marcia L. Branstetter, David J. Erickson III, Shih-Chieh Kao, Olufemi A. Omitaomu, Esther S. Parish, Alexandre Sorokine, Karsten J. K. Steinhaeuser, Ranga Raju Vatsavai, Thomas J. Wilbanks, and Pierre Ngnepieba (partner through HBCU Program)

Project Description

Climate extremes may be defined as severe hydrological or weather events, as well as large regional shifts in climate patterns, caused or exacerbated by climate change or variability. While an individual climate extreme may not be predictable, the statistical properties of certain types of extremes may be predictable with physics-based computational models of climate or sophisticated mathematical analysis. Thus, temperature extremes can be predicted with a relatively higher degree of certainty, while uncertainties dominate for hydrologic predictions. Extreme events like tropical storms, landslides, wildfires and storm surge cannot be directly predicted by the current generation of climate models. However, projections of the statistical properties of extreme events and regional climate change, along with their uncertainties, are among the most critical inputs for climate change preparedness and mitigation. This project attempts to improve the science of climate extremes and uncertainty based on hypothesis-guided analysis and relatively hypothesis-free discovery processes.

Mission Relevance

The DOE Offices of Biological and Environmental Research and Advanced Scientific Computing Research have emphasized the importance of climate extremes, uncertainty, and their impacts through multiple strategic workshop reports and advisory board meetings focused on climate prediction, integrated assessments, and computational requirements. This author attended one such DOE-sponsored workshop entitled "Identifying Outstanding Grand Challenges in Climate Change Research: Guiding the Department of Energy Strategic Planning" in March 2008. The methods and insights developed here are important for multiple agencies such as the Department of Defense (DOD), National Oceanic and Atmospheric Administration (NOAA), Environmental Protection Agency (EPA), and National Aeronautics and Space Administration. The DOD has already funded a synergistic activity through their Office of the Secretary of Defense (OSD), while multiple possibilities are currently at various stages with other federal agencies, including DOE.

Results and Accomplishments

New capabilities have been developed to produce predictive insights on climate extremes along with their uncertainties based on climate model simulations and observations. A set of tools in extreme value theory, time series analysis, nonlinear dynamics, and data mining have been carefully leveraged or improved for this purpose. Novel insights have been developed for temperature extremes, defined as regional warming and heat waves, as well as extreme precipitation events and droughts. Nonlinear data mining algorithms and sophisticated mathematical approaches have been developed which suggest the possibility of extracting data-guided insights from observations to complement climate model observations. The ability to leverage information content in oceanic indices has been suggested, along with the possibility of developing new insights about the science of climate teleconnections. The possibility of developing predictive insights on tropical cyclones based on a combination of data mining and physics-based modeling is being explored. While the bulk of the work has not been published yet, the line of research has already attracted attention in the scientific community and sponsoring agencies, resulting in invited presentations at conferences or workshops organized or sponsored by the American Geophysical Union and the Environmental and Water Resources Institute of the American Society of Civil Engineers, the National Science Foundation (one workshop in next-generation data mining and another in uncertainty quantification), NOAA, EPA, Centers for Disease Control, and Carnegie Mellon University. A presentation at a data mining venue organized by the Association for Computing Machinery won the best student paper award. A new workshop on climate data mining has been initiated at the IEEE International Conference on Data Mining.

Publications

Ganguly, A. R., M. Steinbach. and V. Kumar. 2009. "Knowledge discovery and nonlinear modeling can complement climate model simulations for predictive insights about climate extremes and their impacts." 2009 Fall Meeting of the American Geophysical Union, December, San Francisco.

Ganguly, A. R., E. S. Parish, N. Singh, K. Steinhaeuser, D. J. Erickson, M. L. Branstetter, A. W. Wayne, and E. J. Middleton. 2009. "Regional and decadal analysis of climate change induced extreme hydro-meteorological stresses informs adaptation and mitigation policies." 21st Conference on Climate Variability and Change, 89th Annual Meeting of the American Meteorological Society, Jan. 11–15, Phoenix, Ariz.

Ganguly, A. R., K. Steinhaeuser, D. J. Erickson, M. Branstetter, E. S. Parish, N. Singh, J. B. Drake, and L. Buja. 2009. "Higher trends but larger uncertainty and geographic variability in 21st century temperature and heat waves." *Proceedings of the National Academy of Sciences of the United States of America,* **106**(37), 15555–15559.

Ganguly, A. R., K. Steinhaeuser, A. Sorokine, E. S. Parish, S.-C. Kao, and M. L. Branstetter. 2009. "Demo paper: Geographic analysis and visualization of climate extremes for the Quadrennial Defense

Review." 17th ACM SIGSPATIAL International Conference on Advances in Geographic Information Systems.
Kao, S.-C., and A. R. Ganguly. 2009. "Intensification of droughts in a warming environment." 2009 Fall Meeting of the American Geophysical Union, December, San Francisco.
Kao, S.-C., A. R. Ganguly, and K. Steinhaeuser. 2009. "Motivating complex dependence structures in data mining: Case study with anomaly detection in climate data." 9th IEEE International Conference on Data Mining—Workshops (ICDMW'09).
Parish, E. S., and A. R. Ganguly. 2009. "Risk formulations versus comprehensive uncertainty characterizations for climate extremes and their impacts." 2009 Fall Meeting of the American Geophysical Union, December, San Francisco.
Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2009. "An exploration of climate data using complex networks." 3rd International Workshop on Knowledge Discovery from Sensor Data, 15th ACM SIGKDD Conference on Knowledge Discovery and Data Mining (Best Student Paper Award).
Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2009. "Discovery of climate patterns with complex networks." International Conference on Network Science (NetSci), June, Venice, Italy.
Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2009. "Descriptive and predictive analysis of climate data." SIAM International Conference on Data Mining (SDM), April–May, Sparks, Nev. (Best Poster Award for Doctoral Forum Presentation).
Steinhaeuser, K., A. R. Ganguly, and N. V. Chawla. 2009. "Complex networks as a tool of choice for improving the science of climate extremes and reducing uncertainty in their projections." 2009 Fall Meeting of the American Geophysical Union, December, San Francisco.

05232

Decadal Prediction of the Earth System after Major Volcanic Eruptions

Katherine Evans, Jim Rosinski, Pat Worley, John Drake, and Lianhong Gu

Project Description

If we can accurately determine both the forcing and heat storage of the Earth system, its sensitivity to an impulse can be found. However, the heat storage of the oceans and the land soil moisture are not well known. After the eruption of Mt. Pinatubo, the observed Earth system cooled and then rebounded to the global warming trajectory predicted by models. We propose to use a climate-system model to hindcast the historical eruptions and use the available ocean data to constrain the model. Implicit in this effort is the development of a high resolution modeling capability, which will provide simulation data at the resolution necessary to capture the effects of smaller-scale atmospheric behavior as well and interactions with the global ocean. This project will provide a clear path to improved predictability of the Earth system by developing hindcast capabilities that are poised for the inclusion of (1) the next generation of land surface models and (2) the imminent availability of ARGO data over the next several years.

Mission Relevance

In early FY 2009, the DOE Office of Biological and Environmental Research released a proposal call, LAB09-06, to investigate a number of new aspects to climate change modeling, including the exploration of climate predictability in the climate system. A multilab proposal led by ORNL was submitted to this call, and it included much the work stemming from this project as a base for future work. Funding for ORNL has been provided from this call for FY 2009 to develop decadal prediction simulation capability, with the possibility for follow-on funding. Much of the basis for this capability will be demonstrated using results from this project. Also, a number of climate science efforts are citing increased spatial

resolution as a necessary component to follow-on research, so this work will have a very broad benefit to global simulation capabilities.

Results and Accomplishments

Technical accomplishments include completed production runs of a cyclical 1850 configuration using new high resolution model configuration and datasets. This model output is a resource available to the general climate community from which to perform experiments such as a comparison of high resolution model runs in the industrial period, or to identify model sensitivities from a background state. This is also the base from which the ensemble 1960–2000 simulations to be completed in FY 2010 will be assessed. Performance improvements of 1.8 times the original throughput have been investigated and implemented as well. Currently, we are assessing parameter values that represent subgrid-scale behavior and interactions for the ~37 km resolution model. This tuning is necessary because the climate model closure to treat subgrid-scale effects such as cloud and moisture budgets are resolution dependent. One example of improved model closure is to include a cloud mixed-phase ice fraction ramp that more closely resembles observations. We are currently configuring a testbed version with these adjusted parameters at the new resolution and with the aerosol distribution described above.

A 10-year atmospheric simulation has been performed to generate higher resolution (1 degree) aerosol datasets from state-of-the-art emissions data. These improved aerosol datasets will become the inputs for an improved T341 ~37 km resolution simulation. These datasets contain higher temporal and spatial variability and will provide baseline preindustrial values for follow-on simulations covering 1960–2000.

05241

Prognostic Land-Use and Land-Cover Change for a Coupled Climate–Biogeochemistry Model

Peter E. Thornton, Forrest M. Hoffman, Jiafu Mao, Xiaoying Shi, Wilfred M. Post, Anthony W. King, and David J. Erickson III

Project Description

The purpose of this project is to develop a new capability in coupled climate–carbon modeling by adding prognostic land-use and land-cover change algorithms, drawn from the computational kernels of Integrated Assessment Models (IAM), to a coupled carbon–climate system model (the Community Climate System Model, CCSM). The effect of human land-use and land-cover change on atmospheric concentrations of greenhouse gases is second only to fossil-fuel emissions as a factor responsible for anthropogenic climate change. Changing land use and land cover also has a significant and immediate influence on climate through changes in surface energy budget and hydrology across all spatial and temporal scales. Current climate system models are just beginning to consider the explicit effects of historical and future land-use and land-cover change on carbon, water, and energy budgets. New developments in representing the land surface and terrestrial biogeochemical cycles in coupled climate system models now make it possible to explore previously untested hypotheses concerning interactions of physical and biological climate system components with anthropogenic land-use and land-cover change. IAMs are more advanced in their treatment of this type of change, but they lack the mechanistic details to represent climate–biogeochemistry–land use feedbacks. The integration proposed here will bridge that gap and be used to evaluate critical assumptions and hypotheses in climate change assessments that require full consideration of climate change feedbacks.

Mission Relevance

This project directly addresses the research priorities within the Climate Change Research program of the DOE Office of Biological and Environmental Research (DOE BER), by improving global climate predictions and exploring the interactions between rising CO_2, other anthropogenic factors, and the Earth's climate system. In particular, this pioneering research is a critical step toward strengthening connections between the integrated assessment and climate modeling research communities, an explicit focus of the Climate Change Modeling component of the Chimate Change Research program. The model development tasks for this preliminary effort are designed in part to facilitate the future introduction of additional prognostic components from the integrated assessment modeling (IAM) domain. The proposed coupling interface would be amenable to coupling with components of IAMs other than IMAGE as proposed, allowing investigations of uncertainty arising from the specific assumptions of different IAMs. In addition, this subject aligns with earth science missions of the National Aeronautics and Space Administration but needs proof of principle. Finally, this advanced model will be able to address bioenergy sustainability issues around land-use change, possible benefitting DOE BER, the DOE Office of Energy Efficiency and Renewable Energy, and the Department of Agriculture. Early results from this project were instrumental is securing DOE BER funding for a multi-laboratory collaboration on coupled Earth System and Integrated Assessment Modeling (ORNL PI: P. E. Thornton).

Results and Accomplishments

We have completed development and testing of land use transition logic in the Community Land Model with coupled Carbon and Nitrogen cycles (CLM-CN). This development included introduction of a rotational forest harvest algorithm, shown to be a significant component of land use dynamics at the global scale. A full suite of factorial simulations for the period 1850–2005 has been completed, examining the interactions among land use, rising CO_2 concentration, and changing anthropogenic nitrogen deposition. We have acquired the source code for the IMAGE model from our collaborators in the Netherlands, and have compiled and executed benchmark simulations on local hardware, validating results against known standards from the IMAGE developers. We have rewritten the IMAGE model as a module that can be called directly as a subroutine from CLM-CN, and validated that the module version returns answers identical to the original stand-alone version. We have written and tested the interface to pass climate information from CLM-CN back to the IMAGE module. We have prototyped the interface for processing IMAGE module land use change results in real-time to pass forward to CLM-CN, and we are collaborating closely with George Hurtt at the University of New Hampshire to operationalize this step of the coupling process. Results from offline CLM-CN simulations are being prepared as a manuscript for submission.

NATIONAL SECURITY S&T

05068

Novel Alternative Signatures for Radiation Detection

John S. Neal, Lynn A. Boatner, and Slobodan Rajic

Project Description

This project directly addresses the need for providing alternative signatures for the detection of nuclear materials via new and innovative radiation detection concepts. For this effort, we harnessed expertise within ORNL in the areas of glass science, fiber optics, and radiation detection materials and systems. Our work investigates the effects of gamma rays and neutrons on fiber-optic transmission with the goal of optimizing the sensitivity and specificity of the glass systems to both ionizing radiation and the displacive effects produced by neutrons. In our work, we propose to (1) maximize the sensitivity and specificity of optical fibers to varying forms of radiation (including neutrons), (2) develop a new deployable method for detecting individual ionizing radiation events (real-time neutron detection) in optical fibers, and (3) develop a fieldable method for physically and precisely locating radiation sources by measuring the time-of-flight reflections off of radiation-induced optical fiber perturbations. This new technology will provide alternative signatures for the presence of nuclear materials and can be used in either a real-time or dosimetric mode. The successful completion of this work will provide a new and novel technology with the potential for overcoming the current constraints of an inability to readily distinguish radiation types and to physically locate the position of radiation sources—plus it will offer size, weight, cost, and power consumption advantages.

Mission Relevance

The nuclear detection community has an increasing need to identify alternative signatures for detecting the presence of nuclear materials and for the application of these new alternative signatures to advanced radiation sensors and systems. This project directly addresses the need for providing alternative signatures via new and innovative radiation detection concepts and by harnessing expertise within ORNL in the areas of glass science, fiber optics, and radiation detection materials and systems. Our work will benefit: (1) the DOE/NNSA Office of Nonproliferation Research and Development (NA-22), which conducts applied research and development, testing, and evaluation to produce technologies that lead to prototype demonstrations and resultant detection systems, thereby strengthening the U.S. response to current and projected threats to national security worldwide that are posed by the proliferation of weapons of mass destruction and the diversion of special nuclear material; and (2) the Domestic Nuclear Detection Office, which develops, acquires, and supports the deployment of new systems to detect and report attempts to import or transport a nuclear device or fissile or radiological material intended for illicit uses.

Results and Accomplishments

After synthesizing multiple glass systems and fabricating billets (small cylinders), we determined which glasses (AgCl-doped zinc–borate, and depleted uranium–doped borosilicate compositions) displayed the best radiation sensitivity for gamma and neutron irradiation. This was accomplished by exposing multiple glass types to ^{60}Co gamma rays and thermal neutrons from a moderated Am-Li neutron source. We were successfully able to draw short segments of depleted uranium–doped glass but had difficulties in attaching standard optical fiber connectors to these samples for testing due to inconsistent fiber diameters. Proof of principle measurements of the increased scattering of light in the fiber-optic waveguides due to refractive index changes produced by displacive damage caused by the direct interaction of neutrons with the optical fiber, using the depleted uranium–doped fibers and neutron sources have not been completed at this time. After discovering a previously unknown phase change during the heating of AgCl-doped zinc–borate glass, we developed a procedure for drawing AgCl-doped zinc–borate glass fibers using our fiber optic drawing tower. We developed a fiber optic transmission comparison device that monitored transmission through a fiber segment under test compared to a nearby control fiber segment. We have measured real-time transmission degradation in optical fibers exposed to various X-ray energies with this newly developed capability. These values were correlated with similar material coupon studies and then extrapolated to account for the tremendous length advantage in increasing the radiation sensitivity that is available in long optical fiber segments. We plan to pursue additional sources of funding to continue this research.

05142

Enabling Ubiquitous Information Flows: Real-Time Data Streams Instantiation and Agent-Based Forward Analysis

Mallikarjun Shankar, Yu (Cathy) Jiao, Rick Lusk, and Sreenivas Rangan Sukumar

Project Description

We address two interdependent grand challenges in enabling access to real-time information or processed data when such information is dynamic (i.e., streaming and real time), distributed, and voluminous. These grand challenges have come into sharp focus with the current price points of computing and communications allowing ubiquitous sensing, because the best distributed computing technologies have not kept apace with the volumes and dynamics of data. We pose and address the Wide-Area Dynamic-Data Instantiation challenge: Given a search query specification (i.e., an event or data of interest) and a set of data-descriptors, how does a system automatically instantiate a real-time data overlay network to collect, organize, semantically tag, and retrieve the data? We then address the question of how a distributed processing capability based on an agent paradigm evaluates or "forward analyzes" instantiated streaming data flows in a heterogeneous, distributed, low-bandwidth environment to support the created real-time overlays.

Mission Relevance

There is a growing need for national-scale real-time dynamic data linkage: local, state, and federal information sharing and dissemination. For the federal Departments of Energy, Homeland Security, and Defense, decision makers (e.g., in emergency response or the military theater) and analysts must review vast amounts of information. Data flowing from different sources at high rates can and does easily overwhelm human analysts in the military or in national security organizations. When the amount of data gets large or the network bandwidth is limited (e.g., in wireless settings), the traditional approaches of crawl-index-search breaks down. In addition, the typical approach of pulling data from a central

repository creates a single point of failure and generates unnecessary transmission of data through the network. Also, network traffic to a centralized data repository can be used by an enemy to predict future action. Our effort develops solutions that strategically anticipate the data ingest and analysis challenges facing the above agencies.

Results and Accomplishments

In FY 2008 we formalized and accomplished specific goals in our proposed plan by the creation of a design architecture supported by a preliminary implementation of the infrastructure. In FY 2009, we built on our results of the last year and developed full concepts and prototype applications of the forward analysis approach. Our publications realize the vision of a distributed mobile system infrastructure that may be actuated and support analysis within the network. Our completed preliminary implementations are in two categories: the first of its kind true distributed mobile agent framework, and a suite of applications that validate the vision of distributed actuation.

The new Java-based mobile agent framework, called Knowledge Acquisition Ubiquitous Agent Infrastructure (KAUAI), runs on both standard J2SE Java Virtual Machine (JVM) and a mobile JVM for Windows Mobile called CrE-ME. Response times (time between initiating the search and having received all the search data) ranged from 6 to 16 s for our sample queries where the deployment time of the infrastructure took only 4 s of the total search time. Distributed solutions outperform the centralized solution in terms of speed for each query, and the speed of the distributed search depends on the amount of query-relevant data in the system (that traverses the primary bottleneck—the wireless network capacity).

The applications we have developed allow images to be processed and dispatched to a mobile device test platform (cell phone and palm-top devices). A separate concept prototype application enables an airborne blimp and three robots to coordinate in their movement extending the idea of distributed tasking and actuation. Unlike robotics projects, the goal has been to enable a top-down programming environment of the ubiquitous infrastructure. With cell phones and robots as prototypes of distributed networked realizations of real world infrastructure, we have addressed the problem of forward analysis through contributions in (1) multi-document summarization (by proposing a new technique to assist human analysts in digesting high volumes of data) and (2) data-stream description (by formulating a statistical meta-tagging framework that can reside as middleware within the mobile agent and tag incoming streams with query-able feature summaries over space and time).

Publications

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05216

Multi-Photon Entangled States for Quantum Information Science

W. Grice, R. Bennink, P. Evans, and T. Humble

Project Description

Quantum Information Science (QIS) is a new kind of information technology with the potential to improve communication security and perform complex calculations by exploiting the novel features of quantum physics. An important resource in QIS protocols is entanglement, whereby the properties of individual particles are intimately related, even when the particles are spatially separated. In optical approaches to QIS, information is encoded into photonic degrees of freedom and it is relatively straightforward to generate pairs of entangled photons. However, any QIS protocols of significance require entanglement on a larger scale, i.e., three or more photons. The handful of multi-photon (>3) entangled state demonstrations have been hampered by low generation rates and poor entanglement fidelity and are generally considered impractical for real QIS systems. We are endeavoring to overcome this two-photon barrier with the generation of state-of-the-art multi-photon states with better entanglement fidelity and count rates that are higher by several orders of magnitude. Our approach significantly improves upon previous works by optimizing photon sources not only in brightness, but also in the spatial and spectral properties of the emitted photons.

Mission Relevance

Quantum Information Science (QIS) is a multi-disciplinary endeavor. There is already significant overlap between QIS needs and the missions of DOE, particularly as reflected in ORNL capabilities (computing, quantum optics, quantum dots, nano-science, materials science, etc.). As QIS matures, there will be a greater need for improved sources, making DOE even better suited to play a significant role. This was recently brought to light in the American Competitiveness Initiative (ACI), in which QIS was highlighted as a national priority and DOE was given the task of "overcoming technological barriers to the practical use of quantum information processing." The development of a waveguide entangled photon source clearly addresses the ACI challenge.

Results and Accomplishments

Source design. Using numerical modeling tools developed previously by our team, we studied several down-conversion materials before settling on periodically poled potassium titanyl phosphate (PPKTP) phase-matched for type II SPDC with a pump wavelength of 776 nm. The generated photons have wavelengths of 1.552 μm, which means that they are more difficult to detect due to limitations in single-photon detector technology. However, this difficulty is offset by a couple of distinct advantages. First, group velocity matching can be achieved at these wavelengths in PPKTP, thus making it possible to eliminate virtually all of the spectral entanglement. Second, the pump wavelength is directly accessible with our Ti:Sapphire laser system, with no need for inefficient second harmonic generation. This simplifies the pumping scheme and results in a more powerful pump with better spatial coherence and stability.

Entangled photon source. Photons from our source were entangled using a novel configuration made up of waveplates and polarization beam displacers, which exploit double refraction in calcite to separate orthogonally polarized components of an incident beam into two parallel output beams. The coincidences-to-singles ratio is 1.5%, which compares favorably to the maximum achievable ratio of 3.0% calculated by taking system losses into account. Based on these numbers, we conservatively estimate that the emission rate into the signal and idler collection modes is 44,000 pairs per milliwatt of

pump, making this source one of the brightest demonstrated to date, and perhaps the brightest at these wavelengths.

Publications

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05228

Integrated Navigation System for GPS-Denied Environments

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Project Description

ORNL is exploiting an unusually timely opportunity to implement a significant solution to the vital national problem of Global Positioning System (GPS)–denied navigation (i.e., to navigate accurately in all environments, with or without GPS). This project involves the research and proof-of-concept demonstration of a novel frequency-agile integrated navigation system for individuals and assets that will perform in GPS-denied environments, including canyons, urban settings, underground, and deep inside buildings. The foundation of this system is the reception of appropriate ground-wave radio-frequency (RF) location signals (the Theater Positioning System [TPS] + LORAN), augmented by a breakthrough-technology local inertial navigation system (INS), used to measure motional displacements and rotations of the user to instantaneously and accurately determine his location and bearing. ORNL has conceptually developed several novel radiolocation signal formats and mathematical data-fusion algorithms (U.S. Patents 6,556,942; 7,394,381; and 7,626,544 issued plus six more patents pending), and we are also combining leading-edge techniques in RF-based orientation (azimuth) determination, quartz-based timekeeping and accelerometry, electronic circuitry, software, and measurement science to achieve a new paradigm in reliable, low-power, low-cost INS units. All these components, plus advanced signal modeling and simulation, will be used to assemble a laboratory demonstration of the integrated TPS/INS navigation system. Our overall research and development (R&D) focus is on the next-generation user navigation unit, including the RF receivers, signal processing, and INS and timing modules.

Mission Relevance

A major concern in the tracking of personnel (by agencies such as the Department of Defense [DOD], Department of Homeland Security [DHS], and Department of Justice) and assets (by DOE, National Nuclear Security Administration [NNSA], and DOD) is the heavy dependence on GPS for accurate position information in the field. However, the use of GPS is at times unreliable (typically only ~85% coverage) and even subject to "spoofing" by an adversary. The obvious consequences of inaccurate (or no) position information can be severe, up to and including injury or death of personnel or loss of key assets (i.e., special nuclear materials). Although autonomous INS units have been proposed as short-term backups to GPS reception during outages, these units are too costly (>$5K), heavy, bulky, inaccurate, and power hungry to be deployed except in a few specialized applications. For most venues, a much more

robust, inexpensive technique is needed, especially where GPS outages occur due to jamming or foliated terrain and in buildings and underground scenarios. This project directly addresses this need. Specific U.S. Government agencies that could benefit from applications of this technology include DOE (research facilities, electrical distribution, and environmental monitoring), NNSA (production-plant assets and materials transportation), DOD/DHS (personnel/vehicle tracking, combat and emergency operations, plus logistics), and Department of Transportation/Federal Aviation Administration (reliable navigation and timing).

Results and Accomplishments

We have thus far initiated the R&D of a new, patentable high-performance version of TPS, a terrestrially based RF backup for GPS (designated as LORAN-S), compatibly operating in the existing worldwide 90–110 kHz LORAN-C radionavigation band. The new signal will greatly improve the accuracy, range, and robustness of the existing LORAN protocol (including its new eLORAN enhancement). The LORAN-S format design has been largely completed, and detailed performance simulations are under way. In addition, we began the R&D of a next-generation combined seven-oscillator quartz-based timing system and INS to determine the user's location and orientation; the unit should vastly outperform current INS units (based on optical and microelectromechanical [MEMS] systems technologies) in accuracy, stability, size, weight, power, and cost. A key electronic advancement we have achieved is the use of tightly balanced, fully differential oscillator circuitry to convert DC bias drifts to common-mode effects, thus drastically reducing the long-term phase noise in the differential output signals; coupled with advanced auto-zeroing techniques, we expect nearly a factor-of-100 improvement over standard units and radically better long-term oscillator stabilities. We have also initiated R&D of a novel three-dimensional antenna/magnetometer unit for improved TPS reception, providing receiver location *and* orientation information, which will facilitate integrating the TPS and INS subsystems into a highly reliable, self-calibrating, user-friendly navigation device ideal for GPS-denied environments.

05281

Distributed Computational Intelligence for Active Response to Cyber-Threat

Louis Wilder, Bob Schlicher, and Lawrence Macintyre

Project Description

In recent years, computer and network attacks have grown exponentially, and the insider threat has become more widespread and daunting. Currently, the intrusion detection system is the mitigation technique used to thwart these attacks. Accordingly, misuse detection is the most common type of method or strategy used by the intrusion detection system. Yet, these systems are limited in their ability to detect the zero-day attacks and suffer from high false positives. Additionally, they have poor scalability (network coverage) and have little or no situational awareness.

The goal of this project is to develop and demonstrate a unique capability in anomaly detection and active response to intrusions in Transmission Control Protocol/Internet Protocol (TCP/IP) networks. This novel approach uses statistical learning of normal user behavior at the host level and a distributed computational intelligence for near real-time reaction. Our approach will extend traditional intrusion detection system tools by including advances in statistics for discovering and quantifying normal user interactions with their computer systems (i.e., host-based monitoring) and determining an expected computer response. Quantified normal behaviors will be shared within a distributed learning framework that will allow

distributed monitoring, comparison and storage of normal usage profiles to reduce long-term false positives. This distributed learning framework will also be capable of reacting to perceived threats, isolating network elements, and actively reconfiguring system components to prevent intrusion spread. This kind of analysis and defense capability will be an indispensable aid for system administrators but also an advantage to users who will have the tools to monitor system behaviors with detail not encompassed by existing virus scanners or firewalls. This capability will allow them to detect anomalous (potentially intrusive) behaviors in a faster and much more comprehensive manner than today's technology allows.

Mission Relevance

DOE is responsible for the integrity and protection of the nation's energy delivery systems, where cyber attacks may cause extreme consequences to public health & safety and the nation's economy. DOE's substantial cyber assets, its international visibility, its mission, and its open research make it a target for cyber attack.

This research is directly aligned with the missions of DOE, the Intelligence Advanced Research Projects Activity, the Intelligence Community, and the Department of Homeland Security. These agencies are eager for tools to help analyze and detect suspicious anomalous activities. The proposed research will help establish a capability that is essential for long-term cyber-space security and will establish ORNL as a leader in an area of cyberspace security traditionally deemed too difficult to solve. Additionally, the proposed capability provides a novel application of sensor fusion that does not currently exist at any of the laboratories.

Results and Accomplishments

This research will produce a prototype software framework for distributed anomaly detection with an active response. The framework provides computational intelligence (algorithms that combine elements of learning, adaptation, and evolution) to address the analysis and correlation of intrusion data. In addition, an unsupervised learning system for distributed intrusion detection correlation will be developed. We will be able to identify normal system behavior using probabilistic process modeling. Additionally, data symbolization and time analysis will be used for determining input–output rules associated with purely discrete human–computer interactions.

For this initial year, our efforts focused primarily on the development of core algorithms for the distributed framework. The following sections list accomplishments to date.

Anomaly literature surveyed. Results from the literature survey revealed multiple categories for anomaly detection approaches including machine learning, statistical, and specifications based. Our proposed anomaly detection is a statistical approach that is unique from other approaches. Competing tools use common Bayesian models and pattern detections. The patterns represent known anomalies such as those found in the Snort rules. This is a problem for new or zero-day attacks because the pattern will not be an immediate part of the pattern set. This project is based on Hidden Markov statistics that look for out-of-normal patterns rather than explicit rule patterns. This method is unique because it does not require hard-coded rules or labeled data and characterizes data patterns by automatic discovery and training.

Designed a modernized, lightweight software architecture. To accommodate advancing software technology and the large-volume ingestion requirements to support the computational intelligence for this project, the current framework software architecture was redesigned to reduce the execution footprint, expose a complementary application programming interface, and improve processing performance. The current Java Runtime size is over 88 Mbytes. In contrast, the new C/C++ execution footprint is targeted at 1–3 Mbytes. The design for the performance improvement identifies a component-based system with

better streamlined data handling. The components of the architecture include a core manager for the controller with a scripting language; database for a streamlined data and knowledge base; pre-processor that handles data structures for modeling assets, events and messaging; correlation engine for grouping nodes or collective behaviors; and controls sensor for network data management.

Distributed management, detection, and response analysis. Based on the cyber community behavioral and attack graph modeling, we identified the type of data and knowledge to support the detection and active response profiles. The graph modeling can be used as a mechanism for identifying distributed activities that could be analyzed together for supporting the anomaly detection and a corresponding course of action. This technical review influenced the updated software architecture for intelligently fusing distributed anomaly detector data and supporting distributed active response(s).

Prototype code development. In preparation for the anomaly detector and the IP-based network scanners and sniffers, parts of the modernized software architecture were prototyped in C++ including the core manager with the a scripting programming language, the database algorithm involving an embedded relational database, and a control sensor software data bus for handling incoming sensor data and routing it to subscribed analyzers (e.g., an Anomaly Detector can be plugged in on the bus to ingest and process data).

05575

Design of Control Methodology for Coherent Beam Combining of High Power Semiconductor Laser Arrays

Yehuda Braiman and Bo Liu

Project Description

The motivation of the proposed research is to design a methodology to efficiently control selected elements in large arrays of high power semiconductor lasers. The expectation is that properly designed control will result in significant improvement in coherency of the array. We will test two setups: (1) V-shaped cavity and separated-thermal control to selected lasers and (2) V-shaped cavity and injection of a well-controlled single-mode beam to selected lasers. The goal is to demonstrate an excellent beam quality at high power from a large array of high power semiconductor lasers.

Mission Relevance

High power compact coherent sources are extremely useful in many civil and military applications. Such devices have been built to achieve high coherent radiation for applications such as directed energy, space communication, blue-light generation via frequency doubling, and end-pumping solid-state lasers. Conventional, narrow-stripe (<3–4 μm wide), single-mode lasers provide, at most, 100 mW reliably, as limited by the optical power density at the laser facet. For reliable operation at high power ranges, broad-area laser (BAL) arrays with large aperture (≥100 μm in width) are necessary. However, such BAL arrays usually exhibit multiple spatial (lateral) modes. The output beams are naturally incoherent. Thus, the challenge has been to obtain single-mode operation from large-aperture devices and to maintain stable, coherent behavior to high power levels.

Results and Accomplishments

We designed a laser amplifier for injection locking of a semiconductor laser array and experimentally implemented a V-shaped cavity setup that we modified accordingly to accommodate injection locking by

a master laser amplifier. An important cavity improvement included closing the cavity by using the second grating. We measured the beam quality in the modified V-shaped cavity and achieved a high degree of coherence in the laser array that consisted of 47 high power lasers.

This project was a late LDRD project that began in July 2009. Initially, the project was planned for 15 months; however, we received only the FY 2009 portion of the budget. Because we have not received FY 2010 funding, we spent less than three months on the project. We are ready to proceed with the project when funding becomes available.

GENERAL

05104

Imaging of Molecular Structure and Electron-Driven Dynamics

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Project Description

A broad range of energy-relevant science and technology requires the development of new tools to understand the dynamics of chemical, atomic, and physical structure and change on the molecular scale. In this project, we are developing novel techniques based on creating and storing molecular ions in an electrostatic storage trap long enough that they radiatively cool to a well-defined state or range of states, initiating a reaction via interaction with another particle such as an electron, molecule, or material surface (simulating the relevant environment or as a tool to probe molecular structure and dynamics), and finally imaging the resultant fragments. Proof-of-principle experiments will demonstrate these steps for both a relatively small molecular ion of relevance to atmospheric chemistry and several larger molecular ions important in biological science, utilizing an electrostatic ion beam trap, part of the recently upgraded ion research facility in the Physics Division. These electron-induced fragmentation experiments will involve interfacing an electrospray ion source and low-energy electron gun to the trap, and will probe the dependence of the electron-induced fragmentation processes on the internal state of the molecular ions by varying the cooling parameters of the trap. The work will be carried out by an interdisciplinary team from the Chemical Sciences and Physics divisions and universities with expertise in molecular ion chemistry and molecular ion production and storage technologies, as encouraged by the potential sponsors of the follow-on project.

Mission Relevance

Many of the most important challenges facing society today are related to energy production, usage, and impact, and are central themes in DOE's mission. To answer some of the most basic and pivotal scientific questions underpinning these challenges requires development of new tools to probe structure and dynamics at the molecular level. Of interest to the DOE Office of Basic Energy Sciences, insight into new methods for dissociation of large ions produced by electrospray ionization sources afforded by the unique capabilities of a molecular ion storage ring facility can make tandem mass spectrometry an even more powerful analytical technique. In support of the DOE Office of Fusion Energy Sciences, the tools developed in this project will enable research aimed at answering key questions that underpin successful operation of ITER and other next-step reactors regarding edge and divertor plasma operation and issues such as tritium retention in the walls. Within the DOE Office of Biological and Environmental Research, there is substantial interest in improving the capabilities of mass spectrometry to more comprehensively probe microbial proteomes and protein complexes. A key element of these studies is better understanding and control of ion fragmentation over a wide range of molecular species.

Results and Accomplishments

During FY 2009 a number of improvements and optimizations were completed as we continued to integrate key experimental components, ultimately leading to completion of proof-of-principle experiments during the second year of this project.

The vacuum system for the electrostatic ion trap was improved, and a base pressure of 1×10^{-10} torr was achieved. Extensive optimizations of the ion trap were performed with a variety of singly charged atomic and molecular ions, including argon, potassium, and oxygen; these led to improvements in the ion transport and injection optics and timing and minimization of magnetic fields in the trap region. The advances in trap hardware, electronics, and control software yielded (1/e) storage lifetimes approaching 1.5 s, so that a measurable number of ions remained stored in the trap beyond 7 s after initial injection.

The dissociation fragment imaging system was also improved by adding a timing pickup to the microchannel plate of the neutral fragment detector, reducing the delay between particles striking the detector and triggering of the fast, intensified camera to record the dissociation event, leading to an increased efficiency of data taking.

Ion source development also continued in the second year of the project. Optimization of electron cyclotron resonance source conditions and beam transport optics resulted in beam currents in excess of 5 nA for 10 keV ozone ions (O_3^+) injected and stored in the ion trap. A 10-kV acceleration platform was constructed for the Analytica-type electrospray ion source along with the necessary extraction, focusing, and transport optics for injection of beams into the trap.

Finally, proof-of-principle experiments were performed with ozone ions stored and cooled in the electrostatic ion trap. Lifetimes of greater than 1.2 s were achieved and fragment imaging measurements were made. Comparison of distributions of three-body dissociation fragment displacements, a measure of the internal energy of the molecular ion prior to fragmentation, made in the first 2 ms of ion storage and made after more than 100 ms of storage clearly show the effect of radiative relaxation of vibrational states of ozone. The fragment distributions measured later, after the ions had relaxed (cooled), exhibited more kinetic energy of release than for the distributions measured early with "hot" ions, consistent with molecular ions in lower internal (vibrational) energy states. In addition, the effects of interaction of electrons with stored ozone ions were also demonstrated in the measured two-body fragment displacements resulting from dissociative excitation at an interaction energy of 25 eV. Fragment displacement distributions predicted by Monte Carlo simulations of dissociation of ozone ions stored in the trap are in reasonable agreement with the measured distributions.

05315

Active Control of Surface Plasmonics with Ferroelectricity

Jian Shen, Gyula Eres, Illia Ivanov, Katya Seal, Kevin Shuford, and Zhenyu Zhang

Project Description

The discovery that light can be squeezed into sub-wavelength structures has revolutionized conventional optics. These interactions known as surface plasmons occur when the conduction electrons at a metal/dielectric interface resonantly interact with external electromagnetic fields. In this regime highly conductive metallic layers become transparent, capable of field concentration, tunable spectral response,

and enhanced absorption promising dramatic innovations in renewable energy, single molecule spectroscopy, and signal transmission. Discovery and exploration of plasmonic phenomena have been limited to static (passive) structures. However, the most exciting applications of plasmonic phenomena occur in the visible spectral range with active control of the plasmonic response. In this project, we propose to study the fundamental mechanisms leading to active control of the plasmonic response in the visible range using ferroelectric materials to create extreme field gradients resulting in a highly nonlinear response at the metal/dielectric interface. The wide bandgap and the highly nonlinear behavior of ferroelectric materials coupled with periodic metal structures offers unique access to surface plasmonic phenomena in the visible range. This project represents the first step toward developing a strong ORNL program for plasmonics research based on integrating advanced materials synthesis capabilities with fundamental understanding of materials requirements for active control of plasmonics.

Mission Relevance

The purpose of this project is to explore the fundamental mechanisms leading to active control of surface plasmonics in the visible spectral range. This is an unexplored area of plasmonic interactions that prominently features the scientific principles for developing high efficiency third-generation photovoltaic devices. Much of the surface plasmonics research in United States is presently funded through the Defense Advanced Research Projects Agency (DARPA) and the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE), and it is likely that funding will continue in the years to come. Currently, this project team has established a close working relationship with DARPA manager Dr. Dennis Polla, who is very interested in our ideas of studying surface plasmonics. He is considering funding a major nanosensor program at ORNL based on surface plasmonsics. In addition to DARPA and DOE EERE, the potential impact of tunable surface plasmonics in renewable energy implies that this could expand to become a new ORNL fundamental science program in this exciting area under the new initiatives for energy research program in the DOE Office of Basic Energy Sciences.

Results and Accomplishments

In this project, our goal is to achieve active control of the plasmonic response in the visible range using ferroelectric materials to create extreme field gradients resulting in a highly nonlinear response at the metal/dielectric interface. For this goal, we have prepared gold particles on ferroelectric substrates aiming at controlling the surface plasmonics at the metal/ ferroelectric interface by electric field. Up to date, we have made significant progress in both sample preparation and the active control of plasmonic response in the proposed project.

$LuFe_2O_4$ was selected because it exhibits a high dielectric tunability with quite low electric fields over a broad temperature range around room temperature. For example, a 5 V bias voltage (electric field ~ 50 V/cm) is able to suppress the dielectric permittivity from 12,000 to 5800, more than 50% at 300 K. Gold particles with diameter of 20 μm were prepared by the solvent method. The size distribution is quite uniform as checked by an optical microscope. The surface-enhanced Raman scattering (SERS) spectra were performed on a high sensitivity laser microscopic confocal Raman spectrometer, equipped with a thermoelectrically cooled charge-coupled device detector with spectral resolution of 1~2 cm^{-1}. We first checked the Raman spectrum of Thionine adsorbed on gold particles displays strong signals, underlining the strong SERS character. Then, a 5 V voltage was applied on the side of sample (the relevant electric field is 50 V/cm), the SERS intensity increased significantly, which shows the tunability of the plasmonic response. The physical origin of the asymmetry is yet to be understood. One possible impact factor is the polarization, and we need further study to clarify this issue.

On the theoretical side, preliminary studies have been completed on the optical properties of nanorods composed of a silver–gold alloy. We find that in addition to the well-known aspect ratio dependence of nanorods, the optical properties are sensitive to the relative composition of the alloy. This is particularly

true for the transverse modes, which display a sizeable blue shift upon increasing the percentage of silver in the alloy. The longitudinal modes are much less sensitive to the relative composition, as silver and gold have similar optical constants where these modes are supported. Using alloy nanorods as array components provides a new degree of freedom to tune the plasmon response and may enable an additional avenue to control the coupling to the ferroelectric films supporting the array.

05569

Identification of New, Super-Heavy Element Z = 117 Using HFIR-Produced ^{249}Bk Target Material and Intense ^{48}Ca Beam at Dubna

Krzysztof P. Rykaczewski, Robert K. Grzywacz, Jeffrey L. Binder, Julie G. Ezold, and J. H. Hamilton

Project Description

The project aims to identify a new super-heavy chemical element of the Periodic Table with atomic number Z = 117. The short-lived radioactive ^{249}Bk target produced from curium and americium seed material irradiated at the ORNL High Flux Isotope Reactor (HFIR) is used in this experiment. Over 22 mg of ^{249}Bk, the radioactive isotope having Z = 97 protons and N = 152 neutrons, were chemically separated at ORNL Radiochemical Engineering Development Center in the first half of 2009. At the end of June 2009, the ^{249}Bk was transferred to the Institute of Atomic Reactors at Dimitrovgrad (Russia) for target fabrication. The rotating target wheel containing six ^{249}Bk targets was transferred to the Joint Institute for Nuclear Research (JINR) at Dubna (Russia) in July 2009. The irradiation of ^{249}Bk with an intense beam of ^{48}Ca, a rare stable isotope with Z = 20 protons and N = 28 neutrons, started at the Flerov Laboratory of Nuclear Reactions (FLNR) of JINR at the end of July 2009 and is expected to last well over 100 days. These irradiations with beam energies of 252 MeV and 245 MeV will be followed by an additional round of experiments in 2010 addressing the chemical identification of the longer-lived super-heavy products. The search for new element Z = 117 is performed in collaboration with physicists from Vanderbilt University and Lawrence Livermore National Laboratory (LLNL) participating in the experiment together with K. Rykaczewski (PI of this project) and collaborators from FLNR Dubna.

Mission Relevance

The discovery of a new chemical element is an increasingly difficult high-profile scientific achievement. It helps us to establish and understand the limits of the periodic table of elements and of atomic nuclei. The decay properties and production cross section of new isotopes identified in this study will help us to understand the structure of the heaviest nuclei, and the underlying nuclear forces binding nucleons together.

New ideas related to the search for even heavier new chemical elements have been developed during this project. Upon success of the current experiment, the search for the new element Z = 119 can be performed using the next batch of HFIR-REDC produced ^{249}Bk material and an intense ^{50}Ti Z = 22 beam either at JINR Dubna or GSI Darmstadt (Germany). Future studies of super-heavy elements may use Z = 98 ^{251}Cf targets extracted from old californium probes present in the ORNL inventory of trans-actinides isotopes. The amount of californium material of enhanced purity (1 mg of ^{251}Cf to 1 ng of ^{252}Cf) will allow the search of new isotopes of elements Z = 118 (with ^{48}Ca beam) and for the isotopes of a new element Z = 120 (with ^{50}Ti beam). Since the alpha-decay half-lives of the isotopes of elements heavier than Z = 117 may be in the microsecond region, the use of fast digital data acquisition system designed at ORNL (at Holifield Radioactive Ion Beam Facility) will be essential in future studies of new elements. The development of new detector and digital data acquisition systems, planned to be implemented by the

ORNL Physics Division team at the Dubna Gas Filled Recoil Separator, helps the nuclear security and nuclear forensic fields, where the efficient detection of different kinds of radiation is important. These electronics may be operated in various modes adapting to changing experimental conditions thanks to their digital and programmable circuitry.

While at present there are two laboratories capable and authorized to run intense ^{48}Ca and ^{50}Ti beams on radioactive trans-actinides targets (JINR Dubna, Russia and GSI Darmstadt, Germany), two other laboratories are coming on-line and intending to pursue the super-heavy elements studies, the Spiral 2 part of GANIL at Caen, France, and RIKEN near Tokyo in Japan. The success of the current experiment on element Z = 117 (with ORNL-produced target material) will create a high demand for the continuation of trans-plutonium elements production and chemistry at HFIR/REDC. We expect it will lead to the creation of a new program at DOE targeting the super-heavy element research. Already now, in addition to the ongoing joint project at Dubna, GSI Darmstadt and GANIL Caen are inquiring about collaborating with ORNL, in order to gain access to the trans-plutonium isotopes.

Results and Accomplishments

Over 22 mg of ^{249}Bk activity (having a half-life of 320 days) have been separated at the ORNL REDC, from over 40 g of curium and americium seed material irradiated with neutrons at the ORNL High Flux Isotope Reactor. One of the project investigators, J. Ezold (ORNL NSTD), is the trans-plutonium "campaign 74" manager at HFIR/REDC. Following the Material Transfer and Scientific Collaboration Agreement, established in 2009 between ORNL and JINR Dubna, this material has been transferred to Russia within three weeks after final purification. Several ^{249}Bk targets suitable for irradiation with an intense heavy-ion beam have been made at IAR Dimitrovgrad. The irradiations at the DGFRS with about 1/3 of maximum intensity started in July at the FLNR Dubna. At the end of July, the beam of ^{48}Ca reached full planned intensity on target, of 1 particle·microAmp. The PI participated in the experiment in August 2009 and September 2009.

The status of the project was presented by K. Rykaczewski at Warsaw University (May 2009, Warsaw, Poland), and at the ORNL REDC (July 2009). K. Rykaczewski has presented a talk on the "Search for a New Element Z = 117 Among the ^{249}Bk + ^{48}Ca Reaction Products" at the meeting of American Physics Society (Division of Nuclear Physics) in October 2009.

The new digital data acquisition system foreseen to be used during the search for Z > 117 chemical elements in the future has been designed by two participants of this project, R. Grzywacz and K. Rykaczewski. The first purchase orders related to this novel digital data acquisition system were placed, and the equipment and software were delivered in September 2009. The *in situ* analysis of the signal rates needed for the design of the data acquisition software was done during the August 2009 and September 2009 visits to Dubna. In late August 2009, the first event suggesting the observation of an isotope of new element Z = 117 was recorded. The collaboration has agreed recently to not disclose the details of the results before the end of the experiment, now planned to run till February 2010.

Publication

Rykaczewski, K., et al. 2009. Paper at the APS Division of Nuclear Physics meeting, Oct. 13–17, Hawaii, *Bulletin of the American Physical Society* **54**(10), 128.

05570

Development of a High Magnetic Field Helicon Plasma Source for Fusion Energy Materials and Component Tests

Richard H. Goulding, Frederic W. Baity, and John B. O. Caughman

Project Description

The need for additional facilities to investigate critical issues related to the plasma-material interface (PMI) in fusion devices was a specific conclusion of a DOE strategic review meeting held earlier this year. A facility using a helicon based plasma source offers significant advantages over more conventional sources, since there are no internal electrodes and a large fraction of the injected gas is ionized. An important question, and the focus of this work, is whether the present highly efficient hydrogen helicon performance can be extended to the magnetic field strength ($\geq$ 1 T) and particle flow ($> 10^{21}$ s^{-1}) needed for such a facility. We will resolve these questions through experiments with a new source equipped with suitable diagnostics. The tasks include (1) modeling and design of a helicon source operating at the required parameters; (2) construction of the source and installation in existing facilities modified for higher magnetic fields, RF power, and particle throughput; (3) experimental optimization of the antenna configuration; (4) measurement of performance characteristics during high power tests; (5) study of the effect of magnetic field geometry on performance; and (6) determination of power deposition profiles on critical components to enable the design of a steady-state source.

Mission Relevance

As referenced above, the construction of new PMI research facilities was recommended as an outcome of the DOE Office of Fusion Energy Sciences strategic planning Research Needs Workshop (ReNeW). The ultimate goal of these facilities, as expressed in the "Greenwald Report" to the Fusion Energy Sciences Advisory Committee, is to obtain sufficient knowledge to "*design and build, with high confidence, robust material components that interface the hot plasma in the presence of very high neutron fluence."* Physical phenomena of interest include surface sputtering, erosion, redeposition, and tritium retention and migration. This project will develop a robust, large-diameter particle source for a linear PMI facility that will ultimately deliver a power flux of 20 MW/m^2 and an ITER divertor-like particle flux > $10^{23}m^{-3}s$, over an area of ~100 cm^2. The ultimate facility will allow near term, cost effective studies of plasma interactions with fusion materials, including neutron damaged ones, and plasma facing components, over a wide range of parameters.

Results and Accomplishments

The first goal, scheduled for completion this fiscal year, has been met. RF and thermal modeling of the device have been completed, and have been used to complete the detailed design of the device. The second task, *"construct the high power large area helicon source and control system,"* originally scheduled for completion by early December 2009, is partially complete. Nearly all of the parts have been fabricated, including vacuum chamber parts and the rf antenna. Fabrication of the aluminum nitride vacuum windows and the device support stand will be completed in September, allowing assembly of the system to begin in October. The anticipated date for the start of assembly has been slightly delayed due to a transfer of one-third of the requested FY 2009 funding to FY 2011. However, the project is on track for completion by the extended completion date of September 2011 specified in the project approval letter.

Publication

Goulding, R. H., et al. 2009. "Design of a high particle flux hydrogen helicon plasma source for use in plasma materials interaction studies." *Proceedings of the 18th Topical Conference on RF Power in Plasmas,* June, Gent, Belgium.

Summaries of Projects Supported Through the Seed Money Fund

BIOSCIENCES DIVISION

00472

An All-Optical Plasmonic Pump for Integrated Applications

Ali Passian

Project Description

Based upon the thermal states of nanostructures, we propose a nanopump that will enable a reversible nanoscale pumping action. The proposed process can occur only at the nanoscale in a unique approach that utilizes Knudsen-like forces induced by nonradiative decay of optically excited surface plasmons. Potential applications include integration with micro- and nano-electromechanical systems and a lab-on-a-chip. The proposed plasmonic approach to inducing a nanoscale pumping action is unique and has not been exploited previously. No integrated system is currently capable of establishing a pressure drop across nanostructures by a noninvasive all-optical method. A very powerful feature of plasmonic systems is the ability of confining electromagnetic energy in nanoscale domains. Pumping energy into nanostructures over such length scales is not easily achievable with other means, and even harder to compete with is the superior (almost instant) rate at which plasmonic systems are capable of delivering the needed energy.

Mission Relevance

An integrated pump for small-scale operation will aid the development of compact sensors and on-chip laboratories that are particularly relevant to national security. The proposed approach is of tremendous potential for harvesting and managing energy (e.g., solar radiation, heat waste). The proposed system will be attractive to the Defense Advanced Research Projects Agency and other defense-related agencies. Applications are numerous as providing microscale and nanoscale pressure regulation and control are widespread needs.

Results and Accomplishments

Design parameters were established from the complementary surface modes of a cylindrical nanorod. While the accuracy of this approach is better for thicker films, we gained conceptual understanding of the field distributions. This yielded the modes of a single nanohole. Computational codes were developed to obtain the optical response for an array of nanoholes. We now can compute the field inside, as well as outside the nanohole. The mode decay can be obtained if we neglect the coupling at the top and bottom of the film and whether there is a surface plasmon coupling. The modes propagating in the holes were shown to be independent of the periodicity as long as there is sufficient metallic media between the holes. Porous silicon was manufactured and was characterized using a variation of an AFM (scanning ultrasonic subsurface microscopy) and SEM (scanning electron microscope). The pore diameters have been measured to be in the range 20–100 nanometers (with most holes around 100 nm). From the developed computational codes, the nanohole axial energy gradient and energy propagation rate were determined.

This determines the optimum laser power and wavelength used for the excitation of the surface plasmons. A 30–55 nm gold film was determined to provide sufficient excitation depending upon the wavelength of the excitation source. The manufactured porous silicon were metalized by vacuum evaporation and characterized with AFM and SEM for integrity and uniformity. After establishing the relationship between the photon excitation wavelength and the noble metal film thickness, a successful excitation and coupling of the surface plasmons was demonstrated and measurements of the molecular transport through the nanoholes were attempted in air as a working gas. We identified helium as the working gas since, while in air this approach proved to be capable of producing the sought effect, it demonstrated that the magnitude of the effect was too small to be reliably measured under uncontrolled environmental conditions. Therefore, repeating the experiments under controlled pressure (He) environment was found necessary. As a result a complete vacuum system specialized for the needed measurements was developed that would more suitably allow for the measurements. Test pressure microprobes (an array of tipless cantilevers) were installed and the system was shown to be operational. The developed system features multiple ports for light delivery to the nanostructure and readout laser beams for the pressure probes. Thus the efficiency of the system as a pump and the potential for separation of various molecular species can now be determined.

00492

Development of a Microfluidic Device to Mimic Vasculature for Studying the Mechanism of Tumor Metastasis

Henry K. Lin, Ram H. Datar, Boyd Evans, Thomas Thundat, and Siyang Zheng

Project Description

We are developing a microfluidic device which would mimic the vasculature system to (1) understand the mechanism of circulating tumor cells (CTC) extravasation under controlled environment and (2) distinguish the underlying factors within a subpopulation of CTC that have the ability to form malignant masses at secondary sites. The proposed device consists of a parylene membrane, functionalized with layers of Matrigel to mimic basement membrane, type I collagen and endothelial cells, sandwiched between two microfluidic channels formed in a transparent elastomer material. Such in-vitro microfluidic system will allow real-time monitoring of the extravasation process via imaging, followed by molecular characterization of endothelial cells and CTC to understand the molecules involved in extravasation, which can lead to discovery of novel drug targets.

Mission Relevance

Development of this microfluidic platform falls under DOE's scientific discovery mission that directly leads to improving the quality of life. This project will enable researchers to further understand the mechanism of tumor cell extravasation from blood vessels, which may lead to novel drug development for better cancer patient management. Moreover, this platform has the potential to become a clinical assay for testing the invasiveness of captured circulating tumor cells in blood withdrawn from cancer patients. This project directly benefits the mission of the National Cancer Institute within the National Institutes of Health. The development of this platform enables cancer researchers to better understand the intricate process of tumor cell extravasation from blood vessels. This in-vivo microfluidic platform can also serve as an ideal screening tool for novel drug development for cancer patient management. Specifically, this project responds to Innovative Molecular Analysis Technologies Program for development of a tool for cancer research.

Results and Accomplishments

We have developed a microfluidic device which mimics the vasculature system for understanding the mechanism of CTC extravasation under controlled environment with the hopes of distinguishing the underlying factors within a sub-population of CTC that have the ability to form malignant masses at secondary sites. Microchannels ranging from 25 μm to 150 μm in width were formed by sandwiching a 10 μm thick parylene membrane with rectangular slits in between two layers of polydimethylsiloxane (PDMS) with predefined etched grooves yielding two independent fluidic channels (top and bottom) separated by the parylene membrane. Tumor cell extravasation across the endothelial cells lined parylene membrane was observed when fluorescent labeled culture tumor cells (MDA-MD-231) in DMEM were introduced on the top channel while 10% FBS were flowing in the bottom channel as chemoattractant. Such in-vitro microfluidic system will allow real-time monitoring of the extravasation process via imaging, followed by molecular characterization of endothelial cells and CTC to understand the molecules involved in extravasation, which can lead to discovery of novel drug targets.

Publication

Lin H. K., B. Reese, S. Zheng, B. Evans, C. Koh, R. H. Datar, and T. Thundat. 2009. "Development of a microfluidic device to mimic vasculature for studying mechanism of tumor metastasis." 7th International Symposium on Minimal Residual Cancer, Athens, Greece.

00525

A Nonlinear Plasmonic Nano-Circuit for Data Communications

Ali Passian

Project Description

The extraordinary plasmon coupling and photothermal effects, exhibited by plasmonic nanoparticles, result from the strong photon excitation, long-range fields, field enhancement, and the availability of a decaying channel allowing for rapid conversion of light energy into heat. We propose to develop a novel nonlinear single-nanoparticle plasmonic device for optical modulation and switching with applications in biosensing and high-speed data communications. The outcome of the proposed work is to provide a proof-of-concept for an opto-thermo-plasmonic nano-circuit for data modulations and communications. The proposed work in part entails the understanding of linear and nonlinear small-scale thermal processes and heat transport due to the optical excitation and nonradiative decay of surface plasmons.

Mission Relevance

The project entails developing the next-generation integrated circuit that will have much higher performance, smaller size, and lower power requirements. This is relevant to high technology applications that depend on high performance electronics, such as nuclear security, space research, high performance computing, and other DOE national security missions. The preliminary results, if successful, are expected to attract funds from DOE, Defense Advanced Research Projects Agency, National Aeronautics and Space Administration, the Air Force, and other defense related agencies. These agencies have calls directly related to the proposed technology. Furthermore, the proposed work involves optoelectronics and nanotechnology, which the National Institutes of Health considers will play important roles in cancer research.

Results and Accomplishments

At this time, since the project is a month along, accomplishments thus far include procuring necessary materials, identifying a postdoc, and planning experiments and designing apparatus. The work proposed entails experiments and theoretical modeling of a single-nanoparticle optically excited plasmonic device (nanosystem). Pre-experimental calculations are needed to determine certain properties of the proposed nanosystem to be fabricated. Post-experimental calculations are required in order to interpret the experimental results and optimize the performance of the nanosystem. The theoretical modeling will be ongoing to support the experimental work. The experimental work will be conducted in two phases: (1) far-field optical characterization of the collective response of many nanoparticles and (2) near-field optical characterization of individual nanoparticles. Optical modulation frequency and power dependencies of the proposed nanosystem will be experimentally and theoretically studied.

CENTER FOR NANOPHASE MATERIALS SCIENCE

00481

Novel High-Power Cathodes for Lithium-Ion Rechargeable Batteries

Chengdu Liang, Nancy Dudney, and Jane Howe

Project Description

We propose to develop novel cathodes for lithium-ion rechargeable batteries based on a bimodal porous carbon material that was developed at ORNL. This carbon material possesses a bimodal pore-size distribution at 3 μm and 8 nm. The 8 nm pores will serve as host sites for $LiFePO_4$ particles, and the 3 μm pores will be employed as channels for the mass transport of electrolytes. The entire cathode will be synthesized as rods 5 cm long and 1 cm in diameter. Thin slices will be cut from the rods and assembled into batteries to demonstrate their performance advantages. The proposed cathodes are expected to have low resistances of both electrons and lithium ions because of their bimodal porous structures, which provide tight contact for electron transfer and fast mass transport for lithium ion migration. Therefore, these cathodes will have low electric resistance and high power density compared to traditional micron-sized particle-packed cathodes.

Mission Relevance

This project, which aims at the development of novel cathodes for lithium-ion batteries, is closely linked to DOE's missions related to energy storage, including the Energy Frontier Research Centers, the DOE FreedomCar program, and DOE programs managed by the Office of Electricity Delivery and Energy Reliability. The Defense Advanced Research Projects Agency and other programs have great interest in high-power-density lithium-ion batteries, which are valuable to multiple defense applications. The success of this project could also benefit Department of Defense programs.

Results and Accomplishments

During FY 2008, the first half of this project, we made considerable progress toward the synthesis of $LiFePO_4$ inside porous carbon substrates. We demonstrated that $FePO_4$ can be synthesized inside the mesoporous carbons through both electrochemical and chemical approaches. The electrochemical deposition resulted in an egg-shell structure of $FePO_4$ on the porous carbon monolith, which had an outer layer of 1 μm thickness covered by $FePO_4$ and an inner core free of $FePO_4$. The chemical deposition gave an uniform deposition of $FePO_4$ on porous carbon through a two-step self-limiting reaction. In the chemical deposition approach, MnO_2 was deposited into carbons with pore sizes of 4 nm and 8.5 nm and then replaced by $FePO_4$ via an *in situ* displacement reaction. We found that the pore size significantly affects the displacement reaction. MnO_2 inside the carbon with 4 nm pores can only be partially displaced by $FePO_4$, while MnO_2 inside the carbon with 8.5 nm pores can be fully replaced by $FePO_4$. The $FePO_4$ coatings were further converted to $LiFePO_4$ for a battery test. The $LiFePO_4$-coated carbon with 8.5 nm pores showed a hybrid electrochemical behavior of a capacitor and a battery. The capacitor behavior of

the $LiFePO_4$ coated material has the potential for high power density electric energy storage. We also found that the coated materials have a loading limit of electroactive materials. This limit has been investigated in FY 2009, we found that the maximum loading is less than 30% of active materials. With this loading level, the composite material could have a high power density, but the energy density is low. In FY 2008 this seed project supported a summer student to conduct the synthesis of α-MnO_2 nanowires. We found that α-MnO_2 nanowires can be uniformly coated by $FePO_4$ as a composite material for possible applications in high-power lithium batteries. This was a serendipitous finding during the development of the chemical deposition of $LiFePO_4$ inside the porous carbon. The results of the coated α-MnO_2 nanowires were incorporated in a proposal to the DOE Office of Basic Energy Sciences (DOE BES). The DOE BES project was funded in September 2009. To overcome the loading limit of active materials on the carbon support, we invented a solution based procedure to load sulfur onto a bimodal porous carbon with the pore size distributions of micropores and mesopores. The invention has been elected by ORNL Technology transfer for pursuing intellectual property. A provisional patent application was filed in August 2009. The sulfur-carbon composite materials research was published in 2009. We also discovered some electrolyte additives which can improve the cyclability of the sulfur-lithium battery system. A white paper and annual operating plan (AOP) were submitted to DOE/EE Vehicle Technologies Program for external funding request.

Publication and Patent

Liang, C. D., N. J. Dudney, and J. Y. Howe. 2009. "Hierarchically structured sulfur/carbon nanocomposite material for high-energy lithium battery." *Chem. Mat.* **21,** 4724–4730.

Liang, C. D., N. Dudney, and J. Howe. 2009. *Sulfur-Carbon Composites and Their Application as Cathode Materials in Lithium-Sulfur Batteries.* U.S. Provisional Patent Application 61/239,132.

00487

Laser-Enhanced, Nanoscale-Focused, Electron Beam–Induced Processing

Jason D. Fowlkes and Philip D. Rack

Projection Description

The directed assembly of nanoscale materials is essential for controlled nanofabrication. While standard lithographic techniques will continue to play an important role in nanofabrication, clearly the frontier of nanofabrication is the direct writing of nanoscale features with specified size, shape, location, orientation, and composition. Electron beam–induced deposition (EBID) is one such nanoscale, direct-write approach that has been successfully employed to deposit a diverse host of materials and structures. While EBID makes it possible to synthesize three-dimensional, nanoscale features on textured or complex surfaces, often the subsequent materials are amorphous or nanocrystalline. In addition, the final nanostructures are frequently contaminated with nonvolatile by-products resulting from the electron dissociation reaction sequence. These contaminants compromise material quality and ultimately the nanoscale functionality. We propose to use photon irradiation during EBID to remove adsorbed reaction by-products from the growing deposit to achieve deposits of high purity and controlled composition.

Mission Relevance

This research will benefit the DOE Office of Basic Energy Sciences (BES) programs, particularly those related to nanoscale science, engineering, and technology. Specifically, this technique enables the direct write deposition of two- and three-dimensional features on any substrate material and integrates fully with

current nanofabrication approaches. Thus, the technique provides a new means to deposit unique nanoscale materials as well as prototype features to probe new material properties that are important for BES missions in areas such as solid-state lighting, photovoltaics, and energy storage. The capability to selectively and nanoscopically functionalize our synthetic biological interfaces using well-developed gold–thiol chemistries should benefit programs at the National Institutes of Health.

Results and Accomplishments

A laser–enhanced EBID capability was successfully integrated with a conventional electron/ion beam microscope located at the Center for Nanophase Materials Sciences. The design and construction was achieved in collaboration with Omniprobe, Inc., a leading manufacturer of "nano-lab" accessories for such microscopes. Two Optoprobe^{TM} hardware units worth ~$200K were deployed; one unit facilitating optical imaging for quantifying laser focus while the second unit provides a fiber optic based translation stage for the localized, microlensed (1–2 mm) delivery of laser light to the sample with controlled fluence.

A central goal of this work was to demonstrate the in–situ purification of EBID deposits by substrate laser heating to desorb remnant precursor by-products. Toward this end, a fluence study was conducted using a high power near-IR diode laser (915 nm) to modulate the surface temperature during EBID. Deposit purification was demonstrated at intermediates fluences (50–100 $W \cdot cm^{-2}$), relative to nonirradiated deposits, while the relatively high temperatures produced at >200 $W \cdot cm^{-2}$ prevented EBID altogether—a fluence that was deemed more appropriate for postdeposition annealing.

A detailed EBID simulation was created to fit experimental EBID results. As a result, the complete parameter set governing the Langmuir-based, precursor–substrate interaction during EBID was estimated for the first time; specifically, values for the parameters of the precursor surface diffusion coefficient, the sticking probability and the mean surface residence time were determined. This achievement constitutes a significantly leap in our understanding of the nanoscale assembly aspect of EBID.

00495

Nonlinear Nanomechanical Oscillators for Ultrasensitive Inertial Detection

Nickolay V. Lavrik and Panos G. Datskos

Project Description

This project seeks to combine unique features of nanoscale mechanical oscillators with advantages of nonlinear systems. To minimize parasitic effects of the ubiquitous noise sources, we propose to take advantage of stochastic resonance, the phenomenon characteristic of certain nonlinear systems in which synergistic action of deterministic and stochastic processes is observed. By pursuing this effort we will verify that intrinsically nonlinear nanomechanical oscillators can be operated in the stochastic resonance regime and that this regime would lead to dramatically improved ability of detecting mass changes that are very close to the fundamental limit imposed by thermal noise.

Mission Relevance

The project is relevant to DOE's Materials Science and Technology subprogram within the DOE Office of Science, national security mission, and nuclear security. Several federal agencies expressed strong interest in technologies and devices that could enable ultrasensitive mass measurements. In particular, the

ultrasensitive mass detection is a critical component of advanced on-chip analytical systems of interest to the Defense Advanced Research Projects Agency, the National Institutes of Health, and the Department of Homeland Security. Such systems will have applications in detection of trace amounts of toxic chemicals or hazardous biological species. The potential broader area applications include accelerometers and inertial navigation devices. The project will benefit energy science and sensor technology with applications in environmental quality, nuclear security, and other related areas in which there is a need for detection of trace amounts of chemical or biological species using a highly portable platform. Currently, there is a consensus that future microminiaturized analytical systems will include a scaled down preconcentrator, a microfabricated separation column, and an appropriately small detector with very high sensitivity. The objective of the proposed effort is to develop an innovative platform for the latter counterpart. An additional significant impact of the proposed approaches is expected in the broader area of sensing applications, in which minute forces need to be detected with high accuracy and reliability. Programs under way in the DOE Office of Science will benefit from the knowledge gained during this work. The proposed work has relevance to the mission of other federal agencies. In particular, the Department of Defense and the Department of Homeland Security will benefit from advances made during this research as it applies to chemical and biological detection needs.

Results and Accomplishments

During FY 2009, further significant progress has been made in the following areas. (1) Microcantilever resonator structures have been optimized to achieve the desired type and degree of nanomechanical nonlinearity; we have implemented entirely dielectric resonators with high optical reflectivity using alternating layers of low stress (<50 MPa) SiNx and SiOx, grown by PECVD. (2) We have demonstrated nonlinear resonances of microscale cantilevers with extremely high frequency stability, consistent with the goals of this project. Using an external piezoelectric transducer, we drove cantilever structures into nonlinear regime with oscillations amplitudes in excess of 10 micrometers i.e. greater than 10% of their length and achieved frequency stability of the bifurcation point better than 10^{-6} (i.e., one part per million). (3) We implemented and characterized a new mode of operating a nonlinear resonator with nonlinear elasticity that incorporates both quadratic and cubic terms. We found that such a resonating cantilever can function as a nanomechanical demodulator that converts its oscillation amplitude into readily measurable DC signals. This innovative approach allowed us to precisely measure shifts in the bifurcation point and, in turn, mass loading of the resonator using a combination of a digital sweep generator and a simple low bandwidth readout, eliminating the need for both a position sensitive detector and a lock-in amplifier.

CHEMICAL SCIENCES DIVISION

00467

Development of a Novel Sensor System for Biomarkers of Physiological and Pathological Processes in Biomedicine

Elias Greenbaum and Ram H. Datar

Project Description

The goal of this project is to establish proof of principle for an original idea for the development of an assay system for biomarkers of physiological and pathological processes in humans without pretreatment of the sample. The gist of the project is the use of unicellular green algae or cyanobacteria as the biosensors and chlorophyll fluorescence induction as the readout in the presence of light scattering and attenuating biological components. It is known that fluorescence induction is a quantitative measure of the physiological health of photosynthetic systems. It is also known that human toxins such as cyanide, choline esterase inhibitors, electron transport chain blockers, bulk commodity agrochemicals, oxidants, etc. all alter fluorescence induction with unique signatures. If we could show corresponding effects for the molecular species involved in the onset of human disease, such as reactive oxygen species, using native human serum samples, we would have a simple and rapid early warning diagnostic assay for these disease biomarkers. Alternatively, our ability to screen and quantify the beneficial attributes of the dietary phenolics from fruit or plant extracts will provide an invaluable way to easily screen the dietary elements crucial in disease prevention.

Mission Relevance

This project is relevant to the DOE mission. In particular the DOE Office of Biological and Environmental Research has an ongoing interest in biosensors and the development of advanced instrumentation. It is also of interest to the National Institutes of Health. Reactive oxygen species, such as hydrogen peroxide and superoxide anions, are produced in many physiological and pathological processes in humans, including aging, response to infections such as *Helicobacter pylori*, atheroma, asthma, joint diseases, chronic obstructive pulmonary disease, diabetes, and cancer. The superoxide anion, O_2^-, is the main reactive oxygen species (ROS). Increased ROS production leads to tissue damage associated with inflammation. Superoxide dismutases (SODs) convert superoxide to hydrogen peroxide, which is then removed by glutathione peroxidase or catalase. Thus, SODs prevent the formation of highly aggressive ROS, such as peroxynitrite or the hydroxyl radical. The production of ROS through either endogenous or exogenous insults is common for many types of cancers and is linked with altered redox regulation of cellular signaling pathways. The redox imbalance thus may be related to oncogenic stimulation. DNA mutation is a critical step in carcinogenesis, and elevated levels of oxidative DNA lesions (8-OH-G) have been noted in various tumors, strongly implicating such damage in the etiology of cancer. Measurement of ROS in human serum samples is therefore a method to assess the impact of pathological oxidative stress. It is known that altered redox regulation affects photosynthesis.

Results and Accomplishments

The pulsed amplitude modulated (PAM) fluorometer (Heinz Walz GmbH) has been set up and is fully operational for fluorescence induction measurement. The protocol for measuring the change in fluorescence using PAM has been optimized: a formula to calculate the sample dilution based on chlorophyll density to give appropriate fluorescence intensity range has been developed, fluorescence induction curves were measured in 5 min increments in a 30 min period, and hydrogen peroxide or the same amount of water was introduced 30 s before the 15 min measurements. The marine algae strains *Chlamydomonas* sp. CCMP 222 and *C. parkeae* and the freshwater strain *C. kesseri* did not show expected drops of fluorescence upon peroxide treatments compared to the water controls. It was found that algae produce the enzyme catalase, which spontaneously converts peroxide to water. This self-protection mechanism resulted in the algae's ability to resist photosynthetic disruptions due to low concentration of peroxide. The freshwater algae mutant with catalase deficiency, NL-11, showed a peroxide threshold of 500 μ*M*, at which NL-11 exhibited an obvious drop in fluorescence after peroxide treatment, while the wild types *Chlamydomons* sp. CCMP 222 and *C. parkeae* were still fluorescent normally in response to 500 μ*M* peroxide. Linear regression analysis of 500 μ*M* peroxide treated and untreated algae fluorescence data in NL-11 showed statistically different R2: untreated, 0.97 ± 0.01; treated, 0.71 ± 0.07 (n = 3). These values can be used as quantitative measurements to define the significance of fluorescence changes in further experiments. The expected drop in fluorescence induction proved the feasibility of the concept of the project. The increased peroxide sensitivity of the mutant suggests a path forward for getting a sufficient sensitivity for large clinical screening of human serum with the algae strain that has a complete catalase deletion.

A preliminary study examined the feasibility of algal fluorescence as an indicator of toxicity of nano- and micro-sized particulates. Two eukaryotic green algae, *Chlamydomonas reinhardtii* 137C+ (CC-125) and *Chlorella kessleri*, and one cyanobacterium, *Synechocystis* PCC6803, were tested with commercial gold nanoparticles (Positive NanoGold, Nanoprobes, Inc.; 1.4 nm diameter functionalized with amino groups) and magnetic beads (Magnetite Beads, Novagen, Inc.; 2.5 μm diameter functionalized with oligo-dT). The requirement for cellular uptake appeared to slow the response to particulates of nanometer and micrometer size compared to previous studies with soluble toxins. Dark adaptation before the fluorescence assay increased response. The eukaryotic green algae exhibited greater sensitivity to the particles than did the cyanobacterium. Heat treatment at 37°C or electroporation, treatments which cause transient disruption in cell membranes, shortened response time from days to minutes for algae incubated with particulate materials. Consistent with these observations, a cell-wall mutant of *C. reinhardtii,* CC1278 (cw15 nit1-305 sr1), exhibited immediate fluorescence decrease when exposed to the gold or magnetite particles.

00477

A New Method for Controlling Densification During Chemical Vapor Deposition Production of Carbon Composites

Peter T. A. Reilly

Project Description

This project uses gas-phase pyrolysis of hydrocarbons under controlled conditions to create free radical condensates (FRCs). The idea is to measure and manipulate the chemistry of FRCs to more rapidly deposit pyrolytic carbon onto the surfaces of preforms and measure the kinetics and dynamics of

deposition. This project takes advantage of the chemical equilibria between the FRC and the gas phase and the elemental carbon formed by controlled carbonization of the FRC. We plan to use hydrogen and thermal gradients to perturb the equilibria and cause controlled pyrolytic carbon deposition. Our goal is to precisely define the process in terms of the chemistry and the kinetics and then optimize it.

Mission Relevance

This project is not just about creating faster, better, cheaper carbon composites. It is really about understanding the chemistry of the FRC. FRCs can be used to reversibly abstract hydrogen from hydrocarbons to produce forms of elemental carbon or convert elemental carbon into hydrocarbons. This chemistry opens up a multitude of opportunities in DOE's hydrogen program. FRCs can be used to unlock hydrogen storage in hydrocarbons, produce hydrogen, convert coal into hydrocarbons, and convert biofuels like alcohols into diesel. They can also be used to create ultrastrong, lightweight materials faster, better, and cheaper. The Department of Defense program on Synthesis and Processing of Materials (W911NF-07-R-0003) focuses on the use of innovative approaches for processing high-performance structural materials reliably and at lower costs. Our project, if successful, would be directly applicable to this program. Successful demonstration of this technology would also create new opportunities at other agencies, such as National Aeronautics and Space Administration, and in industry.

Results and Accomplishments

This project is based on the establishment of an equilibrium between FRCs and the production of carbon and hydrogen from them. We set up a reactor and demonstrated the equilibrium by reversing the carbonization process that forms pyrolytic carbon around carbon fibers. Segments of C/C rod were inserted into our reactor containing a white mist generated from the pyrolysis of acetylene at 1 atm pressure. After roughly 1 h in the reactor, the composite was reduced to a collection of carbon fibers. Scanning electron microscopy images of the fibers as a function of time in the reactor show evidence of pitting and exfoliation of the fibers increases with increasing time in the reactor. These results indicate that solid carbon can be converted back to hydrocarbons without a catalyst. This single result has sweeping implications. It implies new paths for preferentially producing the thermodynamically favored forms of carbon such as carbon nanotubes. It suggests that carbon nanotubes can be created by the pound instead of the milligram. Hydrocarbons could be used to reversibly store hydrogen with better storage efficiency than believed possible. Oil could be extracted and refined from oil shale in a single step. Coal and natural gas could be combined to produce diesel fuel. The list goes on. Which of these processes is economically and environmentally feasible is a matter of intensive research; however, the chemistry of FRCs presents a vast number of new possibilities that could greatly change the course of society.

00480

Hydration-Driven Processes in Bioenergy: Testing a Novel Neutron Scattering Approach

Hugh O'Neill, David C. Baker, and Sylvia E. McClain

Project Description

Water plays a vital role in the development of biofuels. Currently the production of cellulosic ethanol is limited by the low solubility of cellulose in water and because natural cellulose contains appreciable amounts of lignin, which is also largely water insoluble. The structural barrier provided by lignocellulose to water hydration in potential biofuel feedstocks is an important factor determining the recalcitrance of biomass to undergo hydrolysis. In fact, studies concerning the economic potential of cellulosic ethanol as

a potential biofuel, cite lignocellulose pretreatment efficiency as a primary factor leading to increased profit and production capability. A microscopic understanding of hydration structure on the atomic length scale (0–10 Å) of lignocellulose and its constituents is critical to understanding fundamental processes of bioenergy production. Using neutron scattering techniques, we aim to synthesize isotopically labeled carbohydrate archetypes to determine the structural and the hydration properties of cellulose.

Mission Relevance

One of the DOE missions and indeed initiatives for the future is to increase the use of alternative fuel sources to help curb our dependence on a gasoline economy. The work for this project will lead to the greater physical understanding of hydration in cellulose based materials, where the recalcitrance of cellulose to water is currently a limiting factor to cellulosic ethanol production. This investigation is a step towards more efficient use of biofuel as a potential fuel source. DOE will benefit most from this research, as it directly falls under one of the DOE directives of enhancing research in biofuels as an alternative fuel source.

Results and Accomplishments

Aqueous solutions of cellobiose (4-*O*-β-D-glucopyranosyl-D-glucose) with molar ratio of 1:63 cellobiose:water (~0.88 *M*) were measured using neutron diffraction enchanced by isotopic subtitution. These measurements were performed using the SANDALS diffractometer, which is specifically designed for measuring liquid diffraction, at the ISIS facility in the United Kingdom. The neutron data analysis from this experiment has been completed, and the modeling of this data is under way. A series of simulations have been performed using a program—Empirical Potential Structural Refinement (EPSR)—specifically designed to model amorphous systems using neutron diffraction data as a necessary constraint to this model. However, the discrepancy between our EPSR measurements and reviously reported nuclear magnetic resonance (NMR) data is larger than expected and could be due to concentration differences. To address this discrepancy, solution NMR measurements at the same concentration of the neutron experiments are currently under way. Studies in the deuteration of methyl cellobioside are being performed to develop methods to incorporate deuterium into cellulosic materials. Using Raney nickel and D_2O, we have demonstrated that the reaction can be controlled, giving up to ten deuterium atoms/cellobiose unit, with minimal, if any, inversion at the carbon centers or scrambling of framework atoms. A milder method that makes use of microwave activation is also being investigated. Analytical technology has developed to assay the products of the exchange by high-performance anion-exchange chromatography coupled with pulsed amperometric detection (HPAEC–PAD). Levels of deuterium incorporation and the precise location of the deuterium atoms will be determined by both ^1H and ^2H NMR spectroscopy.

00497

Ordered Nanoporous Hyperadsorptive Preconcentrators of Threat Agents

Jun Xu, Radu Custelcean, Chengdu Liang, S. Overbury, Seth Cohen, and Erkinjun Nazarov

Project Description

The U.S. Army's goal for the Joint Chemical Agent Detector (JCAD) is to have the minimum detection limits of approximately one part per trillion. Current state-of-the-art detectors have difficulty in reaching this goal due to lack of specificity and sensitivity. We plan to contribute to this goal by incorporating ordered nanoporous materials to advanced chemical sensors (i.e., the differential mobility spectrometer).

The objective of this project is to demonstrate proof of principle for sampling threat agents using ordered nanoporous materials. These novel materials include metal-organic frameworks (MOFs), aperiodic ordered mesoporous carbons (AOMC). Threat agents to be sampled by these adsorbents include chemical warfare agents (CWAs), toxic industrial compounds (TICs), and noble gases associated with nuclear threats. For preliminary proof-of-principle research, this project will be focused on MOFs as adsorbent and dimethylmethyl phosponate (DMMP) simulant for sarin (GB) as adsorbate.

Mission Relevance

The potential advantage of this research will be the development of a new method for building a compact, but more sensitive, device for detection of threat agents, including chemicals associated with nuclear production, chemical warfare agents, and toxic industrial compounds. Recently, DOE NA-22 issued a call for proposals, stating the need for new sampling technologies. Our project is consistent with DOE's proposal calls. The Defense Advanced Research Projects Agency, the Defense Threat Reduction Agency, and the Domestic Nuclear Detection Office have solicited proposals in novel sampling technologies. Successful demonstration of a novel preconcentrator would present a major breakthrough in sensitive detection of the threat agents and allow us to develop a large research program for the agencies.

Results and Accomplishments

In FY 2008, four MOF materials were prepared with and without functional groups attached to ligands. The Sionex DMS sensor has been obtained, and one investigator has been trained. In the next fiscal year, the overall tasks in this project are to (1) functionalize MOF pores so that sorption of the chemical threat agents is maximized and capture of background gas is minimized, (2) identify adsorption and desorption characteristics that will be used to completely extract the adsorbates into micro analyzers, and (3) package the preconcentrator with micro DMS for detecting the chemical threat agents with approximate parts-per-trillion minimum detection limits.

In FY 2009, aperiodic ordered mesoporous carbons (C850A) and metal organic frameworks (IRMOF-3-Urea) have been tested for capturing DMMP in both laboratory reactors and in a field-based detector. C850A, synthesized by C. Liang, consists of surface area of ~1600 m^2/g and two kinds of pore sites: 7.5 nm size mesopores and micropores. IRMOF-3-urea, provided by R. Custelcean and S. Cohen, consists of 2271 m^2/g and pores of 9.6 Å and 18.6 Å. Laboratory reactor experiments were performed using the AMI-200 reactor. The field-based detector was micro GC/DMS analyzer, provided by Sionex Corporation.

In the reactor tests, temperature program desorption (TPD) experiments of C850A show the following: (1) both micropores and mesopores, characterized by two desorption temperature ranges (217~160^oC and ~95^oC, respectively), are responsible for capturing DMMP; and (2) the desorption temperature for micropores decreases for more DMMP adsorbed. The maximum sorption capacity for C850A is found to be 0.55 g/g. This sorption capacity is 26-fold higher than Carbotrap and 41-fold higher than Tenax TA. Similar results are shown for IRMOF-3-urea. The sorption capacity for the MOF is 0.64 g/g, which is 30 times higher than Carbotrapand and 50 times higher than Tenax TA. C850A is found to remarkably recyclable.

In field-based detector tests using gas chromatography with detection by differential mobility spectrometry (GC-DMS), the sampling time varied from 1 s to 40 s for capturing DMMP with concentration of a few PPM. C850A adsorbent was filled into a cylindrical preconcentrator that is incorporated with the detector. Sensitivity for the mesoporous carbons increases sevenfold from using Carbopack-B (60/80) in detecting trace DMMP. Also, the large pore size of mesoporous carbons allows pass of small air constituents, leading to increased selectivity.

Publication

Xu, J., R. Custelcean, C. Liang, Y. Du, H. Li, S. Overbury, S. Cohen, and E. Nazarov. 2009. "Nanostructured porous material preconcentrator." The Knowledge Foundation International Symposium (nanoKAP), Nov. 4, Washington D.C.

00500

Neutron Scattering Characterization of Sol-Gel Drug Delivery Systems

Hugh O'Neill, Gary A. Baker, Eugene Mamontov, and Volker S. Urban

Project Description

The aim of this project is to investigate the diffusive properties of model drugs within sol-gel drug delivery systems of relevance in bone repair and joint replacement, using a combination of quasi-elastic and small-angle neutron scattering. This project addresses a major scientific bottleneck in drug delivery research, namely, the ability to characterize the distribution and diffusion of guest molecules in host carriers. We anticipate that the combination of small-angle and quasi-elastic neutron scattering can provide unheralded benefits in the characterization of both the structural and dynamic properties of realistic drug delivery materials, by providing information where other characterization techniques used to date have provided only indirect or qualitative evidence, or in cases where other approaches have failed entirely. This will be the first demonstration of using quasi-elastic neutron scattering to measure the dynamics and diffusion of pharmaceuticals within confined environments relevant to drug-delivery platforms.

Mission Relevance

The DOE Office of Basic Energy Sciences, particularly the Chemical Sciences, Geosciences and Biosciences Division, has active programs that focus on the investigation of interactions at interfaces and also the influence of weak interactions on transport in complex, real-world materials. It is expected that there will be a call for proposals for single investigator and small-group grants in FY 2009. The work proposed here would be well-suited to these calls. Demonstration of the unique capabilities of neutron science for biomedical research would attract future funding and also generate a new user community at the neutron facilities in ORNL. The National Institute of Biomedical Imaging and Bioengineering (NIBIB) recently had several calls for proposals in areas such as "Biomaterials and Biointerfaces," "Enabling Technologies for Tissue Engineering and Regenerative Medicine," and "Bioengineering Grants." The work proposed here would be well suited to these calls.

Results and Accomplishments

This project addresses a major scientific bottleneck in drug delivery research, namely the ability to characterize the distribution and diffusion of small guests within host carriers. Deuterated diglycerolsilane was synthesized as a model drug delivery material. The structural properties of the material with and without benzoic acid were investigated using small angle neutron scattering on the BioSANS instrument at the High-Flux Isorope Reactor. This allowed characterization of the pore size distribution and morphology of the drug delivery materials. The dynamics of benzoic acid in the sol-gels was measured using quasi-elastic neutron scattering using the BASIS instrument at the Spallation Neutron Source. We were able to identify the three dynamical components related to the diffusion of benzoic acid, glycerol and D_2O in the gels. Currently, we are investigating the properties of lovastatin, a bone growth stimulant, entrapped in sol-gel materials.

00508

Whole-Community Proteomic Characterization of Synthetic Human Gut Microbiomes in Gnotobiotic Mice

Robert Hettich, Alison Russell, and Nathan VerkBerkmoes

Project Description

This exploratory research program focuses on the development and demonstration of advanced mass spectrometry (MS) techniques for the characterization of synthetic microbiomes in gnotobiotic mice. This work will be conducted in collaboration with Prof. Jeffrey Gordon (Washington University) as a key demonstration of a technological approach to characterize the complex microbiomes that influence both health and disease in mammalian systems. The first aim is focused on the experimental demonstration of MS technology to acquire comprehensive proteome data from a variety of synthetic microbiomes from gnotobiotic mouse samples; the second task focuses on bioinformatic analyses conducted with newly emerging microbial genome data; and the third aim seeks to use an isotope labeling approach to examine temporal metabolic activity in the various microbiomes. If successful, our work will provide key scientific information to the gut microbiome research community.

Mission Relevance

This work is directly tied to DOE research objectives, particularly within the Office of Biological and Environmental Research (DOE BER), that are focused on the development and demonstration of advanced technological approaches for characterizing microbes at a systems biology level. In particular, research directives within DOE BER are highly focused on technologies that can reveal DNA and protein information for natural microbial communities. As part of its exploratory roadmap initiative, the National Institutes of Health (NIH) has formulated a research program entitled "The Human Microbiome Project." Funding has been designated and active research proposal calls are in progress. Technologies to impact this high visibility area within NIH are quite likely to receive funding in the next 1–3 years.

Results and Accomplishments

We have completed experimental demonstration of MS technology to acquire comprehensive proteome data from a variety of synthetic microbiomes from gnotobiotic mouse samples, as well as demonstrating bioinformatic analyses that can be used to query the MS datasets with newly emerging microbial genome data, for binary microbial consortia in gnotobiotic mouse cecal samples. In particular, we were able to obtain deep proteomic information to investigate how a bacterial firmicute and bacteroidetes compete and cooperate in a natural environmental system. These proteomic results were a critical component of a co-authored paper (with Prof. Jeff Gordon's group) in *Proceedings of the National Academy of Sciences.* We have extended this work to seven-member microbial consortia in five separate mouse cecal samples and have obtained the first glimpse of more complex, closely related microbial species in a mouse intestinal ecosystem. This required an optimization of cellular lysis methodology and development of new bioinformatic tools to sort out genomic information from related microbes. Current work is focused on a specific study to evaluate a 12-member microbial consortia system from gnotobiotic mice cecal samples, in order to study how these microbial communities impact diet-induced changes in the mouse. For this work, proteomics will be a key aspect of unraveling microbial activity at the protein level. We are employing a new detergent-based cellular lysis method to enable deep proteome coverage, as well as exploit novel bioinformatics techniques developed at ORNL to delineate unique vs. nonunique peptides from closely related organisms.

Publication

Mahowald, M. A., F. E. Rey, H. Seedorf, P. J. Turnbaugh, R. S. Fulton, A. Wollam, N. Shah, C. Y. Wang, V. Magrini, R. K. Wilson, B. L. Cantarel, P. M. Coutinho, B. Henrissat, L. W. Crock, A. Russell, N. C. Verberkmoes, R. L. Hettich, and J. I. Gordon. 2009. "Characterizing a model human gut microbiota composed of members of its two dominant bacterial phyla." Proc. Natl. Acad. Sci. **105,** 5859–5864.

00509

Integration of Analytical Imaging Methods

Peter J. Todd

Project Description

This project will apply image transformation methods and correlation algorithms with chemistry to permit virtual (i.e., mathematical) and practical integration of secondary ion mass spectrometry (SIMS), optical, and scanning electron microscopy (SEM). The strengths of one imaging method will overcome the limitations of the other method(s). For example, an SEM image can display a spatial resolution of about 10 nm routinely, but a SIMS image, only about 1 μm. SEM images of a sample could thus be used to identify very small (<1 μm) regions of interest, for example, a particle or inclusion, relative to other features sufficiently large for identification by SIMS. Correlation will permit the locations of these small regions to be found relative to the larger features. Thus, SIMS could provide isotope ratio and trace element detection, even of particles smaller than 1 μm, if an SEM image showed their relative position.

Mission Relevance

Mathematical integration of analytical imaging data would have a profound effect on non-proliferation efforts. Currently, correlation is done manually, and is expensive, stressful, boring, and generally unreliable. As well, the combination of SEM, SIMS and optical imaging will enhance current efforts to measure diffusion coefficients in MgAl alloys as part of the Integrated Computational Materials Engineering (ICME) initiative. Optical and electron microscopies can be used to identify grains and boundaries necessary because these features play a prominent role in diffusion. SIMS will be used to measure the distribution of stable isotopes as a function of depth. This project will benefit programs of the National Institutes of Health. Much of biomedical research is centered on imaging technology, e.g. optical microscopes. Integration of SIMS and SEM, analytical imaging devices, has not been developed at all, but could significantly add to this effort, as well as profoundly affecting biomedical philosophy.

Results and Accomplishments

Software developed for optical image correlation was installed and tested. SEM images created from backscattered electrons show primarily topographical and secondly compositional features in a sample, while XPS images reflect the distribution of targeted element concentration differences. These images could be correlated manually, as well as by the software, permitting validation of applying software developed for optical image correlation to analytical image correlation.

Extension of automated image correlation to secondary ion images was hampered by instrumental difficulties. In fact, loss of samples prepared for the Cameca IMS4f and lost by instrumental problems consumed much of the effort spent on this very short project. With corrective maintenance outside the scope of this project, these problems will be corrected.

00512

Luminescence of Levitated Individual Semiconductor and Noble-Metal Nanoparticles

William B. Whitten and Stanley Pau

Project Description

The objective of this project is to demonstrate that individual nanoparticles can be electrodynamically trapped and that their fluorescence emission can be used to characterize the particles. We hope to further show that these techniques can be used to study surface photochemical processes on individual nanoparticles. The first task will be to construct a measurement chamber containing an electrodynamic trap with optical access for the excitation laser beam and optics to collect the luminescence from the particles. A laser beam will be passed through the chamber either horizontally or vertically to excite luminescence from a trapped particle. Viewports in the other horizontal direction will permit collection of a portion of the luminescence emission by using a large-aperture microscope objective for spectroscopy and a video microscope for visual observation of the particles in the trap. The latter arrangement avoids ocular exposure to scattered laser light. For trapping, the nanoparticles must be charged. If individual particles can be trapped, their optical emission spectra will be acquired with a grating spectrograph equipped with a charge coupled device (CCD) camera detector.

Mission Relevance

The luminescence of semiconductor and noble-metal nanoparticles is of interest because the luminescence is much more intense than for bulk samples of the same materials and the nanoparticles can be used as fluorescent labels for biomolecules and cells and as catalysis centers. Most of the experimental studies have been conducted on ensembles of particles in solution or deposited onto a substrate. In ensemble measurements, inhomogeneity in particle size can wash out any structure in the luminescence spectrum. For particles on a substrate, interaction between the particle and the surface can produce large perturbations in optical properties such as spectral diffusion and fluorescence blinking. The objective of the proposed project is to study the luminescence of individual nanoparticles levitated in an electrodynamic trap free from the influence of substrate or solvent.

Results and Accomplishments

A measurement chamber containing an electrodynamic trap with optical access for the excitation laser beam and optics to collect the luminescence from the particles was constructed. Earlier measurements on trapped microparticles had been made in air with little attention to possible particle escape into the environment. Safety concerns over possible exposure to airborne nanoparticles made positive confinement of the particles under study a necessary requirement. Consequently, the sample chamber was maintained under negative pressure and the withdrawn air was filtered using a high-efficiency particulate air filter before entering the vacuum pump. The electrodynamic trap was designed by Stanley Pau from the University of Arizona, a coinvestigator. The trap was fashioned by depositing circular gold electrodes on both sides of a thin aluminum oxide plate with a central hole. An oscillating voltage applied to the upper circular electrode produced an ac quadrupole field with a minimum along an axis perpendicular to the plane and passing through the hole in the plate. This ac quadrupole field permits the capture and levitation of suitably charged particles for subsequent optical measurements. Attempts to charge the analyte particles by electrospray resulted in insufficient charge for trapping. Particles were successfully charged by friction on a Teflon substrate. Both submicrometer-sized diamond crystals and particles dried from a suspension of 50 nm gold nanospheres were successfully trapped, as evidenced by visual observation on the video monitor. An emission spectrum of a trapped gold particle was shown to be

largely due to plasma lines from the argon ion excitation laser—further work is needed. Our successful nanoparticle trapping demonstration will, however, enhance a future proposal to the DOE Office of Basic Energy Sciences regarding carbon dioxide photo-degradation on suspended nanoparticle catalysts.

00513

Study of Radio Frequency Critical Magnetic Fields of Superconducting Materials Using Microsecond-Long Pulses

I. E. Campisi, S.-H. Kim, J. D. Mammosser, D. K. Christen, and T. S. Bigelow

Project Description

To date only a handful of data exists on the maximum critical fields that a few superconductors can reach when subject to microwave or radio frequency (RF) fields. The main reason for such lack of data is due to the complexity of manufacturing complete cavities out known or new superconductors which can be operated successfully in continuous wave to fields high enough to be of interest to physics. The method in this project circumvents that problem by using microwave pulses shorter than the thermal relaxation times of those materials and allows one to rapidly tests small samples of materials at various temperatures, thus selecting potential new materials for microwave applications and giving a better insight into nonequilibrium superconductivity. The results will be plentiful databases on the critical magnetic fields at microwave frequencies for many superconducting materials.

Mission Relevance

Better knowledge of the limiting fields in superconductors is of great importance to applications in superconducting particle accelerators, such as the Spallation Neutron Source for Basic Energy Sciences, the Continuous Electron Beam Accelerator Facility for Nuclear Physics, the future International Linear Collider or Project X at FermiLab, or other accelerators for high energy physics. Moreover, the study of the microwave properties of superconductors can also lead to an improved physical understanding of their nonequilibrium properties, knowledge that benefits superconducting materials science.

Results and Accomplishments

A variable frequency TE011 (Transverse Electric mode 011) copper cavity has been designed and built, which allows testing of circular, 1 in. diameter samples of superconducting materials. The cavity has been tested with a high-technitium superconductor at 77 K using a 16 GHz magnetron oscillator which provided about 120 kW peak power for about 200 ns pulse length. No evidence of RF magnetic field penetration has been observed up to about 500 Oe, limited by the energy in the RF pulse.

A dewar insert has been designed and built to allow testing down to below 4.2 K. The system is being commissioned and has passed safety inspections.

An 18 GHz klystron from the Fusion Energy Division is being recommissioned to reach higher pulse energies; this will allow testing of superconductors to higher fields within weeks.

00514

An Ionic Liquids–Based Ion Detector

Peter T. A. Reilly

Project Description

Ionic liquids will be used to create an ion detector whose response is essentially independent of mass. A mass independent ion detector will be created by interfacing an electron multiplier with an ionic liquid reservoir. Ions of any size will impact the surface of the ionic liquid in vacuum whereupon ions from the liquid of the same net charge and polarity will be ejected. The interaction of particulate ions with ionic liquids will be explored as a function of particle kinetic energy, mass and charge. The ability to detect ions without mass dependence is the last major hurdle for the direct analysis of mass specific species such as whole ribosomes, RNA, DNA or even viruses.

Mission Relevance

Part of DOE's strategic plan is to strengthen scientific discovery through innovation. One of the strategies of this theme is to expand efforts in biological and environmental research, including genomic and related biological sciences to create fundamentally new energy sources and conversion processes. The development of a mass independent detector will permit the rapid analysis of biological systems that are relevant to our energy future. The vast improvement in the rate of analysis will increase the rate of discovery of new energy sources and conversion processes.

The mission of the National Institutes of Health will be greatly enhanced by the capabilities this detector will provide. It will enable the direct measurement, characterization, and identification of complex mixtures of proteins, protein complexes, RNA, DNA and even viruses. The ability to analyze complex biological systems rapidly will accelerate the rate of discovery. The Departments of Homeland Security and Defense are greatly interested in rapid analysis of bacteria and viruses. This innovation enhances these analyses.

Results and Accomplishments

This project is still being carried out. An experimental apparatus has been designed, built, and assembled to test ionic liquid media for ion exchange. Our work with low energy ions (<100 eV) suggests that ionic liquids do not eject small ions from the low energy impaction process. Changing the type of ionic liquid seems to have no effect on small ion ejection with low energy impact. Our results indicate that the large ions bounce off the ionic liquid surface without penetration and ejection of small ions. However, our work at higher energy suggests that the ionic liquid medium produces secondary ions at much lower thresholds in comparison to a metal surface. We have been successful at detecting large singly charged ions up to the 200 kDa range with only 2 keV of kinetic energy. There does not seem to be a lower mass limit. It has been theorized that there is a kinetic energy threshold for penetration of the large ion into the ionic liquid bulk. We hope to determine the upper size/mass detection limit as a function of kinetic energy in a final set of seed money experiments. Our work to date suggests that the type of ionic liquid does not significantly affect its effectiveness as an ion conversion medium.

00516

The Effect of Nanoscale Confinement on Properties of CO_2-Rich Fluids Relevant to Carbon Sequestration

Miroslaw S. Gruszkiewicz and David R. Cole

Project Description

The goal of this project is to provide the proof of principle for a novel method of measuring densities and liquid–vapor phase boundaries of fluids confined in nanopores. The principal areas of application are large-scale geological CO_2 sequestration and enhanced geothermal systems (EGS). Complex behavior originating from molecular-scale interactions at the fluid–solid interface cannot be predicted using bulk fluid properties. The new experimental tool will be used to explore properties not directly accessible by existing methods, but necessary for development of realistic molecular-level simulations and universal reactive transport models capable of predicting fluid flow and dissolution/precipitation of minerals. Vibrating tube densimetry (VTD) has been used successfully at ORNL for obtaining pressure-volume-temperature-composition behavior of bulk fluids, but it has never been applied to pore-confined fluids. This project was funded in two steps. The first task (FY 2009) was to (1) reconstruct the existing VTD instrument and test operation with solid-filled vibrating tubes and (2) measure for the first time by VTD the changes of density as a function of pressure-temperature conditions and the locus of liquid-vapor phase equilibrium envelope for a gas contained in the pores of SiO_2 (silica) aerogel. The award of the remaining funding was conditional on the success of this task.

Mission Relevance

The anticipated results of this project and future applications of the new method are directly relevant to the development of energy technologies relying on interactions between fluids and nanoporous solids, such as geological CO_2 sequestration, EGS development using supercritical CO_2 as the primary thermal fluid, catalytic reduction of CO_2 for solar fuels, water splitting in catalyzed cycles, nuclear waste storage, and nanomaterials manufacturing. The project addresses directly DOE basic research needs formulated in the workshop report “Basic Research Needs for Geosciences” (2007). Relevant recent calls for proposals include Energy Frontier Research Centers and anticipated calls for single investigator and small group projects (DOE Office of Basic Energy Sciences [DOE BES]), Research, Development, and Analysis of Geothermal Technologies (DOE Office of Energy Efficiency and Renewable Energy [DOE EERE]), and enhanced coal bed methane recovery (DOE Office of Fossil Energy).

Results and Accomplishments

The existing VTD apparatus was modified accommodate solid-filled vibrating tubes. New Hastelloy tubes, straight and U-shaped, were prepared and filled with silica aerogel (density 0.2 g/cm^3) synthesized *in situ* (Ocellus Inc).

Mounting Alnico magnets and vibrating tubes to the VTD core by welding, as done previously, was not acceptable since (1) porous material could be damaged by high temperature and (2) tubes and magnets need to be replaceable. New vibrating tube mounts and new clamps for magnets were designed, fabricated, and retrofitted in the existing core. The silver core of the VTD was assembled using a U-shaped solid-filled tube and successfully tested for stable vibrations. The resonant frequency of vibration (265 Hz) was in the predicted range. These results show that the porous solid adhered strongly to the tube walls.

Subsequent tests with gas adsorbed in aerogel pores require precise temperature and pressure control, but the existing equipment was nonfunctional or inadequate. Currently the pressure gauges, temperature control and the frequency recording facilities are being reconstructed.

Since this project was started, new funding for vibrating tube densimetry of confined fluids was obtained from two sources: (1) DOE BES (Energy Frontier Research Center for Nanoscale Control of Geologic CO_2 and (2) DOE EERE (Development of Geothermal Technologies related to Enhanced Geothermal Reservoirs). LDRD Seed Money funding provided an important early background advantage for the successful pursuit of these new opportunities and the ability to prove the new method and deliver the expected results faster.

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

00491

The Graphics Processing Unit–Enhanced Computer for Large-Scale Text Mining

Xiaohui Cui and Thomas E. Potok

Project Description

We are quickly reaching an age in which a capability is needed for text mining (TM) of terabyte-scale unstructured text corpora for prompt decision making. Analyzing large-scale text collections requires high-performance computing and various algorithmic changes to current TM approaches. The graphics processing unit (GPU) can solve some highly parallel problems much faster than the traditional sequential processor (CPU). Thus, a deployable system using a GPU to speed up large-scale TM processes would be a more effective choice (in terms of cost/performance ratio) than using a computer cluster. However, due to the GPU's application-specific architecture, harnessing the GPU's computational prowess for TM is a great challenge. The objective of this project is to prove the feasibility of utilizing the computational capabilities of GPUs to speed up TM on large-scale datasets.

Mission Relevance

In addition to the applications outlined for this project, our research result could be applied in intensive computer modeling, for supporting research such as climate change data processing, advanced computing architecture, risk analysis for national energy infrastructure, and confined plasma and high energy particle beams problems currently of concern to DOE. The approach will provide general massive volume data analysis methods and advanced computing architecture that will be beneficial in many other research areas of interest. A successful result will enable us to demonstrate the use of much cheaper GPU-enhanced systems to provide massive document processing capacities. This capability will benefit agencies such as the Department of Homeland Security, the Defense Advanced Research Projects Agency, and the intelligence communities, who have armies of analysts searching text on a daily basis in pursuit of the proverbial needle in a haystack.

Results and Accomplishments

In FY 2008, we developed and presented a parallel latent semantic analysis (LSA) implementation on the GPU, using NVIDIA® Compute Unified Device Architecture and Compute Unified Basic Linear Algebra Subprograms. In this FY 2009 research, we assessed the benefits of exploiting the computational power of Beowulf-like clusters equipped with contemporary GPUs as a means to significantly reduce the runtime of flocking-based document clustering. The GPU computational platform we experimented in this research experiment is a cluster of closely coupled machines connected via a fast network link. There are three levels of parallelisms in our GPU program design. At the top level are the MPI processes, the number of which is the determined by the availability of resources (e.g., the number of physical nodes in

the cluster). In the middle layer are the CPU threads that run in each MPI process. They share one GPU card and launch GPU kernels independently. At the bottom level are the GPU kernels consisting of blocks of many light-weighted threads. The implemented algorithms are based on previous research performed at ORNL and consist of two phases: the Tf-Icf step and flocking-based document clustering simulation.

Our framework scales up to over one million documents processed simultaneously in a sixteen node GPU cluster. Results are also compared to a four-node cluster with higher-end GPUs. On these clusters, we observe thirtyfold to fiftyfold speedups, which demonstrates the potential of GPU clusters to efficiently solve massive data mining problems. Our results show that performance gains stem from three factors: (1) acceleration through GPU calculations, (2) parallelization over multiple nodes with GPUs in a cluster, and (3) a well-thought-out data centric design that promotes data parallelism. Such speedups combined with the scalability potential and accelerator-based parallelization are unique in the domain of document-based data mining, to the best of our knowledge.

Publications

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Cui, X., J. M. Beaver, J. St. Charles, and T. E. Potok. 2008. "Dimensionality reduction for high dimensional particle swarm clustering." *Proceedings of the IEEE Swarm Intelligence Symposium,* September, St. Louis.

Cui, X., J. M. Cavanagh, and T. E. Potok. 2009. "Parallel latent semantic analysis using a graphics processing unit." *Proceedings of the 2009 Genetic and Evolutionary Computation Conference,* July, Montreal, Canada.

Zhang, Y., F. Mueller, X. Cui, and T. E. Potok. 2009. "A programming model for massive data parallelism with data dependencies." The Eighteenth International Conference on Parallel Architectures and Compilation Techniques (PACT), September, Raleigh, N.C.

Zhang, Y., F. Mueller, X. Cui, and T. E. Potok. 2009. "GPU-accelerated text mining." Workshop on Exploiting Parallelism using GPUs and other Hardware-Assisted Methods, March, Seattle.

COMPUTER SCIENCE AND MATHEMATICS DIVISION

00471

Electron Transport at the Nanoscale: Grain Boundary Resistance in Interconnects

Don M. Nicholson, An-Ping Li, Balasubramaniam Radhakrishnan, Xiaoguang Zhang,
Tae Hwan Kim, and Boyd M. Evans III

Project Description

The project addresses the problems associated with the rapid increase in resistivity as copper interconnect lines in integrated circuits become narrower than 40 nm. Circumventing this problem is critical in maintaining Moore's Law growth in computer speed. A basic understanding of grain boundary (GB) resistance in interconnects will be obtained by phase-field crystal modeling of GB distribution and structure, first-principles calculation of the resistance of individual GBs, and the nanoscale measurement of resistance across individual GB of copper lines with carefully controlled geometry. The measurements will be done on copper lines etched from blanket films that have been annealed to form large "bamboo" grains. Characterization and transport measurements will be performed using the four-probe scanning tunneling microscope with cryogenic and ultrahigh-vacuum capability. Electron back-scattering diffraction will be used to determine the misorientation angle of the measured grain boundaries.

Mission Relevance

This project is important for the continued growth in computer speed needed to address DOE's energy and security problems including Basic Energy Science, climate modeling, and transportation. It is important to the Defense Advanced Research Projects Agency for military computing, sensors, control of manned and unmanned vehicles, missile guidance, implantable biodevices and sensors. The National Institutes of Health will benefit from the possible further miniaturization of biodevices and the reduction in power requirements, for example, power from cochlear implants. The Department of Homeland Security will benefit from reduced power and size of explosive detectors. The energy wasted as joule heating in interconnects accounts for several percent of national electricity use. Our work could reduce the waste.

Results and Accomplishments

We upgraded our code for the phase-field-crystal modeling method so that it can run on parallel computers and used it to model microstructure evolution. A coupled finite element Potts Model was used to simulate the effect of stored energy on grain structure in interconnects. We have advanced electron transport codes so that it can model resistance of grain boundaries in metals. We have used a focused gallium ion beam to machine very small copper wires, 250 nm × 400 nm, (less than a hundredth the size of a human hair). We have characterized the orientation of each grain along the wire, and measured the resistance across the boundaries between grains. The cross-sectional area was determined from the

temperature dependence of the resistance and was used to convert the resistance across grain boundaries into the specific resistance of the grain boundaries. A theory for a universal resistance of incoherent high angle grain boundaries was proposed and used to explain the measurements. These are first-of-a-kind measurements.

Publication

Kulkarni, N. S., B. M. Evans, T.-H. Kim, A.-P. Li, E. A. Kenik, and D. M. Nicholson. 2009. "Specific grain boundary resistivity measurements in thin film copper bicrystals." *Advanced Metallization Conference 2008, Materials Research Society Book Series* **24,** 269.

00522

DNA Separation Using Electrophoretic Traps

Fedor Rudakov

Project Description

Ability to separate biomolecules according to sizes is required for wide variety of applications including DNA sequencing, genotyping, mutation analysis, and diagnosis of diseases. Usually, separation by size is achieved by electrophoretical transport of charged biomolecules through a sieving media using uniform electric field. We present an alternative design that allows separating biomolecules of a particular size from a mixture without performing complete separation of the sample by size. Our design allows independent manipulation of biomolecules of different sizes along any pathway in two dimensions while keeping them highly concentrated. By manipulating the speed of the photoelectrophoretic trap, biomolecules of a particular size can be selectively separated from the mixture.

Mission Relevance

This is a basic research program that will benefit ongoing fundamental computational research for the DOE Office of Basic Energy Sciences being conducted by scientists at the Center for Engineering Science Advanced Research (CESAR) and at the Computer Science and Mathematics Division. It will also benefit other DOE research programs in biology and life sciences.

Results and Accomplishments

We have demonstrated (both computationally and experimentally) selective separation of DNA fragments using optically directed transport. Separation is achieved by manipulation of the speed of the photoelectrophoretic trap and is based on the capability of the biomolecules to "keep up" with the trap, which is size dependent. Biomolecules inside the trap remain highly concentrated which prevents band broadening due to diffusion. In addition biomolecules can be translocated along any pathway in two dimensions independently from each other. Our methodology enables tight control over the separation process and can potentially provide very high resolution. The results are summarized in our paper in *Applied Physics Letters*.

We studied dynamics of DNA fragments in a periodic potential and demonstrated their separation. The publication summarizing our results is currently in preparation.

Publication

Braiman, Avital, Fedor Rudakov, and Thomas Thundat. In press. "Highly selective separation of DNA fragments using optically directed transport." *Appl. Phys. Lett.*

ENERGY AND TRANSPORTATION SCIENCE DIVISION

00506

Dissolution of Monoglyceride Precipitants in Biodiesel by the Application of Microwave and Ultrasonic Energy

Michael D. Kass, Samuel A. Lewis, and Raynella (Maggie) Connatser

Project Description

The proposed effort seeks to eliminate monoglyceride precipitants that form in biodiesel fuel at low ambient temperatures. By applying low-level microwave and ultrasonic energy to precipitated biodiesel, we seek to assess whether microwave and ultrasonic energy can be used to redissolve the precipitant. Microwave and acoustic energies have been shown to preferentially heat in interfacial regions. Therefore, heating will be concentrated at the solid precipitant surface, without substantial bulk heating of the solution. The influence of microwave/acoustic energy to promote dissolution of the solid precipitants will be assessed.

Mission Relevance

With the rising cost of petroleum and the recognized need to utilize domestic fuel resources to improve the nation's energy security, biofuels, such as biodiesel, offer a promising alternative to help meet the country's energy needs. Additional concerns about global warming have also led to calls for more renewable energy sources, including alternative fuels. Successful demonstration of the proposed effort will improve the acceptability of biodiesel to the U.S. consumer and lead to the expansion of biodiesel usage. The proposed effort directly supports the DOE Vehicle Technologies Program, which seeks fuel options that contribute to petroleum displacement (such as biodiesel) and to identify environmentally friendly fuels. In addition, the DOE Biomass Program would be supported by this effort since this program seeks to improve the production of biofuels (including biodiesel).

Results and Accomplishments

Neat biodiesel was spiked with 20 ppm steryl glucoside (SG), 40 ppm sodium dodecylsulfate (SDS), and 500 ppm water in order to form precipitates at low temperature. The spiked biodiesel was refrigerated overnight to form precipitates, which are stable at room temperature and contribute to increased filtration time due to filter plugging. Filtration time is the parameter used to determine the level of precipitate formation and the standard method is outlined in ASTM D 6217. The spiked and refrigerated biodiesel increased the filtration time by 12%, which is significant. When the spiked and refrigerated biodiesel was subjected to the application of ultrasonic energy (450 W and 20 kHz), the filtration time was lowered by 20%. This drop in filtration time means that the precipitates were eliminated or altered, such that they did not contribute to filter plugging. A thermal control was also evaluated and the result showed that the precipitates were not eliminated by heat alone and that the thermoviscous forces associated with acoustic attenuation were responsible for the improved performance. Dissemination of the results should lead to

the development of sonic-based techniques to mitigate precipitate formation in biodiesel. Removal of the precipitates is significant and should lead to the expansion of biodiesel as an alternative fuel.

ENVIRONMENTAL SCIENCES DIVISION

00466

Tracing Nanoparticle Transport in Porous Media by Neutron Radiography and SANS

Baohua Gu, Wei Wang, Ken Littrell, Hassina Z. Bilheux, and Xun-Li Wang

Project Description

Understanding of the behavior and fate of engineered nanoparticles in the environment is needed because of growing concerns of potential environmental and health risks of these particles. However, our current understanding is severely limited by available techniques to characterize these nanoparticles once they enter into the environment (e.g., natural sediments and groundwater). This project explored the use of small-angle neutron scattering (SANS) and thermal neutron radiography techniques to determine the deposition and transport behavior of nanoparticles such as silica (SiO_2) and titania (TiO_2) in quartz sand media. Unlike the black-box approach used in early studies, this research provides the first-ever proof-of-principle measurements of the deposition and transport profiles of nanoparticles and particle aggregates *in situ* as a function of particle size and surface chemical characteristics. The study is anticipated to lay the foundation for using a neutron source to study the fate and transport of nanoparticles in the environment and thus benefit the development, management, and risk assessment of engineered nanomaterials.

Mission Relevance

Engineered nanoparticles such as silica, titania, metals, and metal oxides are among the most widely used nanomaterials in advanced energy, catalysis, and commercial applications, but little is known about their environmental, health, and safety implications. Recent studies suggest that they become increasingly harmful at smaller sizes. Studies of the fate and transport of nanoparticles in the environment will benefit the development, management, and risk assessment of engineered nanomaterials and technologies. Programs that may benefit from this research include the DOE Offices of Biological and Environmental Research, Basic Energy Sciences, and Materials Sciences.

Results and Accomplishments

The behavior of both silica and titania was investigated in packed quartz columns under either static or flow-through conditions to mimic environmental conditions where nanoparticle deposition and transport occur in the subsurface sediment. Both labeled and unlabeled nanoparticles with controlled sizes were synthesized to facilitate *in situ*, nondestructive analysis of the deposition and transport processes. We performed the SANS experiment at the High-Flux Isotope Reactor and the neutron thermal imaging experiment separately at the Neutron Research Facility in Garching, Germany. Results from SANS experiments show clear patterns of particle interactions and aggregation behavior during the transport of either SiO_2 or TiO_2 nanoparticles through the quartz media under different pH and ionic compositions. The transport behavior of silica was found to strongly depend on the solution ionic strength but not so on

the pH (from 3.5 to 9.5) because of its low zero point of charge (zpc ~ 2). However, extensive aggregation and deposition of TiO_2 nanoparticles occurred at pH below 7, and transport of TiO_2 was significantly retarded because of oppositely charged TiO_2 nanoparticles and quartz surfaces. These results provided fundamental insights into how engineered nanoparticles may behave and migrate once they enter into the subsurface environment.

Using neutron-absorbing gadolinium- and cadmium-doped silica nanoparticles, the transport behavior of these nanoparticles were also studied, for the first time, by thermal neutron imaging. While the transport of these nanoparticles was clearly observed, we found that the image resolution and contrast were unsatisfactory, especially at relatively low particle concentrations. Future studies using neutron imaging will require improvements both in imaging resolution and sensitivity. Nonetheless, our results indicate that SANS is useful to elucidate the effect of geochemical properties on the deposition and transport of nanoparticles *in situ*, which would otherwise be impossible to obtain by using conventional techniques.

Publication

Gu, Baohua, Kangjoo Kim, Liyuan Liang, and Wei Wang. 2007. "Transport of nanoparticles in heterogeneous systems: Methodology and applications." American Geophysical Union Annual Meeting, Dec. 10–14, San Francisco.

00496

In Situ Neutron Imaging of Roots and Rhizosphere Water Exchange

Stan Wullschleger, Jeff Warren, and Hassina Bilheux

Project Description

Despite years of investigation, *in situ* imaging of roots and a dynamic evaluation of root water uptake from soil and transport within the plant have not been undertaken. In the past, root imaging and analysis of water exchange at the root-soil interface or rhizosphere have relied on isotope or dye tracers, or X-ray analysis. These approaches are labor intensive and either cause disturbance to the system or lack adequate spatial and temporal resolution to be informative. Our research explores the use of neutron imaging to create high-resolution images of plant roots and water dynamics in the root zone. Specifically, we are using the Spallation Neutron Source (SNS) and the High-Flux Isotope Reactor (HFIR) facilities to determine temporal patterns of water exchange in a root system and transport through plant xylem. Our research will evaluate (1) whether neutron imaging can be used to determine physical and chemical boundaries between root, the root-soil interface, and soil; and (2) whether neutron imaging can resolve patterns of water flux to and from roots. Our research is directed at resolving basic biological principles regarding water, carbon, and nutrient flux dynamics within and between soil, plants, and fungi.

Mission Relevance

Our research is directly relevant to several areas of interest to the DOE, especially as it relates to the integration of neutron facilities into areas of biological research, including bioenergy, carbon-cycle science, and global climate biology. This project attempts to address programmatic goals and objectives of the DOE Office of Biological and Environmental Research through their Genomic Science Program, their Terrestrial Carbon Program, and through their Program for Ecosystem Research. Many agencies support research that would benefit from new technology for the analysis of root images. Examples include evaluation of crops (Department of Agriculture, Agricultural Research Service), forest trees

(Department of Agriculture, Forest Service), and basic research conducted by the National Science Foundation.

Results and Accomplishments

The goal of this research is to evaluate neutron imaging for nondestructive, quantitative analysis of root structure, and soil, root, stem, and foliar xylem water flux. Towards this goal, in FY 2009 we proposed to conduct further research at beam line 3 (SNAP) of SNS, and at the development imaging beam line constructed at HFIR; however, SNAP was not available. Therefore, we continued to develop our sample chambers for use in imaging roots and root water uptake by plant roots and leaves. Neutron imaging successfully distinguished between nondeuterated or deuterated poplar leaf samples. Fine leaf veins (<200 μm) were visible in the nondeuterated sample, in comparison to the deuterated sample. This difference in contrast establishes the potential for tracking a pulse of water though plant xylem. Results from this SEED proposal will be presented at the 2009 ASA–CSSA–SSSA International Annual Meetings in Pittsburg.

00511

Investigation of Ionic-Liquid Attachment to Charged-Carbon Electrodes by Surface-Enhanced Raman Spectroscopy for Energy Storage

Shannon Mahurin

Project Description

In this project, we propose the use of surface-enhanced Raman spectroscopy (SERS) to investigate interactions between an ionic liquid electrolyte and a carbon electrode surface as a function of applied potential. SERS offers a method of determining the structure and nature of surface interactions by exciting characteristic vibrations of the adsorbing molecules. Nanostructured SERS-active substrates will be synthesized by thermal evaporation to form silver-island films on glass supports. Thin, optically transparent carbon films will then be deposited onto the SERS-active silver by thermal evaporation to use the Raman enhancing mechanism of the silver film to study interactions with the carbon. The silver/carbon film will then be immersed in the ionic liquid electrolyte where adsorption and bonding between the carbon surface and the ionic liquid will be probed by SERS as the voltage to the carbon electrode is increased.

Mission Relevance

DOE recently issued a Basic Energy Needs for Electrical Energy Storage workshop report that targeted the need for greater understanding of fundamental interactions at the electrode-electrolyte interface of capacitive storage devices. This report shows a DOE interest in new techniques for improving our understanding of capacitive devices, which is addressed in this proposed work. In addition, the DOE Office of Energy Efficiency and Renewable Energy has a long-standing interest in the development of energy storage systems and is expected to have a significant increase in R&D related to energy storage devices. The recently funded Energy Frontier Research Centers include work related to surface interactions at carbon/electrolyte interfaces.

Results and Accomplishments

In this project, we measured the Raman of the ionic liquid, [bmim][Tf_2N], at both a silver and a carbon-coated silver surface. The Raman of bulk [bmim][Tf_2N] was measured and compared to the SERS spectrum of the ionic liquid at a silver surface with no applied voltage. Shifts in SERS spectrum compared to the bulk spectrum allowed us to precisely determine the binding of the ionic liquid to the silver. We also discovered that the enhancement factor for the ionic liquid was less than 100, which is relatively small. Ultra-thin carbon layers were successfully deposited on the SERS silver substrate. However, the background Raman signal from the carbon and the low enhancement factor for the ionic liquid prevented us from measuring a strong enough Raman spectrum from the ionic liquid on the carbon surface both at zero potential and at an applied potential. This results because the enhancement factor decreases exponentially with distance from the silver surface.

00517

Ecological Effects of Fly Ash Exposure to Sentinel Fish Species

S. Marshall Adams

Project Description

Using an integrated bioindicator approach, developed and applied by Environmental Sciences Division staff over the past 20 years, we conducted field studies in Watts Bar Reservoir to establish baseline conditions for determining long-term biological and ecological effects of fly ash exposure on the health and fitness of three sentinel fish species in the area of a massive fly ash spill near the Kingston fossil fuel plant. We measured a suite of biological responses, including biochemical, physiological, histopathological, hematological, nutritional, and reproductive indicators, in these fish to assess their overall health and fitness. In addition, we also measured body burden levels of 25 metals, some of which are typically associated with fly ash, to evaluate possible causal relationships between heavy metal exposure and various indicators of fish health. Such studies serve to establish baseline conditions for future long-term ecological effects studies and to provide important information for helping to promulgate environmental regulatory standards for the utility industry relative to the treatment and discharge of fly ash effluents into receiving water bodies.

Mission Relevance

Fossil fuel generating plants are an important component of our nation’s electric power production, and our bioindicator approach, modified and calibrated in this study to investigate the biological effects of the fly ash spill at the Kingston fossil fuel plant, would be of value at other fossil fuel facilities (and thus to other power utilities) across the nation to assess the environmental and ecological issues associated with fly ash exposure to natural resources. Information provided by this baseline study, which has already generated almost $700K (with another approximately $350K to follow in spring 2010) of additional research funds to continue such studies, should immediately assist and benefit the Tennessee Valley Authority (TVA) in their assessment of the ecological effects of the fly ash spill. This study should also provide valuable environmental regulatory information for the Environmental Protection Agency (EPA), not only in their ecological risk assessment process, but also such information could provide critical data relative to their current considerations regarding regulating coal ash as a hazardous substance. In addition, results from these studies would also benefit the U.S. Fish and Wildlife Service (USFWS) in their Natural Resource Damage Assessment process.

Results and Accomplishments

Because of the time-critical nature of this study related to the assessment of possible effects of the coal ash spill on the biological resources of the Emory and Clinch River systems, these LDRD funds were instrumental in providing a "jump start" to this study, allowing us to get out into the field and collect baseline samples a few weeks after the massive fly ash spill. Obtaining these baseline samples (or preliminary data) has served as a platform for allowing us to expand the scope and nature of this project, which has subsequently resulted in funding support of almost $700K from TVA with another approximately $350K expected in spring 2010. In addition, we currently have a proposal submitted to another agency for almost $300K which builds upon the results of this baseline study and also benefits from the information generated from our follow-up related studies. Specifically, the results of the baseline studies, supported primary by LDRD, indicate that no definitive short-term effects of fly ash exposure were observed on the health of the sentinel fish species and no bioaccumulation of metals in these fish were detected above background levels (above the natural variability of the system). Possible implications and applications of these studies, including the support of the LDRD to collection of baseline samples, are relevant to (1) promulgating and setting regulatory standards for discharge of fly ash effluents into the environment (EPA and the Tennessee Department of Environment and Conservation), (2) prioritizing sites in aquatic systems for cleanup and restoration by the utility industry, (3) providing critical data for use in the ecological risk assessment process by the EPA, and (4) serving as a basis for the Natural Resource Damage Assessment process by the USFWS.

00524

Nanoparticle-Hydrogel Sensors for Trace Detection of Explosives in Groundwater

Wei Wang and Liyuan Liang

Project Description

This research will develop and synthesize a simple, inexpensive intelligent sensing material with high sensitivity and selectivity to rapidly detect explosives in contaminated groundwater *in situ*. We propose to fabricate the sensing material by simultaneously introducing colloidal photonic crystal nanostructure and molecular recognition functions into network of polymer hydrogel. The color of the synthesized hydrogel is designed to vary according to the changes in volume or lattice spacing of the embedded photonic crystal structure upon interaction between specific explosive molecules such as TNT and designed functional groups in the polymer hydrogel, thereby allowing the identification and determination of explosive molecules in water. The new technique potentially reduces the labor and analytical costs associated with sampling and laboratory analysis.

Mission Relevance

One of the key needs of the DOE Environmental Remediation Science Program is developing new methodologies for detection and identification of organic and inorganic contaminants in groundwater at DOE sites. Techniques for rapid screening and detection of explosives are needed by many federal agencies such as the Departments of Energy, Defense, and Homeland Security. For example, the DOD Strategic Environmental Research and Development Program has a statement of needs in FY 2009 on "advanced technologies for detection, discrimination, and remediation of military munitions" and "predictive techniques for assessment of the environmental impact of new munition compounds."

Results and Accomplishments

This project started in the last month of FY 2009. We have designed technical routes for fabricating SiO_2 nanoparticles and hydrogels, and are in process of procuring necessary materials, assembling apparatus, and hiring a postdoc. Future results will be reported.

GLOBAL NUCLEAR SECURITY TECHNOLOGY DIVISION

00504

Lu_2O_3-Based Transparent Polycrystalline Ceramic Scintillators: A New, High-Density Inorganic Scintillator for Improved Positron-Emission Tomography

John S. Neal, Lynn A. Boatner, and John J. Henry, Jr.

Project Description

The objective of this project is to synthesize and characterize a new, high-density inorganic scintillator based on lutetium oxide (Lu_2O_3, density = 9.4 g/cm^3) solid solutions for use in nuclear nonproliferation, homeland security, and positron emission tomography (PET) applications. Production of the high-density scintillating bodies would be made at a relatively low cost and in high quantity in a transparent polycrystalline ceramic form. The improvements in cost and availability are a result of (1) producing these new scintillators in a transparent polycrystalline ceramic form and (2) the need for thinner crystals (less volume of scintillator). Ceramic processing of these new scintillating bodies would also allow the realization of functionally graded scintillators in a single body. A successful demonstration of this new scintillator would also lead to applications in national security—i.e., as low-cost, medium-energy-resolution spectrometers for detection systems ranging from hand-held radioisotope identifiers to portal monitors.

Mission Relevance:

These new scintillator materials, when used for gamma-ray spectroscopy, directly address the need for medium-energy-resolution spectrometers within the NA-22-defined ConOp categories (characterize, contain/screen, and search). Cadmium zinc telluride (CZT) semiconductor detectors and lanthanum tribromide ($LaBr_3$:Ce) scintillators continue to be very expensive with limited commercial availability. The successful development of Lu_2O_3-based scintillators will meet the user requirements for room-temperature energy resolution at a cost that is significantly lower than that for single crystals and will allow for rapid, economical, and efficient commercial availability. These improvements in cost and availability are a result of producing these new scintillators in a transparent polycrystalline ceramic form and directly in near-net-shapes and sizes. The open-literature base supports the need for PET detector systems that incorporate depth-of-interaction (DOI) information and allow time-of-flight (TOF) PET for medical diagnostics. This project will benefit agencies supporting a wide range of medical applications including the National Institute of Biomedical Imaging and Bioengineering, the National Cancer Institute, and the National Institute of General Medical Sciences.

Results and Accomplishments

It should be noted that this work, along with our work on ZnO-based ceramic scintillators, were our first efforts to produce ceramic scintillators on ORNL's recently installed Spark Plasma Sintering (SPS)

equipment. After an initial break-in period for the SPS device, the equipment appeared be operating properly, but within a few months of the start of this project, equipment response became erratic, requiring long downtimes for repairs. Various temporary measures often led to confusing or nonreproducible results. Not until the end of the project did the vendor provide comprehensive equipment replacements/repairs. In spite of these equipment difficulties, we made significant progress towards producing transparent ceramic bodies that incorporated various lanthanides in an attempt to change the band structure in order to make Ce^{3+} fluorescence possible. The following paragraphs describe our accomplishments.

Because our previous work with lutetia ceramics was performed using a uniaxial hot press, we first sintered undoped lutetia (Lu_2O_3)ceramics using the SPS equipment in order to determine the best pressing conditions (times, temperatures, force) for producing transparent bodies. After finding the optimum pressing conditions for Lu_2O_3, we proceeded to study the effects of silica as a ceramic sintering agent. We established that silica doping did, in fact, produce samples with improved transparency and found a range of doping levels that produced the highest levels of transparency.

As a starting point for investigations of changing the band structure of lutetia-based ceramics, we investigated compositions similar to those reported by another group of researchers who claimed they had produced lutetia-based ceramics (produced using nanoparticle precursor particles and vacuum sintering techniques) that allowed Ce^{3+} fluorescence. Like these other researchers, our samples repeatedly turned out deep red in color, indicating Ce^{4+} (an optically inactive form of Ce). Maintaining cerium in the 3+ charge state in the highly reducing atmosphere of the SPS equipment has turned out to be one of greatest technical challenges for this project. Additionally, as with our undoped lutetia ceramics, we found that silica acted as a beneficial sintering agent.

With the refurbishment of the SPS device and subsequent improvement in the control and recording of sintering parameters, we are now able to observe the sintering behavior of lutetia-based ceramics. We believe that we are close to determining both the optimum conditions for making transparent lutetia-based ceramic scintillators and a method for maintaining cerium in the 3+ charge state. We plan to pursue additional sources of funding to continue this research.

00518

Passive Coded-Aperture Imaging of Fission-Spectrum Neutron Sources

Paul A. Hausladen and Matthew A. Blackston

Project Description

This small seed project constructed and demonstrated the first fission-spectrum neutron imager based on the coded-aperture technique. The imager was assembled with minimal investment from a repurposed array of ORNL-developed pixelated fast-neutron detectors with the addition of a coded-aperture mask and a modified detector fixture. The coded-aperture approach enables directional resolution that is an order of magnitude better than that reasonably achieved with neutron scatter cameras. This capability enables noncontact quantification of neutron sources that was not previously possible, such as counting distinct neutron sources in storage or deployed configurations from a distance or measuring the configuration of plutonium in a drum without opening it. Such capabilities would be useful for purposes of nuclear material control and accountability, treaty confirmation, or emergency response. The excellent angular

resolution and high efficiency of the imager compared with that achieved via neutron scatter cameras make this new class of applications potentially viable.

Mission Relevance

The ability to image and track individual neutron sources can potentially support DOE Safeguards, Nonproliferation, Transparency and Dismantlement, and Emergency Response missions. The capability can also potentially support the missions of the Department of Homeland Security and the U.S. Department of Defense to discover illicit nuclear material within and outside the United States. The fission-spectrum coded-aperture imager assembled in the present work was used immediately after commissioning for measurements of safeguards-related sources at the Idaho National Laboratory's Zero-Power Physics Reactor as part of the Advanced Fuel Cycle Initiative Safeguards Campaign. These measurements indicated the feasibility of using fast-neutron imaging for safeguards-related tasks such as monitoring storage, evaluating holdup deposits *in situ*, and identifying individual leached hulls still containing fuel. Follow-on funding will be sought to support DOE Safeguards and Dismantlement and Transparency missions.

Results and Accomplishments

The present work demonstrated the feasibility of coded-aperture imaging of fast neutrons from californium-252 (^{252}Cf), deuterium-tritium (D-T), and americium-beryllium neutron sources. Follow-on work demonstrated the feasibility of coded-aperture imaging of fast neutrons from plutonium mixed-oxide reactor fuel. In addition, active measurements with a pulsed D-T neutron source interrogating highly enriched uranium metal indicated that fast fission die-away neutrons from differential die-away measurements could be imaged between interrogating D-T neutron pulses. The passive and active imaging measurements represent the first-ever coded-aperture measurements of intrinsic and induced sources of fast fission neutrons. Measurements with the present mask-detector configuration showed that it was capable of spatial resolution of a few centimeters at the neutron source for close-up diagnostic images. The imager was demonstrated with ^{252}Cf fission neutrons to have an angular resolution of about 1° full width at half maximum and approximately an order of magnitude more sensitivity for fission neutrons than for fission gamma rays. Analysis of the measurements indicated that the imager would be much more sensitive than that used for the feasibility demonstration, provided neutrons and gamma rays could be distinguished via pulse-shape discrimination. Applications for the coded-aperture fast-neutron imaging could include monitoring of storage of secured vaults through the facility walls, evaluating fuel processing holdup deposits *in situ*, or noncontact counting of distinct neutron sources on deployed missiles as part of treaty confirmation measurements.

MATERIALS SCIENCE AND TECHNOLOGY DIVISION

00454

An Innovative Low/High-Temperature, Repetitive Pressure-Pulse Apparatus for Cavitation Damage Research

John Jy-An Wang, Fei Ren, and Hong Wang

Project Description

Cavitation damage has manifested itself as a major obstacle in many advanced technology developments either at room or at high temperatures (e.g., in spallation sources, modern high-speed turbomachinery, rocket engines, gas and steam turbines, diesel engines in heavy vehicle propulsion, spacecraft and high-speed marine vehicles, commercial power generating systems, propellers, pumps, bearing components). In this project, the feasibility of developing a novel, laser-assisted repetitive pressure-pulsed apparatus able to generate controllable cavitation events has been successfully demonstrated. In support of this demonstration, procedures to determine the cavitation parameters, such as pressure magnitude, and estimate the associated cavitation damage have been developed. This undertaking will support efforts to elucidate some of the fundamental hydraulic-mechanical processes associated with cavitation and its effects on target materials. With the main focus on the controllable cavitation parameters, such as pressure magnitude and temporal characteristics, as well as on damage characterization, the research carried out will have a wide-ranging impact on several important industrial sectors and their supply chains.

Mission Relevance

The success of this project will greatly increase our understanding of the underlying mechanisms of cavitation damage and our ability to develop strategies that would prevent or mitigate this form of damage. This work will impact programs within DOE and the Department of Defense (DOD) that focus on advanced engine development, advanced materials development, and their effective lifetime estimates considering cavitation damage (e.g., mercury target cavitation in the DOE Spallation Neutron Source project, potential plasma cavitation in the International Thermonuclear Experimental Reactor fusion reactor environment, naval fleet and aircraft integrity surveillance, National Aeronautics and Space Administration space propulsion program, DOD gas turbine engine development, DOE Office of Nuclear Energy nuclear power reactor system, and DOE Heavy Vehicle Propulsion Materials program).

Results and Accomplishments

Three prototypes of a Repetitive Pulsed-Pressure Apparatus (RPPA) were developed. The first generation was a small-scale apparatus, which was used in the proof-of-principle study. The second and third generation apparatuses were capable to test bulk samples, which were different in terms of the relevant orientation between the laser beam and the test samples. The synergistic effect combining cavitation and the pulse-heating/media-cooling induced thermal cycling fatigue to the target surface damage was

demonstrated with the second generation apparatus; while the third generation apparatus was suitable to study the cavitation damage without laser thermal interaction. The verification experiments on stainless steel and aluminum samples were carried out both in tap water and distilled water. The key parameters of the cavitation environment, such as pressure and temperature, were calibrated and benchmarked during the experiments. Cavitation damages such as pitting and indentation were observed on sample surfaces using scanning electron microscopy. The synergistic effect of combining cavitation and the pulse-heating/media-cooling induced thermal cycling fatigue to the target surface damage was also demonstrated in this project. The developed novel systems have many distinctive advantages compared to the present experimental devices for cavitation research, in particular (1) it has no external driver (pump) or moving part, (2) the miniature design avoids the large water channel loop required in conventional approaches, (3) it can be tailored to evaluate multiple design variables to mimic cavitation environment, and (4) it has low testing time and cost.

Publication

Wang, Jy-An, Fei Ren, and Hong Wang. 2009. *An Innovative Low/High-Temperature, Repetitive Pressure-Pulse Apparatus for Cavitation Damage Research.* Technical Report ORNL/TM-2009/260, Oak Ridge National Laboratory, Oak Ridge, Tenn.

00463

Atomic-Level STEM Imaging of Bias-Induced Phase Transformations: Applications to Information Technology

Albina Y. Borisevich and Sergei V. Kalinin

Project Description

We propose to develop an experimental framework to address the role of individual defects on the dynamics of first-order phase transitions in ferroelectrics on the atomic level. The combination of scanning transmission electron microscopy (STEM) with scanning tunneling microscopy (STM) or atomic force microscopy (AFM) experiments, implemented on a recently acquired Nanofactory (S)TEM-STM and (S)TEM-AFM systems, will allow us to combine the atomic resolution and electronic sensitivity of STEM with the local electrical/mechanical excitation capabilities of STM/AFM. The unique feature of this setup is that electrical bias or force can be applied *locally* to a chosen point of the sample, providing the means to compare dynamics of switching (e.g., at and away from a dislocation or a structural defect). The local observations of polarization dynamics will allow elucidation of the mechanisms for domain wall motion, domain nucleation, polarization-induced changes of interface properties, and contact effects.

Mission Relevance

Electrically based phase, structural, and chemical transformations underpin multiple areas ranging from ferroelectric and phase-change materials in information technology to areas such as fuel cells, solid-state electrolytes, solid-state lighting, and photovoltaics, subjects of critical importance for DOE. The properties of these materials are controlled by defects that act as nucleation centers for new phases and pinning centers for moving transformation fronts. Understanding these dynamic phenomena on a single-defect level and elucidation of associated mesoscopic and atomictic mechanisms require the capability to probe the local aspects of these transformations *in situ*. This knowledge, once acquired, can be used to design new generation of materials with controlled defect populations to control and direct the phase transformation mechanism, and will lead to new generations of information and energy storage ematerials

and high-life time energy conversion systems. This research combining STEM and STM/AFM capabilities will directly fall under auspices of current and future programs in this direction and has initiated a new independent FWP on the interface between two techniques.

Results and Accomplishments

In the course of the project, the primary effort has been focused on the installation and operation of the STEM-SPM holders as well as development of model systems. The single-tilt STM and AFM holders, as well as a double-tilt STM holder, were successfully delivered and installed. The results on *in situ* characterization of electronic transport in SnO_2 and ZnO nanowires as a function of applied strain (i.e., piezogalvanic effects) were obtained. Preliminary studies in VO_2 nanowires, which possess a bias-induced metal-insulator phase transition, have been performed; the results will be reported at the fall 2009 meeting of the Materials Research Society. We have performed extensive characterization (STEM/EELS) of $BaTiO_3$, PZT, and $BiFeO_3$ samples for STEM-SPM studies and demonstrated (1) atomic resolution structure imaging, (2) EELS imaging across the interface, and (3) imaging dislocation structure. We were able to track structural intricacies such as polarization and octahedral tilts across the interface. For this work we received a lot of exposure at the international meetings (see list), and the first of the series of papers is now submitted to *Science*. We have developed and tested sample preparation routines for thin-film samples with a free-standing edge and 10° miscut, required for experiments with the double tilt STM holder. The preliminary results on bias-induced ferroelectric phase transition and domain wall motion were obtained. On $BiFeO_3$ thin films, we were able to demonstrate tip-induced domain switching and characterize shape and time evolution of the domains. The short summary of first results is now submitted as *Science* Brevia. The ideas utilized in this project were further developed as a part of a bigger proposal submitted to a Single Investigator/Small Group call from DOE and successfully initiated in August 2009.

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00474

Development of a Device for Low Cost In-Reactor Loading of Materials

Lance L. Snead, Thak Sang Byun, Roger G. Miller, and Joel L. McDuffee

Project Description

Strong interest has been demonstrated by domestic and international programs for the development of an inexpensive, conceptually simple vehicle for irradiation-creep measurements in the High-Flux Isotope Reactor (HFIR). In its simplest case, within a HFIR rabbit a pressurized bellows would transmit force to a sample to induce creep strain during irradiation. The rabbit capsule is a unique capability of HFIR, and the successful completion of this device would give ORNL competitive advantage. The technical and programmatic benefit of such a design is that upon creep the bellows internal pressure, hence applied load, undergoes negligible change and, in principle, the vehicle could be examined and reirradiated. The current state of the art is for an irradiation campaign of several years and several million dollars. Successful demonstration of this technology would allow for a much more rapid and inexpensive means of obtaining critically needed data. Moreover, as the cost for in-reactor sample loading has to date been prohibitive, this design would allow new opportunities for the basic science of irradiation effects to be carried out. The main goals of this project are to construct a creep load-train with a pressurized bellows and to demonstrate that the principle works.

Mission Relevance

Through discussion of the preliminary concept, interest has been indicated by ongoing DOE programs (U.S. Fusion, International Fusion Collaborations, Generation IV, and Naval Reactors) as well as by outside interests (British Energy [BE] and Pebble Bed Modular Reactor [PBMR] in South Africa.) In preparing the proposal, letters of support have been provided by the U.S. Fusion and Naval Reactors programs indicating interest in using this vehicle for future irradiations in the HFIR. This implies that construction, irradiation, post-irradiation examination, and evaluation of data would be carried out at ORNL. Moreover, an expression of interest for carrying out graphite irradiation, if successfully demonstrated, has been transmitted by both PBMR and British Energy (though likely in a collaborative BE/PBMR program.)

Results and Accomplishments

Stage 1. The first prototype load frame using pressurized bellows was designed and constructed. The materials for parts, pure molybdenum and Inconel 718, were selected for high temperature applications. An Inconel 718 open-ended bellows was selected and purchased, and also Inconel 718 end-caps were machined and welded to the bellows in an electron beam welding machine. An SS-3 type steel tensile specimen and the end-capped bellows were assembled in the molybdenum frame and the bellows was pressurized by helium gas through a pin hole in an end-cap to about 15 MPa. After pressurization, the pin hole was closed by laser welding to contain the gas pressure in the bellows. One of the end-caps was designed to protrude out of the end of the molybdenum frame so that the bellows can be loaded in a testing machine to measure load-displacement response. This capability is important because the actual load applied during irradiation can be experimentally measured after irradiation at the same temperature.

The load-displacement response of the pressurized bellows in the load frame was measured in a mechanical testing machine at different temperatures. A set of testing jigs was manufactured to hold the creep frame in the vacuum furnace. The creep frame was capable of a load of about 400 N at room temperature and about 500 N at 300°C, which can apply, respectively, about 350 and 450 MPa tensile stresses to the tensile specimen. Since actual irradiation creep tests are performed at higher temperatures, a higher stress can be introduced by the same pressure due to gas expansion. In most cases, irradiation creep will occur at less than 100 MPa (110 N) for a SS-3 metallic specimen and 10 MPa (or 500 N) for a rod-type graphite specimen with 8 mm diameter (500 N). This result demonstrates that the bellows-loaded creep frame can easily induce irradiation creep. For a typical ferritic steel specimen, the stress level is enough to induce even instant plastic deformation at higher temperatures.

The main hurdle we faced in construction of the load frame was leak after welding. The elastic deformation by internal pressurization produced failure at the welded and thus constrained edges of bellows when the welding chamber was depressurized. The internal pressure, 15 MPa, is believed to be nearly maximum pressure at which the weldment can sustain up to 300°C. Also, the buckling of the end-confined bellows at high temperature resulted from the high internal pressure. Both of these problems should be resolved by reducing the internal pressure to ~5 MPa or lower. In FY 2009, the load-displacement curves will be produced over a full range of temperatures up to 850°C using a load frame with a lower internal pressure. As a final task, the design will be optimized and thermal and safety performance calculations will be made for the optimized design.

Stage 2. Two prototype vehicles were designed, constructed, and began irradiation in HFIR. This vehicle was designed to apply 10 MPa stress to a 6 mm diameter nuclear graphite cylinder. The nominal irradiation temperature was 600°C. The first of these vehicles was removed from the reactor after one cycle of irradiation. The second vehicle is still under irradiation and will receive three reactor cycles. Funding has been identified to carry out post irradiation examination of these capsules from internal and external sources. The external sources include British Energy and the Japanese Atomic Energy Agency. Follow-on funding will be dependent on results of this post irradiation examination.

00476

Development of Inorganic Membranes for Water Reclamation from Wet Gas Streams—An Opportunity to Simplify Water Management Operations

M. Moses-DeBusk, B. Bischoff, and K. D. Adcock

Project Description

Our water reclamation system is designed to simplify water management operations by removing water from wet gas streams (i.e., diesel exhaust). The method we are evaluating for water reclamation permits a greater quantity of water to be removed at a given temperature compared to traditional direct condensation methods. Additionally, this process will limit water–gas contact time, reducing dissolution of gas-phase contaminants present in diesel exhaust and further enhancing this method's use in obtaining high purity water fit for human consumption.

Mission Relevance

The results of this project will impact national security missions related to energy resources by reducing fuel consumption required by the U.S. military for transport of potable water for soldiers' daily basic needs. Efficient use of fuel and personnel by the Army are impeded by the need to transport large amounts of bottled water, ~5 gal per soldier per day. The results of this project will promote the development of high efficiency on-vehicle water or stationary reclamation systems, reducing resources required for bottled water transport. The project results are of great interest to the Army and the Department of Defense.

Results and Accomplishments

Our project began with the fabrication of an inorganic membrane and construction of a test system. A holder was designed that could efficiently transfer the heat of condensation to a cooling jacket in order to remove the heat of condensation and reduce the membrane temperature for improved condensation.

Multiple studies were carried out to investigate the effect of water concentration and flow rate on the membrane's efficiency of reclaiming water from the wet gas stream. Additionally, to simulate acidity present in water condensed from diesel exhaust, NO_2, a primary contributor to diesel acidity, was added to the gas flow, and the pH of both the reclaimed water and the exhaust water was monitored.

Lower gas flow rates resulted in increased membrane efficiency for water reclamation. A greater reduction in the dissolution of acid causing NO_2 was also observed at lower flow rates. These results suggest that the membrane efficiency at higher flows would have been higher if the water displacement process could have kept up with the rate of water condensation. In summary, our method of water reclamation can reduce gas-phase contamination of reclaimed water promoting its use in production of potable water.

00482

Novel Infrared-Processed Titanium Composites for High-Temperature Galling Resistance

Peter J. Blau, Evan K. Ohriner, Brian C. Jolly, and Donald L. Erdman III

Project Description

Galling is a severe form of bearing surface damage that can result in plastic deformation and seizure. It is problematic for metals under high contact pressures and at elevated temperatures. The objective of this effort was to develop a novel infrared (IR) surface treatment and use it to synthesize a hard layer of particle-reinforced composite material to improve the high-temperature galling resistance of titanium alloys. The goal of this effort was to enable the use of lightweight, corrosion-resistant titanium alloys for bearing surfaces in fuel-efficient vehicle engines, aerospace applications, and power generation. ORNL's unique, high-intensity IR lamp system was used to synthesize multi-phase surface layers containing hard ceramic particles. A new high-temperature galling test method was developed. The torsional response of a metal couple is combined with surface roughness changes to quantify galling resistance. Behavior of the novel titanium composite was compared to that of a commercial galling-resistant alloy and an oxygen diffusion–treated titanium alloy. Results of this effort provided two major benefits: (1) the promising, new IR surface treatment may enable wider use of lightweight titanium alloys in energy conversion systems, and (2) a new and unique capability to assist U.S. industry in developing improved high-temperature, galling-resistant materials was developed.

Mission Relevance

Recent developments in the primary processing of titanium promise to reduce raw material cost and broaden the application of titanium alloys to component parts for energy-efficient, low-emissions automobiles, trucks, and power generation systems. By enhancing the resistance of titanium alloys to surface damage at elevated temperatures, these lightweight aerospace alloys can be more widely utilized in surface load-bearing applications, seals, and fasteners. Therefore, this project has multi-sector benefits while also serving the missions of energy efficiency and renewable energy. For example, the development of galling-resistant titanium surfaces is expected to benefit the aerospace and the defense sectors (National Aeronautics and Space Administration, Defense Advanced Research Projects Agency, Air Force, Army, Navy) through its applicability to variable-nozzle turbochargers, jet engine compressor section vanes, aircraft control surface linkages, anti-jamming lightweight rifles, and wear-resistant arresting cable sheaves on aircraft carriers.

Results and Accomplishments

This project began in mid-year FY 2008 and was completed in FY 2009. A high-temperature galling test configuration was designed, and fixtures were custom-machined from high-performance nickel-based alloys. A furnace chamber was fitted to an existing torsion testing machine. Using infrared heating, hard composite layers containing micrometer-sized TiB_2, HfB_2, and ZrB_2 particles were prepared and microstructurally characterized. Some of these layers were as much as twice as hard as the base titanium alloy. The surface-engineered composite found most suitable for use in galling tests contained TiB_2 particles. Over 20 separate galling experiments were performed. A cobalt-based alloy (Stellite 6B), known for its elevated temperature wear resistance, was used as a reference material. While not attaining the performance of the cobalt alloy, tests conducted at 485°C indicated that the IR surface-engineered titanium composite did reduce the friction of nontreated titanium by 20%. This improvement in sliding behavior could expand the use of titanium, which is about 15% lower in density than the Stellite 6B, in bearing applications where light weight is important. For example, the titanium alloy composites could be

used for high-temperature, galling-critical surfaces in truck engines and drivetrain components, or in aerospace applications. The findings from this work will support a new project on the replacement of steel components with titanium alloys in energy-efficient diesel engines sponsored by the Vehicle Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy.

Publications

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00483

Tip-Enhanced Optical Assembly of Plasmonic Nanostructures

Zhenyu Zhang, Katyayani Seal, and Gyula Eres

Project Description

Metallic nanostructures offer immense opportunities for conceptual discoveries in fundamental research and may also enable a myriad of novel technological applications. Materials with ordered arrangements of metallic nanostructures promise exotic phenomena, such as optical cloaking and lensing, and are of vital importance in diverse areas such as optical circuiting, chemical and biological sensing, and nanoelectronics. Recent advances in nanofabrication have witnessed the development of a variety of innovative methods for controlled engineering of metallic nanostructures, but each has its own limitations. In this project we are developing a new approach for deterministic growth of metallic nanostructures, the initial purpose being plasmonic device applications. The method, tentatively termed optical-tip lithography (OTL), is rooted in the ability to achieve plasmon-mediated growth of metal, and the proof of the principle is to be demonstrated on ferroelectric surfaces by utilizing an atomic force microscope tip and an elegant optical illumination scheme. Our approach provides new control mechanisms to fine tune the growth process, providing access to new functionalities for plasmonic nanostructures. The active role of the ferroelectric will further demonstrate the novel use of "smart" substrates in controlling the synthesis of plasmonic nanostructures as well as their device performance. Our novel OTL method has tremendous scope for advancing technology related to plasmonic applications, from chemical sensing to high-speed data transfer. This work will combine several existing research directions, providing a strong impetus for further research in the area of nanoplasmonics, a consequence that will help ORNL to better position itself in this important area of research.

Mission Relevance

This project is directly relevant to DOE's research portfolio in basic science. It is particularly relevant to DOE initiatives in nanoscience and materials science. The capacity to be developed may prove an essential component of the Center for Nanophase Materials Sciences at ORNL. The project may also benefit the Defense Advanced Research Projects Agency and the National Institutes of Health.

Results and Accomplishments

Progress has been made towards the basic proof of principle of using an AFM tip to enable localized growth of metal nanostructures. The main impediment to direct evidence of this process is the complex

tip and tip-holder interaction in the aqueous $AgNO_3$ environment. As an alternative to the use of an AFM tip, arrays of micron-sized pyramids with aspect ratios similar to an AFM tip have been synthesized by FIB, with and without hydrophilic coatings in order to circumvent the hurdles encountered due to the AFM tip in an aqueous environment. This approach shows more promise and further efforts in this direction are under way. In auxiliary research directions, the current method of photodeposition of silver on $LiNbO_3$ (in contrast with previous attempts) utilizes white light illumination through the crystal by using evanescent illumination, which allows for a slower and better controlled growth process. This setup therefore allows the monitoring of the process of growth of silver nanoparticles by measuring their absorption spectrum during the deposition process and their morphology by using atomic force microscopy. Specific results from these studies include key information such as the kinetics of light-induced nanoparticle production, nanoparticle size and nanoparticle aggregation dependent shifts in plasmon frequency and local refractive index-dependent shifts in plasmon frequency. The domain selectivity of the deposition process may be used for the synthesis of metallic nanostructures for photonic devices. This work will be showcased in scientific conferences and relevant publications are in progress.

Publications

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00493

Novel, Hafnium-Doped Al_2O_3 Permeation Barriers for Oxygen and Hydrogen Barrier Applications

Theodore Besmann, James Haynes, Karren More, and Bruce Pint

Project Description

The objective of this project is to form thin films of highly adherent, hafnium-doped α-Al_2O_3 on conventional iron-based alloys via microstructural control of thermally grown alumina. Due to their chemical stability, dense layers of stable, adherent α-Al_2O_3 have potential to be very effective oxygen permeation barriers in oxidizing environments and are a candidate hydrogen permeation barrier. However, the adherence and stability of alumina films to conventional structural alloys are problematic.

The most effective approach to forming dense, adherent alumina barrier films on structural alloys is to aluminize the alloy and then oxidize the surface at a specific temperature and atmosphere to form thermally grown alumina. Recent work at ORNL has shown that hafnium doping of the oxide grain boundaries is extremely effective in improving α-Al_2O_3 adhesion to metallic surfaces.

Diffusion aluminide coatings are being fabricated on hafnium-doped, iron-based substrates by chemical vapor deposition (CVD), followed by controlled oxidation of the surface of the coatings to form α-Al_2O_3 permeation barriers. The microstructure, phases, hafnium content, and adherence of the resultant Al_2O_3 films are being characterized.

The goals of the work are to demonstrate that (1) hafnium additions to alloys can significantly improve the quality of the α-Al_2O_3 layer by changing the microstructure and improving adhesion and (2) preoxidation conditions are critical in the formation of durable α-Al_2O_3 layers by characterizing the oxide thin films via analytical TEM.

Mission Relevance

Improved oxygen and hydrogen permeation barriers are critical to the success of a number of energy-related technologies of vital interest to DOE, including gas turbine engines, fuel cells, nuclear power plants, and potential fusion applications. Improved oxidation barriers would provide the capacity to further increase firing temperatures in gas turbine engines, thus improving efficiency. Alumina permeation barriers in fuel cell applications eliminate the problems associated with chromium poisoning of fuel cells. Hydrogen barriers in nuclear applications significantly improve hydrogen containment. For hydrogen permeation, in the nuclear energy area, the results of this work and the demonstration of ORNL expertise and capabilities could be brought to the attention of the DOE program related to tritium-producing burnable absorber rods. This concept also could be applied to containment for hydride fuels to increase their operating temperature.

Results and Accomplishments

One of the clear results from this work was that alloy sulfur content plays a significant role in thermally grown alumina adhesion on both aluminized iron- and nickel-based alloys. The laboratory cast materials with hafnium additions also tended to have higher sulfur contents, resulting in poor adhesion of the thermally grown surface alumina layer despite the hafnium addition. To address this shortcoming in our initial hypothesis, additional alloys were cast with yttrium and hafnium additions, as yttrium is known to have a stronger affinity for sulfur than hafnium. For both the iron- and nickel-based materials, the proper combination of yttrium and hafnium resulted in a more adherent thermally grown oxide that appears to be a good candidate for further development. Also, for the coatings on iron-based alloys, an increase in alumina activity during the coating process resulted in a smoother coating surface, which also improved the alumina adhesion. Our work also showed very poor alumina adhesion when commercial type 316 stainless steel with 68 ppma sulfur was aluminized. In contrast, the ORNL-cast 316 with hafnium and yttrium additions formed an adherent alumina scale when aluminized by the same process. Characterization by transmission electron microscopy showed that a denser (fewer voids) thermally grown α-Al_2O_3 layer was formed at 1100°C than at 1000°C. However, microprobe showed that the higher oxidation temperature resulted in greater alumina interdiffusion. These results will help illustrate ORNL expertise in aluminide coatings, composition effects on coating performance and characterization.

00499

Fabrication of Single-Crystal Thin Films: The Missing Link in Understanding High-Temperature Superconductivity in the Iron Pnictides

Jian Shen, Pengcheng Dai, Zheng Gai, Lifeng Yin, and Wenguang Zhu

Project Description

The recent discovery of superconductivity in the iron pnictides, LnOMPn (Ln = La, Pr, Ce, Sm; M = Fe, Co, Ni, Ru; and Pn = P and As), has generated such an excitement that most condensed matter physicists consider it the biggest observation since the discovery of high-temperature superconconductivity in

cupurates. Despite the initial success, further advances rely critically on the synthesis of single-crystal samples. Here we propose to use laser molecular beam epitaxy to grow single-crystal, iron-pnictide, thin films on GaAs(001) substrate. Our goal is to optimize the growth condition of the thin films, manipulate the surface, and compare with bulk polycrystal transport and magnetic measurements. As proof of principle, we will initially study the CeOFeAs parent compound and fluorine-doped superconductors. The tools and procedures that we develop in this project will be applicable to a range of other iron-based pnictides that have exciting possibilities for understanding high-temperature superconductivity.

Mission Relevance

As a part of the energy strategy for the future, there is a clear need for understanding superconductivity, as revolutionary new power transmission and control solutions based on superconductors will provide instantaneous power regulation without energy loss and, therefore, solve the challenge facing the current electricity grid to provide abundant, reliable power to the increasingly large populations. The discovery of the iron pnictides gives a boost to research along this direction. This project will help to understand the mechanism of high-temperature superconductivity and develop future solutions to efficient use and transmission of electricity. Although the technology associated with traditional low-temperature superconductivity (LTS) materials is relatively mature, the scientific foundations for the newly discovered high-temperature superconducting (HTS) materials are in a more rudimentary state, and the engineering parameters required for definition of possible realms of exploration are largely unknown. Within the limitations imposed by these unknown factors, a five-year program has been opened by Department of Defense, Superconductivity Research and Development Program.

Results and Accomplishments

This project started in the last month of FY 2008. We have successfully grown epitaxial thin films of CeOFeAs and observed a previously unknown robust ferromagnetic phase in the ultrathin regime. To ensure perfect epitaxial growth, we selected GaAs(001) as the substrate because the lattice mismatch is negligibly small (~0.03%) and the surface polarities are similar. The latter helps to decrease the interfacial energy and is thus beneficial for epitaxial growth. The epitaxial relationship between the film and the substrate is $[100]_{CeFeAsO}$ // $[110]_{GaAs}$ and $[001]_{CeFeAsO}$ // $[001]_{GaAs}$. Within a narrow growth temperature window around 560°C, we can achieve high-quality epitaxial thin films as confirmed by reflection high energy electron diffraction, which is used for monitoring the growth. Direct dc magnetization measurements from the CeFeAsO thin films demonstrate a clear ferromagnetic behavior. The magnetic susceptibility of a 23 monolayer thin film is almost three orders of magnitude larger than that of the bulk parent compound. This means that the thin film is not in an antiferromagnetic spin density wave state. In fact, the film is in a typical ferromagnetic state as indicated by both the magnetic hysteresis loop and the saturated field cooling curve at 22 K. The ferromagnetic T_c is close to room temperature. The easy axis is lying in plane, and no out-of-plane component can be detected.

00505

Nanoporous Inorganic Membranes for High-Efficiency Organic Separations

Ramesh R. Bhave

Project Description

The goal of this project is to demonstrate the feasibility of organic separations in the viscous flow regime with high throughput and selectivity. Once demonstrated, it would be an innovative approach to achieve

dramatic improvements in productivity of organic processes. Our focus will be on the study of transport and separation mechanisms using ORNL nanoporous inorganic membranes with precisely controlled characteristics and robust morphology. Dense polymer membranes have been used for organic separations but lack the long-term reliability and operating characteristics required for large-scale industrial applications. We aim to demonstrate an order of magnitude increase in permselectivity compared to the best available polymer membranes. Estimated energy savings for a 10,000 barrels/day lube oil plant are significant (>10 billion BTU/year).

Mission Relevance

Membrane separations are energy efficient as compared with distillation and for several years have been a part of call for proposals from the Industrial Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE). The goals of this project are aligned with the DOE EERE mission to improve the efficiency of separation and energy-intensive processes. We anticipate that successful completion of this project could result in novel cost-effective technology to reduce energy consumption and increase efficiency of many energy-intensive industrial processes such as chemical/petrochemical, a key DOE mission. Research in inorganic nanoporous membranes for the purpose of developing energy-efficient alternatives to traditional separation processes such as distillation and extraction would have broad applications. The Environmental Protection Agency would benefit as membrane processes reduce waste volumes and have the potential to significantly improve air quality and minimize environmental impact. Many food and agricultural processes involve use of organic solvents and require efficient separations at the molecular level. Thus, results of this study could be beneficial to the Department of Agriculture.

Results and Accomplishments

We have completed benchmarking state-of-the-art commercially available nanoporous membranes with pore diameters ranging from 1 nm to 10 nm. We have also fabricated and characterized nanoporous membranes with pore diameters as low as 3 nm. We have evaluated the ability of synthesized and commercially available membranes to retain polyethylene glycols with molecular weights ranging from 200 to 6000. A 1 nm membrane showed >90% retention of substances with molecular weight as low as 1000 and demonstrated high permeability up to 30 L/hr-m^2-bar at 25°C. The membranes were fully characterized using gas and liquid permeance supported by dynamic pore size (DPS) distribution and gel permeation chromatography (GPC). DPS analysis revealed microstructure consisting largely of uniform pores with narrow pore size distribution. GPC analysis confirmed retention characterized reported in the literature for membranes with pore diameter of 1nm. We are preparing to study the separation performance with organic mixtures such as lube oil and solvents. Although the permeation characteristics of inorganic nanoporous membranes are significantly superior to polymer membranes, these results also indicate that membranes with pore diameter less than 1 nm are needed to achieve separation of organic substances with molecular weights in the range 100–400. We have identified several potential approaches, which are currently under evaluation. These include functionalization and pore size reduction using both inorganic and organic precursors.

00520

Comparison of ORNL Plasma Arc Lamp Decontamination to Existing U.S. Air Force Aircraft Decontamination Procedures

Chad Duty, Gilbert M. Brown, Marcus B. Wise, Richard Schoske, Patrick Kennedy, and Rich Stouder

Project Description

In previous experiments the ORNL Plasma Arc Lamp technology using a TiO_2 catalyst was effective in the destruction of chemical weapons agent simulants. However, these preliminary experiments were limited to only glass surfaces, only involved G-series simulants, and were not compared to decontamination methods currently in practice. The purpose of this project was to develop a better understanding of the decontamination mechanism and to demonstrate the effectiveness of the ORNL Plasma Arc Lamp technology for decontaminating surfaces applicable to military applications (i.e., C-17 composite material). Additionally, a direct comparison of the ORNL Plasma Arc Lamp technology decontamination to existing U.S. Air Force aircraft decontamination tactics, techniques, and procedures will be made. The use of the plasma arc lamp for decontamination of chemical and biological warfare agents is referred to as the High Energy Arc Lamp (HEAL) system.

Mission Relevance

The proposed research will demonstrate proof of principle for the decontamination of aircraft following exposure to chemical or biological weapons. The proposed technique will provide a much more energy efficient method for aircraft decontamination as well as a reduced logistical and manpower requirement. The proposed research will benefit the Department of Defense, specifically the Chemical and Biological Defense Program, by providing an alternative approach for aircraft and large area decontamination. The project is also directly applicable to the Defense Threat Reduction Agency and the U.S. Air Force.

Results and Accomplishments

The primary goals of this project were to (1) develop a more complete understanding of the mechanism by which chemical warfare agents decompose in the presence of TiO_2 when exposed to radiant energy from the plasma arc lamp, and (2) demonstrate the effectiveness of this decontamination system on "real world" materials in comparison to the currently accepted decontamination practices. The results from the initial goal are embodied in the ORNL technical report listed below. This publication is an important milestone for demonstrating technical expertise and fundamental understanding in the chemical/biological warfare community and will be a useful reference point in securing future funding.

The HEAL decontamination strategy was also demonstrated on materials relevant to military applications, specifically the wing section of a C-17 airplane. Sections of the composite wing structure were spiked with known concentrations of a chemical warfare simulant (DIMP) and then exposed to the HEAL system or washed repeatedly with hot soapy water (HSW—the current Air Force protocol). Based on a limited number of off-gassing measurements from the sample, it appears that the HEAL approach was not as effective as the HSW method. Potential reasons for this result are (1) ineffective interaction of the simulant with TiO_2 due to improper application of the catalyst and (2) the lack of a quantitative method to allow accurate analysis of the residual simulant material on the working surface. The research team is currently pursuing follow-on funding to address these concerns.

Publication

Schoske, R., P. W. Kennedy, C. E. Duty, R. R. Smith, T. J. Huxford, A. M. Bonavita, P. G. Engleman, A. A. Vass, W. H. Griest, R. A. Jenkins, R. H. Ilgner, and G. M. Brown. 2009. *Decontamiation*

Strategy for Large Area and/or Equipment Contaminated with Chemical and Biological Agents Using a High Energy Arc Lamp (HEAL). Technical Report ORNL/TM-2009/08, Oak Ridge National Laboratory, Oak Ridge, Tenn.

MEASUREMENT SCIENCE AND SYSTEMS ENGINEERING DIVISION

00459

Quantitative Imaging of Subcutaneous Veins with Multispectral Illumination and Three-Dimensional Modeling

Kenneth W. Tobin, Jr., and Vincent C. Paquit

Project Description

We aim to demonstrate that it is feasible to perform optical imaging of subcutaneous veins, including estimation of the relative vein depth and diameter. We approach the problem using (1) multispectral imaging, since the propagation of light in tissue has been characterized as a function of wavelength in previous research; (2) laboratory experiments on phantoms and human subjects in order to validate theoretical approaches and hypothesis regarding the skin structure selected and the optical phenomena to be considered; (3) three-dimensional Monte Carlo photon transport modeling to simulate light propagation in tissues (reflection, absorption, transmission) method used to link experimental results and theoretical formulations; and (4) investigate inverse imaging approaches, including parametric and pattern recognition techniques. If successful, we expect this project to enable the near-term development of devices to assist humans with venipuncture and catheterization procedures. In the longer term, we envision this technology as one component of a fully automated, robotic venipuncture device.

Mission Relevance

This basic research project can be associated with Strategic Theme 3 (Scientific Discovery and Innovation) of the DOE Strategic Plan: Strengthening U.S. scientific discovery, economic competitiveness, and improving quality of life through innovations in science and technology. With the potential applications in military healthcare, this project will be beneficial to national security needs as well.

This project will be beneficial to the program areas of several federal agencies, in particular the U.S. Army Telemedicine and Advanced Technologies Research Center (Medical Imaging Technologies, Hospital/Operating Room of the Future programs); the National Institute of Biomedical Imaging and Bioengineering (Image-Guided Interventions and Optical Imaging and Spectroscopy programs); and the National Institute of Justice (Biometric Technologies).

Results and Accomplishments

To demonstrate the feasibility of the proposed approach, we undertook four research tasks: (1) We constructed, optimized, and quantified a laboratory imaging system required for accurate venous imaging. By combining a digital camera and a broadband light source associated with a monochromator, we capture hyperspectral images of the skin, from which the location of the subcutaneous veins' centerlines are extracted. By combining the two-dimensional location of the veins with the three-dimensional

location of the surface of the arm obtained by active optical triangulation using a projected structured light pattern, one can compute the three-dimensional path that will guide the robotic needle inserter to the vein. (2) To improve the response of our system according to the skin structure variations, we performed multispectral analysis on a limited number of skin datasets captured with our vision system. We defined a multispectral image processing method for subcutaneous structure classification based on linear data reduction techniques. (3) To evaluate the influence of the topography and molecular structure of the skin surface using image processing techniques and to simulate intensity images as seen by an imaging camera, we developed a tri-dimensional Monte Carlo light propagation model. (4) Focusing on the tri-dimensional reconstruction of the subcutaneous vascular system, we combined the three first tasks with tissue phantom imaging in order to solve the inverse problems of locating the major subcutaneous veins and therefore estimating their relative depth and diameter from the observed multispectral images.

Publications and Patent

Paquit, V. C. 2008. "Imagerie multispectrale et modélisation 3D pour l'estimation quantitative des vaisseaux sanguins sous cutanés." Ph.D. thesis, Université de Bourgogne, Le Creusot, France.

Paquit, V. C., et al. 2008. "3D multispectral light propagation model for subcutaneous veins imaging." SPIE Medical Imaging 2008: Physics of Medical Imaging, February, San Diego.

Paquit, V. C., et al. 2008. "Multispectral imaging for subcutaneous structures classification and analysis." *Proceedings of International Topical Meeting on Optical Sensing and Artificial Vision,* May, Saint Petersburg, Russia.

Paquit, V. C., et al. 2008. "Improving light propagation Monte Carlo simulations with accurate 3D modeling of skin tissue." *Proceedings of the IEEE International Conference on Image Processing,* October, San Diego.

Paquit, V. C., et al. 2008. "Simulation of skin reflectance images using 3D tissue modeling and multispectral Monte Carlo light propagation" *Proceedings of the 30th Annual International Conference of the IEEE Engineering in Medicine and Biology Society,* August, Vancouver, Canada.

Paquit, V. C., et al. 2009. "3D and multispectral imaging for subcutaneous veins detection." *Opt. Express* **17,** 11360–11365.

Price, J. R., et al. 2008. *"Improved Device for Assisted Venipuncture.*" UT-Battelle, LLC, Invention Disclosure 1300002067, March 31.

00461

Combined Real-Time Quantitative Phase and Fluorescence Biological Microscopy by Digital Holography

Christopher Mann, Philip Bingham, Jeffery Price, Yisong Wang, John Biggerstaff, and Michael Zemel

Project Description

Biological processes and structures in transparent objects that produce refractive index changes or variations of the shape are of particular interest in the field of life sciences. For most existing phase contrast techniques, the phase-to-amplitude conversion is nonlinear and the phase information is not quantitative. Digital holography offers an excellent approach to quantitative phase imaging, providing an optical thickness resolution of a few nanometers. On the other hand, while digital holography provides nanometer precision and morphological information about a sample, the application of fluorescence imaging reveals specificity and functional details. Currently, instrumentation for generating fluorescence and quantitative phase information simultaneously is lacking. The objective of this research is to construct and develop a new, combined, dual-mode quantitative phase and fluorescence instrument that will enable

robust, real-time imaging, and also develop and apply total internal reflection digital holographic microscopy (TIRHM) to visualize and quantify cellular interactions.

Mission Relevance

This research in biological microscopy and imaging analysis supports the DOE Office of Biological and Environmental Research. The underlying technology being leveraged for this project was developed at ORNL through research supporting the DOE Office of Energy Efficiency and Renewable Energy and the Industrial Technologies Program. The original work was performed in the area of industrial automation and is now being applied to cellular and biological imaging. We are currently in the process of submitting proposals to the National Institutes of Health and the Department of Defense for follow-on funding and are collaborating with a number of biological institutions to apply the developed technology.

Results and Accomplishments

The dual-mode holographic-fluorescence microscopic system is constructed and has been fully tested and optimized. The microscopic system incorporates a newly designed fiber-optic delivery system in a conventional microscope. This novel and robust system is highly attractive to biomedical researchers who require three-dimensional morphological information from their samples in combination with functional cellular information. We are currently collaborating with a number of biological research groups. So far our research has yielded unparalleled sub-nanometer resolution measurements and excellent image clarity. This bodes well for future metrological analysis and application to biological problems. This work has resulted in two conference presentations, the submission of three invention disclosures, and the publication of a journal paper. We have solved some of the wider issues that had precluded the day-to-day use of this technology in conventional real-time biological microcopy. Some of the problems we have solved include wave-front aberration correction, auto focusing, and accurate mounting of the sample. With the promising image quality and resolution we have so far achieved, we expect that our instrument will provide high-resolution, real-time, unambiguous imagery and that the utilization of the proposed techniques will generate new scientific knowledge in the biosciences.

Publications

Mann, C. J, et al. 2008. “Three-wavelength phase imaging digital holography of MEMS motion.” OSA Digital Holography and Three-Dimensional Imaging (DH) Conference, St Petersburg, Fla.

Mann, C. J, et al. 2008. “Quantitative phase imaging by three-wavelength digital holography.” *Opt. Express* **16,** 9753–9764.

Mann, C. J., et al. 2009. “Quantitative analysis of living cells by digital holographic microscopy.” Biomedical Science & Engineering Conference, BSEC 2009 (first Annual ORNL).

00469

Nanostructured Materials for Enhanced Radiometric Forces at Atmospheric Pressure

Brian D’Urso, Slobodan Rajic, Nickolay V. Lavrik, and Panos G. Datskos

Project Description

Radiometric forces are the result of thermal effects in gases in the presence of a temperature gradient. Crookes’ radiometer, which is enclosed in a low-pressure chamber and operates by sunlight, is an example that utilizes these forces. For the past century, Crookes’ radiometer found no practical

application because of the small mean free path of air molecules at atmospheric pressure (<100 nm), which necessitates operation in a partial vacuum. Recent advances in nanofabrication enable the fabrication of nanostructured surfaces with features of the order of the mean free path in air under ambient conditions. In addition to operation in atmospheric pressure, such structures experience much larger radiometric forces in the presence of temperature gradients. We seek to develop nanostructured materials and objects with the appropriate geometry to experience drastically enhanced radiometric forces. A team with experience in nanofabrication and measurement of small forces will develop nanostructured surfaces and measure the enhanced radiometric forces. Potential applications include micro-electro-mechanical systems (MEMS) devices, cooling, and waste heat recovery.

Mission Relevance

If successful, this research will result in a material that can convert small temperature gradients into mechanical motion. This could be relevant to the DOE energy security mission by leading to the development of devices that could extract useful work or energy from low-grade waste heat from power production or other industrial processes. The potential enabling feature of these materials for waste heat energy recovery is the large force that potentially could be produced from even a 1°C temperature difference. This project will benefit agencies in the Department of Defense, particularly the Defense Advanced Research Projects Agency. By converting temperature differences to mechanical motion, the material we develop may provide a means of propelling micro-air vehicles for use in surveillance or offensive systems.

Results and Accomplishments

We have completed most of the nanofabrication of materials for enhanced radiometric forces and we have prepared a system for measuring the Knudsen forces on those materials in a temperature gradient. We have fabricated membranes with nanoscale thickness and porosity over approximately 1 cm^2, and we have separated these membranes from their original substrate. One critical step, opening the pores from the back side of the membrane, remains in the fabrication. The system for measuring Knudsen force on the membranes using a calibrated torsion pendulum has been prepared and is awaiting completion of the membrane fabrication process. We have also planned the remainder of the project. We expect to complete the nanofabrication of materials for enhanced radiometric forces and measure the forces on those materials in a temperature gradient with the apparatus we have developed. This will include opening the pores on the back side of the membranes to complete the fabrication of membranes with nanoscale thickness and porosity over areas of at least 1 cm^2. The material will be characterized by exposing it to temperature gradients at different pressures from atmospheric pressure to a partial vacuum while it is suspended on a torsion pendulum. An optical readout of the deflection will provide a measurement of the Knudsen force enhancement due to the material nanostructure for comparison to the current theory of thermal transpiration and a measure of the success of the project.

00484

Novel Method to Achieve High-Resolution Neutron Microscopy

Philip Bingham

Project Description

The goal of this project is to develop and demonstrate a coded source imaging system for neutron radiography that will significantly improve the resolution for neutron microscopy. The world's best resolution achievable through conventional neutron radiography is on the order of 100 μm, with

significant progress being made towards achieving 10 μm resolution using expensive, experimental refractive optics and new detector technologies. The goal of this project is to demonstrate resolution in the 25 μm range and provide a clear path forward to achieve <1 μm resolution using conventional technologies. We propose a new implementation of the coded aperture for neutron radiography that uniquely encodes the source of neutrons passing through an object as opposed to an encoding of radiation emitted from an object.

Mission Relevance

It is anticipated that this project will provide a proof of concept that supports the investigation of microscale structures such as microchannel heat exchangers, fuel cell components, and biological microscopy for pharmacology and drug delivery research. The application areas for the neutron microscopy method being developed cover many DOE missions. In particular, heat exchanger and fuel cell research both fall under energy resources and environmental quality; biological microscopy imaging is a valuable tool for biofuel research, environmental quality study, and basic sciences research. One key goal of this project is to establish the technical feasibility for a neutron imaging instrument at the Spallation Neutron Source. If successful, the capabilities developed in the project will provide an instrument useful to many federal agencies.

Results and Accomplishments

This seed money resulted in several key accomplishments that have provided significant capabilities to obtain follow on funding. First, the project developed a relationship with Dr. Ayman Hawari at North Carolina State University and his students involved in neutron imaging at their reactor. This group has the flexibility to easily test new system configurations as we move toward higher resolution. Second, simulation and testing has resulted in the development of a filter that reduces gamma noise by reducing the gammas seen from the NC State source that has a direct view of the reactor. Third, a coded source mask was developed, simulated, and tested on the NC State imaging beam line. Fourth, calculations were performed for initial designs of a system for 1 μm resolution. Finally, the results of the previous accomplishments were assembled into an early career proposal to the DOE Office of Science.

Publication

Ziao, Z., K. K. Mishra, A. I. Hawari, H. Z. Bilheux, P. R. Bingham, and K. W. Tobin. 2009. "Investigation of coded source neutron imaging at the North Carolina State University PULSTAR reactor." IEEE Nuclear Science Symposium, Oct. 25–31, Orlando, Fla.

00488

Actuation and Control of Wearable Robotics

Lonnie Love, Peter Lloyd, and Randy Lind

Project Description

The focus of this project is the development of high-pressure (> 2000 psi), microfluidic actuation (<0.063 in. diam) that will enable a new class of compact, lightweight wearable robotic devices. Our first task focuses on the development of a high-pressure (>2000 psi), very-low-flow (0.5 mL/s) control valve. Actuator motion is controlled by this valve. Due to the very small orifices (<0.003 in. diam), flow is controlled by pulse width modulation rather than a variable orifice area. This introduces our second problem, pressure pulsations in the fluid that will introduce noticeable vibration on the actuators. Our

second task is focusing on controlling the timing between adjacent flow control valves to mitigate vibration. The final task is the development of a single-joint, wearable, finger mechanism to demonstrate the compactness and fidelity of fluid-based wearable robotics.

Mission Relevance

The primary relevance of this project is the development of a new class of actuators suitable for miniaturized fluid power systems. The utility of such actuators to DOE is in the area of wearable haptic devices to aid in remote handling of hazardous materials. The relevance for the medical community is in the area of physical rehabilitation for stroke recovery, active orthotics, and advanced prosthetic devices. This work has already led to two new programs: a $150K collaboration with OrthoCare Innovations in the area of prosthetic alignment devices, and a $602K collaboration with Boston Dynamics on a robotic arm and hand for testing chemical/biological suits. In terms of military relevance, this technology has utility in morphing wing technologies for advanced flight control surfaces.

Results and Accomplishments

This project consisted of three tasks: development of a high pressure/low flow control valve, development of a control methodology to accommodate pressure pulsations, and the development of a force controlled wearable finger mechanism. For the first task, we successfully developed a control valve that is suitable for wearable robotics. For the second task, mitigation of pressure pulsations, we demonstrated the fidelity of the approach through simulation. However, we discovered a revolutionary new approach to the control of fluid based wearable robotics that simultaneously mitigates pressure pulsations while changes the behavior of fluid powered actuators. This approach is more mechanical in nature and enables the control of the wearable device to be more like traditional haptic interfaces. There are two distinct characteristics of this approach. First, the actuation consists of a pair of antagonistic actuators driving an involute cam. The antagonistic actuators eliminates backlash in the system and the need for a rod seal (reduced friction and complexity). The involute cam provides a constant transmission ratio which likewise reduces complexity and actuation size. Second, each actuator has a fixed orifice between the supply pressure and actuator chamber and a control valve between the actuator chamber and return pressure. This control approach enables direct torque control of the joint (a radical departure from typical fluid controlled devices). We demonstrated this on a wearable finger mechanism and developed a prototype glove to show prospective sponsors.

Program Development Accomplishments

During the past year, we demonstrated the technology to a number of prospective sponsors. This resulted so far in two funded projects. The first is a new National Institutes of Health (NIH) program with OrthoCare Innovations using the technology to develop an automated prosthetic alignment device. This project, DOE NFE-09-02180, is for $150,132 spent over 2 years. The second project is with a robotics company, Boston Dynamics. We are using the technology to develop an anthropomorphic arm and hand. This project, DOE NFE-09-02437, is a one-year project for $602,520. We also submitted a $1M NIH proposal on pediatric prosthetics (teaming with OrthoCare Innovations). Dr. Michael Weinrich, the director of the National Center for Medical Rehabilitation Research at NIH, suggested that we develop a BioEngineering Research Partnership (BRP) directed at maturing the wearable technologies and transitioning to industry. The BRP is a 5-year, $10M program. We have discussed the concept with OrthoCare Innovations and Fillauer Companies (a leading orthotics company) and are presently working on a proposal. Finally, one member of the project team was invited to demonstrate the technology to Senator James Inhoffe in Oklahoma City. Senator Inhoffe is a strong supporter of prosthetics and rehabilitative systems for the military.

Publication and Patents

Lind, R. F., J. F. Jansen, and L. J. Love. 2008. *A Hydraulic Flow Control Device by Means of a Two-Stage Digital Poppet Valve.* Invention Disclosure 200802083.

Love, L. J., J. Jansen, and R. Lind. 2009. "Mesofluidic actuation for articulated finger and hand prosthetics." *Proceedings of the 2009 International Conference on Intelligent Robots and Systems,* pp. 2586–2591.

Love, L. J., J. F. Jansen, and R. F. Lind. 2009. *Fluid Powered Wearable Device*. Invention Disclosure 200902240.

Love, L. J., J. F. Jansen, and R. F. Lind. 2008. *Hydraulic Wrist Mechanism Based on Involute Cam.* Invention Disclosure 200802078.

Love, L. J., J. F. Jansen, and R. F. Lind. 2008. *Mesoscale Fluid Digital Valve.* Invention Disclosure 200801983.

Love, L. J., and R. F. Lind. 2008. *Hydraulic Involute Cam Actuator.* Invention Disclosure 200802073.

00494

Novel Method for Three-Dimensional, Depth-Resolved Imaging of Highly Scattering Samples

J. S. Baba, P. R. Boudreaux, and S. J. Lee

Project Description

Depth-resolved, three-dimensional (3D) imaging of highly scattering samples (e.g., aerosols, the atmosphere, murky water, subterrain, and biological tissues) is significant for varying segments of commercial and military/law enforcement arenas. Althouth the literature is full of endeavoring approaches based on elimination of multiply scattered photons from the image plane via spatial, time, or coherence gating techniques, we propose a paradigm shift. Our approach exploits underlying scattering physics to detect varying degrees of radiation scatter as a means to generate 3D images of samples. Our technique utilizes state of polarization gating (SOPG) to localize reflected radiation from varying depths to generate stacked two-dimensional (2D) images. Depth imaging performance of this novel technique is expected to be 2–3 times greater than that of optical coherence tomography but less than that of ultrasound, with the added advantage of simplicity for easy miniaturization and future low-cost implementation.

Mission Relevance

This development will be applicable to DOE energy, environmental, atmospheric, aerosol, and oceanic research that requires imaging through highly scattering samples (e.g., air pollutants, aerosol particles, and murky waters). This development is applicable to the National Institutes of Health and the Department of Defense (DOD) (medical imaging of highly scattering tissues for rapid assessment of skin pathologies, wounds, and burn conditions); to law enforcement efforts (locating objects in murky waters); and to DOD and the Department of Homeland Security (imaging subterranean and other high scattering sites or objects for explosive devices).

Results and Accomplishments

This project focused on the development of depth resolved 3D imaging of highly scattering samples utilizing state of polarization gating (SOPG) to localize reflected radiation from varying depths to generate stacked 2D images. This also required the application of SOPG to concurrently develop an

accurate scattering sample refractive index system. Monte Carlo simulations were developed to test the anticipated system performance and to investigate possible methods for volumetric data segmentation and analysis. It was determined that the depth of imaging would be ~3 mm for most biological tissues but could be more for less scattering samples. The scattering sample refractive index was developed with accuracy to the second decimal place for the proof of concept. An Air Force sample embedded below varying thickness of scattering samples was imaged to demonstrate the ability to utilize SOPG for depth resolved imaging in highly scattering samples.

00498

Optical Resonance Disk–Based Infrared Thermal Detectors

S. Rajic and P. G. Datskos

Project Description

Detection of infrared radiation (IR) is important for a variety of activities, and microdisc resonators are proposed as very sensitive thermal detectors. The quality factor of microdisks can be greater than 106, which would provide excellent thermal IR sensitivity. A thermal microdisk detector consists of a waveguide, a microdisk resonator, and a thermal isolation region. When probe light with wavelength λ is introduced into the microdisk of radius r and refractive index n, for example, by side-coupling it with an optical waveguide, a substantial reduction of photon transmission will occur in the waveguide at the resonance wavelength. The thermal absorber converts incident IR photons to thermal power, causing a rise in temperature of the resonant microdisk. Thus a very small thermal expansion shift in the microdisk dimensions would produce a substantial perturbation in the probe transmission wavelength. This is the detection mechanism we plan to exploit in this project.

Mission Relevance

There is relevance in this project to the DOE Office of Science in exploring this general phenomenon of optical resonant microdisc and to the DOE national security mission due to the ultimate development of this approach into an infrared imaging sensor tool. The Department of Defense (DOD) has obvious interest in this area of sensor development in the infrared. In fact, once the basic feasibility of this approach is established, we anticipate additional collaborative work with several DOD and Department of Homeland Security programs in the future.

Results and Accomplishments

The micro-fabrication and modeling/design tasks have been begun during FY 2008 and the project was completed during FY 2009. System architectures have been explored that would be both amenable to our fabrication techniques and relatively optimized for the role of sensitive IR detectors. Many wafers have been processed with the circular glass layer and substantially undercut supporting structure. The supporting structure needed to be as small in diameter as possible to provide substantial thermal isolation. This goal was in conflict with the need to next melt the exterior part of the glass disc and reform it into a perfect toroid of glass. This glass then becomes the ultra-low-loss waveguide that has been shown to exhibit optical resonant Q-values in excess of ten million. The challenge we faced was that the well thermally insulated glass can very quickly melt in whole and not just at the edges as desired. Small diameter variations in the supporting structure can have large thermal conductivity implications and thus very quickly produce a thermal run-away situation in the entire device. Our approach to this first fabrication challenge has been to produce a uniform energy density CO_2 laser beam and illuminate a two dimensional array of test structures. These test device arrays varied in glass diameter in one direction and

in supporting structure diameter (thermal isolation) in the other array direction. The optimal laser illumination conditions found during this project were max power, 23.75 W; divergence, 4 mRad; defocused spot size, 0.5 mm; and linear write speed, 1.25 in./s. The structures were subsequently evaluated for both dimensional integrity and thermal infrared sensitivity. Since the structures were far from optimal for an infrared detector, the ultimate performance was not impressive for the individual pixels. However, the feasibility of the approach has been demonstrated.

00501

Cell-Borne Chip for Controlled Therapeutic Protein Production and Delivery

Anatoli V. Melechko, Timothy E. McKnight, Scott T. Retterer, and Ilia N. Ivanov

Project Description

Nanomaterial-enabled protein delivery shows promise for therapeutic intervention in a large number of pathologies. The effectiveness of these strategies, however, is often reduced due to the limited amounts of peptides and proteins that can be carried by the nanomaterial vector. A significant challenge is delivery of sustained doses of therapeutic proteins at a targeted tissue or organ. In contrast to conventional protein delivery, an attractive alternative method is to co-opt the host's own cells for localized transgenic protein production, thereby enabling sustained doses at therapeutic levels over longer time periods. The goal of this project is to design and demonstrate a *nanostructure-based cell-borne chip* enabling such controlled gene delivery and site specific production of therapeutic proteins. Cellular-scale elements will be designed to penetrate into individual cells and detach from a larger macroscale device during interfacing with tissue. These detached elements will remain resident within cells for subsequent biochemical manipulation of those cells whereby transgenic proteins are produced from DNA template carried by the penetrant structure. Modulation of the DNA-bearing device via localized heating using noninvasive laser irradiation will provide means to modulate transgenic protein production within the host cell. We anticipate this novel hybrid cell-chip technology will provide for blood-borne and tissue-based deployment of cellular agents that may be genetically reprogrammed for therapeutic production of proteins via remote, noninvasive stimuli.

Mission Relevance

The DOE mission statement includes the overarching theme to promote scientific discovery and innovation in order to strengthen U.S. scientific discovery, economic competitiveness, and to improve the quality of life through innovations in science and technology. Alternatives to existing methods for therapeutic protein production are relevant to the DOE mission from at least two significant viewpoints: economic competitiveness and quality of life. With respect to economic competitiveness, therapeutic proteins are more difficult, time-consuming, and expensive to produce, being approximately 20 to 100 times more expensive to manufacture than synthetic drugs. It is critical to develop improved means of producing and administering therapeutic proteins that will maintain a competitive edge for domestic pharmaceutical interests. Second, with respect to improving quality of life, production of therapeutic proteins within localized regions of tissue has the potential to be an improved therapy for a large number of pathological conditions, including a large subset of neurological disorders which represent over 6.3% of the world health burden according to the 2006 WHO report *Neurological Disorders Public Health Challenges.*

Results and Accomplishments

Methods have been developed for growth of high aspect ratio, cell-penetrant structures upon solid substrates of fused silica and upon releasable membranes of sacrificial silicon nitride bridges. Both methodologies yield detachable, cell-penetrant structures that may be deployed into cell and tissue matrices to provide controlled failure and release of the nanostructure into biological tissue.

Methods have been developed for chemically modifying these cell penetrant structures with covalently attached DNA template and for delivering these DNA templates into viable tissue for transgenic protein production. As a demonstration of these approaches, transgenic production of nerve-growth factor has been realized within localized regions of interfaced tissue in-vitro, resulting in morphological differentiation of cells into a neural phenotype indicative of sustained production and dosing of the neuroprotective and neurophilic nerve growth factor protein. In addition, these penetrant nanostructured elements have been functionalized with plasmonic nanostructured gold films and evaluated with respect to their spectral absorption. Results indicate that plasmon-mediated excitation of our cell penetrant structure is possible, therefore validating the proposed concept of using light to deliver excitation for modulation of transgenic protein production from DNA tethered to the cell-penetrant scaffolding nanomaterial.

Publication

Peckys, D. B., A. V. Melechko, M. L. Simpson, and T. E. McKnight. 2009. "Immobilization and release strategies for DNA delivery using carbon nanofiber arrays and self-assembled monolayers." *Nanotechnology* **20,** 14.

00510

Development of Computational Methods for Neurobiological Imaging Research

Shaun Gleason, Ryan Kerekes, Richard Ward, Barbara Beckerman, Michael Dyer, David Solecki, and Stanislav Zakharenko

Project Description

Neurobiologists are interested in understanding how neurons form complex synaptic circuits during development and how these processes are perturbed in diseases. Neuronal migration and maturation during development play a critical role in how neurons ultimately function. Development of computational methods to extract pertinent information from the large three-dimensional (3D) and four-dimensional (4D) image data sets has not kept pace with available imaging technologies. We propose to develop a set of analysis methods that allow researchers to discover relationships between the anatomical and migratory characteristics of neurons and their ability to function in a network of cells. These methods will provide a foundation upon which a comprehensive suite of tools can be developed. The biological questions that these tools will address strike at the foundation of many neurological disorders including Alzheimer's, Parkinson's, and schizophrenia.

Mission Relevance

Although the initial application of this research is for analysis of cellular morphology and migration within animal models, the results may be applicable to cellular analysis of morphology and migration for plant materials targeted for bioenergy. In addition, the techniques learned during development of motion

tracking methods for neuron cells may be useful for motion detection in security applications where people must be monitored in a facility. This same concept may be applied to intelligent energy delivery (light, HVAC) by monitoring and tracking the location of people within a facility and delivering energy based on location and activity, or task. This work will benefit the National Institutes of Health (NIH). This project addresses the needs of a program entitled "NIH Blueprint for Neuroscience Research," which looks for new methods, tools, instrumentation, etc. that will benefit multiple National Institutes (NI), such as Neurological Disorders and Stroke (NINDS) and Biomedical Imaging and Bioengineering (NIBIB). Also, this project can benefit the Department of Defense, particularly in the areas of neuronal interfacing for prosthetics and traumatic brain injury (TBI).

Results and Accomplishments

Our collaborators at St. Jude Children's Research Hospital provided us with a large data set of retinal horizontal neuron imagery. The dataset consists of 95 confocal image stacks of developing mouse retinas, each covering an area of 200 μm × 200 μm and a depth of roughly 150 μm and containing on the order of 10–20 neurons. The images were acquired from both wild-type and knockout genotypes at various stages of development, ranging from postnatal day 1 to postnatal day 13. Three individual cells were manually cropped from each volume, resulting in a total of 285 single-cell volumes in addition to the original whole-field volumes. We developed new algorithms to automatically detect and segment the soma (cell body) and dendrites of each neuron in the single-cell volumes. For the somas, we detected the center of the soma using morphological grayscale erosion, and we segmented the soma using a level-set segmentation technique. For the dendrites, we developed a technique for finding an appropriate threshold that separates the fluorescent cell material from the background to create a binary volume. We developed an intensity-based 3D skeletonization technique to thin the resulting binary volume and localize the centerlines of the dendrites while preserving their structure and topology. We compared a small subset of our detected dendritic centerlines to those generated manually on the same cells by our collaborators at St. Jude, and we observed 80% similarity of dendrite position on average between our results and the manual results. In most instances, the differences were due to missed branches or false branch detections in one of the algorithms. Using the segmented soma and dendrite skeleton, we developed an algorithm to compute the graph structure of the dendrites in terms of nodes and edges. From this structure, we were able to compute several features of the cells, including dendrite positions, angles, lengths, and branching order, that may be discriminatory with respect to genotype. We are currently working to develop this feature set and quantitatively characterize all the neurons in our dataset with respect to these features. In addition, we have developed neuron migration analysis tools that can track the motion of multiple neurons in culture in a completely automated fashion. Tracking is performed on the soma, the leading and trailing processes, and the centrosomes within the cell. Time lapse movies of moving cerebellar neurons in culture were captured on a fluorescent microscope by our collaborators at St. Jude.

Publications

Kerekes, R. A., S. S. Gleason, N. Trivedi, and D. J. Solecki. 2009. "Automated 3-D tracking of centrosomes in sequences of confocal image stacks." *Proceedings of IEEE Engineering in Medicine and Biology Conference.*

Solecki, D. J., N. Trivedi, E. E. Govek, R. A. Kerekes, S. S. Gleason, and M. E. Hatten. 2009. "Par6 α regulated Myosin II motors drive the coordinated movement of centrosome and soma during glial-guided neuronal migration." *Neuron* **63**(1), 63–80.

00515

Remote Microfluidic Platform Using Smart Materials and Structures: A Diagnostic and Interventional Tool for Critical Structural Anomalies During Fetal Development

Boyd McCutchen Evans III

Project Description

This is a multidisciplinary project involving the development of a remotely activated, microfluidic valve system. This project involves investigating thermally responsive polymer materials based on poly(*N*-isopropylacrylamide), or p(NIPAAm). When in aqueous solution, this polymer has the interesting characteristic that it exhibits a dramatic reduction in size as its temperature increases through a specific temperature known as the lower critical solution temperature (LCST). This property will be used to create a "normally closed" valve that can be wirelessly activated. This valve will be useful in a range of devices including miniature total analysis systems. We will explore the use of thermally responsive polymers as types of smart materials. This project will use microfluidic techniques to fabricate nanoscale and microscale beads of the thermally responsive polymer. The initial applications that we will investigate involve medical conditions requiring implantation of remotely activated valve devices using minimally invasive surgical techniques, including the birth defect congenital diaphragmatic hernia (CDH).

Results and Accomplishments

A valve has been designed and fabricated comprising a thermally reactive polymer annulus surrounding an internal heating element and an external solid valve body. The current embodiment of this configuration has been designed to insert into the 0.060 in. inner diameter valve lumen of a dual-lumen balloon implant, supplied by our commercial collaborator, NuMed Inc. A flow stand has been assembled enabling the simultaneous evaluation of three independent valves. In flow tests simulating the operating pressure of the fetal trachea (80 mm water column pressure), the current embodiment of this normally closed valve has demonstrated stopped flow in the closed condition (room temperature) and 80 mL/h in the fully open condition (45°C). This embodiment uses a reactive polymer valve body of poly-*n*-isopropylacrylamide with a transition temperature (LCST) between the closed and open state at 32°C. Continued effort includes optimizing the polymer formulation to provide a higher transition temperature with a target of 42°C for biomedical applications, including the demonstration system of fetal tracheal occlusion therapy.

Concurrently, a radio-frequency resonant heating circuit has been designed and demonstrated to remotely actuate the polymer valve. This system is comprised of external driving electronics and a miniaturized coil pickup that will be integrated as the power source for the heating element of the implantable valve system. The current embodiment of this system uses a commercially available, off-the-shelf ferrite core (1.5 mm diameter, Fair-rite Type 78) and has been demonstrated to inductively couple >30 mW of power wirelessly from an external coil antenna to the implanted series resonant circuit, consisting of the coupling inductor, a series capacitor, and an impedance-matched resistive heating element. Thermal actuation of our existing valve body using inductive power coupling has been demonstrated by visual observation of phase transition in the reactive polymer valve material.

Program Development Accomplishments

This effort is a collaboration between a medical team (Baylor College of Medicine), a commercial biomedical device manufacturer (NuMed Inc.), and ORNL. Baylor and NuMed have both made significant in-kind contributions to the effort. NuMed has designed and fabricated a number of custom

balloon valves, compatible with our valve design. Our surgical collaborators at Baylor have procured animals for preliminary animal tests of the tracheal occlusion approach using the NuMed balloon implant. These tests are scheduled to begin on December 7, 2009, and will provide data for subsequent valve optimization based on fully occluded and partially occluded trachea in twin fetal sheep. Based on these data, subsequent tests using the fully integrated valves are expected in Spring 2010. These tests have been approved under ORNL-ACUC Tracking Protocol 0390, October 28, 2009.

With support from the ORNL National Institutes of Health Program Office, we have been conducting the project under the observation of Dr. Carol Blaisdell, Medical Officer in the Lung Developmental Biology and Pediatric Pulmonary Diseases Division of Lung Diseases at the National Heart Lung Blood Institute (NHLBI). Dr. Blaisdell has been very encouraging of our research and is in support of our pursuit of preliminary data necessary for an R01 proposal. Also, once we have established preliminary data, Dr. Blaisdell has volunteered to coordinate interactions between this project's researchers and the Federal Drug Administration. Dr. Gail Pearson, NHLBI's Branch Chief for the Heart Development and Structural Diseases Branch in the Division of Cardiovascular Diseases Branch, has also shared her support and enthusiasm for this project in its early stages and has stated "I agree fully that this project is consistent with NHLBI's mission, and having taken care of a few of these kids during my pediatric residency, it is a significant pediatric problem in terms of health care dollars and years of life lost due to premature mortality." Dr. Pearson has also been in discussion with Dr. Weinman, NHLBI's Deputy Director of the Division of Lung Disease, who also shares interest in this project. Based on this support, we are optimistic that an R01 to NIH will be well received following the completion of year two effort on this project.

00519

Dual Waveband Passive Longwave Infrared Uncooled Imager

Scott R. Hunter and Nickolay V. Lavrik

Project Description

The project is to develop an entirely new and innovative technique for obtaining infrared imagery that can be overlaid with visible images in the same device. In our technique, photon tunneling is utilized with thermally actuated bimorph structures to passively convert midwave or longwave infrared (LWIR) to visible radiation that is then overlaid on the visible light image. This can be accomplished by fabricating the IR imaging structures using optically transparent materials (400–750 nm range). Visible light from the scene will pass through the structures and can be used to image the scene in the visible, while the IR detector structure simultaneously converts the incoming infrared radiation to a visible signal that is overlaid on the visible image. This technique allows very high sensitivity imaging with near background limited performance (no electronic readout noise sources) using small pixel pitches and scalable to large pixel array sizes (1000×1000 pixels or larger; there are no inherent constraints on the upper array size limits) in an extremely low power, low cost imager. The goal of the project is to explore the unique advantages of this dual wavelength imaging approach with the modeling and fabrication of a well-developed proof-of-principle device.

Mission Relevance

The value of dual waveband infrared cameras is particularly apparent under low ambient lighting conditions, or when a target or individual is camouflaged or hidden in the surrounding environment, such as in perimeter security situations. Under these conditions, potential targets and individuals are not easily

recognizable using either visible of infrared imaging techniques separately, but the combined images give a clearer image of the potential target and surrounding threats. Since this device images thermal signatures, there are many energy conservation applications, such as building heat loss and manufacturing process controls, where heat loss can be monitored and controlled. Research and development of dual wavelength infrared imagers is an active research area with funding from the Department of Defense. These dual wavelength imagers can be used for rifle sights, vehicle navigation, perimeter security, ground and aerial reconnaissance and other night vision applications. The Defense Advanced Rsearch Projects Agency and the Army's Night Vision Labs are actively funding R&D on innovative dual wavelength imaging techniques to achieve their missions. Present imagers use two separate cameras that are bulky, power and computer processing hungry, and expensive.

Results and Accomplishments

The following research tasks were performed on this project during FY 2009 to demonstrate the unique advantages of the present dual wavelength imaging technique and to show the feasibility of the approach. We are in the process of demonstrating feasibility by modeling, fabricating and testing various structures, single test pixels and small linear arrays of pixels. Extensive modeling of the operation and theoretical limits of the bimorph actuated infrared pixel has been performed. These studies have been performed on technically feasible pixel structures. Three iterations of small (100–400 μm long, 100 μm wide) test cantilever and bridge structures have been designed, fabricated, and process flows designed and implemented to release these structures. These structures variously include thermal isolation and bridge support arms, arrays of etch holes to improve structure release yield, and multiple thin films to control stress. These structures have been fabricated using low thermal expansion coefficient silicon dioxide thin films (1–2 μm thick) and a much higher thermal expansion coefficient SU8 polymeric material (~0.6 μm thick). A photon tunneling test rig has been fabricated and we have observed photon tunneling through these test structures using this test setup. This is an important test of the concept in that we can observe evanescent field coupling between the laser illuminated substrate and the suspended test structures. We are presently fabricating thermally sensitive bimorph cantilever and bridge structures and small arrays, which we will test and characterize during the next phase of this project.

NUCLEAR SCIENCE AND TECHNOLOGY DIVISION

00489

Surface Interactions of Radioactive Particles and Radioactivity Effects on Transport and Deposition

Costas Tsouris, Joanna McFarlane, Mark Walker, Eunhyea Chung, and Sotira Yiacoumi

Project Description

This project has been focused on testing the hypothesis that radioactive particles behave differently from nonradioactive particles by means of direct surface-force measurements using atomic force microscopy (AFM). An AFM system has been purchased and assembled in our laboratories for this purpose. After a series of surface force measurements in air, including adhesion force measurements and force-distance profile measurements between two nonradioactive surfaces, i.e., the cantilever tip and a planar surface, experiments were conducted with a radioactive gold foil that was activated at the ORNL High-Flux Isotope Reactor (HFIR). The gold foil was used as a planar surface, and the adhesion force between a cantilever tip and the gold foil was measured at a constant relative humidity environment. This was the first attempt to determine *in situ* the effect of radioactivity on surface forces. Force measurements showed that the adhesion force decreased with time or increased with radioactivity dose rate. Further studies are needed to elucidate radioactivity effects on particle interactions and help formulate mathematical expressions for the prediction of these interactions. It is expected that this project will help predict the behavior of radioactive aerosol plumes, as well as particle suspensions in aqueous solutions.

Mission Relevance

In this project, we obtained proof-of-principle data revealing the effects of radioactivity on surface interactions between radioactive surfaces. This work is relevant to nuclear reactor accidents, deliberate explosions of radioactive dispersal devices, radioactive particle behavior in waste tanks at DOE sites, and fate of radioactive particles in the environment. Besides DOE, the project will benefit the Department of Defense (DOD), the Department of Homeland Security (DHS), and the Environmental Protection Agency (EPA). DOD and DHS are interested in how radioactive particles will spread in the event of an explosion of a radiological dispersal device (RDD). A number of explosions have been designed with “cold” particles to simulate explosions of RDD devices and the transport of plumes formed by such explosions. The question remaining is whether radioactive particle plumes would behave differently from “cold” particle plumes. EPA is interested in protecting the environment from the release of radioactivity.

Results and Accomplishments

The work included two main tasks: (1) developing an experimental setup involving an atomic force microscope (AFM) to directly measure surface forces and (2) obtaining surface force measurements and analyzing the data. For the first task (i.e., AFM setup), after consultation with a representative of VEECO, a U.S.-based company specializing on AFM technology, we purchased a new Caliber AFM system. This

system was set up in November 2008 by a VEECO representative, who also provided training to investigators on this project. After this task was completed, we proceeded with the second task, which involved surface force measurements. Initial plans involved the use of ammonium molybdophosphate particles (AMP) that would be loaded with radioactive and nonradioactive cesium cations, at varying ratios, via sorption. For this task, we would have to attach AMP particles on tipless AFM cantilevers. After consultation with safety personnel, we decided to revise this task for safety reasons, because of the risk of inhaling the AMP particle if it was detached from the AFM cantilever. A simpler system was used instead, in which the radioactive surface was a planar gold foil. The gold foil was activated at the HFIR reactor and was transferred to the AFM laboratory once the radioactivity dose rate was 90 mrem/h. Several measurements were conducted between the nonradioactive cantilever tip and the radioactive, planar gold surface at a low relative humidity (<25%). The results show that the adhesion force increases with radioactivity, demonstrating that the hypothesis that radioactive surfaces behave differently from nonradioactive surfaces is correct. This result may be explained by the charging of the cantilever tip due to the bombardment of electrons and the formation of an image charge when the tip approaches the gold surface that increases the attraction. However, further studies are needed to further investigate the mechanism behind this behavior, which is expected to have a significant effect on surface interactions; aggregation, sedimentation, and filtration of radioactive particles; transport of radioactive plumes; as well as particle interactions in aqueous systems.

Publications

Tsouris, C. 2008. "Hydrodynamics and interfacial phenomena in separations of nuclear materials." Invited presentation, G. W. Woodruff School Nuclear & Radiological Engineering and Medical Physics Programs, Georgia Institute of Technology, October.

Walker, M., J. McFarlane, E. Chung, S. Yiacoumi, and C. Tsouris. 2009. "Effects of radioactivity on surface interaction forces." 16th Symposium on Separation Science & Technology for Energy Applications, October, Gatlinburg, Tenn.

00502

The Development of a New Field of Organic-Based, High-Temperature, Heat Transfer Fluids

Joanna McFarlane, Marc A. Garland, Rodney D. Hunt, Huimin Luo, A. Lou Qualls, and William V. Steele

Project Description

Greater thermodynamic efficiency and new thermochemical cycles are dependent on equipment that can run at higher temperatures than current power plants. Both nuclear and solar power generation would benefit from heat transfer fluids for cooling or energy transport that are stable to 600°C, have good thermal characteristics, and do not react with the vessels in which they are contained. The possibility of using substituted polyaromatic hydrocarbons in heat transport was demonstrated in this work. Physical properties were measured that are key to performance as high-temperature heat transfer fluids, such as melting point, critical point, heat capacity, thermal stability, and radiolytic behavior. Fluids tested in this project will eventually be run in an ORNL high-temperature loop, to advance technology in both solar and nuclear power.

Mission Relevance

Innovations in the generation of electricity are often dependent on equipment that can run at higher temperatures than current power plants. Both nuclear and solar power generation would benefit from heat transfer fluids for cooling or energy transport that are stable to temperatures close to 600°C, have good thermal characteristics, and that do not react with the vessels in which they are contained. Development of substituted polyaromatic hydrocarbons as high temperature heat transport fluids supports the efforts of the DOE Offices of Basic Energy Sciences, Fossil Energy, Nuclear Energy, and Energy Efficiency and Renewable Energy. In addition to DOE, high-temperature heat transfer fluids are of interest to a variety of government agencies. These include the resource-conscious military and National Aeronautical Space Administration. In addition, this work will provide the basis for collaborative fundamental studies of the nonequilibrium molecular dynamics of fluids between ORNL and academic institutions. Development of new "virtual" techniques may lead to applications throughout the oil industry for enhanced oil recovery from unconventional sources.

Results and Accomplishments

The thermodynamic properties of 1- and 2-phenyl substituted polyaromatic hydrocarbons have been measured and estimated almost to the critical point. Densities, vapor pressures, and heat capacity measurements were used to derive critical temperature, pressure and density for the phenylnaphthalenes. The thermal and radiolytic stability of 1-phenylnaphthalene was examined using thermogravimetric analysis, differential scanning calorimetery, and gamma irradiation. Low vapor pressure and resistance to thermal decomposition may make phenylnaphthalenes suitable for heat transfer applications involving parabolic solar collectors, high-temperature chemical separations, and recovery of unconventional oil from shales and sands. The 1-phenylnaphthalene has an advantage over high temperature inorganic salts for applications up to 800 K because it is a liquid at temperatures at or close to ambient. However, 100 kGy irradiation of 1-phenylnaphthalene in a ^{60}Co irradiator indicates 1.7% degradation, which, although lower than tributylphosphate/kerosene benchmark fluids for nuclear applications, is higher than that observed for imidazolium ionic liquids. Also, 1-phenyl and 2-phenylnaphthalene compounds appear to isomerize at temperatures slightly below their critical points, which may mean that the properties of mixtures need to be investigated.

00503

Development of an Advanced Light Water Reactor Analysis Capability

Kevin T. Clarno, Matthew A. Jessee, Emilian L. Popov, Guillermo Ivan Maldonado, Jack D. Galloway, Hermilo Hernandez-Noyola, and Johnathan D. Chavers

Project Description

Through the support of the Nuclear Regulatory Commission (NRC), the Nuclear Science and Technology Division (NSTD) develops, maintains, and applies nuclear analysis methods for many aspects of the nuclear fuel cycle using the SCALE code system. The capability to simulate a full-core nuclear reactor has been a missing component of the SCALE code system. The purpose of this project is the development of a coupled neutronics/thermal-hydraulics/isotopic depletion models capability and integration with the SCALE code system. This will provide a comprehensive, open-source capability that is currently not available at any other DOE national laboratory.

Mission Relevance

Through this project, the capability at ORNL to analyze the performance and safety of light water reactors (LWRs) will be greatly enhanced for several key sponsors, including the DOE Office of Nuclear Energy (DOE NE) and the Nuclear Regulatory Commission (NRC) Office of Nuclear Reactor Regulation and New Reactor Office. The development of enhanced and expanded capabilities for LWR reactor analysis is essential for ORNL to secure key roles in support of several major initiatives at the DOE Office of Nuclear Energy, including Light Water Reactor Sustainability to extend plant lifetimes from 60 to 80 years and Advanced Fuel Cycle R&D to explore options for recycling nuclear fuel. In addition, the integration of SCALE with a full-core analysis capability may greatly simplify the NRC reactor design certifications and review of existing nuclear reactors. This project has provided the fundamental capabilities and framework needed to address many of our sponsor's reactor analysis needs.

Results and Accomplishments

The NESTLE core simulator code has been fully integrated with the ORNL SCALE code system. Developments include enhancements to the NESTLE input file format to be consistent SCALE input and an auxiliary computer code (T2N) to automate the processing of nuclear data between SCALE and NESTLE. NESTLE and T2N will be released separately to the public as complementary reactor analysis tools to SCALE through the Radiation Safety Information Computational Center.

Several enhancements have been made to both NESTLE and the SCALE lattice physics code (TRITON) to extend our reactor analysis capabilities. We have implemented a two-phase (liquid and vapor water) thermal-hydraulic model into NESTLE to simulate BWR systems. We also successfully implemented a boiling water reactor flow redistribution model that was beyond the scope of the original proposal. Significant progress has been made in the integration of ORIGEN-S into NESTLE, which is the first implementation of a comprehensive nuclide depletion capability into a core simulator to meet the needs of modeling advanced fuel depletion. This task objective will be finalized as part of a co-author's Ph.D. research.

Demonstrations of integrated reactor analysis capability using SCALE-NESTLE have been presented at the 2009 American Nuclear Society (ANS) Conference in Atlanta. The code system has also been implemented into a graduate course in Nuclear Reactor Physics at the University of Tennessee and will be demonstrated in a Training Workshop at the 2010 ANS reactor physics (PHYSOR) topical meeting.

Publication

Maldonado, G. I., J. Galloway, H. Hernandez, K. T. Clarno, E. L. Popov, and M. A. Jessee. Accepted. "Integration of the NESTLE core simulator with SCALE." *Transactions of American Nuclear Society*.

00507

Advanced Variance Reduction Methods for Active Interrogation Modeling

Douglas E. Peplow, Thomas M. Miller, and John C. Wagner

Project Description

Active interrogation systems are designed to detect illicit nuclear materials (uranium and plutonium) hidden in cargo containers. These systems work by sending radiation into the container, causing fissions in nuclear material, which then emit detectable radiation. Extensive computer simulation is required to design these systems and analyze their effectiveness in different situations. Because of the large quantities of material in a cargo container (e.g., 55 gal drum, tractor-trailer, or ocean-going vessel), these systems are very difficult (and sometimes impossible) to simulate with ordinary Monte Carlo codes. Advanced variance reduction can help speed up simulations via the use of an importance map. This project will develop a method for using multiple importance maps to cause source particles to first interact in the fissionable material and then move out towards a detector. This type of improvement should drastically reduce the simulation time and greatly increase the number of simulations possible.

Mission Relevance

Creating methods for performing rapid computer simulation of active interrogation systems will benefit a wide array of DOE/National Nuclear Security Administration (NNSA) programs, particularly NA-22 (Nonproliferation Research & Development) and NA-24 (Nonproliferation & International Security). NA-22 currently funds efforts related to the development of active interrogation systems, hence, the ability to analyze and improve these systems through faster computation is of interest to that agency. The methods developed through this project are also expected to have relevance to other DOE/NNSA applications in which it is necessary to distinguish between individual components of radiation signals (e.g., direct and scattered radiation components). The Domestic Nuclear Detection Office of the U.S. Department of Homeland Security has programs to detect and prevent nuclear materials from entering the United States. The Defense Threat Reduction Agency of the U.S. Department of Defense also has responsibilities related to detection and prevention of the flow of illicit nuclear materials. Improved computer simulation capabilities would increase the ability of these agencies to design and evaluate proposed active interrogation systems.

Results and Accomplishments

A simple model of a barrel-scanning system that was made showed that a two-step approach could be used to model interrogation particles entering the barrel and fission neutrons leaving the barrel. Preliminary results showed that using the variance reduction decreased the computation time by a factor of 300 to 400 compared with that achieved via analog techniques.

00520

Comparison of ORNL Plasma Arc Lamp Decontamination to Existing U.S. Air Force Aircraft Decontamination Procedures

Chad Duty, Gilbert M. Brown, Marcus B. Wise, Richard Schoske, Patrick Kennedy, and Rich Stouder

Project Description

In previous experiments the ORNL Plasma Arc Lamp technology using a TiO_2 catalyst was effective in the destruction of chemical weapons agent simulants. However, these preliminary experiments were limited to only glass surfaces, only involved G-series simulants, and were not compared to decontamination methods currently in practice. The purpose of this project was to develop a better understanding of the decontamination mechanism and to demonstrate the effectiveness of the ORNL Plasma Arc Lamp technology for decontaminating surfaces applicable to military applications (i.e., C-17 composite material). Additionally, a direct comparison of the ORNL Plasma Arc Lamp technology decontamination to existing U.S. Air Force aircraft decontamination tactics, techniques and procedures will be made. The use of the plasma arc lamp for decontamination of chemical and biological warfare agents is referred to as the High Energy Arc Lamp (HEAL) system.

Mission Relevance

The proposed research will demonstrate proof-of-principle for the decontamination of aircraft following exposure to chemical or biological weapons. The proposed technique will provide a much more energy efficient method for aircraft decontamination as well as a reduced logistical and manpower requirement. The proposed research will benefit the Department of Defense, specifically the Chemical and Biological Defense Program, by providing an alternative approach for aircraft and large area decontamination. The project is also directly applicable to the Defense Threat Reduction Agency and the U.S. Air Force.

Results and Accomplishments

The primary goals of this seed money project were (1) to develop a more complete understanding of the mechanism by which chemical warfare agents decompose in the presence of TiO_2 when exposed to radiant energy from the plasma arc lamp, and (2) to demonstrate the effectiveness of this decontamination system on “real world” materials in comparison to the currently accepted decontamination practices.

The results from the initial goal are embodied in the ORNL technical report referenced below. This publication is an important milestone for demonstrating technical expertise and fundamental understanding in the chemical/biological warfare community and will be a useful reference point in securing future funding.

The HEAL decontamination strategy was also demonstrated on materials relevant to military applications, specifically the wing section of a C-17 airplane. Sections of the composite wing structure were spiked with known concentrations of a chemical warfare simulant (DIMP) and then exposed to the HEAL system or washed repeatedly with hot soapy water (HSW, the current Air Force protocol). Based on a limited number of off-gassing measurements from the sample, it appears that the HEAL approach was not as effective as the HSW method. Potential reasons for this result are (1) ineffective interaction of the simulant with TiO_2 due to improper application of the catalyst and (2) the lack of a quantitative method to allow accurate analysis of the residual simulant material on the working surface. The research team is currently pursuing follow-on funding to address these concerns.

Publication

Schoske, R., P. W. Kennedy, C. E. Duty, R. R. Smith, T. J. Huxford, A. M. Bonavita, P. G. Engleman, A. A. Vass, W. H. Griest, R. A. Jenkins, R. H. Ilgner, and G. M. Brown. 2009. *Decontamiation Strategy for Large Area and/or Equipment Contaminated with Chemical and Biological Agents Using a High Energy Arc Lamp (HEAL).* Technical Report ORNL/TM-2009/08, Oak Ridge National Laboratory, Oak Ridge, Tenn.

00521

Development of a Machinable SiC-BN Ceramic Composite Compatible with High-Temperature Molten Fluoride Salts

David Holcomb, Steve Nunn, Dane Wilson, and David West

Project Description

The overall project task is to evaluate the mechanical and fluoride salt corrosion properties of a recently developed silicon carbide-boron nitride (SiC-BN) composite material. Key to the new composite material being useful for engineering applications is combining the high hardness, mechanical strength of silicon carbide with the ease of machinability of boron nitride while preserving their chemical inertness. If the new material performs as anticipated, this work will serve as leverage for ORNL to create a larger program focused on developing this material to the point where it can be used in engineered systems in support of high-temperature, energy transfer processes.

The project methodology is to fabricate a set of SiC-BN composite samples and experimentally measure their molten fluoride salt corrosion performance. As a new composite material, the fabrication methodology for producing SiC-BN has several variants with unresolved performance differences—notably including corrosion properties. Two fabrication routes are being explored to create suitable material test coupons. The first fabrication method employs reaction synthesis followed by hot pressing. The second fabrication technique utilizes pressureless sintering instead of hot pressing, with the final porosity being removed from the material by impregnating with a carbon bearing liquid.

Mission Relevance

Effective high-temperature thermal energy exchange and delivery at temperatures over 600°C has the potential of significant national impact by reducing both capital and operating cost of energy conversion and transport systems. Today, no standard, commercially available, high-performance heat transfer systems exist for temperatures above 600°C. Liquid fluoride salts offer good heat transport properties at high temperatures with low vapor pressures, toxicities, and reactivity at reasonable costs and are, therefore, leading candidate fluids for increased heat transport efficiency. Both pure SiC and pure BN are compatible with high-temperature molten fluoride salts and high-temperature air exposure (up to 850°C).

Results and Accomplishments

This project is still in process with no substantial results as of yet. Coupons of the SiC-BN have been fabricated using both of the proposed fabrication routes. None of the coupons produced thus far exhibit the desired mechanical properties. The coupons produced in the initial fabrication batch via the hot pressing method are mechanically hard and very difficult to machine. Work continues to alter the constituent material ratios, hot pressing conditions, and binder phase amounts to obtain material with the desired mechanical properties. The coupons produced thus far via the carbonaceous liquid impregnation

route continue to exhibit substantial interconnected porosity. Work continues on improving the impregnation process to completely fill the porosity.

Only planning efforts have been made thus far for salt exposure testing. An available moisture- and oxygen-controlled glove box, fluoride salt, and crucible combination have been identified and will be available when suitable coupons have been fabricated.

00523

Feasibility of Increasing the Thermal Conductivity of UO_2 by the Addition of High Thermal Conducting Material for Performance Improvement

Daniel F. Hollenbach, Larry J. Ott, James W. Klett, Peter J. Pappano, and Theodore M. Besmann

Project Description

The purpose of this project is to develop a new type of nuclear reactor fuel that has a significantly increased thermal conductivity compared to standard UO_2 fuel, and that can be manufactured with minimal changes to existing fuel fabrication facilities. The proposed new fuel is composed of high thermal conductive graphite fibers randomly mixed with UO_2 powder, then compressed and sintered. The addition of graphite fibers to the UO_2 matrix should increase the overall bulk thermal conductivity of the fuel. Since there is a concern associated with the interaction of graphite and UO_2, there is a parallel project that develops a method to create a SiC layer on the graphite fibers, which will hinder any graphite/UO_2 chemical interaction. The increased bulk thermal conductivity will be demonstrated by manufacturing UO_2/graphite thread fuel compacts at up to 5 vol% graphite threads. The increase in thermal conductivity as a function of graphite thread volume will be determined using flash laser diffusivity techniques.

Mission Relevance

The maximum power of a nuclear reactor is limited by the rate at which energy can be removed from the fuel. Existing light water reactors (LWRs) use UO_2 fuel because it is stable, chemically inert, and cheap to manufacture. However, it has a very low thermal conductivity, ~3–5 W/mK. Conversely, highly ordered graphite has a thermal conductivity of ~2000 W/mK, and certain graphite fibers have thermal conductivities in excess of 600 W/mK at room temperature. Additionally, carbon has a very low thermal neutron absorption cross section. Combining minimum amounts of graphite threads with UO_2 should significantly increase the bulk thermal conductivity of the mixture without degrading its neutronic or chemical properties. Using this new type of fuel in existing reactors should enable them to operate at ~20% higher power levels. Maximum reactor power would be limited by the balance of plant characteristics instead of the thermal conductivity of the fuel.

Results and Accomplishments

This year we used only $40,000 of the total $183,000 authorized for this project. This preliminary funding was used to write and obtain approvals for all necessary radiological work permits and research safety summaries. Work also began on both the manufacture of UO_2/graphite compacts and creating a SiC layer on the graphite threads. The following progress was made in FY 2009:

1. The research safety summary has been changed to accommodate UO_2 compaction work.
2. The radiological work permit has been changed to accommodate UO_2 compaction work.

3. Approximately 100 g of UO_2 in the form of UO_2 pellets were obtained. These will be used for benchmark measurements and as feed material for the UO_2/graphite compacts.
4. Six thin slices were cut from an existing UO_2 pellet for benchmark measurements.
5. Thermal diffusivity measurements were taken on the six slices, which are currently being evaluated.
6. A first run at creating a SiC layer on graphite fibers was attempted with limited success. The silicon did not react with the graphite but deposited on the surface, probably because the temperature was too low.

Beginning next fiscal year work will continue on creating and analyzing UO_2/graphite pellets and applying a SiC layer on graphite threads.

PHYSICS DIVISION

00455

Computing the Electric Dipole Moment of the Neutron and the Schiff Moment of the Nucleus

D. J. Dean and M. Ramsey-Musolf

Project Description

This project begins a theoretical program "beyond the Standard Model physics" which will closely tie to the new experimental efforts at the Fundamental Neutron Physics Beam (FNPB) at the Spallation Neutron Source (SNS). The project allows initial progress on two problems relevant to experimental effort at the SNS: a new neutron electric dipole moment measurement and parity-violating (PV) neutron scattering measurements.

Mission Relevance

The operation of the FNPB at the SNS represents a new forefront in nuclear physics research funded by the DOE Office of Nuclear Physics. The high intensity source of monochromatic neutrons provided by this facility will allow experimental nuclear physicists to perform measurements of fundamental properties of the neutron and its interactions with unprecedented precision. These experiments will test basic features of the Standard Model of the electroweak and strong interactions and search for evidence of physics going beyond the Standard Model. This world-leading effort represents an important and fundamental area of experimental nuclear physics research at ORNL.

A number of theoretical computations are needed to help interpret the FNBP experiments. In the case of the neutron electric dipole moment (EDM) search, the implications of this experiment for different scenarios for charge-parity (CP) violation require a comparison of the results, with complementary searches being carried out for the EDMs of the electron and neutral atoms. A comprehensive phenomenological analysis of these EDM searches in models for new CP violation remains to be completed. Similarly, new computations of the Schiff moments of neutral atoms are needed. A similar comprehensive analysis of neutron decay parameters and their implications for "new physics" remains to be performed. Finally, the theoretical framework for interpreting the hadronic PV experiments has recently been reformulated using the methods of effective field theory (EFT). In particular, the sensitivity of the different hadronic PV experiments to the "low energy constants" in the EFT must be delineated for the broad array of measurements that will be performed at the FNPB and elsewhere. In short, there exists an opportunity for significant theoretical advances by performing these computations and analyses.

Results and Accomplishments

We developed a plan to study a new formulation of the Schiff moment operator in both nuclei with an equal number of neutrons and protons and in asymmetric nuclei in the coupled-cluster method at the

singles and doubles excitation level (CCSD). Our approach to the Schiff moment calculation requires us to also utilize the particle removed operators within CCSD. This is called particle removed (PR) CCSD. We developed the formalism and also coded the PR-CCSD operations. We implemented the PR-CCSD formalism in both an m-scheme (all symmetries broken) code, and in a spherically symmetric code for CCSD. The results of these efforts are being written for publication in *Physical Review.*

We also made progress in studying the permanent EDM. A permanent EDM of a physical system requires time-reversal (*T*) and parity (*P*) violation. Experimental programs are currently pushing the limits on EDMs in atoms, nuclei, and the neutron to regimes of fundamental theoretical interest. Here, we calculate the magnitude of the *P,T*-violating EDM of ^{3}He and the expected sensitivity of such a measurement to the underlying *P,T*-violating interactions. Assuming that the coupling constants are of comparable magnitude for π-, ρ-, and ω-exchanges, we find that the pion-exchange contribution dominates. Our results suggest that a measurement of the ^{3}He EDM is complementary to the planned neutron and deuteron experiments and could provide a powerful constraint for the theoretical models of the pion-nucleon *P,T*-violating interaction.

Publication

Stetcu, I., C.-P. Liu, J. L. Friar, A. C. Hayes, and P. Navratil. 2008. *Phys. Lett. B* **665,** 168.

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