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

ORNL/PPA-2012/1

Laboratory Directed Research and Development Program

FY 2011 Annual Report

UT-BATTELLE
ORNL-27 (4-00)

ORNL/PPA-2012/1

Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2011 ANNUAL REPORT

March 2012

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UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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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 of all ORNL LDRD research activities supported during FY 2011. The associated *FY 2011 ORNL LDRD Self-Assessment* (ORNL/PPA-2012/2) 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, nuclear energy 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 four components: the Director's R&D Fund, the Seed Money Fund, Wigner Fellowship Fund, and Weinberg Fellowship Fund. As outlined in Table 1, these four funds are complementary. The Director's R&D Fund develops new capabilities in support of the Laboratory initiatives, the Seed Money Fund is open to all innovative ideas that have the potential for enhancing the Laboratory's core scientific and technical competencies, and the fellowship funds allow building of staff capability with exceptional new scientists. 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	Wigner Fellowship Fund	Weinberg Fellowship Fund
Purpose	Address research priorities of the Laboratory initiatives	Enhance Laboratory's core scientific and technical disciplines	Provide research opportunities for exceptional new scientists in honor of Professor Wigner	Provide research opportunities for exceptional new scientists in honor of ORNL Director Alvin Weinberg
Reviewers	Focus Area Review Committees (FRCs) 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 two to three technical reviewers for each proposal	Candidate and full proposal are reviewed by Wigner Fellowship Review Committee (WGRC) composed of ORNL corporate fellows, senior technical manager, and subject matter experts	Candidate and full proposal are reviewed by Weinberg Fellowship Review Committee (WNRC) composed of ORNL corporate fellows, senior technical manager, and subject matter experts
Review process	Preliminary and full proposal review, including a presentation to the FRC, 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	Full proposal review and presentation to the WGRC	Full proposal review and presentation to the WNRC
Review cycle	Annual	Monthly	Once per quarter	Once per quarter
Project budget	Typically ~$618,000	<$128,000	Typically ~$450,000	Typically ~$150,000
Project duration	24–36 months	12–18 months	24 months	24 months
LDRD outlay	~80% of program	~18% of program	~1% of program	~1% 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 some of the initiatives 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; these are called focus areas. ORNL uses the resources of the Director's R&D Fund to encourage the research staff to submit ideas aimed at addressing focus-area 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 focus areas and research priority areas for FY 2011 were as follows.

- *Advanced Materials and Interfacial Processes for Energy.* Materials and interfacial processes are critical to break through today's technical bottlenecks to realize the full potential of producing clean, abundant, and affordable energy. The combination of the ability to design materials at the nanoscale and to tailor interfacial phenomena that control materials properties and associated chemical processes show extraordinary promise for achieving the revolutionary advances needed for meeting

future energy demands. The goal of this focus area is to develop concepts that will lead to the design, discovery, synthesis, and processing of materials with desired functionality and control of interfacial processes at the atomic and molecular level that will lead to new intellectual property and scientific breakthroughs relevant to solar energy and electrochemical energy storage. Achieving this goal will also require new capabilities for *in situ* characterization and modeling atomic and molecular processes that occur at multiple length and time scales. During the year, the Laboratory invested $5.24 million in 20 LDRD projects. FY 2011 LDRD investments were made in projects to accomplish the following.

  - Tailored materials: design, discovery, and synthesis of materials and interfaces with atomic and molecular control that lead to novel properties and/or functionality for revolutionary breakthroughs in electrochemical energy storage (EES) and solar photovoltaic performance. Materials of interest include but are not limited too thin-film and nanostructured materials, polymers, and hybrid materials for both applications and electrolytes for EES.
  - Systems integration and materials processing: concepts for enhanced design and cost-effective production of efficient solar and EES systems
  - Theory/modeling/simulation: understanding the interactions of photons, electrons, ions, reactive chemicals and energetic particles with materials over multiple length and time scales
  - Nanoscale imaging and spectroscopy: enable the study of interfaces (both buried and at surfaces), including dynamic systems, at atomic and molecular levels and under realistic conditions

- *Neutron Sciences and Technology.* ORNL is in a unique situation with world-class capabilities for neutron science and technology utilizing both the most intense pulsed spallation neutron source in the world (SNS) and a high flux isotope reactor (HFIR) matched only by the Institut Laue-Langevin (ILL) in Europe. The goals of this focus area is to ensure that these facilities are used to their maximum advantage for science in the USA and at ORNL by investing in the facility infrastructure, neutron scattering instruments, ancillary equipment, and scientific application of neutron techniques and maintain these at world-leading standards. In 2011, $2.39 million of LDRD funds supported 12 projects in this area. FY 2011 LDRD investments were made in projects to accomplish the following.

  - Novel neutron scattering instruments and spectrometer elements; new concepts for polarized neutron scattering, micro-bending of neutron beams, and other techniques to maximize the use of available neutron fluxes; innovative concepts to significantly improve either accelerator or reactor neutron sources in support of the scientific programs; and new and unique experimental capabilities, for example expanding the realm of accessible experimental conditions to enable non-equilibrium experiments including pump-probe experiments, multiple simultaneous probe measurements, and extreme conditions such as simultaneous application and control of pressure, low temperature, and magnetic field.
  - Develop new signature science programs making the best possible use of existing and soon-to-be-available neutron instrumentation, especially those implementing innovative experimental methods, leading to new capabilities that support the science programs.

- *Ultrascale Computing and Data Science.* To solve the computational problems that the scientific community deems critical to the advancement of science and of the most benefit to the nation will require computers with hundreds of petaflops by 2015. Systems of this capability will present a set of new challenges that must begin to be addressed today. These challenges include an exponential increase in system concurrency, memory bandwidth and latency shortfalls (the memory wall), increase in failure rates with the need for improved resilience at all levels of the software stack, and exponential increase in data that requires new data analysis and knowledge discovery capabilities.

The goal of the LDRD investment is to address these challenges by developing new algorithms for scientific applications and system software; developing fault and performance monitoring, modeling and analysis tools; enhancing knowledge discovery techniques; and significantly rethinking available concurrency in scientific applications. Toward this goal, the Laboratory invested $4.01 million during FY 2011 to support 15 projects to accomplish the following.

- — Exascale applications development tools for ultrascale systems, including programming models and translation technologies
- — Performance tuning investments including auto-tuning tools, productivity enhancements, new methods for performance measurement, modeling, and analysis applied to both systems and applications
- — Advanced algorithms and methods including new libraries and other tools that will be needed to support the effective use of ultrascale systems
- — System software technologies to improve resilience, virtualization, operating system structures, runtime systems, and I/O and storage systems
- — Tools and methods for processing large-scale data sets, developing methods needed to analyze and manage large scale scientific data sets, including ontology, acquisition, curation, indexing, sharing, transmission, representation, and visualization
- — Innovative information systems and environments that address the issues that would scale across a wide range of disparate types on information networks
- — Disparate data fusion techniques — innovative analytic techniques for fusion of text, images/video, and digital data
- — Modeling and simulation tools for distributed mobile systems; innovative real-time data driven modeling and simulation systems based on sensor network data ingestion with applications to understanding behavior of and status of critical infrastructures at the facility and national scales and emergent behavior in complex social systems
- — Analysis and fusion of disparate sources of information such as text, bots, network sensors, network traces, switch information and traffic analysis for the purpose of discovering early indications of potential threats or rapid analysis of currently unfolding events and/or classifying sensitivity of the data so corrective action can be performed before it leaves a protection zone
- — Security and trust of complex systems that are often comprised of un-trusted components
- — Predictive algorithms, and protocol-related issues connected to transmission, retrieval, and protection of information encoded and manipulated from the analysis phase

- *Biomass Production and Conversion for Energy and Materials.* This focus area seeks to strengthen our leadership and depth in the assessment of biomass resources and infrastructure and position ourselves for a biofuels deployment and a "beyond bioethanol" strategy and science. It is strategically designed to focus, integrate, and strengthen the comprehensive bioenergy-relevant research capabilities of ORNL to support the nation's creation of a sustainable bioenergy generation and delivery infrastructure. The term *infrastructure* is defined here in its broadest sense to encompass all the technology, and its underlying science, needed to ensure sustainable, reliable, and secure production of bioenergy and bio-products. During FY 2011, LDRD investments totaling $2.12 million were made to support 15 projects to accomplish the following.

  - — Research into the logistics of transportation, handling, and distribution of feedstock and products to support the emergence of a comprehensive lignocellulose industry

  - Development of an integrated sustainable feedstock supply chain and its interface with other sectors by investing in the following areas: (1) understanding and optimizing the bioenergy supply chain from land through demand, including food impacts; (2) developing analytical and visualization tools to optimize and forecast the bioenergy supply chain at local to national scales; (3) developing methods for coping with multiple optimization objectives as required by a complex systems model of bioenergy; (4) developing analytical approaches to understand the competition between vehicle technologies such as flex-fuel, electric, and conventional; and (5) developing comprehensive analysis of all options for biomass substitution for fossil energy to answer the question "What is the best use of biomass?"
  - Development of new products beyond bioethanol using all components of lignocellulosic materials and so they can be merchandized. Developing core capabilities in catalysis of biomass and synthetic biology leading to industrial partnerships
  - Research for end user validation, including (1) optimization of internal combustion engines for alcohol fuels; (2) materials science to address both hygroscopic and corrosion challenges associated with bio-products; (3) emissions after-treatments for alcohol-based fuels; and (4) environmental implications of bioenergy products

- *Electric Grid Technology*. Investment goals are to seek to stimulate research areas that will result in technologies for modernizing the electric delivery system. The objective is to support the development of a highly reliable and secure electrical grid. Toward this goal, the Laboratory invested $2.01 million in FY 2011 to support six projects. Efforts focused on development of the following.
  - Modeling and simulation tools to enable real-time monitoring, analysis, and prediction of electrical outages.
  - Technology for energy storage and storage control on the electric grid, including compressed air energy storage, pumped hydro, and grid scale ultra-capacitors and flow batteries.
  - Advanced resilient control methods and topologies to monitor essential components, enabling rapid diagnosis and precise solutions appropriate to any event
  - New methodologies and fault detection algorithms to detect high-impedance faults.
  - Novel approaches to dynamically detect disturbances and control power flow to reduce major disruptions on the grid.
  - Innovative materials and processes for the grid, including cables, conductors, transformers, motors, and solid-state devices.
- *Global Security Science and Technology.* The strategic intent is to bring ORNL research and scientific applications to bear on national security challenges in a way that produces exceptional solution sets and extends the bounds of science. In support of this goal, seven LDRD projects were funded for $2.19 million to develop (1) energy and sustainability for national security; (2) information and communication technologies that create, analyze, and distribute knowledge exactly where and when it is needed; (3) built environments of every scale to solve complex weapons of mass destruction (WMD) challenges, leading to integrated system solutions; (4) unique systems solutions to the need for ubiquitous understanding of the location, use, and potential disposition of nuclear materials, for both nuclear nonproliferation and counterproliferation; and (5) understand and control, at the nanoscale, physical and chemical phenomena of materials and interfacial processes in developing sensor networks, tagging, tracking, and locating systems.
- *Nuclear Energy Science and Technology.* The objective of this focus area is to address three specific challenges that must be overcome if nuclear energy is to achieve its potential: (1) new generations of

high-temperature, highly efficient nuclear electric and nuclear process heat systems; (2) reducing the cost of nuclear electric and nuclear process heat systems; and (3) addressing integrated nuclear fuel cycles (the *integrated* fuel–reactor– reprocessing – material storage and transport– material disposition *system*) issues. In support of this goal, 10 LDRD projects were funded for $2.40 million. Efforts focused on the following: (1) improving ORNL high-temperature fuel and materials experimental capabilities (physical and computational); (2) expanding ORNL modeling and simulation capabilities for nuclear energy systems and relevant phenomenology; and (3) further strengthening ORNL's reputation on full fuel cycle to include chemistry, engineering, materials, radiation environment, computations, etc.

- *Understanding Climate Change Impacts.* The goal of investment in this area is to address the many questions facing climate change science requiring the development of new generation of comprehensive climate models, frequently referred to as Earth System Models, to predict the coupled chemical, biogeochemical, and physical evolution of the climate system. In support of this goal, five LDRD projects were funded for $1.95 million. Efforts focused on (1) improving formulation of earth system modeling and developing methods to quantify regional-scale climate predictability on seasonal to decadal time scales; (2) expanding multiple-scale (genome to ecosystem) in ecological systems and to assess how insights derived from these investigations can improve models that forecast change at multiple levels of biological organization; (3) improving capability for the integration of model and experimental data and develop interface with both the advancement of high-resolution models and the application of results to assessing impacts and aiding decision-support; (4) developing an improved understanding of the climate system, and the commensurate improvements in predictive capability, with a focus on impacts and consequences for "critical infrastructures" including the energy sector, water resources, agriculture and land use, natural ecosystem goods and services, carbon sequestration strategies, and coupled feedback that also reflect population response to climate change.

- *Scientific Discovery and Innovation.* Scientific discovery and innovation investment goal is to maintain and advance all of the Laboratory's distinctive capabilities, and for the accomplishment of the Laboratory's science strategy. In support of this goal, seven LDRD projects were funded for $0.9 million. Efforts focused on giving staff researchers an opportunity to communicate potentially breakthrough research ideas and proposals directly with Laboratory leadership and to possibly research Laboratory discretionary investment in these ideas.

To select the best and most strategic of the ideas submitted, the Deputy Director establishes committees for each focus area 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 2011, $32.14 million was allocated to the ORNL LDRD program to support 173 projects, 74 of which were new starts (Table 2). About 80% of the fund's annual allocation is awarded to projects at the beginning of the fiscal year. The remainder, about 20%, 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 focus area are summarized in Fig. 1.

Table 2. ORNL LDRD by fund

	Director's R&D Fund	Seed Money Fund	Wigner Fellowship Fund	Weinberg Fellowship Fund
Costs	$25,091,775	$4,963,163	$1,794,114	$316,886
Number of projects	97	58	10	8
Number of new starts	39	28	5	2
Continuing (2nd & 3rd year of funding)	58	30	5	6
Average total project budget (1–3 years)	$477,470	$123,338	$219,595	$72,668
Average project duration	24 months	16 months	24 months	24 months

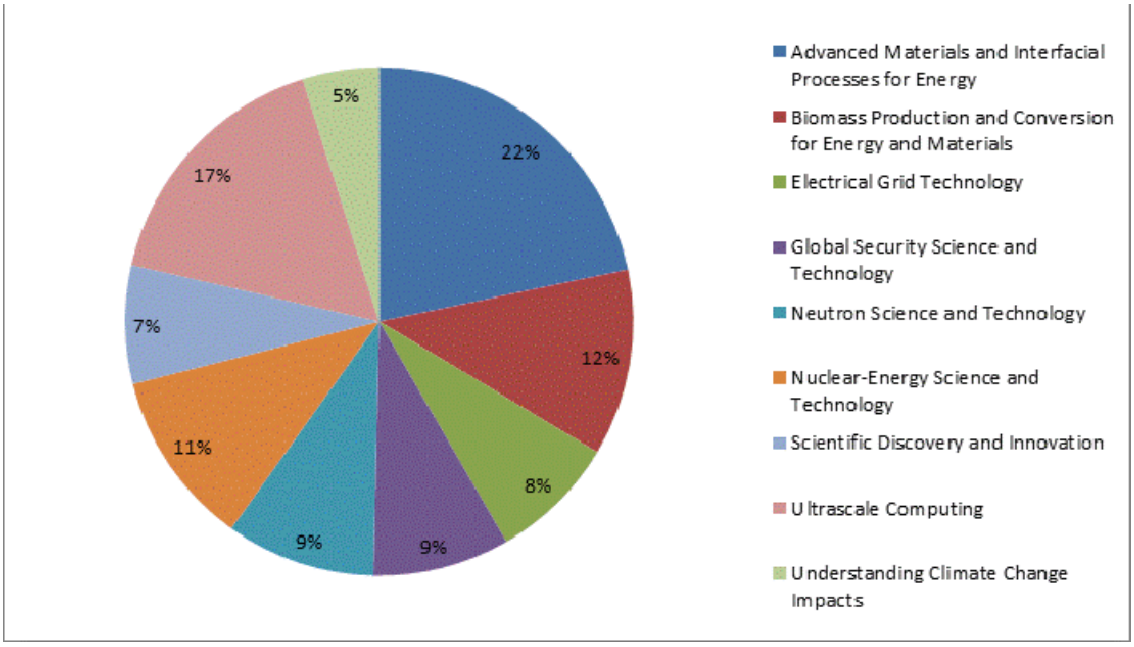

Fig. 1. Level of Director's R&D Fund investment in the Laboratory Focus Area for FY 2011.

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 focus areas. 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 directorates 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 2011, $4.96 million of the LDRD program was apportioned to the Seed Money Fund to support 58 projects, 28 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

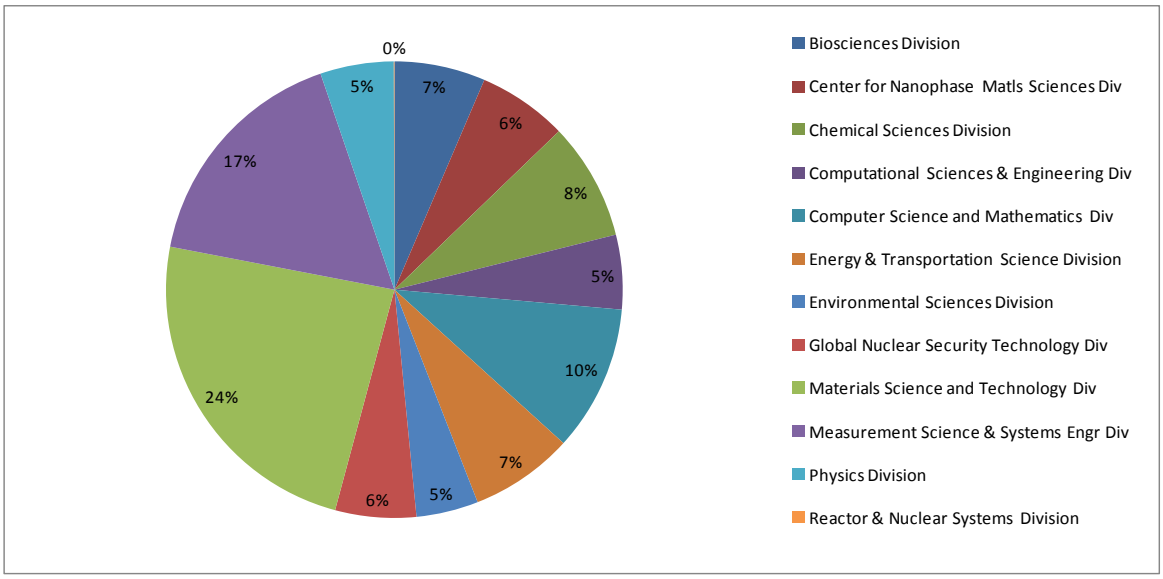

Fig. 2. Distribution of Seed Money Fund by research division for FY 2011.

Fellowship Money Fund

In FY 2011, the awardees of the Laboratory's Alvin M. Weinberg and Wigner Fellowship programs received funding through the LDRD Program. The fellowship programs were formed to provide research opportunities for exceptional new scientists in honor of Professor Wigner and Dr. Alvin Weinberg (former ORNL director). The appointment of Fellows to ORNL's staff provides an opportunity for outstanding life, physical, computer, computational, social scientists, engineers, and applied scientists to select and pursue research in an area related to national energy problems and interests. Fellows are exceedingly well qualified in their fields of expertise and are no more than 3 years beyond the doctorate. There are no application deadlines for the Fellowship. Each application package, consisting of a fellowship research plan, is considered based on how it meets the criteria for the position. Applications are reviewed by special selection committees once per quarter during the year. The Wigner Fellowship is full-time 2 year appointment, and the Weinberg Fellowship is quarter-time 2 year appointment.

Fellowship proposals are reviewed by Fellowship committees. When candidates apply for a fellowship, they are required to submit their research statement. Once the candidate is selected, a mentor is assigned, who helps him/her prepare the LDRD project proposal that is aligned with the fellow's research statement. Wigner Fellowship proposals are reviewed by the Wigner Review Committee (WGRC), and Weinberg Fellowship proposals are reviewed by Weinberg Review Committee (WNRC). After the reviews are completed, the committees' recommendations are sent to the Deputy Director for Science and Technology for approval. The proposals also go through DOE concurrence.

In FY 2011, $2.11 million of the LDRD program was apportioned to the Fellowship Fund to support 18 projects—8 Weinberg and 10 Wigner Fellowship proposals.

Report Organization

This report, which provides a summary of all projects that were active during FY 2011, is divided into 12 sections: one for each of the eight Laboratory focus area discussed above, a Scientific Discovery and Innovation category of projects funded through the Director's R&D Fund by the Deputy Director for Science and Technology, the Seed Money Fund, the Wigner Fellowship Fund, and the Weinberg Fellowship Fund. The Seed Money Fund 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 2011. Publications resulting from the project are also listed.

SUMMARIES OF PROJECTS SUPPORTED THROUGH THE DIRECTOR'S R&D FUND

ADVANCED MATERIALS AND INTERFACIAL PROCESSES FOR ENERGY

05195

Controlled Hierarchical Self-Assembly of Robust Organic Architectures

B.P. Hay, R. Custelcean, and N.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 (1) involving 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 DOE Office of Basic Energy Sciences (BES) initiatives 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 of organic crystals using reversible imine formation as the coupling reaction. This involved the reversible coupling carbonyl compounds (aldehydes or ketones) with

amines. The strategy used 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. Five tetracarbonyl nodes and five tricarbonyl vertices have been prepared and purified in gram quantities. 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. Novel algorithms were derived and coded to generate powder diffraction patterns for comparison with experimental data. Systematic studies were conducted to identify general reaction conditions (solvent, added water, pH, temperature, and time) to optimize imine formation. Although it was possible to reproduce the formation of a DCC framework that appeared in the literature after this project was initiated, all attempts to form new crystalline frameworks have thus far been unsuccessful, leading instead to amorphous polymers or gels. A manuscript documenting the preparation and characterization of these highly cross-linked materials has been submitted to a peer-reviewed journal.

Information Shared

Duncan, N. C., B. P. Hay, E. W. Hagaman, and R. Custelcean. "Thermodynamic, Kinetic, and Structural Factors in the Synthesis of Imine-Linked Covalent Organic Frameworks." *Tetrahedron*, submitted for publication.

05342

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

F.A. Reboredo, M. Eisenbach, M. Kent, P.R. Nicholson, D.M. Stocks, and G. Malcolm

Project Description

This project aims to overcome one of the major stumbling blocks in theoretical condensed matter physics and materials science, namely, 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 propose to attack this failure on two fronts. First, we will perform 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. The purpose of solving this model is to (1) understand the role of electronic correlations as they become dominant, (2) understand the features that exchange correlation functionals must poses in order to describe strongly correlated materials, and (3) provide an accurate benchmark to test new DFT-type approximations. Second, we will use our new theoretical insights that we have obtained to develop new DFT approximations that overcome one of the major failures of LDA theories, namely, incorrect treatment of the so-called self-interaction. Success in developing a self-interaction free DFT has the potential to revolutionize electronic structure theory.

Mission Relevance

The goal of the proposal is to obtain basic information on 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.

The QMC calculations in the homogeneous electron gas have had an impact that extends beyond condensed matter and material science; the basic papers in this field are among the top four cited articles in *Physical Review B* and *Physical Review Letters* of all time. Our aim is to produce data of a similar range of applicability and thereby provide the underpinnings of a significant advance in the ab initio theory of strongly correlated materials.

Results and Accomplishments

The LDRD funds during the third year were used to partially support the work of Michal Baldish. During that time we concluded the final calculations requested by the referees. Our paper reported specifically and extensively on the scientific project for which the LDRD was requested. Our article was published August 9, 2011, in *Physical Review B,* volume 84, Issue 7, Article Number: 075131 DOI: 10.1103/PhysRevB.84.075131 It was submitted to the PTS system with ID number 27721.

In summary, we reported the study the electronic structure of a spherical jellium in the presence of a central Gaussian impurity. We tested how well the resulting inhomogeneity effects beyond spherical jellium are reproduced by several approximations of DFT. Four rungs of Perdew's ladder of DFT functionals, namely, LDA, generalized gradient approximation (GGA), meta-GGA and orbital-dependent hybrid functionals were compared against our QMC benchmarks. We identified several distinct transitions in the ground state of the system as the electronic occupation changes between delocalized and localized states. We examine the parameter space of realistic densities ($1 < rs < 5$) and moderate depths of the Gaussian impurity ($Z < 7$) and constructed a phase diagram of the electronic ground state configuration. The selected 18 electron system (with closed-shell ground state) presents $1d$ to $2s$ transitions, while the 30 electron system (with open-shell ground state) exhibits $1f$ to $2p$ transitions. For the former system, the accuracy for the transitions is clearly improving with increasing sophistication of functionals with meta-GGA and hybrid functionals having only small deviations from QMC. However, for the latter system, we find much larger differences for the underlying transitions between our pool of DFT functionals and QMC. We attribute this failure to treatment of the exact exchange within these functionals. Additionally, we amplify the inhomogeneity effects by creating the system with spherical shell, which leads to even larger errors in DFT approximations.

Information Shared

Bajdich, M.F. A. Reboredo, P. R. C. Kent, "Quantum Monte Carlo calculations of dihydrogen binding energetics on Ca cations: An assessment of errors in density functionals for weakly bonded systems," *Physical Review B*, 82(8), Article Number 081405, DOI: 10.1103/PhysRevB.82.081405 (August 10, 2010).

Bajdich, M., M. L. Tiago, R. Q. Hood et al., "Systematic Reduction of Sign Errors in Many-Body Calculations of Atoms and Molecules," *Physical Review Letter*, **104**(19), Article Number 193001, DOI: 10.1103/PhysRevLett.104.193001 (May 2010). Times cited: 3 (from Web of Science).

F. A. Reboredo, "Systematic reduction of sign errors in many-body problems: Generalization of self-healing diffusion Monte Carlo to excited states," *Physical Review B*, **80**(12), Article Number 125110, DOI: 10.1103/PhysRevB.80.125110 (September 2009).

05388

Multiphase Self-Organized Interfaces for Polymer Photovoltaic Technologies

S.M. Kilbey II, B.B. Sumpter, D.L. Pickel, W.T. Heller, M. Fuentes-Cabrera, J. Ankner, R. Shaw, J.-G. Chen, N. Ramanathan, J.A. Calderon, and M. Dadmun

Project Description

Through a joint experimental and theoretical/computational effort, we tackle the underlying science needed to develop nanoparticle-polymer photovoltaic (PV) devices having tailored heterojunction interfaces comprising self-organized blends of semiconducting conjugated polymers and semiconductor quantum dots (SQDs) as well as conjugated polymer/fullerene composites. Understanding how to manipulate the donor/acceptor morphology and tailor heterojunction interfaces in bulk heterojunction thin films is crucial for optimizing photocurrent generation and creating low-cost, efficient polymer-based PV cells. Research activities aimed at understanding the nanoscale structure and properties of polymer-nanoparticle interfaces will yield fundamental knowledge of the links between electronic and morphological states of the systems, ultimately enabling the ability to tailor blends comprising semiconducting quantum dots or fullerenes (acceptors) and semiconducting polymers (donors) that make up the photoactive layer of a PV cell. This project addresses major needs in the fundamental design of photoactive layers and integrates expertise in computation, scattering, spectroscopy, and polymer science and physics to address challenging problems in soft and hybrid materials for energy conversion technologies.

Mission Relevance

Driven by the need for energy security and reinforced by the need for a cleaner environment, technologies that harness renewable energy sources are receiving increased interest. In this regard, the development and deployment of large-area, low-cost, and efficient PV systems are of considerable importance and wholly consistent with Laboratory and DOE Office of Science missions. Through this research program, barrier issues in polymer-based PV systems are being addressed, existing capabilities across the Laboratory in computational, neutron, and soft matter sciences are being integrated, and new capabilities in these areas are also being developed. The interdisciplinary research team developed here will be well positioned to respond to future, anticipated calls in the area of materials for energy conversion technologies (solar, battery, etc.).

Results and Accomplishments

A variety of accomplishments related to understanding morphology development and excitonic processes and improving charge transport in PV systems based on conjugated polymers and nanoparticles, including both SQDs and fullerene-based derivatives, have been attained during this research program. New capabilities in the synthesis of well-defined conjugated polymers with appropriate chain-end functionality have been developed, which has enabled studies of block copolymer-based compatibilizers to optimize the nanoscale morphology of donor-acceptor blends. Insight into the thermodynamic origin of the ability of the block copolymer compatibilizer to tune morphology has been gained using computational methods. The photophysics of oligomeric paraphenylenes (OPPs) was investigated using large-scale quantum density functional calculations, and results from computation were compared to measured optical absorbances of OPPs in thin film form and end-tethered poly(para-phenylenes) used to compatibilize electrode-like surfaces. Particularly impressive changes in performance, ostensibly related to photocurrent generation, have been revealed in bulk heterojunction blends containing conjugated polymer-modified electrodes. New capabilities in spectroscopic imaging of donor-acceptor blends, light- and thermal-aging

studies of PV blends, and sample environments for carrying out neutron scattering studies have been developed and used to examine the nanoscale morphology of organic PV systems. These results as well as the underlying new capabilities, for example, electrical current atomic force microscopy, developed through this research program are being used to advance the understanding of the intimate links between assembly, structure, and optoelectronic properties.

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Other information shared: four invited presentations, four contributed presentations, and three conference proceedings.

05423

New Multinary Materials for Solar Energy Utilization

M.A. McGuire, A.F. May, G.E. Jellison, Jr., D.J. Singh, and M.-H. Du

Project Description

The goals of this work are to expand the frontiers of inorganic photovoltaics and our understanding of fundamental physics and solid state chemistry of multinary semiconductors, and to use these advances to develop new classes of complex materials with enhanced photovoltaic properties. We will achieve this by using our combined expertise in materials synthesis, optical and photovoltaic measurements, and first-principles calculations. State-of-the-art photovoltaic materials CdTe and CIGS ($CuIn_{1-x}Ga_xSe_2$) have relatively simple crystal structures, related to that of silicon. We will investigate more complex ternary structure types as candidate photovoltaic materials. Increasing complexity often leads to discovery of enhanced properties and even new phenomena. Target compounds will contain electropositive cations (*A*) embedded in a covalent framework. The *A* cations may provide doping and alloying sites coupled only indirectly to the conducting framework and allow enhanced chemical control over properties such as carrier concentrations, mobilities, and band gaps. Specific systems that will be studied include ACd_xTe_y and ACu_xSe_y. In addition, we will explore how the incorporation of strongly electropositive elements can be used to increase the gap in small band gap materials, opening up new chemical systems as candidate photovoltaics.

Mission Relevance

The project will investigate new inorganic compounds as candidate photovoltaics materials. Development of these materials would provide a new direction in solar cell research and could lead to significantly higher device efficiencies. This would greatly benefit the DOE Office of Energy Efficiency and Renewable Energy (EERE) solar energy program. This work will involve careful experimental and theoretical characterization of new materials and will lead to advances in our understanding of complex semiconductors in terms of their crystallographic, chemical, optical, and electronic properties. Thus, the work is relevant to the DOE Office of Basic Energy Sciences (BES) goal of advancing our understanding of matter in ways that support the energy missions of DOE.

Results and Accomplishments

Many chemical systems were studied in an effort to explore new compounds with the structural and chemical properties required for potential photovoltaic materials. In FY 2011 we completed our study of the $BaCu_2Q_2$ (Q = Se, Te) system, examined new and known materials in the AMg_2Bi_2 system, grew and characterized single crystals of the kesterite Cu_2ZnSnS_4, and developed analytical techniques and programming required to study the optical properties of monoclinic materials using generalized ellipsometry.

The results of our study of $BaCu_2Q_2$ are reported in an article entitled "Transport and optical properties of heavily hole-doped semiconductors $BaCu_2Se_2$ and $BaCu_2Te_2$" in *Journal of Solid State Chemistry* (doi:10.1016/j.jssc.2011.08.021). First-principles calculations show these materials to be semiconducting with band gaps of appropriate magnitude for solar applications; however, high naturally occurring carrier concentrations (10^{18}–10^{19} cm^{-3}), relatively low mobilities (15 $cm^2V^{-1}s^{-1}$), and a resistance to doping via chemical substitutions suggest these materials have little potential for photovoltaics. Moderately high Seebeck coefficients were observed in these materials, in good agreement with models based on the calculated electronic structure. The noted difficulty in doping these materials will likely also preclude good thermoelectric performance.

High-quality single crystals and polycrystalline samples of $CaMg_2Bi_2$ and the related new compounds $EuMg_2Bi_2$ and $YbMg_2Bi_2$ were synthesized and characterized by x-ray and neutron diffraction, thermodynamic and transport properties measurements, and first-principles calculations. The three materials adopt the same crystal structure and form as p-type single crystals with carrier concentrations near 10^{19} cm^{-3}. The transport behavior suggests strong defect scattering, and good mobilities in the range of 100–300 $cm^2V^{-1}s^{-1}$. Band structure calculations suggest a band gap near 0.7 eV for the Ca-compound, but significant optical absorption only for photon energies above about 2 eV. Study of the heat capacity and magnetic behavior revealed an antiferromagnetic transition near 7 K in $EuMg_2Bi_2$. A manuscript reporting results of this study has been accepted for publication in *Inorganic Chemistry*. A report on the high-temperature properties of these materials is in preparation.

Single crystals of the kesterite phase Cu_2ZnSnS_4 were grown by vapor transport reactions. Kesterites are known to perform well in photovoltaic devices, but studies of fundamental properties of single crystals are scarce. Our crystals formed as thin (~0.5 mm) needles up to 1 cm in length, growing along the (1–1 0) crystallographic direction. X-ray diffraction showed the crystals to be well-crystallized Cu_2ZnSnS_4, and optical characterization indicated a band gap near 1.4 eV. The crystals displayed semiconducting transport properties with room temperature resistivities of 0.04–0.5 Ωcm. Growth of larger crystals will allow more detailed optical analysis. We expect the results of these studies will be published in the scientific literature.

As more complex materials make their way into applications, the tools necessary to study their optical properties must be developed. In particular, the optical properties of crystals with monoclinic symmetry have received little attention. The dielectric tensor $\boldsymbol{\varepsilon}$ relates the electric displacement to the applied electric field ($\mathbf{D} = \varepsilon_o \boldsymbol{\varepsilon} \mathbf{E}$, where ε_o = the permittivity of free space) and describes light propagation in a material. For monoclinic materials, there are four components of $\boldsymbol{\varepsilon}$. Below the band gap, the tensor can only be diagonalized at a fixed energy, and changing the energy changes the principal axes. For higher energies the tensor components contain both real and imaginary components, and diagonalization is not possible. Thus, to describe a monoclinic material, the real and imaginary parts of all four components must be determined. We have done this for the first time by measuring the complex reflection coefficients for 12 orientations of a crystal of monoclinic $CdWO_4$. This work is an important step in developing an understanding of the optical properties of asymmetric, complex materials and demonstrates world-leading capabilities in this area. A manuscript detailing this work has been submitted for publication.

05428

Tough Electrolytes for Batteries–Composites Inspired by Nature Storage of Electrical Energy

N.J. Dudney (ORNL); W. Tenhaeff, A. Sabau, and S. Kalnaus; E. Herbert, and G. Pharr (UTK); K. Hong and X. Yu (CNMS); K. Perry and K. More (MST); J. Anker (SNS); J. Mays and S. Deng (UTK); S. Paddison and B. Habenicht (UTK) *JDRD funding*

Description

All solid state batteries will be far safer than current Li-ion technology containing flammable electrolytes. However, dry polymer, glass and ceramic electrolytes are all at least ten-fold too resistive; plus they are prone to fail by fracture or by incursion of lithium dendrites. Forming a composite may be the solution, particularly if both components are Li-ion conductors. Composites with submicron laminar and fiber features will be fabricated using poly(ethyleneoxide)-based electrolytes, poly(cyclohexadiene)-based block co-polymer, and lithium phosphorus oxynitride (Lipon) glass. Ion transport within and across the phase boundaries will be studied with particular attention to the effect of the second phase on the polymer crystallinity, which can have a huge effect on the cation and anion transport. Simulation of the transport and mechanical properties will guide design of promising materials and structures. Mechanical properties will be evaluated by microindentation and by cycling performance in battery half cells. Success will open new options for Li-air battery and advanced battery architectures.

Mission Relevance

This project will investigate the scientific and technical potential of preparing composites of inorganic and polymer materials as solid state electrolytes for rechargeable lithium batteries. Electrical energy storage is identified as a critical need for the US energy portfolio and as such is highly relevant to the DOE mission (BES and EERE) and other federal agencies including the DOD and DHS. With an improved solid electrolyte, development of batteries using a metallic lithium anode should become safer and cost-effective. This will provide enhanced energy density and cycle life for transportation as well as storage for renewable energy.

Results and Accomplishments

During the first year, bilayers of thin films of Lipon and two different PEO+$LiClO_4$ based electrolytes (<~1μm each) were prepared with both Lipon-top and PEO-top configurations. Much effort was required to control these thin films, their interface, and to accurately measure the transport across and along the interface. The PEO structure was modified to prevent crystallization and provide a reasonable ionic conductivity. In addition, the mechanical properties of Lipon were determined by nanoindentation. The most important properties of the bulk materials and interfaces will soon be available for input into simulation of composite structures. The basic codes for the simulation of the ionic transport and mechanical properties are in place and refinements, particular for the complex ion transport and adhesion at the interface, are being implemented. The only shortcoming is that attempts to synthesize a conductive copolymer of PCHD+PEG have so far been unsuccessful. This effort is now focused on preparing a homopolymer of sulfonated-PCHD with good single ion Li^+ transport. Progress towards a composite electrolyte can proceed with the PEO-based polymer electrolyte and Lipon glass barrier films.

During the second year, we expanded work in all areas. Mechanical properties of highly conductive crystalline PEO samples from Peter Bruce (Univ. St. Andrews) were investigated by nanoindentation while under SEM vacuum. Simulations were expanded and published with examples of mechanical and ion transport analysis for the same composite structure. Bilayer work addressed polymer films cast onto

ceramic plates of a commercial electrolyte. Initial work to prepare ultra-thin and ultra-smooth films for neutron reflectometry was successful, and bilayer interfaces will be analyzed with upcoming beamtime. Many attempts were made to prepare composites of ceramic electrolyte powders dispersed in a polymer electrolyte matrix. Unfortunately, the interface was resistive, even with sonication and other processing to "activate" the interface. Analysis by high-resolution SEM and TEM of cryogenically prepared cross sections showed no evidence of interfacial reaction. Ongoing effort is directed to chemical modification of the interface for improved transport and adhesion.

The composite fabrication and electrochemical analysis will be continued with follow-on funding from DOE-EERE Vehicle Technologies. This effort will emphasize the performance of the electrolyte films in contact and upon cycling with lithium metal. A proposal to continue the work on evaluation of the mechanical properties of solid electrolytes, again with respect to the fresh and cycled lithium, is pending

Information Shared

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"Electrochemical and Mechanical Characterization of Composite Nanostructures of Solid Glass and Polymer Electrolytes," Wyatt E. Tenhaeff, Erik Herbert, Hunlun Hong et al.

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"Electrochemical and Mechanical Characterization of Composite Nanostructures of Solid Glass and Polymer Electrolytes," Wyatt E. Tenhaeff, Erik Herbert et al.

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05451

Designing High-Efficiency Photovoltaic Heterostructures by Interfacing Polar and Nonpolar Oxides at the Atomic Scale

H.N. Lee, S. Okamoto, G.E. Jellison, Jr., M.F. Chisholm, and D.J. Singh

Project Description

This project is aimed at obtaining fundamental understanding of oxide interfaces in a photovoltaic (PV) context. If successful, these insights will be enabling for new approaches to high-efficiency generation III

PVs. Of necessity, these high-efficiency cells require new materials with appropriate band gaps and electronic properties, and entirely new approaches may be required. Although complex oxides are normally quite stable, there has been very little interest in their applications to PVs because most oxides have a large optical band gap. Furthermore, doping both n-type and p-type to obtain high-mobility materials is not yet possible in typical oxides, so charge separation is more difficult. However, recent advances in complex oxide synthesis have demonstrated that the interfaces in polar-nonpolar heterostructures can be electronically reconstructed, leading to conducting layers with high carrier mobility. Here, we will strive to gain fundamental insight into the role of the interface on PV properties by investigating transition metal oxide heterostructures. The ultimate goal of this project is to show that polar interfacial oxide heterostructures can yield efficient PVs. We will investigate perovskite-based interfacial oxide heterojunctions seeking systems that offer (1) high mobility, (2) efficient solar light absorption, and (3) charge separation. The focus of this program is entirely new, will build on strengths, and will fundamentally differentiate ORNL from other PV programs, thereby giving ORNL a competitive advantage in pursuing new funding opportunities.

Mission Relevance

The quest for new energy materials is central to a broad range of research programs. Thus, the methods and prototype materials developed in this project will undoubtedly impact the mission of the DOE Office of Basic Energy Sciences (BES) in both directly and indirectly related fields. Moreover, the work undertaken here is a DOE BES opportunity for world leadership in a new class of materials for high-efficiency PV applications. Since 50% efficient PV is the stated DOE goal for third-generation PVs, this will give us a comparative advantage for understanding and developing new energy materials.

Results and Accomplishments

Based on atomic scale p-n junctions, we have found that the electronic ground states are strongly influenced by the potential difference between the p-and n-type interfaces imposed by the layer thickness. This implies that when the interfaces are properly constructed, the charge carriers generated from the solar light illuminating can be separated. While superlattices with very thin individual layers (n = 1 and 2) are highly resistive (>10^6 ohm), superlattices with greater individual layers (n = 5 and 10) have shown semiconducting behaviors with a carrier density ~10^{13}/cm^2. Moreover, by using recently developed density functional theory for accurately determining an oxide's band gap, we have determined for the first time the band gap of $Bi_4Ti_3O_{12}$ theoretically, which has been also confirmed to match well with the experimentally determined E_g. We also have found that when atomic layers are substituted by perovskites with a high absorption coefficient, the overall band gap can be systematically tuned. For this, we employed the layered ferroelectric $Bi_4Ti_3O_{12}$ and demonstrated that its band gap could be narrowed as much as 1 electronvolt while maintaining strong ferroelectricity by site-specific substitution with the correlated insulator $LaCoO_3$. It was found that when a specific site in the host material is preferentially substituted, a split-off state responsible for the band gap reduction could be created just below the conduction band of $Bi_4Ti_3O_{12}$. The demonstrated approach paves a new route to controlling band gap in complex oxides desired for emerging oxide opto-electronics and energy applications. An invention disclosure has been filed based on the outcome of this approach on the band gap tuning in complex oxides, which has been considered as a formidable task.

Information Shared

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05483

Development and Verification of Multi-Scale, Multi-Physics Models to Enable the Design of Safe Rechargeable Batteries

H. Wang, E. Lara-Curzio, and W. Cai

Project Description

Li-ion batteries are used widely in mobile applications due to their high energy density, a feature that makes them attractive for plug-in hybrid and all-electric vehicles. However, high energy density has important safety implications and Li-ion batteries are prone to thermal runaway that could have serious safety consequences. While developing a safe battery that will never go to thermal runaway is the ideal solution, all the application records and field failure evidences have shown the combination of high energy density and Li-ion cell chemistry cannot eliminate the possibility of a thermal runaway event. Therefore, studies on battery safety, especially under conditions leading to internal short and thermal runaway, are critical to enable the widespread deployment of Li-ion batteries in transportation applications. Our goals are to develop multi-physics, multi-scale models to assess the propensity of cells and batteries to thermal runaway events; to establish experimental verification of those models; and ultimately to have a suite of tools to enable the design of robust, safe batteries. In FY 2011, the project funding was reduced to $100K. The main focus of the project was on experimental investigation of Li-ion cells.

Results and Accomplishments

Internal short circuit (ISCr) testing: A series of ISCr tests were performed to create internal shorts on various Li-ion cells.

1) *Internal short circuit tests of regular Li-ion cells:* 800 mAh prismatic cell phone cells were subjected to the pinch test using balls with diameter of 1 in. Eighteen cells were tested at 1–3 V return voltage to minimize the short size. Short size of 1–2 mm in diameter was achieved. A total of 48 cells were tested at 3.8–4.2 V for the complete thermal runaway study.
2) *Internal short circuit tests of Li-ion polymer cells with regular separators:* Li-ion cells with 1.5 Ah capacity were charged to 3.8–4.2 V. A total of 18 cells were tested in a study of thermal runaway induced by ISCr.
3) *Internal short circuit tests of Li-ion polymer cells with special separators:* Li-ion cells with 1.5 Ah capacity and special separators were charged to 3.8–4.2 V. A total of 18 cells were tested in a study of thermal runaway induced by ISCr.
4) *Separator study of Porous Power materials:* Twenty-five Li-ion cells made by Porous Power were tested for a study of resistance to thermal runaway using the pinch test. Cells made by commercially available separators were used for comparison.
5) *Internal short circuit tests of large format Li-ion cells:* In collaboration with GM and Naval Surface Warfare Center (NSWC), large format cells for electric vehicles were tested using the ORNL pinch technique. In three preliminary tests, 15Ah, 21Ah, 24Ah, 35Ah and 60Ah cells were tested using a portable ORNL system at NSWC.

Hsin Wang is an ORNL participant of the USABC technical committee and actively involved in the development of internal short circuit testing methods. A formal three-way information exchange has been started among ORNL, Motorola, and UL to develop a standard test method for prismatic Li-ion cells. Collaboration with GM and NSWC has generated two new projects:

1) WFO with GM on Li-ion cells ($200K total from August 2011; $100K for ISCr tests)
2) DOE Vehicle Technologies Program FY12 AOP on ISCr development for electric vehicles: $150K

Modeling efforts of ISCr were removed due to budget reduction.

Information Shared

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05484

Novel Nanostructured Photovoltaic Solar Cells

J. Xu, S.H. Lee, B. Smith, X. Zhang, C.M. Parish, C.E. Duty, H.N. Lee, and G.E. Jellison, Jr.

Project Description

Aiming to increase photovoltaic (PV) efficiency, we proposed to create a nanocone-based three dimensional (3D) heterojunction for solar PV conversion and to obtain fundamental understanding of the key phenomena necessary for its function. The 3D heterojunction will be matrix structure formed by n-type ZnO nanorods that are surrounded by p-type semiconductor. ORNL's advanced capabilities in (1) synthesis of cone-shaped nanorods, (2) II-VI pulsed laser deposition (PLD), (3) nanostructure modeling, and (4) pulsed thermal processing (PTP) will enable us to produce a prototype PV device using our novel concepts. Our deliverables are (1) demonstration of a working nanocone-based solar cells and (2) key insights into the functionality of nanostructure-based PV devices. Upon completion of the project, we will be able to provide a benchmark for the efficiency of a nano-architecture PV cell (none exists at present) and we will possess the basic knowledge of how to push PV efficiency beyond the Shockley-Queisser limit.

Mission Relevance

DOE Basic Energy Sciences Advisory Committee (BESAC) assessed the scope of fundamental scientific research that must be considered to address the DOE missions in energy efficiency, renewable energy resources, and other future energy areas. Research for highly efficient and low-cost photovoltaic (PV) solar cells is one of the "Basic Research Needs." To contribute to this mission, the objective of this project is to develop a novel PV device that is based nanocone interdigitated p-n junctions. This approach holds promise for very high efficiency cells.

Results and Accomplishments

In the first year (FY 2010), the major achievements included (1) theoretical study of morphological effect of 3D nanojunction on carrier transport, (2) successful synthesis of n-type ZnO nanocones on ITO,

(3) fabrication of nanocone heterojunctions by depositing p-type CdTe layer on the ZnO nanocone surfaces, and (4) a functional nanocone PV with a low conversion efficiency of 0.14%.

In the second year (FY 2011), we demonstrate that efficient carrier transport is realized in nanocone-based heterojunction with n-type ZnO nanocone tips implanted in p-type poly-crystalline (PX) CdTe film. The nanocone tip-film junction yields 3.2% power conversion efficiency without optimization. This is 80% improvement of PV efficiency (1.8%) obtained for a related planar ZnO-PX CdTe cell. This is among the highest PV efficiency in nanostructured PV solar cells. This is also 22-fold increase from the PV efficiency in the first year. Theoretical calculation shows that electric field in CdTe generated by the nanocone tip is much higher than that given with the planar junction. Such a high field is believed to be responsible for the high conversion efficiency.

Information Shared

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05506

Achieving Rechargeable Lithium-Air Batteries through Metal Oxide Electrocatalysts

Y. Xu, W.A. Shelton, G.M. Veith, N.J. Dudney, J.Y. Howe, and J.P. Hodges

Project Description

Lithium–oxygen has one of the largest theoretical energy densities of any practical electrochemical couple at nearly 12 kWh/kg of lithium. Prototype lithium-oxygen cells suffer substantial overpotentials in both discharging and charging and rapid capacity loss with cycling. Several recent studies have reported improved electric efficiency and capacity retention by including organometallic compounds, metals, and metal oxides to carbon cathodes. The improvements nonetheless remain quite insufficient, and the existing studies are very limited in the mechanistic understanding that they provide of the cathode oxygen reduction reaction (ORR)/oxygen evolution reaction (OER). By using a combination of state-of-the-art density functional theory (DFT)–based modeling techniques and synthesis, characterization, and electrochemical testing methods, we propose to study Li-ORR/OER on representative model catalytic materials. Our study will generate understanding for the fundamental cathode-side electrochemistry and will provide valuable insights for the identification of cathode materials that substantially improve the cyclability of lithium-air batteries.

Mission Relevance

Lithium-air battery chemistry has been described by DOE as one of the few viable approaches toward reaching the energy density of a liquid hydrocarbon fuel and is one of the very few available battery chemistries that has the potential to extend the range of battery electric vehicles (BEVs) sufficiently to reach the DOE target of 200–300 miles per charge without adding significant weight to the vehicle and therefore reducing the overall energy efficiency. As such, an efficiently cyclable lithium-air cathode should be of strategic interest to the DOE Office of Energy Efficiency and Renewable Energy vehicle program in the long run, although funding priorities may only partially reflect that in the short run. The fundamental aspects of the lithium-air chemistry should also be aligned with Basic Energy Sciences programs in chemistry. Overall, it represents an important new area worthy of exploration as part of our nation's future electrical energy generation and storage strategies.

Results and Accomplishments

During the course of this project we have shed important new light on the fundamental electrochemistry that occurs on the air cathode. We developed a theoretical framework to evaluate the intrinsic reaction mechanism and activity of lithium-ORR on gold, platinum, and carbon based on DFT calculations. The direct reduction of molecular O_2 occurs at 1.5 and 1.9 V (vs. Li/Li^+) on flat and stepped gold surfaces and 2.0 V on platinum surfaces. Lithiation of O_2 significantly weakens the O-O bond, so contrary to the established views, Li_xO species, not peroxides (Li_2O_2), are what form directly on the metal sites. The interfacial Li_xO layer should decompose during the charge process to leave behind atomic oxygen. The reduction of atomic oxygen occurs at 2.4 V on Au and 2.0 V on Pt. Therefore the activation overpotential for the ORR on Pt and Au sites is expected to be controlled by the stability of *atomic* oxygen during cycling and *smaller* on Au than on Pt. Further, our calculations suggest that water significantly affects the Li-ORR activity on metals, and we are pursuing experiments and calculations to clarify the mechanism. Our work has also revealed that carbon itself plays an active role in the ORR. Model structures, including graphite/graphene(0001), the (8,0) single-wall nanotube, the armchair-type edge, and the di-vacancy, are used to represent prevalent graphitic carbon structures. The inertness of the basal plane limits O_2 reduction to 1.1 V, and 1.2 V on the curved nanotube. In contrast, the graphene edge and di-vacancy are significantly oxidized at ambient conditions, and various CO_x groups can catalyze O_2 reduction at up to 2.3 V, in line with the observed onset potential for ORR on carbon cathodes (2.5 V and higher). These findings provide an important context in which to interpret experimental results obtained with carbon-based cathodes. In addition, we have initiated theoretical studies of the ORR/OER on several oxides, including different spinels of Mn. Preliminary results indicate that the oxidation state of the Mn cation is an important reactivity descriptor for the electrocatalytic activity of Mn spinel surfaces.

We also pioneered the application of multiple surface characterization techniques to determine the nature of the actual discharge products. We made the significant discovery that nickel current collectors, which were employed in most previous studies, decompose carbonate-based organic electrolytes at above 3.5 V and are thus not suitable for non-aqueous rechargeable Li-air cells because the charge process routinely requires over 4 V. Furthermore, the major solid discharge products in such organic electrolytes Li-air cells are found to be polymeric and result from the reaction of electrophilic carbonyl bonds in the presence of Grignard-like Li-F species, as well as from the decomposition of the inorganic Li salts that gradually lowers the conductivity of the electrolyte and reduces the capacity. Based on these results we have designed new electrolyte compositions, based on ether species as well as solid compounds, which should be more resistant to electrolyte and salt decomposition and allow the formation of solid Li_2O_2. The identification of the severe limitations in the prevalent Li-air cell composition and design and the description of the fundamental ORR activities of the metals and carbon are the major achievements of this project.

Ongoing catalyst development work is focused on testing carbon nitride/graphene composites, which contain high concentrations of electropositive carbon sites. These materials have been shown to be potential oxygen reduction catalysts for fuel cells. Preliminary results show that they have close to 100 percent Coulombic efficiency with cycling, whereas the MnO_2 and carbon-based materials have efficiencies close to 10 percent. Mechanistic studies will be completed in the near future. Work has also progressed in developing ways to protect the Li anode from reaction with CO_2, O_2, N_2, and H_2O. These anode architectures are being exploited to create solid-state Li-Air batteries that will enable the in situ characterization of reaction products and to identify how the products differ from those formed in liquid electrolytes.

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05512

Low-Cost Materials and Manufacturing of CIGS Thin-Film Solar Cells

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Project Description

Today's highest efficiency thin-film solar cell converts solar energy to electricity at a rate of ~20%. The absorber layer is composed of an expensive and complex compound of copper indium gallium diselenide (CIGS). A unique process has recently been developed at ORNL for producing CIGS nanoparticles at an extremely low cost. The nanofermenation process uses specialized bacteria to naturally produce nanoparticles in a culture medium at moderate temperatures (~60°C), making it ideally scalable for high-volume manufacturing. Although the production of CIGS nanoparticles has been demonstrated with this process, the nanoparticles have a high density of defects and poor shelf life. Fundamental research is required to adjust the stoichiometry of the CIGS nanoparticles for optimal photovoltaic performance and develop an in situ chemical passivation technique for reducing surface defects. The nanoparticles will be formed into a thin film solar cell using ORNL's unique Pulse Thermal Processing (PTP) facility. The PTP technique generates extremely high surface temperatures during short energy pulses, permitting sintering of semiconductor materials on flexible, temperature-sensitive substrates. The combination of these unique manufacturing capabilities presents an extremely low-cost approach for producing high-quality thin film CIGS solar cells, which is an important capability for pursuing future research on affordable thin-film photovoltaics.

Mission Relevance

Thin-film solar cells based on CIGS benefit from lower fabrication cost and a significantly smaller amount of materials utilization (hundreds of nm layer thickness are needed for thin films compared to microns for silicon cells). Furthermore, the future of thin-film solar cells is highlighted by the recent

breakthrough in their performance: CIGS research shows a PCE approaching 20%. More attractive features of thin-film solar cells are the low requirement on material morphology. Even the most efficient thin-film solar cells reported have a multicrystalline structure with grain boundaries of micrometers. This indicates the possibility of utilizing materials with low cost and imperfect quality. While current nanocrystal synthesis requires costly high temperatures and vacuum, nanofermetation boasts synthesis at near room temperatures using inexpensive solvents. This project may create a paradigm shift in the synthesis of low-cost, highly efficient solar cells.

Results and Accomplishment

In the first year, we were successful in bacterial synthesis of CdS and CIGS nanoparticles with varying stoichiometry. CIGS ($CuIn_xGa_{1-x}Se_2$) and CIGSu ($CuIn_xGa_{1-x}S_2$) have been synthesized from stock solutions having x = 0.2 to 0.6. The finding that *Desulfovibrio desulfuricans* (G-20) can also produce CIGSu strengthened position that the application of nanofermentation is not limited to only fermentative thermophiles. Product purification was successful with respect to the removal of biomass through filtration and the removal of salts through multiple washings. Surface passivation of CdS quantum dots was accomplished with the addition of sodium oleate. The second year's efforts focused on deposition and consolidation of CdS and CIGS nanoparticles into thin films using PTP with the goal of creating a functional solar cell. This project successfully delivered the very first functioning photovoltaic cell based on bacterially synthesized particles. Bacterially synthesized CdS nanoparticles, serving as the emitting layer, were deposited on a conventional cell made up of a CIGS absorbing layer and moly back contact on a glass substrate. The cell generated approximately 500 mV (standard devices are 600 mV) and approximately 10 mA/cm^2 with a measured efficiency of 4.1%. This cell was not optimized, had a fill factor of approximately 50%, illustrated that bacterially synthesized particles could be harvested, deposited, and consolidated, and shows tremendous opportunity for significant improvement.

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05547

A Transformational, High-Energy-Density Secondary Aluminum Ion Battery

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Project Description

The objective of this project was to develop an aluminum ion battery that has the voltage and capacity to can make a transformational change in energy storage. Aluminum has attractive properties as an anode for a secondary storage battery, with a theoretical voltage comparable to lithium. Aluminum also has a distinct advantage in energy density (8140 Whr/kg vs 1462 Whr/kg for Li) due to its trivalency. Previous attempts to utilize aluminum anodes in batteries were plagued by high corrosion rates, parasitic hydrogen evolution, and sluggish response due to the formation of an oxide layer on the aluminum electrode surface. To overcome these deficiencies, we have taken advantage of new developments in electrolytes, and we utilized an advanced electrolyte/electrode composition employing room-temperature ionic liquids, resulting in significant improvements in anodic efficiency and therefore battery performance. In this ionic liquid medium, the $AlCl_4^-$ ion will be the predominant anion as well as the chemical form of Al(III) in solution. The initial plan was to choose a cathode electrode material such that the mobile $AlCl_4^-$ species would be directly intercalated or intercalated as an Al(III) ion into the cathode material. Thus far we have been unable to experimentally realize this goal, but we have developed a rechargeable Al-MnO_2 battery, consisting of reversible aluminum dissolution-deposition at anode (Al) and lithium insertion-extraction at cathode (λ–MnO_2) in a room-temperature ionic liquid electrolyte (lithium chloroaluminate in 1-ethyl-3-methyl imidazolium chloroaluminate). We have characterized the fundamental cell performance (voltage) and optimized electrolyte composition, anode composition, and cell kinetics. A prototype battery in a coin cell format was constructed, and this novel battery architecture shows an average discharge voltage of 2.0V, rechargeable capacity with tens of cycles, and good stability without self-discharge.

Mission Relevance

There is great interest and motivation for the United States to make a transition from fossil energy–based electricity to the generation from renewable sources such as solar or wind. These sources offer enormous potential for meeting future energy demands. However, the use of electricity generated from these intermittent sources requires efficient electrical energy storage. For large-scale solar- or wind-based electrical generation to be practical, the development of new electrical energy storage systems will be critical to meeting continuous energy demands and effectively leveling the cyclic nature of these energy sources. Among the most critical needs for this nation's secure energy future are transformational developments in electrical energy storage for use in vehicles to include batteries made from novel materials that would increase the level of energy storage per unit volume and mass. In this project we have carried out research aimed at the development of a battery based on an aluminum anode that has the potential to have sufficient specific energy to be transformational. Aluminum is a very attractive electrode material for batteries, due to its advantages in abundance, cost, and theoretical energy density. As a battery anode, aluminum features a trivalent electrochemical redox reaction, with a theoretical specific capacity of 2980 mAh/g and volumetric capacity of 8040 mAh/cm^3, values which are close to and four times those of lithium, respectively.

Results and Accomplishments

Good progress has been made toward the development of a high-specific-energy-density, rechargeable battery with an aluminum anode, a MnO_2 cathode, and a room-temperature ionic liquid ethylmethylimidazolium chloride-aluminum trichloride (EMImCl-$AlCl_3$) as the electrolyte. We initially tested the concept in which Al(III) would intercalate in λ-Mn_2O_4 cathode during discharge. The net reactions would be as follows:

$$\text{Anode: } Al + 7\,[AlCl_4]^- \leftrightarrow 4\,[Al_2Cl_7]^- + 3\,e^-$$

$$\text{Cathode: } Mn_2O_4 + 4\,[Al_2Cl_7]^- + 3\,e^- \leftrightarrow AlMn_2O_4 + 7\,[AlCl_4]^-$$

$$\text{Net reaction: } Al + Mn_2O_4 \leftrightarrow AlMn_2O_4$$

Investigations of the columbic efficiency of aluminum deposition and dissolution and the cycleability of aluminum dissolution and deposition were determined by voltammetry measurements in an acidic melt of EMIC-$AlCl_3$ (rich in $AlCl_3$). A sequence of 100 cyclic voltammetry cycles at a low scan rate demonstrated the good coulomb efficiency and cycleability of the aluminum dissolution and deposition on an aluminum anode. Two cathode material candidates, spinel λ-MnO_2 and $AlMn_2O_4$, did not demonstrate good cycleability, apparently due to reactions with the electrolyte.

We were successful in demonstrating a novel concept of a hybrid aluminum anode-lithium ion battery, a concept that allowed us to demonstrate the feasibility of a rechargeable Al-MnO_2 battery system. The operation principle of this new battery is aluminum metal as the anode, λ–MnO_2 (spinel structure) as the cathode, and lithium chloroaluminate dissolved in 1-ethyl-3-methyl imidazolium chloroaluminate as the electrolyte. During charge-discharge cycle, the electrochemical redox reactions are reversible as aluminum dissolution-deposition, which occurs at the anode and lithium insertion-extraction occurring at the cathode. The cathode reaction is a typical intercalation process that is well established to occur in lithium-ion batteries. The electrolyte works as a reservoir to provide and store lithium cations and chloroaluminate anions. The imidazolium cations in the electrolyte serve as charge carriers to neutralize the charge balance. The reactions are described as the following:

$$\text{Anode: } Al + 7AlCl_4^- \leftrightarrow 4Al_2Cl_7^- + 3e^-$$

$$\text{Cathode: } 2MnO_2 + Li^+ + e^- \leftrightarrow LiMn_2O_4$$

$$\text{Overall: } Al + 7AlCl_4^- + 6MnO_2 + 3Li^+ \leftrightarrow 4Al_2Cl_7^- + 3LiMn_2O_4$$

CR2032 coin cells were used as prototypes to evaluate the performances of Al/MnO_2 batteries in ionic liquid electrolytes. The charge and discharge curves appear as a two-stage process, which corresponds to the dual-peak redox behavior typical of Li-ion battery cathodes. The first discharge plateau is around 2.15 V and the second around 1.95 V. The specific charge and discharge capacity are 65 mAh/g and 74 mAh/g based on MnO_2 weight. The cell is charged to 2.4 V by a current of 15 mA/g and kept at 2.4 V until the current was less than 1.5 mA/g. The discharge capacity is 94 mAh/g at the first cycle, and it decreased to 54 mAh/g after 50 cycles. The capacity decreases in the first 10 cycles, and then remained relatively stable after 20 cycles. The open circuit voltage (OCV) of the battery is 2.12 V, and the value is quite stable in an observation at open circuit condition for up to 24 hr.

In summary, this project has developed the new concept of a hybrid aluminum-lithium ion battery to experimentally realize the goal of a rechargeable battery with an Al anode. This is the first demonstration of a rechargeable Al-MnO_2 battery in ionic liquid-based electrolyte.

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05566

Predictive System Simulation Capability for Evaluating Safety and Performance of Batteries

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Project Description

The batteries of the future require higher energy/power densities (e.g., to displace the gasoline engine), lower cost, longer life, and a smaller footprint (e.g., store solar energy) while retaining safety. These improvements will be primarily the result of new materials, device architectures, and processing techniques. There are significant safety concerns associated with an increase in performance as the electrodes pack more energy and are in closer proximity to each other (e.g., 3D architectures). In this project, we are developing a predictive system-level (macroscopic) 3D petascale simulation tool, based on rigorous averaging procedures, to model batteries. This detailed simulation capability will model the coupled multiphysics phenomena (charge and thermal transport, electrochemical reactions, and mechanical stresses) across the porous 3D structure of the electrodes (cathodes and anodes) and the solid or liquid electrolyte system while including the nanoscale effects through closures based on resolved quantities. The simulation tool will be validated both at the full-cell level as well as at the secondary particle level, and give an unprecedented capability to study the interplay between the particle-scale effects to the overall performance and the safety of the batteries. This tool fills a critical void in the simulation space and gives ORNL a unique capability.

Mission Relevance

Advanced batteries are critical to solving the nation's quest for clean energy and independence from foreign oil. This has become a central Department of Energy (DOE) mission, and through this project we are planning the development of predictive models for system-level simulations of batteries, both at the cell level and the pack level. In particular, this project will address the issue of safety and performance of batteries by providing insight into particle and cell-level interactions. The project is of direct relevance to the proposed energy innovation hub for electrical storage, Advanced Research Projects Agency–Energy

(ARPA-E) solicitations, and many other programs in the DOE Office of Energy Efficiency and Renewable Energy, and the DOE Office of Basic Energy Sciences. In addition, there is tremendous interest in portable storage for Department of Defense needs.

Results and Accomplishments

The milestones for the first year are (1) derivation of a consistent set of multidimensional governing equations for batteries for mass, species, charge, and energy conservation, (2) implementation of the same, in a scalable computational framework, and (3) validation of the simulations against data available from cell experiments, micro-Raman, and neutron tomography. During the first year, parallel but well-coordinated and integrated activities have been pursued to not only develop multidimensional simulation tools for batteries but to also pursue novel experimental techniques in order to gather necessary data to validate the models. We pursued activities to (1) develop unified formulation for electrochemical storage devices, (2) implement this formulation in two different codes: a multiphase flow code (MFIX) and a derivative of a nuclear fuel simulation code (AMP), (3) apply the above to a lithium-ion battery (LIB), supercapacitor, and Li-Air cathode, (4) obtain cell-level characteristics from experiments to get necessary in-house validation data, (5) perform a detailed spatial map of the lithium using neutron imaging and micro-Raman to obtain data beyond cell-level global characterization, and (6) to explore the Cantera chemical reactions database and evaluate the same and generate a plan for adopting the same for electrochemical reactions. The developments listed above have laid down a foundation not only for successfully finishing the goal set in the original proposal to construct validated multidimensional simulation capability but also for securing follow-on funds to continue this effort on further development of computational capabilities for modeling batteries.

During the second year, we have worked on the integration of the computer modeling and experimental efforts. One area where we have made significant progress is in the neutron imaging of discharged air-cathodes, and corresponding modeling to understand the competition of kinetics and diffusion that leads to non-uniform deposition of lithium products. For the first time, we report the results from neutron tomographic imaging of lithium product species in porous carbon foam electrode under both chemically passivated and electrochemically discharged conditions. Analysis of the bulk lithium 2D image reconstructed slices, and the subsequent 3D tomographic volume provide a semi-quantitative (relative) estimate of the lithium concentration across the bulk of the electrode. Further using this approach, we also studied the spatial distribution of discharged products in Li-air cathodes in order to understand the effect of discharge kinetics, diffusion, and electrolyte decomposition products that eventually lead to the reduction of the effective electrode porosity. We observe a non-uniform spatial distribution of lithium discharge products, for discharge Li-air cathodes that could arise due to transport and kinetic limitation in thick porous electrodes as proposed in modeling of the experimental data. Our studies point to the importance of using neutron imaging based methods for studying the electrochemical transport, and reaction mechanism under both ex situ and in situ conditions for novel electrical energy storage devices. We have also made some progress in capturing the effects of microstructure on the effective transport of lithium in complex electrodes including fractals, 3D, etc. In addition, the Cantera package has been adopted for electrochemical systems and currently linked with DualFoil code. We will be coupling the same with the AMPERES code by the end of this project, and plans are under way to release any resulting software as open source.

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05608

Fundamentals of Ionic Conductivity in Polymeric Materials for Energy Storage Applications: How to Decouple Ionic Motions from Segmental Dynamics

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Project Description

Polymer membranes have attracted much attention during the past several decades because they provide elegant solutions to many difficulties in battery technology. However, the relatively low ionic conductivity in polymer membranes has become the bottleneck for developing batteries with higher power density, shorter charging time, and better operations at low temperatures. Despite numerous studies in the past, a clear understanding of the ion transport mechanism in polymer electrolytes is still missing. In this project, we demonstrated that contrary to the widespread belief that segmental motion controls ionic conductivity, the ion motion can actually decouple from the structural relaxation of the polymer matrix. Moreover, our study revealed the connection between the chemical structure of polymers and the degree of decoupling. We showed that the decoupling phenomenon could be utilized to design polymer membranes with extremely high ionic conductivity. The principles demonstrated in this research will provide a "game-changing" approach to the development of solid polymer electrolyte batteries for energy storage applications.

Mission Relevance

Development of efficient electrical energy storage systems has been identified as a critical task for addressing national energy needs in the United States. This project is aiming to obtain a clear understanding of the fundamental principles governing ionic conductivity in polymeric materials for energy storage applications. The results of this project will serve as guidelines for design of next-generation batteries and fuel cells with dramatically improved performance. Our ongoing research is therefore highly relevant to the DOE mission and will put ORNL at the forefront of the polymer electrolyte field. In addition, we expect that the developed knowledge and new concepts will be helpful in addressing the problem of CO_2 capture, and thus help ORNL to secure funding for CO_2 sequestration from DOE and industry.

Results and Accomplishments

We synthesized a series of polymer electrolytes with different chemical structures and studied their ionic conductivity and segmental relaxation using dielectric spectroscopy. Our results showed that the ionic conductivity strongly decouples from the segmental motion in polymers with rigid backbone structure. We observed that ionic conductivity in one of the samples was nearly six orders of magnitudes higher than what would have been expected in the scenario of no decoupling. We were also able to determine the ion diffusivity from both electrode polarization effects and pulse field gradient nuclear magnetic resonance (PFG-NMR) measurements. Similar decoupling was found between ion diffusion and segmental motion. Further analysis revealed that the degree of decoupling correlates with the steepness of the temperature dependence of segmental relaxation (the so-called fragility). This result supports our idea that the loose packing structure in fragile polymers can provide pathways for ion transport even when the segmental motion is completely frozen. Computer simulations confirmed the proposed connection between polymer chain rigidity and frustration in packing. Overall, we have made significant progress during this first year of our project. We have not only demonstrated the validity of the proposed concept but also reveal the key parameter that controls the degree of decoupling. This proof of the concept has placed us on a solid ground for developing polymer electrolytes with significantly improved ionic conductivity.

Information Shared

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05716

Why Coatings Work: Nanoscale View of High-Voltage Cathode Surfaces

G.M. Veith, L. Baggetto, M. Chi, A. Payzant, J. Browning, M.K. Miller, and N.J. Dudney

Project Description

The goal of this LDRD project is to demonstrate the ability to determine the structure and conductivity paths through the polyhetero protective coatings on high-voltage cathode materials and predict ways to improve coatings. Accomplishing this goal requires utilization of advanced techniques to deconstruct the structure and composition of the complex multiphase protective coating. Therefore, we will integrate the subnanometer spatial and chemical resolution of the Local Electrode Atom Probe (LEAP) and aberration-corrected Scanning Transmission Electron Microscopy (STEM) to determine the mosaic of phases that comprise the surface of the high-voltage $LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$ cathode material with and without protective Al_2O_3 or $AlPO_4$ coatings. Critically for follow-on opportunities and novelty, other National Laboratories (ANL, LBL, BNL, SRNL) do not have LEAP or the sample synthesis expertise needed to execute the proposed line of research. Most importantly, this LDRD project lays the foundation for a more comprehensive program focused on developing both an understanding and predictive ability to design and fabricate the protective coatings essential to lithium-ion batteries for maximum rate, capacity lifetime, safety, and other technologies such as photovoltaics and catalysis.

Mission Relevance

The proposed project directly addresses DOE and the nation's needs to identify new mechanisms to increase energy utilization and storage. The ability to design protective coatings will be of direct interest

to EERE, which is seeking new ways of protecting electrode surfaces and improving the cycleability of battery materials. Furthermore the corrosion issues we are investigating are fundamental problems in a number of energy storage and utilization technologies including nuclear reactors and photocatalysts, which are areas of fundamental research supported by the Office of Science.

Results and Accomplishments

The first accomplishment of this project was the development of the DUST method to prepare polycrystalline composite electrodes which can be electrochemically cycled then disassembled for analysis by using the atom probe. This was a critical challenge to analyzing real battery cathodes; these are normally buried under many layers of polymer binders which attenuate X-ray signals and limit the use of microscopy. Second, we have developed the methodology to prepare atomically smooth battery cathodes over a 2 in. wafer for use in the neutron reflectometer and performed the first reflectometry experiments. These measurements have shown the formation of a diffuse layer on the surface of the cathode in contact with the electrolyte. This demonstrates our ability to measure surface reaction layers, their thicknesses, and densities. We have developed in situ electrochemical cells to perform transmission diffraction measurements in an X-ray spectrometer. These cells are enabling us to follow structural changes in both cathodes and anodes as they are cycled, providing fundamental insight to the degradation mechanisms of batteries. Finally, we have developed the methodology to prepare needle-like cathode particle specimens for the atom probe and identified the evaporation protocols to determine the three-dimensional atomic composition of the cathode. We have collected the first data sets on uncycled cathodes and are working to develop a model of surface segregation of Mn ions.

05836

Femtosecond Electronic Spectroscopy of Complex Nanostructures and Their Functional Assemblies

Y. Ma

Project Description

The novel chemical and physical properties associated with semiconducting nanoparticles, nanowires, and single-walled carbon nanotubes (SWNTs) make them appealing building blocks for designing a new generation of photovoltaic components such as high-efficiency solar cells. Realization of this technological innovation, however, critically depends on a detailed understanding of their optical properties and fundamental electronic processes, in particular, how and where excitons move. The goal of this project is to study ultrafast exciton dephasing and diffusive motion of localized excitons in semiconducting nanostructures and their assemblies employing femtosecond two-pulse photon echo and frequency-resolved transient absorption spectroscopic techniques. These are sensitive to exciton dynamics in the coherent and incoherent regimes, respectively. Our objectives are to determine experimentally the dephasing timescales and diffusion coefficients and lengths, and to explore their intrinsic correlations to the dimensions of system confinement. We will also seek quantitative information about exciton motion between proximal nanostructures in chosen assemblies, which should provide basic insights into the nature of electronic couplings and mechanisms governing the energy transfer processes. We envision this seminal work to develop into a future larger research program in this area that will be supported by the DOE Office of Basic Energy Sciences (BES). Our experiments open a new area of investigation at ORNL, as we will be able to investigate coherence dephasing of interesting systems on a very short timescale. This capability will favorably impact other ORNL researchers who are investigating a variety

of solar energy conversion materials and techniques and will strengthen ORNL's ability to compete in this funding arena.

Mission Relevance

Our project seeks fundamental understanding of exciton migration in complex nanostructures and their functional assemblies. The information gained will provide important basic insight for future electronic and optical applications of these nanomaterials, in particular high-efficiency photovoltaic solar cells. The research directly addresses the challenges outlined in the DOE BES report on the Basic Research Needs for Solar Utilization. Successful completion of this project will give us the opportunity to obtain future funding from the DOE BES. Since other federal agencies such as NASA and the military branches also have a tremendous interest in seeing efficient solar energy conversion come to fruition, we anticipate that the information gained from our research will benefit the relevant research and development programs sponsored by these agencies.

Results and Accomplishments

Two ultrafast optical spectrometers, namely, femtosecond transient absorption (TA) and picosecond time-correlated single-photon-counting (TCSPC), have been built and tested. The former employs a high-precision DC motor-driven optical delay stage with a 0.3 fs resolution and dual lock-in amplifiers and therefore enables weak signal detection with an absolute change of the sample optical density on the order of 10^{-5} (limited by the laser stability) and a time resolution of ~50 fs. By using either single or dual optical parametric amplifiers, or in combination with a broadband white-light continuum (460 to 1100 nm), measurements at various combinations of pump and probe wavelengths can be performed. The TCSPC system is based on a tunable femtosecond laser excitation source, an actively quenched single-photon avalanche diode, and a TCSPC module. It has a typical instrumental response of 40 ps (full-width at half maximum) and can be applied to resolve fluorescence emission decay with a time resolution of ~10 ps. These two spectroscopic tools enable elucidation of electronic relaxation processes from both bright and dark excited states that occur within timescales ranging from 50 fs to tens of nanoseconds and are ready to study various fundamentally important and technologically relevant materials. A detailed femtosecond TA study was performed on copper-phthalocyanine (CuPc) single-crystal nanowires, which have been considered to be perfect building blocks for molecular electronics and photovoltaics. As the CuPc nanowires with different diameters/lengths were grown successively on an opaque silicon substrate (provided by Dr. Kai Xiao, Center for Nanophase Materials Sciences), the measurements were carried out with a reflective pump-probe configuration. We found that the exciton relaxation is very sensitive to the growth temperature (from 192 to 204°C), which affects not only the molecular structure (α- or β-phase) but also the nanowire diameter (from 90 to 110 nm) and length (from 19 to 24 μm). Measurements at different excitation intensities for the wires grown at selected temperatures further showed that the exciton relaxation accelerates markedly with increasing excitation intensity. The observed intensity dependence arises from an exciton-exciton annihilation process, and quantitative analysis of this nonlinear phenomenon was conducted in Year 2. We found that the annihilation in the CuPc nanowires is diffusion limited and involves intra-chain exciton diffusion along one-dimensional (1D) molecular stacks. Although the diameters of these CuPc nanowires are at least an order of magnitude greater than the Bohr radius, exciton diffusion along the molecular stacking direction is strongly favorable owing to the relatively large intra-chain interactions. This behavior is similar to what was found for other metallophthalocyanine polymorphs such as colloidal particles and thin films. The long-lived excitons with a mean lifetime of ~200 ps make CuPc nanowires strikingly distinct from any other MPc polymorphs, which typically have lifetimes on the order of a few picoseconds only. The significantly long-lived excitons and their favorable 1D diffusion in CuPc nanowires in comparison to other crystalline polymorphs suggest that they are particularly suitable for photovoltaic applications.

Revision to the research plan was made in Year 2 in order to focus on photovoltaic materials because of potential follow-on funding opportunities. The first new project initiated in Year 2 is time-resolved spectroscopic characterization of selected water-soluble polythiophene derivatives with variable side-chain lengths, which are considered as potential candidates for high-efficiency photovoltaic applications. A particularly attractive feature of these polymers is reversal, large shift of their absorption spectra with the change of temperature. In order to understand the physical mechanism underlying this spectral feature, we performed picosecond time-resolved fluorescence and anisotropy measurements under different sample temperatures. We found that, at any given temperature, the excited-state lifetime depends strongly on the side-chain length. A common observation for all the polythiophene derivatives studies is that both the isotropic and anisotropic fluorescence decays accelerate remarkably with the increase of sample temperature, which provides direct evidence for a temperature-induced conformation change of these polymer molecules.

The second new project initiated in Year 2 is ultrafast excited-state dynamics in benchmark poly(3-3-hexylthiophene):methanofullerene derivative (P3HT:PCBM) bicontinuous blends. Time-resolved fluorescence data were collected at different wavelengths upon optical excitation of P3HT at 550 nm. We found that both the fluorescence lifetime and the peak intensity decrease with the time of laser illumination. The lifetime and peak intensity reach the half of their values within ~30 minutes. We believe that the observed changes arise from P3HT photo-degradation owing to the presence of trace amount of water/oxygen in the sealed sample cell. Our results demonstrate the critical need of keeping these blends free from water and oxygen in order to conduct reliable optical spectroscopic experiments.

In summary, this LDRD has enabled us to initiate ultrafast spectroscopic studies on both fundamentally important and technologically relevant materials. It also creates a unique capability at ORNL.

Information Shared

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05837

Cryogenic Development for a Measurement of the Neutron Electric Dipole Moment at the Spallation Neutron Source

W. Yao

Project Description

Next-generation experiments aim to improve our knowledge of the neutron electric dipole moment (nEDM) by two orders of magnitude. An nEDM can be detected by measuring the difference in the precession frequency of a population of polarized neutrons in a magnetic field (10 mGauss) when subjected to a strong electric field (50 kV/cm) aligned parallel or anti-parallel to the magnetic field. One proposed technique utilizes ultra cold neutrons (UCNs) confined inside a box filled with superfluid liquid ^{4}He via superthermal process. Spin polarized ^{3}He atoms, simultaneously introduced into the box and mixed with the UCNs, serve as a frequency monitor of neutrons precession via the spin-dependent

neutron absorption by ^{3}He. The liquid ^{4}He, a substance believed to have very high intrinsic dielectric strength, also serves as a scintillation medium, converting the energy released from a neutron-^{3}He absorption event into a detectable light signal.

This technique has several challenges directly related to the large-scale low-temperature requirements. We are preparing a series of R&D projects to address these challenges. The following are those related to this LDRD project.

- Study the high-voltage performance of electrodes inside liquid helium below 1 K.
- Demonstrate injection of polarized ^{3}He into a volume of liquid ^{4}He.
- Demonstrate the movement of ^{3}He inside superfluid ^{4}He using heat flush.
- Design large dilution refrigerator and cryogenic components to maintain a temperature below 0.3 K for a bath of liquid helium of 1.2 m^3.

Mission Relevance

A significantly more precise measurement of the neutron EDM is a high priority for nuclear physics. This is because such a measurement would greatly improve our understanding of the "Baryon Asymmetry of the Universe," the fundamental yet unexplained observation that matter exists. The importance of improving the measurement of the neutron electric dipole moment is documented in long-range plans for the nuclear physics community issued by the Nuclear Science Advisory Committee, and in performance milestones accepted by the DOE Office of Nuclear Physics. In addition, one of the primary motivations for the construction of the Fundamental Neutron Physics Beamline at the Spallation Neutron Source was that it would provide a source of neutrons necessary to carry out world-class measurement of the neutron electric dipole moment.

Results and Accomplishments

- **^{3}He cryostat for high-voltage test in superfluid ^{4}He below 1 K**
  To facilitate the study of the high-voltage behaviors of electrodes in superfluid ^{4}He at temperatures below 1 K, we set up a ^{3}He cryostat with high cooling power by modification of a decommissioned dilution refrigerator. After the construction and some primary tests in MIT Bates Lab, the system was moved to LANL and went through a full performance test. It will be connected to the high-voltage test system, which contains a pair of electrodes of 46 cm in diameter submerged inside 150 liters of liquid ^{4}He.

- **Different approach for testing injection of ^{3}He into superfluid liquid ^{4}He**
  When injecting ^{3}He into superfluid liquid ^{4}He at 0.35 K, the residual ^{4}He vapor due to superfluid film flow can block the path of incoming ^{3}He. A device called a film burner had been designed and constructed to suppress the film flow and thus reduce the residual helium vapor by our colleagues in Duke and LANL. The method detects the ^{3}He NMR signal inside liquid ^{4}He after spin polarized ^{3}He is injected from an atomic bean source passing through the film burner. Recently, we proposed two simplified approaches for the test. In the first method, we plan to detect the incoming ^{3}He atoms using a bolometer located on the injection path. ^{3}He flux is directly measured through the heat deposition on the bolometer due to the incoming atoms, which does not need to be spin polarized. In the second method, we monitor the vapor pressure of the residual ^{4}He via a sensitive pressure sensor near the film burner at low temperature. By knowing the vapor pressure, we will be able to calculate the efficiency of ^{3}He injection indirectly from the ^{3}He–^{4}He scattering cross section. We have been pursuing some technical details for the two approaches.

- **Locate new resources for carrying out low-temperature R&D**
  Both the injection test described above and the heat flux test, which measures the efficiency of phonon stream in moving ^{3}He inside superfluid ^{4}He, need to be done in facilities with substantial cooling power below 0.35 K. We have been working on locating new facilities in order to carry out those tests in a timely manner. As a direct progress for such an effort, Professor Silvera's group at Harvard University joined the collaboration and provided us with a dilution refrigerator. We are designing the modifications to make his system suitable for either the injection test or the heat flush test.

05842

Highly Polar Oxides for Photovoltaics Beyond p-n Junctions

H.M. Christen, G.E. Jellison, Jr., H.-S. Kim, and D.J. Singh

Project Description

The goal of this proposal is to show that highly polar oxide materials can yield efficient photovoltaics without the need for p-n junctions. This is motivated by the realization that cost-competitive, high-efficiency photovoltaics will only be realized if a radically new and scalable approach is found to go beyond converting all absorbed photons to electrons of identical energy. Recent reports of photovoltaic effects in ferroelectrics and our development of highly polar oxides by pulsed-laser deposition motivate an approach that is fundamentally different from current PV methods: separating the electron-hole pairs by the permanent polarization of highly polar oxides. With this proposal we seek to (1) understand the fundamental mechanism of the PV effect in polar materials; (2) determine the stability of the polarization of ferroelectrics and pyroelectrics under illumination; (3) find pyroelectric materials with a large polarization and an appropriate absorption spectrum; and (4) enhance their electronic mobility by tuning the dielectric permittivity.

Mission Relevance

The work seeks to find completely new approaches to solar photovoltaic energy conversion by introducing polar oxides as cost-effective alternative to existing photovoltaic device structures. It thus directly supports the mission of DOE to explore new pathways of providing affordable, renewable energy to the nation.

Results and Accomplishments

The work within this project achieved the following results:

1) Clear and definite observation of a link between dielectric constant and electronic mobility in complex-oxide materials, using the test system of doped (conducting) ferroelectic crystals.
2) Implementation of a substrate heater designed for growth at higher temperatures than achievable in conventional pulsed-laser deposition systems.
3) synthesis of Ni-doped lead zirconate-titanate films to reduce band gap in this perovskite material: a complex, undesired phase separation mechanism was observed, making it impossible to verify theoretical predictions of bandgap lowering. However, the results led to a better understanding of phase stability and epitaxial control of such materials.

Information Shared

A manuscript tentatively entitled *Dielectric constant enhanced Hall mobility in doped ferroelectrics* (W. Siemons, M. A. McGuire, V. R. Cooper, M. D. Biegalski, I. N. Ivanov, G. E. Jellison, Jr., L. A. Boatner, B. C. Sales, and H. M. Christen) is being prepared and will be submitted before the end of the fiscal year.

05843

Theoretical Studies of Decoupling Phenomena in Dynamics of Soft Materials

A. Sokolov and V. Novikov

Project Description

Understanding dynamics of soft materials is the key to understanding and controlling their unique properties. However, current knowledge of the dynamics in these materials is very limited, and many phenomena are not yet understood even on a qualitative level. Among them is a decoupling of various processes from a structural relaxation. It includes (i) decoupling of chain relaxation from segmental relaxation in polymers, (ii) decoupling of ionic conductivity from the structural relaxation, (iii) decoupling of protein's biochemical activity from the solvent's viscosity, etc. The major goal of the proposed research is to develop a solid theoretical foundation that can address and explain these decoupling phenomena. The work will be done mostly on an analytical level using theoretical models of polymer dynamics and the concept of dynamic heterogeneity in disordered materials. It will help in guiding the experiments and in explaining results accumulated using various techniques, including neutron scattering studies performed at SNS. This fundamental understanding is crucial for the development of new materials for energy applications (such as batteries, fuel cell, organic photovoltaic cells, carbon capture), for bio-related technologies (enzymatic activity, bio-inspired catalysis), and processing of lightweight materials (polymers).

Mission Relevance

Soft materials (polymers, colloids, biomaterials, etc.) attract significant attention of researchers because of their potential application in many fields, from energy and lightweight materials, to biotechnologies and bio-medical applications. Molecular motions play the key role in most of the unique properties of soft materials. However, understanding and controlling the microscopic mechanisms of molecular motions still remains a great challenge. The project is focused on development of fundamental understanding of decoupling phenomena in dynamics of soft materials. It has direct connections to DOE missions because it addresses problems important for electrical energy storage (batteries), carbon capture, and fuel cells. Also, explanation of decoupling of segmental and chain relaxations in polymers and its dependence on polymer structure is necessary for a broad variety of applications, from polymer processing to biotechnologies.

Results and Accomplishments

One of the possible sources of the decoupling phenomena in dynamics of soft materials is the dynamical heterogeneity. However, little is known about its origin and the characteristic length scale L_{het}. We found arguments connecting L_{het} to the characteristic length associated with the boson peak vibrations ξ. We analyzed pressure, temperature, and materials dependencies of ξ in several molecular and polymeric glass formers. We found a good agreement for the pressure and materials dependencies of ξ and activation

volume $\Delta V^{\#}$ measured at the glass transition temperature T_g. These results provide evidence for a possible relationship between sensitivity of structural relaxation to density and the heterogeneity volume. However, contrary to the expectations for L_{het}, ξ does not significantly change with temperature above T_g. Possible reasons for the observed difference are discussed. We demonstrate that the ionic diffusion decouples from the structural relaxation process in ionic liquid [C4mim][NTf2] as the temperature decreases toward T_g. The strength of the decoupling is significantly lower than expected for a liquid of similar fragility. We estimated the dynamic crossover temperature in [C4mim][NTf2] to be $T_c \sim 225 \pm 5$ K. However, our analysis reveals no sign of the dynamic crossover in the ionic diffusion process. This observation provides important insight into the diffusion process in soft materials. We also focused on development of other approaches to study dynamic heterogeneities. In particular, we study how neutron scattering spectroscopy can be used to analyze dynamic heterogeneity at the nano-scale.

Information Shared

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05970

Large Scale Graphene Sheet Production by Chemical Vapor Deposition

I. Vlassiouk

Project Description

In this project we will synthesize large sheets of graphene by chemical vapor deposition. We propose and outline details of graphene sheet synthesis with the targeted dimensions compatible to those that can be employed in large scale applications, such as construction of large photovoltaics panels, electrochromic windows, solid state lightning devices, and others.

Mission Relevance

The project outcome will constitute a cornerstone for successful development of various applications based on a single layer of graphite—graphene. Graphene has great potential in many DOE mission areas, such as biotechnology and sensing, energy, computing, and waste treatment. Graphene possesses remarkable electronic properties, and membranes from this material show high potential in separations (for example, great selectivity towards hydrogen). Graphene can be potentially used as a substitute for expensive indium tin oxide (ITO) in various applications requiring transparent conductor, such as photovoltaics and electrochromic windows.

Results and Accomplishments

In this project we have (1) constructed a large chemical vapor deposition tube with 6 in. tube diameter and 96 in. in length, (2) adjusted the growth recipe for synthesis of high quality graphene using atmospheric pressure CVD, (3) characterized grown graphene by Raman spectroscopy and scanning

electron microscope, and (4) demonstrated large 36 × 17 in. (40 in. diagonal) polycrystalline graphene sheet.

06241

High Energy Rechargeable Magnesium Batteries Based on Nanostructured Materials

S. Dai (CSD/CNMS) and X.-G. Sun (CSD)

Project Description

Magnesium is light (density 1.74 g/cc), inexpensive, and available, being the eighth most abundant element in the Earth's crust. Unlike lithium, magnesium is stable in wet environments and has a high melting point (650°C vs. 178°C for lithium). Both factors contribute to the vastly improved safety of batteries based on magnesium metal anodes. However, there are two major obstacles to the development of a practical rechargeable magnesium battery: (1) slow magnesium intercalation kinetics into cathode materials and instability of the crystal structure of the cathode materials during repeated cycling and (2) passivation of magnesium in common electrolytes and low magnesium dissolution/plating efficiency. The goal of this project is to reduce the intercalation length of the magnesium into the cathode and improve the insertion kinetics by developing a magnesium battery that utilizes ultra-thin vanadium oxide and other oxide films grown on mesoporous carbon frameworks. In addition, novel electrolytes based on magnesium imide salts in ionic liquids will be explored to enable reversibility at the magnesium anode.

Mission Relevance

Electrochemical energy storage (EES) is one of the most important technologies for a sustainable energy future. The development of transformational EES systems is central to the DOE mission. Any future EES system must possess the following essential characteristics: (1) high energy density, (2) sufficient power, (3) reasonable cost, and (4) optimized safe operation and minimum environmental impacts (see J. B. Goodenough, H. D. Abruña, and M. V. Buchanan, Basic Research Needs for Electrical Energy Storage, DOE Office of Basic Energy Sciences, July 2007). In addition to DOE, electrochemical energy storage (EES) is also the key to many other funding agencies outside DOE. For example, the U.S. Army Office of Research and DARPA have the continuing interest in development of advanced batteries.

Results and Accomplishments

As soon as the project started in August 2011, we prepared to jump start the project by ordering the necessary materials for making the magnesium batteries, such as magnesium rod, magnesium foil, magnesium triflate, and some reagents for preparation of electrolyte, such as ethylaluminum dichloride solution 1.0 M in hexanes, aluminum chloride [anhydrous, crystallized, ≥99.0% (AT)], butylmagnesium chloride solution 2.0 M in THF, di-*n*-butylmagnesium solution 1.0 M in heptane. We also synthesized pyrrolidinium and piperidinium based ionic liquids as electrolytes for the magnesium battery. The preliminary tests on magnesium deposition/stripping in different electrolytes are currently under way. At the same time, the synthesis of magnesium-hosting cathode V_2O_5 is also under way with atomic layer deposition on mesoporous carbon materials.

NEUTRON SCIENCES AND TECHNOLOGY

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

Y.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, as well as 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 of the molecular mobility under confinement and 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 have recently performed proof-of-principle experiments and demonstrated the exceptional potential of the small-angle neutron scattering (SANS and USANS) technique 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. We have conducted systematic fundamental studies of the fluid-surface interactions, and the 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. In the year 2011 we applied 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 20 coals from R. Sakurov's collection at elevated pressure. As a result, seven papers were published/accepted/submitted to international journals and reported at several international conferences and meetings. The results of SANS and QENS studies performed within this project in 2011 resulted in three highlights being submitted to DOE (Dr. Brinkman's office) and highlighted on the front page of the ORNL web site: http://www.ornl.gov/info/features/get_feature.cfm?FeatureNumber=f20110822-00.

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 Science, Basic Energy Sciences Program. 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 to understand the reasons of 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 USA and elsewhere.

Results and Accomplishments

A new method of SANS and USANS data analysis and interpretation was developed. The method makes it possible for the first time to evaluate the volume fraction of pores inaccessible to a particular greenhouse gas as a function of pore sizes. This information is invaluable for more accurate estimation of the sorption capacity of CO_2 in a particular coal seam and appropriate modification of the existing calculation models. This method was applied to investigate total and closed porosity in coal samples obtained from a seam (Tanquary site) into which CO_2 has 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. Similar experiments have been conducted using a collection of 20 various coals that were obtained from R. Sakurovs (CSIRO, Australia).

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 CH_4 molecules in carbon aerogel were obtained and analyzed using complimentary SANS data on the phase behavior and adsorption of methane in the same aerogel sample. The data revealed strong suppression of the methane molecule mobility due to liquefaction of methane gas in small pores of aerogel. Recent QENS experiments on the methane mobility in confined CO_2+CH_4 mixtures have shown that replacement of the adsorbed methane by CO_2 starts to occur at an unexpectedly low CO_2 pressure of the order of 25 bar. This result can be understood based on SANS studies of the methane adsorption from CO_2+CH_4 mixtures. SANS has been used for characterizing shape of nanoporous carbons and the developed new methods of SANS data interpretation were applied to monitor phase behavior of hydrogen in nanopores of activated carbon, which revealed abnormal densification of H_2 in small pores (with the densification factor of ~50). SANS was also applied to characterize phase behavior of carbon dioxide in a model porous system—silica aerogel—with well characterized porous structure in the vicinity of the bulk gas–liquid critical point. The first structural characterization of tight gas shales, which represent enormous resource of natural gas in the United States, has been conducted and a manuscript submitted to *Energy & Fuels*.

Information Shared

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05246

Neutron Scattering and Osmotic Stress to Study Intrinsically Disordered Proteins

C. Stanley, E. Rowe, H. O'Neill, and V. 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 aims to make progress in biomedicine and is consistent with the DOE mission to promote scientific and technological innovations that improve quality of life. This project also takes particular advantage of the unique neutron facilities within the Neutron Scattering Science Division

(NSSD) 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 this project has been enhanced by the participation of three undergraduate students: Laura Grese (UT), Zac Enderson (Georgia Tech), and Amanda DeBuhr (UT), along with two graduate students working through the Laboratory for Conformational Diseases and Therapeutics (V. Berthelier), UT Graduate School of Medicine: Tatiana Perevozchikova and Dimitriy Smolensky. Overall, this research fosters collaborations, such as the recent one formed with Dr. Pratul Agarwal (Computer Science and Mathematics Division, ORNL) 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 for FY 2011 have been (1) the continued development of our combined SANS and osmotic stress approach for studying protein hydration, conformation, and protein-protein interactions, and (2) SANS characterization of an IDP pair that undergoes coupled folding and binding.

1) **SANS and Osmotic Stress.** We are developing a combined SANS and osmotic stress approach to directly correlate protein structure and structural transitions with the associated hydration and energetics. Our first SANS studies were on the preferential hydration of hexokinase (HK) monomer and dimer states by osmolytes. Using SANS and three hydrogenated osmolytes—betaine, triethylene glycol (TEG), and poly(ethylene glycol) of MW 400 (PEG 400)—that vary in size and chemistry, we were able to quantify the amount of protein-associated water, N_w, for each osmolyte solution condition. This was found from the zero-angle neutron scattering intensity ratio with and without solute, $I_S(0)/I_0(0)$, as a function of solute volume fraction, f_v. Changes in the radius of gyration, R_g, with f_v also correlate with $I_S(0)/I_0(0)$. HK preferential hydration follows the osmolyte series: TEG < betaine < PEG 400, where steric exclusion is the predominate effect for PEG 400. Despite the greater surface area of the dimer, the HK monomer at pH 9 has a larger N_w compared to the dimer form at pH 5 for all three osmolytes. The net change in water, $\Delta N_w = N_{w,D} - 2N_{w,M}$, that accompanies the measured monomer-dimer transition (2M→D) therefore reflects not only the burial of protein surface area but also the change in surface charge with the change from pH 9 to 5 where HK has an isoelectric point, pI ~ 5.3. Indeed, we performed calculations of the HK monomer solvent-accessible surface area, which indicated the surface is composed of 22% negatively charged residues. Interestingly, although ΔN_w depends on both the burial of protein surface area and change in surface electrostatics, the hydration change measured for this reaction by betaine, TEG, and PEG 400 are the same ($\Delta N_w \sim -1600$). This suggests that the measured ΔN_w is independent of the osmolyte used and we are probing the true hydration properties of the system. These studies have been instructive toward applying our SANS and osmotic stress method to understand the hydration properties and structural transitions in IDPs.

2) **SANS Characterization of an IDP Pair.** Using circular dichroism (CD) spectroscopy and SANS, we investigated the structure and binding interaction properties between the 59 residue IDP region of CBP: nuclear-receptor co-activator-binding domain (NCBD), and its binding partner: activator for thyroid hormone and retinoid receptors (ACTR), which also is an IDP. CD indicates that NCBD alone retains some α-helical secondary structure while ACTR alone contains more random coil. Both

NCBD and ACTR undergo an osmotically induced conformational transition toward increased α-helix with the addition of osmolytes, and the effects can be quantified by the osmotic stress method. *Ab initio* shape reconstruction from the SANS data demonstrates the NCBD/ACTR dimer to possess a folded domain matching the previously determined NMR structure and a disordered ACTR N-terminal tail. Ensemble optimization method (EOM) analysis was performed using the SANS curves as constraints to assess the conformational landscape of ACTR in the NCBD-bound and unbound states. The data in both cases are best fit by an average of multiple models that capture the range of dynamics in structure. Conformational fluctuations in the tail of bound ACTR exhibit bimodal distributions in the radius of gyration (R_g) and maximum linear dimension (D_{max}). Unbound ACTR also contains these two modes with an additional larger mode from the gain in conformational freedom. These results suggest that unbound ACTR either preferentially samples the bound state conformation or adopts compact conformations similar to the bound state and most favorable for binding to the NCBD region of CBP.

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05404

Asynchronous In Situ Neutron Scattering Measurement of <10 μs Transient Phenomena at Spallation Neutron Source

K. An, R.A. Riedel, S.D. Miller, J.A. Kohl, H. Choo, and J. Jones

Project Description

The advent of extremely high neutron flux, unique time event data acquisition, and novel instrumentation at the Spallation Neutron Source (SNS) opens up new possibilities, especially for in situ dynamic and kinetic studies. Unlike conventional histogram data at other time-of-flight neutron sources, the time event data acquisition scheme at SNS records neutrons with an intrinsic timing resolution of 100 ns. The objective of this project is to develop a transformational asynchronous in situ neutron measurement method that enables unprecedented <10 μs time resolution. A new technique will be developed making use of both neutron scattering and pump parameters in time event data acquisition mode, as well as real-time data analysis and visualization algorithms. A demonstration study will examine dynamic ferroelectric domain reorientation behavior in piezoelectric ceramics, which occurs at timescales from 1 to ~100 μs during application of electrical fields. The proposed asynchronous approach will increase timing resolution on the SNS instrument suite by three orders of magnitude from 10 ms to 10 μs; fundamentally change the way to measure time-dependent materials behavior using neutrons; and allow study of transient phenomena otherwise not possible. These advanced capabilities will open new scientific and program-development opportunities in broad areas of dynamic mechanical behavior, in structural materials, and phase transformation and energy-conversion processes in functional materials.

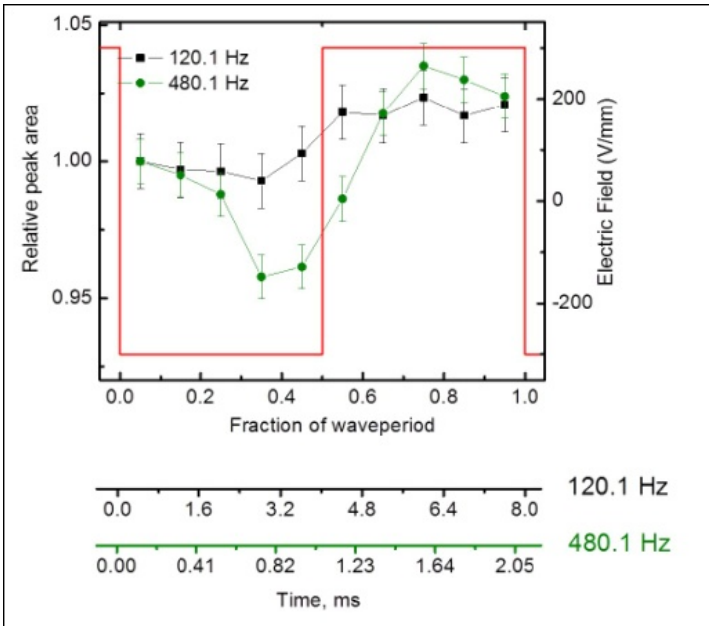
Mission Relevance

DOE has new research areas in the Office of Science Financial Assistance Funding Opportunity Announcement (DE-PS02-09ER09-01): In Basic Energy Sciences, Part (a) Materials Sciences and Engineering "Major research areas include fundamental dynamics in complex materials, correlated electron systems, nanostructures, and the characterization of novel systems." Part (b) Chemical Sciences, Geosciences, and Biosciences seeks the following: "New experimental techniques are developed to investigate chemical processes and energy transfer over a wide range of spatial and temporal scales: from atomic to kilometer spatial scales and from femtosecond to millennia time scales." Both parts can leverage the pump-probe technique, providing novel approaches to experimentation. The new and unique capabilities developed from this project will strongly position DOE-funded SNS to pursue scientific problems that cannot be handled at other neutron scattering facilities. It will strengthen the in-house scientific capability and also attract high-quality collaborative research projects. It will benefit scientific programs related to "real-time, in situ, time-dependent materials phenomena studies" from the DOE Office of Basic Energy Sciences and the DOE Office of Energy Efficiency and Renewable Energy, the Department of Defense (DoD), Army, Navy, Air Force, and industry.

Results and Accomplishments

In this year, a high temporal resolution (HTR) sample environment data acquisition (SE-DAQ) technique and a new "meta event" data structure, which consists of high temporal resolution for the SEDAQ, are developed. This new technique allows 100 ns HTR for SE-DAQ. New asynchronous data reduction codes are developed to post-synchronize both the meta and neutron event data. With those newly developed capabilities, time-resolved asynchronous neutron diffraction measurements of scientific phenomena were performed with different time resolution from minutes to microseconds. SNS users already benefit from this unique capability to capture fast transient phenomena.

HTR SE-DAQ is required for intrapulse synchronization of fast transient phenomena. The proposed intrapulse synchronization is the main development effort of this year including 1MHz HTR DAQ for sample environments by utilizing the neutron event DAQ with 100ns time resolution, which will satisfy the proposed <10 μs temporal resolution requirement. To implement the meta event DAQ for multiple analog signals of generic sample environments, a new 16-bit analog to digital (ADC) conversion system was developed to record fast meta events. This innovative design integrates seamlessly the detector and SE-HTR DAQ with same time resolution as well as similar data structure, which allows robust data reduction and post-synchronization by implementing the new data reduction code to the existing VDRIVE program.



As proposed, a new in situ high-voltage AC field sample environment is built for studying ferroelectric materials. The structural change of $BaTiO_3$ under different AC frequency is explored with the new capability. Time-dependent μ-second temporal scale transient phenomena are observed. Using the technique of asynchronous data collection, we measured the structural changes in a 111-oriented domain-engineered

$BaTiO_3$ single crystal during the application of square-wave ac electric fields at two different frequencies 120.1 Hz and 480.1 Hz on VULCAN. The phase variation of 0.1Hz allows the neutrons to probe continuously and reversibly in pulses with a maximum time resolution close to an instrument bin width until statistically significant data are collected. This reduces the effort of synchronized experimental control with complex sample environments, as in the conventional pump probe approach. Meta and neutron event data are reduced to 10 segments in one waveform cycle with 800 μs and 200 μs temporal resolution for 120.1Hz and 480.1 Hz, respectively. The integrated peak areas as a function of time are shown in the figure, which exhibit time-dependent relaxation. This suggests extrinsic phenomena, that is, other than intrinsic piezoelectric lattice distortion, contribute to intensity changes within 444 diffraction peaks. Extrinsic phenomena can include domain wall broadening among other things.

The new developed technique is introduced to SNS users. Time-resolved experiments at VULCAN benefit from this novel technique, including studies of in situ deformation under load, phase transformation during heating, and lithium intercalation of batteries during charge. For example, phase transformation of steel specimen was heated as fast as 30°C/s and data are resolved within 0.1 s (3°C/pattern) by applying this new technique. More approved user proposals will benefit from the unique capability to perform time-resolved study on wide range of scientific topics.

Information Shared

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Five invited talks at international conferences.

05432

The Search for Common Themes in Unconventional Superconductivity: Spin Excitations in Organic Superconductors

A.D. Christianson, G. Ehlers, M.D. Lumsden, T.A. Maier, D. Mandrus, S.E. Nagler, and C. Wang

Project Description

Organic metals, molecular magnets, and superconductors have attracted considerable attention due to the possibility of designing materials for specific applications with the vast array of organic complexes available through modern synthetic techniques. Despite this, very little is known about the pairing mechanism or the magnetic interactions found in organic superconductors and related molecular magnets. Here we propose to remedy this through inelastic neutron scattering studies of the excitations in organic superconductors and closely related materials with particular emphasis on the evolution of the spin excitations from the antiferromagnetic to the superconducting side of the phase diagram. The project consists of three components: (1) sample synthesis and characterization, (2) theory and simulation, and (3) experimental inelastic neutron scattering studies. The combination of these components will lead to an unprecedented understanding of the excitations in organic superconductors and may yield common themes for the investigation of unconventional superconductivity.

Mission Relevance

The project will provide key additional knowledge of the physical behavior of organic superconductors and related molecular magnets and will contribute to the broader understanding of unconventional superconductivity and magnetism and consequently has the potential to contribute to a materials-based solution to the energy crisis. As such this project 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

We have made steps towards optimizing the synthesis of deuterated organic superconductors and organic charge coordination polymers; for example, a jumbo-sized growth cell was developed. Sizeable crystals of [Cu(pyz)2(HF2)]X (X = ClO_4, BF_4, PF_6, SbF_6) have also been synthesized. We have performed comprehensive neutron scattering measurements employing several instruments at the Spallation Neutron Source and the High Flux Isotope Reactor of the magnetic coordination polymer $CuF_2(D_2O)_2$-(pyz) and are working to finalize data analysis in preparation for a publication. The theoretical modeling component of this project has made substantial headway on the simulation of the magnetic properties of the organic superconductors and has calculated the expected response for inelastic neutron scatting based upon a model with d-wave pairing.

05445

In Situ Neutron Scattering Studies of Fuel Cell Materials

A. Huq, M.P. Paranthaman, J.-H. Kim, Z. Bi, C.A. Bridges, J.P. Hodges, and S. McIntosh

Project Description

The goal of this project is to study a variety of solid oxide fuel cell (SOFC) materials using a combination of materials synthesis, electrochemical characterization, in situ powder neutron diffraction, and inelastic scattering. The driving goal is to develop comprehensive structure-function relationships that describe the oxygen ion/proton conducting and electrocatalytic properties of materials being developed as electrolyte and electrode materials for high-temperature electrochemical devices, including fuel cells and electrochemical reactors. Historically neutron diffraction has played a crucial role in the study of metal oxides (e.g., high Tc superconductors) due to its high sensitivity towards oxygen in the presence of heavier elements; however, neutron scattering has not been widely applied to SOFC materials. In situ neutron scattering studies under conditions that simulate the dynamic fuel cell operating environment can provide unique information that cannot be obtained by any other means such as structure; defect location, concentration and ordering; phase transitions as a function of chemical composition, temperature and oxygen partial pressure; phase separation and decomposition; phase behavior in in situ dynamic ion-conducting environments; and vibration and diffusion properties of mobile species. These parameters directly determine the cell performance and must be understood in order to move towards intelligent materials design.

Mission Relevance

The proposed research plan fits in very well with the plans for the "Center for Materials Chemistry" which can be the launching point for future funding. To expand the use of clean and renewable energy sources and reduce America's dependence on foreign oil, Energy Secretary Steven Chu announced $41.9 million in American Recovery and Reinvestment Act funding for fuel cell technology on April 15, 2009. While in the proposed budget for FY 2010 fuel cell technology is no longer being considered for

onboard automobile applications, DOE will continue to fund research for stationary fuel cell applications, such as backup power on power grids, auxiliary power units on heavy duty trucks and RVs, etc. In addition to funding directly related to fuel cells, once developed the in situ capabilities will also be attractive for research in other fields such as catalysis, gas absorption materials, energy storage, solar energy conversion, phase mapping of correlated electron materials and synthesis of solid state materials. In the 2011-B cycle of SNS, 15 days of beam time (four experiments) was awarded for proposals which requested the newly developed sample environment that was commissioned resulting from this LDRD. These included three projects on SOFC and one on Li-ion batteries. In cycle 2011-A two successful neutron experiments showcasing the capability of the system were performed. One of these was carried out on $NdBaCo_2O_{5+\delta}$ layered perovskites, which have attracted great interest due to their good mixed oxide-ion and electronic conducting (MIEC) properties as well as fast surface oxygen exchange property. The next experiment was done in collaboration with a user where the reduction properties of two promising anode material $SrMgMoO_{6-\delta}$ and $La_{0.75}Sr_{0.25}Mn_{0.5}Cr_{0.5}O_{3-\delta}$ were studied. This work resulted in the submission of a pre-proposal to DOE that is now being developed to a full proposal.

Results and Accomplishments

Project I: The electrical conductivity, crystal structure, and phase stability of $La_{0.99}Ca_{0.01}Nb_{1-x}Ta_xO_{4-\delta}$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5, δ=0.005), a potential candidate for proton conductor for SOFCs, have been investigated using AC impedance technique and in situ X-ray powder diffraction. Partially substituting Nb with Ta elevates the phase transition temperature (from a monoclinic to a tetragonal structure) from ~520ºC for x = 0 to above 800ºC for x = 0.4. AC conductivity of the $La_{0.99}Ca_{0.01}Nb_{1-x}Ta_xO_{4-\delta}$ both in dry and wet air decreased slightly with increasing Ta content above 750ºC, while below 500ºC, it decreased by nearly one order of magnitude for x = 0.4. It was also determined that the activation energy for the total conductivity increases with increasing Ta content from 0.50 eV (x = 0) to 0.58 eV (x = 0.3) for the tetragonal phase, while it decreases with increasing Ta content from 1.18 eV (x = 0) to 1.08 eV (x = 0.4) for the monoclinic phase. By removing the detrimental structural phase transition from the intermediate-temperature range, consequently avoiding the severe thermal expansion problem up to 800°C, partial substitution of Nb with Ta brings this class of material closer to its application in electrode-supported thin-film intermediate-temperature SOFCs.

Project II: $InBaCo_{4-x}Zn_xO_7$ oxides have been synthesized and characterized as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC). The effect of Zn substitution for Co on the structure, phase stability, thermal expansion, and electrochemical properties of the $InBaCo_{4-x}Zn_xO_7$ has been investigated. The increase in the Zn content from x = 1 to 1.5 improves the high-temperature phase stability at 600°C and 700°C for 100 h, and chemical stability against a $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) electrolyte. Thermal expansion coefficient (TEC) values of the $InBaCo_{4-x}Zn_xO_7$ (x = 1, 1.5, 2) specimens were determined to be 8.6×10^{-6}–9.6×10^{-6}/°C in the range of 80–900°C, which provides good thermal expansion compatibility with the standard SOFC electrolyte materials. The $InBaCo_{4-x}Zn_xO_7$ + GDC (50:50 wt. %) composite cathodes exhibit improved cathode performances compared to those obtained from the simple $InBaCo_{4-x}Zn_xO_7$ cathodes due to the extended triple-phase boundary (TPB) and enhanced oxide-ion conductivity through the GDC portion in the composites.

Information Shared

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05511

Addressing Fundamental Challenges in Modeling the Recrystallization of Metallic Polycrystals through In Situ Neutron Diffraction Studies

B. Radhakrishnan, S.B. Gorti, X.-L.Wang, G.M. Stoica, and G. Muralidharan

Project Description

Structural and functional materials used in energy applications often derive their unique properties by preferred grain orientation (texture), obtained through precise thermo-mechanical processing routes. An important processing step is recrystallization, the formation and growth of specific texture components from a deformation substructure consisting of many dislocations. Despite years of research, a comprehensive understanding of the characteristics of recrystallization has been elusive. Even with the availability of the most sophisticated computers and simulation tools, a direct dislocation level simulation of recrystallization is nearly impossible. The project seeks to exploit the unique features of the VULCAN diffractometer at the Spallation Neutron Source, to perform in situ neutron diffraction investigation of the kinetics of texture evolution. The texture data in conjunction with the existing advanced microstructure evolution modeling, and high-performance computing capabilities at ORNL will be used to develop an integrated, predictive, and process modeling tool for structural materials. The tool will be used to devise a new annealing procedure for wrought magnesium alloys by inducing and controlling the development of unique texture components for enhancing their room temperature formability. The successful completion of this research will lead to enhanced use of wrought magnesium sheets in automobiles resulting in significant energy savings through weight reduction.

Mission Relevance

The project focuses on the development of lightweight materials for structural and energy applications, and is therefore of relevance to the mission of DOE's Industrial Technology Program and Vehicle Technology Program. It is also of interest to the Department of Defense, and the National Aeronautics and Space Administration, because of the unique applications that the proposed approach might generate in defense and aerospace components.

Results and Accomplishments

A second round of in situ neutron diffraction studies was carried out this year, through additional beam time obtained through a successful Neutron Scattering Sciences Division user proposal. Two sets of samples were investigated. The first set of samples was from Mg alloy AZ31 that were deformed through a combination of compression and shear using asymmetric rolling. The second set of samples was from aluminum alloy 5052 which is essentially an Al-2Mg alloy with minor additional solute. The samples were continuously heated in the recovery temperature range using a newly developed induction heating facility at VULCAN. The aluminum samples were also subjected to an external stress roughly below the yield stress at temperature using the newly developed load frame at VULCAN. The AZ31B samples were also rotated about the mounting axis in order to explore a wide range of diffraction angles. Post-annealing textures were also measured using X-ray diffraction, and the High-Pressure-Preferred Orientation facility at Los Alamos. AZ31B showed significant weakening of all the major deformation components during recovery anneal, with the basal texture component showing a significant weakening. A crystal plasticity–Monte Carlo technique was used to model the texture changes during shear deformation and annealing. The model was able to observe the weakening of the textures as observed experimentally. The results have been presented and a publication in *Metallurgical and Materials Transactions* is in press. In the Al-2Mg alloys, an important finding is that the Cube texture component decreased during the recovery

stage. However, the rate of decay of the Cube component decreased upon increasing the heating, or in the presence of an external stress. A new nucleation model based the relative recovery rates of various texture components has been developed and implemented within the crystal plasticity-Monte Carlo code. The results will be presented at The Minerals, Metals and Materials Society (TMS) spring meeting in Orlando, FL, March 11–15, 2012, and published. The work carried out as part of the LDRD was leveraged to obtain DOE funding from the Office of Vehicle Technologies. The proposal, "Low Cost Magnesium Sheet Production using the Twin Roll Casting Process and Asymmetric Rolling," has been funded at $400K for FY 2012.

Information Shared

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05567

Protein Dynamics: Neutron Scattering Methodological Development

J.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 Oak Ridge National Laboratory. 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. In the first 2 years computational methods were developed. In the third year experiments were performed on activity: dynamics relationships.

Results and Accomplishments

Water is widely assumed to be essential for life, although the exact molecular basis of this requirement is unclear. Water facilitates protein motions, and although enzyme activity has been demonstrated at low hydrations in organic solvents, such nonaqueous solvents may allow the necessary motions for catalysis. To examine enzyme function in the absence of solvation and bypass diffusional constraints, we tested the ability of an enzyme, pig liver esterase, to catalyze alcoholysis as an anhydrous powder, in a reaction system of defined water content and where the substrates and products are gaseous. An understanding of the role of hydration in enzyme activity is a central question in molecular biophysics. Previous work has indicated that the hydration required for activity is below the monolayer coverage. For instance, for this study, pig liver esterase studies (PLE; molecular mass of monomeric form ~60,070 Da) have been found to have hydrolytic activity at a hydration level of 0.03 g water/g enzyme (h) at room temperature (i.e., ~100 water molecules per molecule of protein). PLE is useful for low hydration studies because water is

neither a substrate nor a product in the alcoholysis reactions catalyzed. For our study, the acyl transfer between methyl butyrate and propanol was followed by headspace analysis. The isotopic labeling of water molecules and its quantification by mass spectrometry is one of the most sensitive methods of water determination and is used here to quantify low levels of PLE hydration and, accompanied by activity measurements and neutron spectroscopic experiments, has allowed the correlation of protein hydration with flexibility and activity. The role of water as a reactant or as a diffusion medium for the products and substrates of the reaction was precluded by the use of a gas-phase transesterification catalytic system.

At hydrations of 3 (52) molecules of water per molecule of enzyme, activity is several orders of magnitude greater than nonenzymatic catalysis. Neutron spectroscopy indicates that the fast (nanosecond) global anharmonic dynamics of the anhydrous functional enzyme are suppressed. This indicates that neither hydration water nor fast anharmonic dynamics are required for catalysis by this enzyme, implying that one of the biological requirements of water may lie with its role as a diffusion medium rather than any of its more specific properties.

A solid basis has now been established for the interpretation of elastic incoherent scattering from globular proteins. This should provide the basis for future successful research proposals.

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05604

Novel Resistive Plate Avalanche Chamber for Neutron Detection

Y. Diawara, L. Crow, J.P. Hayward, V. Sedov, M. Kocsis, and X. Zhang

Project Description

A novel neutron detection technology employing solid materials as neutron converter is proposed here. It retains the desirable performance characteristics of gaseous detectors (direct conversion) and scintillators (no parallax) while offering high count rate capability. Gaseous and scintillator-based detectors are the most widely used for neutron detection technologies. He-3 gaseous detectors have a number of very attractive features for neutron scattering including large active area, direct conversion process, high dynamic range and low gamma sensitivity. However, the spatial resolution and the parallax errors of these neutron detectors are fundamentally limited, respectively, by the particle (protons and tritons) range and the conversion volume design; moreover, the He-3 shortage will limit its future use in neutron detection. The scintillators, when coupled to PMTs, achieve large active area, single-neutron sensitivity, and no parallax broadening. Unfortunately their dynamic range and their detective quantum efficiency are limited. The low rate capability of these detectors limits their applications in high flux experiments such as in SANS and reflectometry. The proposed neutron converter, integrated in a resistive parallel plate avalanche chamber, will offer some unmatched characteristics, including high counting rates, better

position resolution than present gas detectors, and the possibility of matching the shape of detectors to specific applications.

Mission Relevance

The proposed project addresses the issue of the He-3 replacement by a solid converter, a growing need for neutron scattering facilities worldwide. Its application could also expand beyond neutron scattering to many other fields (Homeland security, medical, etc.). Therefore, the proposed detector design is deemed to be of primary importance to neutron science. It is a versatile detector that will meet the counting rate requirements of present neutron scattering instruments. Its relevance to ORNL is pointed out by the following aspects:

- It is a design tailored to the needs set by the experiments on high-intensity neutron beams provided by SNS and HFIR.
- Applications where the combined features of space resolution and throughput rate capabilities will play a fundamental role are protein crystallography small-angle scattering, and time-resolved observations of kinetic processes.
- The development of this detector technology will reinforce the recognition of ORNL as a leader in neutron detection among the community of users of neutron source facilities.

Results and Accomplishments

Some significant technical and scientific accomplishments have been achieved on the first prototype of the He-based gaseous detector:

- The detector design has been completed. It consists of two prototypes of 20 cm resistive plate detectors and a prototype for testing.
- The first detector has been tested at two of ORNL's high neutron current beamlines: CG1A at HFIR and BL4B at SNS. The tests confirmed the high rate capabilities of the resistive plate detectors: 0.5 million counts per second global rate. A direct beam was measured from BL4B with a 0.5 mm × 30 mm slit size and the measured local rate was over 300,000 counts per second, which is 100 times higher compared to the maximum local counting rate of the present detector used at this beamline.
- The position resolution was measured using a 2 mm mask.
- A background level below 0.1 counts per second was achieved.
- The second detector prototype will use a solid nanostructure (aerogel) layer as a neutron converter. We have identified The National Institute of Aerospace (NIA) as a partner, and we are collaborating in this project to develop an effective neutron converter layer based on porous nanostructure films.
- Finally, all the detector components have been ordered and the budget for the aerogel development has been committed. The electronics components, mainly the time to digital converter, need to be designed and tested.

Information Shared

A patent application based on this technology and entitled "A porous material neutron detector" has been filed: US Patent Application No. 12/844,960.

Because of the high rate capabilities, the resistive plate can be used as a beam monitor since all present monitors saturate at high rate. An invention disclosure based on this application and entitled "High Rate Neutron Beam Monitor" has been submitted to ORNL. ID number: 201002497.

05777

Enhanced Directionally Selective Moderator for SNS

E.B. Iverson and F.X. Gallmeier

Project Description

The Directed Moderator combines moderating material and single-crystal layers to enhance the brightness of neutron beams emitted in selected directions, chosen to align with the beamlines served by that moderator. This enhancement may result in increased beam brightness by a factor five over all wavelengths greater than 1 Angstrom, and additional gains (by as much as a factor ten overall) between 1 and 4 Angstroms and at very long wavelengths. These gains result from neutron refraction, reflection, and Bragg scattering within the crystalline material in such a way as to dramatically increase the likelihood that any given scattering event results in a neutron emitted in a useful direction. The physics associated with these gains is not present in currently available general-purpose neutron transport codes. If successful, we will provide a moderator concept that enhances the beam brightness at SNS by an order of magnitude.

Mission Relevance

This research is directly aligned with ORNL's intent to "design, construct, and operate neutron sciences facilities of the highest efficiency and effectiveness… [and] further the state of the art of neutron … source technology to enable leading-edge research." Order-of-magnitude increases in source performance can open fundamentally new avenues of research, and dramatically improve the throughput of studies currently underway.

Results and Accomplishments

We have implemented and tested refraction and reflection in a standard neutron transport code system. We have tested currently available crystallographic capabilities and found them to be adequate for powder materials but not for oriented materials; we are implementing crystallographic scattering from oriented materials. We have designed and tested the Laminated Stack Moderator, composed of alternating layers of moderating material and multi-layer crystalline vanes. Both the newly developed simulation capabilities and the testing of the control moderator described above significantly influenced this design. The Laminated Stack Moderator has confirmed the gains coming from Bragg scattering within the Directed Moderator's crystalline vanes, and provides ample quantitative results suitable for validating simulation methods.

Information Shared

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05901

New Neutron Scattering Experiments at the SNS

L. Kszos

Project Description

ORNL has the world's highest flux user facilities for neutron scattering, the Spallation Neutron Source (SNS) and the HFIR. Neutron scattering is a powerful tool to study the structure and dynamics of materials. Several specialized techniques at SNS and HFIR provide information on materials at a wide range of length (0.1–100's nm) and timescales ($10^{-}6–10^{-15}$ s). The information gleaned from neutron scattering experiments is invaluable in characterizing materials for a variety of technological and scientific applications. Because of the diversity of studies that can be performed at the SNS and HFIR, to fully utilize the capabilities of this unique national facility, collaborations need to be established with researchers from many disciplines and institutions. This project proposes to support new experimental studies of advanced materials utilizing a broad suite of instruments at the SNS and HFIR.

Results and Accomplishments

In FY 2011, we supported 24 students to work on experiments at the SNS on BL-18 (ARCS), BL-4A (Magnetism Reflectometer), BL-7 (VULCAN), BL-4B (Liquids Reflectometer), BL-3 (SNAP), BL-11A (POWGEN), and BL2 (Backscattering Spectrometer),and at HFIR on CG-2 (GP-SANS), CG-3 (Bio-SANS), HB-3A (Four-Circle Diffractometer), CG-1D (Imaging), HB-1 (Triple Axis). The students were from the University of Minnesota, University of Pennsylvania, California Institute of Technology, University of Florida, Georgia Tech, Drexel University, McMaster University, California Institute of Technology, Lehigh University, and University of South Florida. The experiments were performed to study thin-film structure, ion transport in porous electrodes, structural studies of ferroelectric ceramics, nucleosome complexes, fuel cell anodes, and hydrogen diffusion in hybrid materials.

Information Shared

As this effort targeted graduate students, expected future publications will be thesis dissertations and publications co-authored with their major professor.

06233

Development of the Neutron Based Biomembranes Initiative at NScD

J. Katsaras

Project Description

This proposal outlines a science plan to establish the Neutron-Based Biomembranes Initiative (NBBI) within the Neutron Sciences Directorate (NScD) and ORNL. In broad terms, NBBI will be comprised of two major thrusts, namely, (1) the elucidation of structure and its relation to the function of biological membranes. This will be accomplished through the use of biologically relevant membrane systems (both model and real), and the unique characterization capabilities offered by thermal and cold neutrons (e.g., contrast variation); and (2) the development and fabrication of systems with utility to the pharmaceutical and medical industries (e.g., liposomal-based targeted drug delivery and imaging systems). Ancillary aims and benefits will include the development of novel techniques, samples and sample environments,

especially those that will exploit the capabilities of the SNS. Both thrusts will involve collaborators from NScD and other organizations within ORNL, and from outside of ORNL (i.e., universities, government agencies, and industry). The science described in this proposal will have a significant strategic impact on neutron scattering at ORNL. It will not only act as a nucleus for leading-edge science within ORNL, and the training of highly qualified personnel (HQP), but will also provide a critical "point of entry" and interface that will make neutron scattering visible and accessible to the biomembranes communities located at universities, DOE and other government labs, and industry. The goal is that NBBI will become an international center of excellence for biomembranes.

Mission Relevance

Throughout the biological world, cell membranes are crucial to the existence of individual cells. In animal cells the plasma membrane is a selectively permeable barrier composed primarily of proteins and lipids, which separates the cytosol from the extracellular environment. Membranes also surround the various cell organelles (e.g., mitochondria, endoplasmic reticulum, Golgi apparatus, etc.), enabling them to maintain their characteristic differences from the cytosol. In addition to its barrier function, the plasma membrane acts as an anchor for the cytoskeleton, a cellular network of fibers contained within the cytoplasm that imparts to the cell structure, shape, and movement.

With the diverse and in-depth expertise offered by the various groups at ORNL, including the nanomaterial characterization and fabrication resources available at the Center for Nanophase Materials Sciences (CNMS) and the modeling and computing capabilities at the Center for Molecular Biophysics, NBBI will have a significant strategic impact on neutron scattering at ORNL and beyond. This will position the NBBI team to pursue and successfully compete for continued support from agencies (DOE BER, especially Genomic Science, Bioenergy, Structural Biology and Subsurface Biogeochemistry programs; DOE BES, especially User Facilities, Physical Biosciences, Biomolecular Materials, and Chemical Physics areas; NIH research (e.g., biofilms, antibiotics, microbiomes, infectious disease); DOD (biodefense, sensors, corrosion); and DHS (biodefense). In addition, and equally important, the capabilities developed by NBBI will become part of a suite of approaches available to NSSD's user community.

Results and Accomplishments

The first order of business was to hire two post-doctoral fellows. This was accomplished by attracting to NBBI Fred A. Heberle, a recent graduate in biophysics (2011) from Cornell University (Supervisor: Gerald Feigenson), and Jianjun Pan, who graduated in physics (2009) from Carnegie-Mellon University (Supervisor: John F. Nagle). Since their arrival in 2011, ORAU Fellows Heberle and Pan have carried out a number of experiments at SNS (Liquids Reflectometer) and HFIR (Bio-SANS) and have successfully competed for neutron beamtime. As a result of their Bio-SANS experiments, they are now in a position to determine the structural parameters of commonly used phosphatidylglycerol biomimetic bilayers.

Bilayer parameters, such as area per lipid and the overall bilayer thickness, can be obtained together with intrabilayer structural parameters (e.g., hydrocarbon region thickness) through the simultaneous analysis of small-angle neutron and X-ray scattering data using a technique developed by Kučerka et al. [*Biophys. J.* **95,** 2356 (2008)]. The area per lipid is a key parameter required to accurately determine bilayer structure, lipid-lipid, and lipid-protein interactions in biomembranes. In addition to playing a key role in describing membrane structure and its associated functions, knowledge of lateral lipid area is central to fine tuning the force fields used in molecular dynamics (MD) simulations. Therefore, in combination with x-ray diffraction and MD simulations, neutrons can be used to accurately and unambiguously determine the lipid areas of biologically relevant systems, thus reconciling long-standing differences found in the lipid literature.

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06242

Re-engineering Xylanase

P. Langan, D.E. Graham, R. Upton, and L. Coates

Project Description

In this proposal we will pioneer the use of neutron crystallography in combination with molecular biology mutagenesis and in silico design to guide the re-engineering of the enzyme xylanase to allow for the more efficient hydrolysis of hemicellulose to xylose over a broader range of conditions. Five-carbon sugars such as xylose from hemicellulose represent up to 30% of lignocellulosic biomass, and their efficient hydrolysis is important for cost-efficient production of biofuels and other bioproducts. We expect that our innovative multidisciplinary approach will be readily applicable to other bioengineering problems of industrial importance and will position ORNL with unique capabilities and expertise to attract programmatic funding.

Mission Relevance

The results will provide fundamental scientific insights into an enzyme with important applications in DOE science and energy resources missions. An improved enzyme is expected to have an impact on the cost and efficiency of the production of biofuels. Biofuels are of direct relevance to DOE missions in renewable energy. The impact of this mission on our energy security and environment is widely appreciated. This proposal will broaden the science and capabilities of the DOE-funded Center for Structural Molecular Biology by adding a new crystallography component to its present capabilities in deuteration and small-angle neutron scattering. The approach and capabilities developed here will be applicable to other bioengineering and synthetic biology problems, some of which may be of interest to NIH when applied to enzymes of biomedical importance. The DOE missions in renewable energy are also of interest to USDA. USDA and DOE jointly fund programs in this area.

Results and Accomplishments

Developing an enzyme expression and activity assay pipeline at Bioscience Division: The genes (with C-terminal His-tags) encoding xylanase homologs from bacterium *Clostridium cellulolyticum* and fungus *Trichoderma reesei* were cloned into *E. coli* expression vectors. *E. coli* cells containing the recombinant plasmids expressed substantial amounts of protein, but the protein was mainly in an insoluble form. Initial attempts to improve solubility by changing expression conditions or altering extraction parameters were unsuccessful. However, some xylanase activity was detected in an assay that measured reducing sugars released by the hydrolysis of Birch tree xylan. Alternative protein expression conditions were developed using the dipeptide glycylglycine as an additive to *E. coli* culture medium resulting in substantially increasing the solubility of the *T. reesei* protein. Protein from these cells demonstrated significant endoxylanase activity in a continuous spectrophotometric assay, using the soluble, chromogenic substrate 4-nitrophenyl-beta-xylobioside and is being prepared for crystallization.

Developing a crystallization and structure analysis pipeline at the Center for Structural Molecular Biology: Commercially available xylanase from *Trichoderma reesei* was purified on a desalting column with 0.1 M TRIS buffer at pH of 8.5. Crystallization trials optimizing around previously determined conditions using PEG8000 and NaI were successful (10% PEG8000, 0.2 M NaI and 0.1 M TRIS (pH = 8.5), enzyme concentration 30mg/mL). Crystallization growths were scaled up by using 9-well siliconized glass plates and the sandwich-box setup (Hampton Research Corp.). The large setup involved 200 μL crystallization drops (100 μL enzyme + 100 μL mother liquor) and 50 mL reservoir solution and have produced crystals as long as 3–4 mm^3 in volume, more than sufficient for neutron crystallography.

ULTRASCALE COMPUTING AND DATA SCIENCE

05282

High-Throughput Computational Screening Approach for Systems Medicine

P.K. Agarwal

Project Description

High performance computing continues to revolutionize biology. Computational thinking and techniques will have a significant impact on the 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 (at ORNL) and medicinal and computational drug design chemists (at the Genome Research Institute) to develop new high-throughput methods for approaching rational drug design and drug discovery. High performance computing 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 DOE's GTL:Genomics initiative. The proposed research will allow development of HPC tools and software for characterization of biomolecular-biomolecular interactions, which is an important components of GTL:Genomics 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 BER as well as ASCR. The proposed research for the development of tools and software for systems medicine is relevant to human health. Therefore, it is relevant to the mission of NIH (in particular to the NIGMS). The outcome of the proposed research would lower time and cost for discovery of new medicine and, therefore, promote human health.

Scientific/Technical Accomplishments

Our approach for improving the speed of discovery of new medicine was based on a two-pronged approach. First, we hypothesized that developing a fundamentally new paradigm of protein structure, dynamics, and function will allow us to discover new allosteric sites. Second, by using new computational methodology we have improved the performance of software for computational modeling of bio-molecules and high-throughput computational drug screening.

Using a new paradigm allowed us to discover novel aspects of enzyme function and therefore enabled us to identify surface sites with high conformational flexibility. These are the potential allosteric sites. Using the developed approach, we have successfully investigated a number of medically important target enzymes. 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 widely studied enzyme both theoretically and experimentally. FabG reduces the beta keto-acyl 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 achieved by characterizing the reaction coupled protein flexibility and gradually mapping the network of residues involved in promoting the reaction. Note that in addition to identification of the allosteric sites, our computational studies also enabled us to obtain detailed insights into the mechanism of catalysis for the target enzymes [–1–2, 4–10].

On the other hand, we also developed and optimized computational software that improved the performance of computational modeling software [2–4]. A high-throughput computational drug screening approach was designed and implemented on ORNL's supercomputer. The high-throughput docking was used for determining the best binding pose of the ligands with the enzyme targets given the receptor binding (allosteric) sites. In the first phase, 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. In the second phase of this project, a full compound library (with about 625,000 drug-like compounds) was screened against the two medical targets. For FabG, a list of 400 compounds has been prepared (100 compounds each for four allosteric sites) based on the use of the high-throughput screening methodology. Currently, these compounds are being further investigated as potential inhibitors and use as medicine.

Overall, the proposed work allowed us to develop a high-throughput computational infrastructure for characterization of enzymes/proteins for the identification of allosteric sites and screening of large chemical libraries to rapidly identify a list of potential drug molecules. The results of this research will enable further investigations of protein targets involved in human health.

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05387

Soft-Error Resilience for Future-Generation High-Performance Computing Systems

C. Engelmann and S.S. Vazhkudai

Project Description

The premise of this project is that soft errors, that is, uncorrected bit flips in computer chip logic caused by thermal and voltage variations as well as natural radiation, will be the main cause of interruptions in future high-performance computing (HPC) systems due to smaller circuit sizes, lower voltages, and increased component count. Based on the exa-scale roadmap, vendors have to find the right balance between resilience and power consumption. While they will offer extensive soft error detection support to avoid silent data corruption (SDC), soft error correction will be limited to save power. This has two consequences. First, fewer soft errors will be masked by the hardware. Second, the risk of SDC remains as its prevention is still an active area of research. This project targets two different solutions to alleviate the issue of soft errors: (1) checkpoint storage virtualization to improve checkpoint/restart times and (2) software redundancy to eliminate rollback/recovery.

Mission Relevance

This project focuses on urgently needed research and development in soft error resilience for future-generation HPC systems housed at ORNL's National Center for Computational Sciences (NCCS) and similar DOE and National Science Foundation (NSF) facilities. This work aims at developing a soft error resilience strategy for next-generation HPC systems by prototyping software solutions and evaluating them in terms of performance overhead, provided resilience, additional financial cost, and power consumption impact. The ultimate objective of this project is to increase the efficiency of next-generation HPC systems, thus improving return on investment and time to solution for scientific breakthroughs.

Results and Accomplishments

We have developed an aggregated checkpoint storage prototype using either memory or solid-state disk storage (SSD) for faster checkpoint/restart times. The memory and SSD resources are arranged as tiers, each providing different characteristics such as performance or reliability. The checkpoint data is also drained to a parallel file system in an out-of-band fashion, in between checkpoints. If space is a concern on this storage system, then the draining is overlapped with checkpointing. We have also developed a static scheme to provision the memory and SSD tiers on the checkpoint storage so as to satisfy a desired checkpoint rate. Our results indicate that this solution is extremely viable for future extreme-scale machines. We have further developed the modular-redundant Message Passing Interface (MPI) solution, MR-MPI, which transparently executes HPC applications in a redundant fashion. The overhead for the employed message replication can be 0% for embarrassingly parallel applications or 70–90% for communication-intensive applications in a dual-redundant configuration. MR-MPI also offers file I/O under redundancy using coordination protocols with a redundancy-oblivious mode for accessing a node-local file system and a redundancy-aware mode for accessing a shared networked file system. The results demonstrate the capability to improve performance by utilizing MPI communication between replicas and parallel file I/O. The recently developed redMPI solution is a follow-on to MR-MPI that additionally offers SDC detection and correction. The employed replication protocols further improve on performance.

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05410

Massively Parallel Algorithms for Scalable Exascale Data Analysis

Y. Jiao, E.M. Ferragut, S.S. Vazhkudai, S. Campbell, M. Hagen, S.D. Miller, C. Griffin, and C. Steed

Project Description

We have developed scalable algorithms for the analysis of moderate size (gigabytes ~ terabytes) measurement/observational data that require petascale/exascale computational resources. Specifically, we have proposed solutions to the data analysis problems of two applications: (1) nonnegative matrix factorization (NMF), a dimension reduction method fundamental to many data mining applications and

(2) the parameter estimation problem faced by neutron scientists. These two applications share the common mathematical and algorithmic challenge: scalable nonconvex optimization. In the past decade, NMF has been successfully applied to high-dimensional data analysis. It is shown to be more effective than PCA in dimension reduction tasks such as document clustering and gene expression analysis. However, the major obstacle for its use in practical scales lies in its computational intensity. Our goal is to mitigate this problem by accelerating the least-squares-type NMF algorithms on GPUs. In neutron scattering sciences, the parameter estimation problem is extremely challenging due to the large parameter space and the sheer amount of experimental data. To the best of our knowledge, very little progress has been made on the first problem and there are no systematic approaches to the second problem.

Mission Relevance

Exascale data analysis is a multidimensional problem: "Exascale" can refer to the size of the data or the computational requirement for the analysis; data may come from simulations or experimentations; and some analyses need to be interactive, while others do not. Much attention has been devoted to analyzing exascale data generated by complex simulations, and parallel algorithm development has been the primary focus. However, many problems faced by measurement sciences and data mining applications that require interactive analyses have remained largely unexplored. We focus on developing scalable algorithms for interactive analysis of moderate size (gigabytes ~ terabytes) measurement/observational data that require petascale computational resources. The target architecture is the CPU/GPU–hybrid supercomputing platform, which is widely considered the most promising exascale computing hardware alternative. The success of this project will showcase the important role that supercomputing can play in accelerating knowledge and scientific discoveries.

Results and Accomplishments

In FY 2010, we showed that the Inelastic Neutron Scattering data analysis problem can be solved by using full 4D numerical integration and the Sequential Quadratic Programming (SQP) optimization algorithm. We demonstrated the solution on the Oak Ridge Institutional Cluster (OIC) by using a simplified simulation model. During the investigation, we identified two specific challenges.

- The 4D numerical integration routine is the performance bottleneck, which limits the highest data resolution that the software can handle in tractable time.
- In the initial proof-of-concept study, we used a simulated data set that has zero noise. A practical solution must be robust in the presence of noise.

In FY 2011, we took a two-step approach to address these challenges. First, we further parallelized the high dimensional numerical integration routine by using the General Purpose Graphics Processing Units (GPGPUs). The final software package was tested and validated on LENs. Secondly, we applied the software on an experiment that Dr. Andrei Savici conducted in 2009, the data analysis of which was hindered by the absence of scalable software. More specifically, we accomplished the following in FY 2011.

1) Implemented a flexible multi-GPGPU Monte Carlo Integration algorithm that can handle the convolution of any two given functions. In practice, one of these two functions represents the instrument resolution function and the other is the sample scattering function.
2) Extended our repertoire of optimization algorithms from SQP to a wide range of Pattern Search, Parallel Genetic Algorithms, and Ant Colony Optimization Algorithms.
3) Achieved more than 200 times speed-up by exploiting multiple levels of parallelism: using hyper-threading on GPGPUs, using multiple GPUs, and using MPI programming for data parallelism.
4) The solution was tested and validated on multiple platforms: Mac, OIC (Linux cluster), and GPU-enabled LENs. We applied the software to an existing experimental data set. This task involved performing the background fitting and removing the background from measured data, computing the

resolution factor and adjusting the algorithm for better results, testing the sample scattering function using different configurations, testing the convolution correctness and scalability, and (ongoing) final parameter fitting.

The exercises we conducted in FY 2011 lead us to conclude the following.

1) The GPGPU-based software we developed can handle the expected experimental data resolution (10^{10}–10^{12}) in tractable time (about 2 weeks).
2) With the presence of noise in most experimental data set, the number of random samples taken by the Monte Carlo Integration routine becomes less important. Our experience showed that $5*10^4$ random samples are sufficient for most problems.
3) The most time-consuming component of the data analysis process is not computing but the pre-processing of raw experimental data. Significant domain knowledge and expertise of the instrument are crucial for background clean up.
4) Determining the form of the sample scattering function is more of an art than a technique. Most of the trial-and-error iterations happen in this step.

Information Shared

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05413

Wavelength-Division Multiplexed Quantum Communication Network

R.S. Bennink, D.D. Earl, P.G. Evans, W.P. Grice, T.S. Humble, and R.C. Pooser

Project Description

Quantum Communication (QC) is a next-generation technology for transferring information encoded in the quantum states of particles. Applications of QC include ultra-secure communication and quantum computing, a potentially revolutionary form of computing. Deployment of QC has been held back by questions of practicality, and the fact that present systems offer no networking capability. We propose the development of an entangled photon QC testbed at ORNL to explore implementation issues and to advance the capabilities of this nascent technology. Our approach will add network functionality to QC by using spectrally entangled photons and commercially available wavelength-division multiplexing (WDM) technology to provide quantum communication resources to multiple users simultaneously. In addition, the completed testbed will give ORNL a unique capability for long-term quantum communication technology research and development. With several defense contractors and US agencies having

expressed interest in quantum communication networks, the proposed testbed represents a timely opportunity to highlight ORNL's quantum information expertise and develop an important research asset.

Mission Relevance

Quantum Information Science (QIS) supports DOE's mission of cross-cutting science integration and discovery, particularly advanced computing technologies for progress in clean energy, nuclear security, complex materials, etc. The development of a network for transporting quantum information between distant locations directly addresses the challenge of "overcoming technological barriers to the practical use of quantum information …" issued to DOE in the 2007 American Competitiveness Initiative (ACI). This project also directly benefits other federal agencies with active interest in quantum computing and quantum communication, such as the Department of Homeland Security, Intelligence Advanced Research Projects (IARPA), National Security Agency (NSA), Central Intelligence Agency (CIA), and the Department of Defense Army Research Office (ARO).

Follow-on funding has recently been secured from the Cybersecurity for Energy Delivery Systems (CEDS) program in DOE's Office of Electricity. In addition to continuing development of the prototype LDRD system, the ORNL team is tasked with identifying quantum communication strategies for protecting information on the electric grid.

Results and Accomplishments

We have designed, constructed, and characterized a state-of-the-art source of broadband entangled photons that forms the heart of our QC network. This source is extremely bright (inferred quantum efficiency of 10^{-8}), covers a substantial portion of the telecom C and L bands (1530 nm to 1625 nm), and possesses strong wavelength correlations ($\Delta\lambda = 2$ nm) suitable for use with WDM systems. This source has the capacity for secret bit generation at a total rate of 20 MHz (2 MHz for 10 pairs of users). (The net secret bit rate is expected to be significantly lower due to limitations that commonly affect other network components.)

We have demonstrated the principles of multichannel functionality using commercially available tunable spectral filters. The filter bandwidth (200 GHz) is consistent with conventional WDM channel spacing and provides users with highly correlated photons at selectable wavelengths. Simulations show that cross-talk can be reduced by reducing the pump laser bandwidth. Nonlocal interference (a quantum effect underlying QC) with a visibility exceeding 80% was demonstrated over the telecom C and L bands. Due to non-local dispersion cancellation, the interferometers require minimal stabilization and compensation.

We have designed, fabricated, and tested a photon detection system that is cheaper and performs better than existing detectors for telecom-band photons. By self-differencing signals from a standard InGaAs/InP APD, we obtain 30dB of noise cancellation, detection efficiency up to 25%, and an operation rate of 228MHz. Additionally, our detectors do not require cryogenic cooling. A field-programmable gate array (FPGA) has been programmed to time stamp detected photons and output a stream of detection data for subsequent processing. The in-house development of a detection system not only makes a many-user QKD network more affordable but also enhances all ORNL's efforts in telecom photonics.

We have also developed QITKAT (Quantum Information Toolkit for Application Testing), a software library for testing quantum information protocols. QITKAT can support a variety of signal processing routines specific to QKD, including data acquisition, time synchronization, inter-user communication, and various diagnostic measures. The library currently supports BB84, a point-to-point QKD protocol. QITKAT is built on top of GNU Radio, an open source software-defined radio library.

Information Shared

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05429

DRTI: Data-Integration and Runtime Infrastructures for Discrete Event Execution at Petascale and Beyond

K.S. Perumalla, S.K. Seal, V. Tipparaju, and S.B. Yoginath

Project Description

Discrete event style of execution is a highly natural mode of execution and often a significantly more runtime-efficient framework in many important applications (e.g., agent-based social behaviors, epidemiological models, and Internet simulations). In an unmistakable trend, increasing numbers of discrete event application scenarios are lately being formulated and attempted at unprecedented scale. However, few frameworks or implementations exist to enable effective use of peta-scale or larger computing platforms. Here we propose to design, develop, test, and benchmark an efficient runtime infrastructure that forms the crucial core for parallel discrete event simulation (PDES) at peta and larger scale. Theoretical stability of large-scale discrete event execution will be analyzed and resolved for efficient rollback dynamics. Novel latency-hiding algorithms will be developed and implemented to efficiently incorporate dynamic input. The runtime will be demonstrated with at-scale application scenarios derived from large-scale epidemiological simulations, Internet simulations, supply-chain logistics simulations, and social behavioral simulations. The runtime will form our differentiating solution as the critical core needed in a range of sponsor opportunities for large discrete-event-based solutions.

Mission Relevance

The basic research of this project is aligned with the current needs of DOE and several other federal agencies. Mission relevance with DOE includes efficient design and operation of high-performance computing installations, efficient numerical analysis for scientific applications, and highly detailed simulations of energy-related questions and policies. Mission relevance to other agencies includes designs for efficient cyber infrastructure and security for the Department of Defense (DoD) National Security

Agency and Defense Information Systems Agency (DISA) and the National Science Foundation (NSF). Our research is also relevant to the missions of the National Institutes of Health (NIH) and the Department of Homeland Security (DHS) in efficient epidemiological simulations, and simulations of bio pathways. Our engine and runtime data-integration frameworks are all applicable to many of the applications that span multiple agencies.

Results and Accomplishments

As a result of the first-year effort, we made the first-ever demonstration at-scale execution of non-trivial PDES-based models. In the research community, we have regained the claim to the capability for the *largest* PDES execution (considering non-trivial benchmarks) to date and are working towards the claim to the *fastest* PDES execution, to be achieved simultaneously in conjunction with the *largest* scale. The demonstrated scale in actual models represents some of the largest non-trivial PDES executions published to date (Perumalla 2010; Perumalla and Seal 2010). Two of our publications were selected as best paper finalists in two international conferences (Aaby, Perumalla et al. 2010; Perumalla and Seal 2010).

Accomplishments in the second year included (a) optimizations incorporated into the runtime using the lower-level Portals messaging interface on the Cray XT5 (Jaguar), enabling the claim to the *fastest* PDES execution at scale, (b) novel discrete event simulation synchronization with virtual machines for high-fidelity cyber infrastructure simulations, (c) chairing an international expert panel at ICST SimuTools'11 on "Discrete Event Execution Meets High-End Computing," and (d) documentation of research results as publications in IEEE, ACM, SCS and ICST journals and conferences.

Information Shared

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05550

Computational Biology Toolbox for Ultrascale Computing

I.B. Jouline, B. Rekepalli, A.A. Gorin, and C. Halloy

Project Description

Insufficient capability to translate the exponentially growing genomic data into useful knowledge is the single most pressing grand challenge in biology. The goal of this project is to dramatically improve biological function prediction by building new and improved models for mining genomic data. This goal will be achieved by using the most sensitive data mining tools organized in a robust, massively parallel computational infrastructure. We will port these tools to a Cray XT5 supercomputer and adopt their usage for developing cloud computing, thus enabling mining not only the existing genomic data but also the future data sets that will be larger by orders of magnitude.

There are two types of the project deliverables: (i) a newly developed toolbox containing most useful computational biology software implemented for Cray supercomputers and (ii) a set of new and improved models for biological function prediction that will become available worldwide through major national and international databases. By investing in this project, ORNL will seize the opportunity to become a leader in ultrascale computational biology and will position our team strategically to successfully compete for major funding from the National Institutes of Health (NIH) and DOE.

Mission Relevance

This project aims at establishing ORNL as a world leader in dynamic knowledge discovery based on capabilities for handling diverse genomic data. It will also contribute to developing focused research communities in biology, because the computational biology toolbox developed by the project will be used by a large community of biomedical scientists. This project also addresses the major problems of the DOE (bioenergy) and NIH (human health), because improved biological function prediction is urgently needed to solve these problems.

Results and Accomplishments

BLAST. We optimized the BLAST code. First we installed the BLAST tool on the Kraken supercomputer and profiled the code to understand the I/O. The database broadcasting to all the nodes in the job was optimized and then the I/O was optimized in two phases. First, a buffer was created in which all the input query sequences were stored and a dynamic load balancing algorithm was designed to distribute the work optimally between all the cores of the node. Second, the outputs from each core were put into separate buffer to produce continuity of the results. Then, all buffers were combined and sent to the lustre file system in optimal chunks. This helped us to scale the code to 50,000 cores.

HMMER. We made code changes to HMMER3.0 that achieved a 100× speedup on Kraken when compared to HMMER2.0. We tested an ideally parallel approach with each core working on a different dataset with the entire reference database in its own memory. With this implementation we were able to scale up to only 16,000 cores as the bandwidth saturates with more communications. This implementation was improved by having a dedicated node for I/O, where all the nodes send the results to this node and once the buffer is full the results are then sent to lustre file system in optimal chunks. With this implementation we can scale parallel HMMER3 achieving near linear scaling until 48,000 cores.

MUSCLE. The most popular multiple sequence alignment tool, but it is not a parallel code. The freely downloadable serial version of the code is installed on Kraken and profiled. We used OpenMP to parallelize MUSCLE on signle node, which achieved a ~2X speedup. Since there are no large data

transfers involved with the MUSCLE tool, a ideally parallel distribution wrapper was written in MPI that scales linearly to 48,000 cores on Kraken without major bottlenecks. We also installed and profiled phylogenetic tree building tools on Kraken such as MrBayes and PhyML since the results generated from MUSCLE will be used as inputs to these Phylogenetic tree building tools for further model development on a large scale.

Based on the results of this project, we have submitted a 4 year proposal (requested costs $1,025,000) to the National Science Foundation: "ABI innovation: Improving Biological Function Predicion Using Ultrascale Computing" (Igor B. Jouline, PI, Robert Harrison, co-PI and Bhanu Rekepalli, co-investigator).

Information Shared

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05561

Evaluating the Role of Cloud Computing for Scientific Discovery

R. Gillen and S.S. Vazhkudai

Project Description

Delivering Open Scientific Interfaces to the Cloud for Climate and Biology. We will make available petascale biology and climate datasets through open cloud interfaces and integrate them with all three major cloud providers (Google, Amazon, and Microsoft). Through a partnership with the vendors and the scientific community, we will develop optimum methods to process these datasets with distributed cloud resources. We will further explore open parallel extensions to all three vendors' cloud computing APIs.

Mission Relevance

The DOE has an interest in mid-sized computing through the use of cloud computing. Our project specifically targets this area by conducting initial exploratory work to study the suitability of cloud platforms for high-performance computing applications, data, and workloads. In addition to DOE, the National Science Foundation (NSF) also directs a broad scope of work related to cloud computing, which is very germane to our proposed work.

Results and Accomplishments

In the area of data movement, we evaluated cloud data movement APIs and performed code enhancements to the vendor-supplied storage access libraries. We developed parallelized file transfers, chunked transfers, cloud-local data proxies, adaptive compression, etc. We made minor changes to the vendor-supplied libraries to not only reduce the total amount of bits transferred but also to significantly improve bandwidth utilization when accessing the entire file, thereby reducing overall transfer time. We evaluated the intra-cloud data accesses further by studying transfers from EC2 to data stored in S3 and

compared it against transfers from EC2 to a local distributed file system. Finally, we tested and evaluated the existing Fuse over S3 provider and built a Fuse over Azure provider.

Supporting our goals of publishing data in the cloud, we developed a set of tools that, in conjunction with Walrus (the storage component of Eucalyptus, an open source cloud infrastructure), enables an organization to take any data available to the Walrus server and expose it in situ as an Amazon S3-compatible storage endpoint. Additionally, we published a subset of the US contribution to the CMIP3 climate data set and exposed it as an ODATA service.

In support of additional research into cloud computing at ORNL, we have established two cloud computing test beds so that user groups within ORNL can access these resources for cloud-enabling their applications. Also we built a lightweight framework in support of data-parallelized applications being auto-deployed to the cloud.

In the area of technical applications in the cloud, we developed a technical prototype for computer forensics using a centralized cloud platform as a means of aiding local police departments and ICE officers in the rapid processing of confiscated hard disks to speed the prosecution of child predators. We also developed a patent-pending approach to using cloud primitives to enable massive scaling of memory-resident tree structures such as those utilized within the document clustering tool Piranah (developed by ORNL's computational data analytics group). Finally, a project that spans the cloud storage and HPC application space is a novel approach to utilizing public cloud intrinsics to forward stage and later handle the egress of large data to/from HPC centers. This work is summarized in the published paper "CATCH: A Cloud-based Adaptive Data Transfer Service for HPC."

This project has helped to establish ORNL as a leader in the use of cloud computing for technical workloads. Our team members have been asked to serve on the program committee of several cloud-related workshops and conferences. One of our team members has also been recognized as a Windows Azure "MVP," and ORNL has been invited to participate as a member of the Windows Azure Customer Advisory Board. We have also established a strong relationship with the technical team at Amazon Web Services (AWS) that is manifested by the establishment of an NDA between AWS and ORNL, our invitation to participate in their private beta program, and request to provide feedback on future product directions.

Information Shared

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05630

Scalable and Efficient Infrastructure for Exascale Analysis and Visualization

J. Meredith, S. Ahern, and D. Pugmire

Project Description

Analysis and visualization of the data generated by scientific simulation codes is a key step in enabling science from computation. However, a number of challenges lie along the current hardware and software paths to exascale scientific discovery. First, only advanced parallelism techniques can take full advantage of the unprecedented scale of the coming machines. In addition, as computational improvements outpace those of I/O, more data will be discarded and I/O-heavy analysis will suffer. Furthermore, the limited memory environment, particularly in the context of in situ analysis which can sidestep some I/O limitations, will require efficiency of both algorithms and infrastructure. Finally, advanced simulation codes with complex data models require commensurate data models in analysis tools. However, the de facto standard Visualization Toolkit (VTK), supporting open-source scientific tools such as VisIt and ParaView, has simplistic parallelism, a demonstrated lack of efficiency, and a data model incapable of supporting paradigms used in many simulations. We propose research and development towards a new library, with infrastructure and key algorithms to support advanced parallelism and efficiency, as well as a robust data model and native in situ support needed by the coming generation of exascale hardware and software.

Mission Relevance

This project is relevant to the US Department of Energy (DOE) and other agencies on several levels. First, the path to scientific discovery via exascale supercomputing is fraught with obstacles in terms of massive parallelism, unique hardware environments, and heavy I/O burdens. As visualization and analysis is key to extracting scientific results from simulation, our proposal will investigate solutions to these obstacles in this context. Furthermore, the models and capabilities of DOE simulation codes are surpassing those of current visualization libraries, and we propose an initial investigation into the support infrastructure to address these needs. Other DOE funding calls and workshop reports highlight the importance of increased funding for analysis and visualization systems capable of exploiting the potential of simulations at the extreme scale, and this goal aligns directly with those of our proposal.

Results and Accomplishments

In year 1, we have completed the base design of the data model that will support the use cases that we anticipate during the move to exascale computing. This includes both efficient representation of simulation data and flexibility in the computational model, in order to support a limited memory, heterogeneous environment. Care was taken to include sufficient descriptiveness in the data model to make support of unanticipated uses cases in the future more straightforward. Next we have completed a base implementation of the design in C++ and have created a prototype end-user tool for testing and visualization of results, and several data format readers and writers. Next, we implemented several data operation algorithms, from framework algorithms supporting the new data model to algorithms running on graphics processors with transparent field data transfers. We were able to validate tremendous memory footprint savings in several common visualization operations over traditional VTK-based tools, and we demonstrated large improvements in analysis tasks on real data using our library with a more advanced parallelism model compared to existing tools. We also built a prototype end-user tool using this library which can load the data from these simulations in a traditional post-processing manner, perform a selection of common visualization tasks, rendering the results or exporting them for further analysis.

05653

Ultrascale Algorithms for Verifying Security Properties of Compiled Software

S.J. Prowell, M. Pleszkoch, K. Sayre, J. Horey, and R. Linger

Project Description

We propose to develop a system, deployed on high-performance hardware, to automate the extraction of a catalog of a computer program's behavior. This machine-readable catalog can be manipulated to determine program characteristics or verify behavioral constraints. The ability to rapidly analyze unknown programs to verify security constraints is a fundamental and significant contribution to national security. Only through direct analysis of the compiled program can precise and provable security claims be established. Our fundamental research hypothesis is that it is possible to automatically determine certain binary program characteristics in order to verify that important security constraints are not violated, and that this analysis can be done sufficiently rapidly to enable its use on dynamic or downloaded content.

This project takes advantage of Oak Ridge National Laboratory's (ORNL) leadership capabilities in computational science and will create a unique capability for rapid analysis of software. This capability has wide applicability, including vulnerability discovery for embedded systems (e.g., smart meters), rapid and automated reverse engineering of unknown programs (e.g., PC or HPC binaries), and verification of software for critical infrastructure (e.g., energy grid control software).

Mission Relevance

This effort directly addresses the DOE mission for energy security—specifically it addresses milestone two of the DOE Roadmap to Achieve Energy Delivery Systems Cybersecurity, which calls for "tools for real-time security state monitoring and risk assessment of all energy delivery system architecture levels and across cyber-physical domains commercially available." The effort also directly addresses ORNL's missions in national security and high-performance computing by advancing computational cyber security methods, enabling the rapid assessment of the security properties of software that is an irremovable–and often outsourced–part of our national critical infrastructure.

Results and Accomplishments

A library, PFX, has been developed that enables the deployment of the behavior computation system on high-performance hardware. This library has been specially tailored to the needs of the project, requires minimal modification of existing algorithms to take advantage of parallelism, and supports the specific form of parallelism—branch and bound—exhibited by the critical behavior extraction algorithms.

We applied our behavior computation system to the malware used in the April attack on ORNL and generated information used to provide advice to the incident response team.

Information Shared

Three publications are under way: one on the parallel FX framework, one on the system call trace analysis for malware, and a general behavior computation paper. We expect these to be completed and submitted in the coming month. A publication on using our system's computed behavior has been accepted at the HICSS conference in January.

05665

Distributed Computational Framework for Massive Heterogeneous Data Fusion

J. Horey, T. LaClair, D. Randeniya, C. Liu, and H.-S. Kim

Project Description

We propose to build a distributed computational framework to fuse large-scale, heterogeneous, streaming data sources. Such a framework is needed because current state-of-the-art tools, such as geographic information systems (GIS), do not operate in a parallel manner and do not scale to large datasets. Applications that integrate large volumes of streaming geospatial sensor data, such as Intelligent Transportation Systems (ITS) from the US Department of Transportation's (DOT) IntelliDrive℠ initiative, would clearly benefit from such a framework. Our framework, *SenseReduce*, employs a functional paradigm that integrates streaming sensor data and geospatial datasets to enable developers to write parallel applications with minimal effort. In addition, our system will be the first distributed knowledge discovery framework that enables data fusion algorithms to operate over a variety of geospatial data types and computational substrates.

Mission Relevance

The proliferation of sensing technologies and the increased volume of geospatial data provides unique knowledge discovery opportunities. Potential applications range from scientific (studying climate change) to industrial (discovering regional power grid trends) and urban safety. For example, the DOT Intelligent Transportation Systems program envisions applications integrating real-time data from sensors to improve the safety, mobility, and efficiency of highway transportation. In addition, the DOE Smart Grid initiatives envision sensors and actuators embedded within the electric grid. For both sets of applications, sensor data must be fused rapidly with geospatial data (e.g., roads, line topologies, etc.) to make some set of computational decisions (e.g., change traffic light patterns, re-route power, etc.). Key enabling technologies needed by both sets of applications include a distributed, computational framework to fuse streaming data sources.

Results and Accomplishments

A. SenseReduce

We have made significant progress in the SenseReduce programming interface, architecture, and core datastructures. With respect to the API, users specify two functions: a *map* function that operates over locally partitioned data and a *reduce* function that operates over the sorted output of the *map* functions. The core datastructures are usable and can actively manipulate real-world spatiotemporal data. Versions of the scheduler, data storage, and compute nodes exist that can execute user-defined jobs locally (via multiple threads/processes).

We have implemented the datastructures and architecture as a set of Java modules. The major modules include the following.

- The base computation classes where user-defined computation is specified.

The IntelliDrive℠ Logo is a service mark of the US Department of Transportation.

- Datastructures: vector features (e.g., polygons, etc.) and raster data (e.g., imagery)
- Schedulers: responsible for tasking computation to the available hardware
- Data stores: responsible for storing and accessing the spatiotemporal data
- Compute nodes: responsible for executing the computation

B. Traffic Modeling and Optimization

To validate the SenseReduce platform, we have started development of a distributed traffic simulator. The simulation effort is divided into two different models. The first is based on discrete cellular automata. This model has been implemented and demonstrated in Matlab. We are also investigating a second model based on a continuous agent (i.e., vector features) model. This model replicates agent behavior used by other well-known traffic simulators. We are also incorporating sensors associated with infrastructure and mobile devices into our traffic simulator. To handle unreliable sensor measurements, we have developed a systems-level model of the underlying sensor systems. Currently we have three separate modules implemented in Matlab that identifies possible faults and estimates the probability of faulty sensor readings.

In conjunction with sensor data fusion, we have developed algorithms to predict and control vehicles and infrastructure with the goal of reducing traffic congestion and vehicle fuel. These algorithms analyze the speed of lead vehicles and account for elevation changes along the travel route. We developed a method to efficiently calculate a speed profile for each vehicle, and implemented the method in Matlab.

C. Joint Directed Research and Development (JDRD)

Our LDRD has served as the basis for two University of Tennessee JDRD grants. One with Professor Lee Han (Civil Engineering) funds a PhD student to investigate scalability issues in current traffic simulation tools. Another with Prof. Charles Cao (Computer Science) funds one PhD student and one master's degree student to instrument vehicles with sensor devices, and to investigate the use of sensor data in optimizing driving performance and comfort.

Information Shared

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05749

Hercules: A User-Guided Translation Tool to Facilitate Application Porting to New Peta/Exascale Architectures

O. Hernandez, C. Kartsaklis, W. Joubert, C.-H. Hsu, and R.L. Graham

Project Description

The goal of this project is to help scientists improve the performance of applications on new platforms by building a translation tool to help identify new sources of parallelism, rearrange data layouts, and control the compilation process. The tool, code named HERCULES, will have a user interface to display static analysis results such as interprocedural dependencies and parallel dataflow information, with a transformation menu to perform parallel loop optimizations, memory layout rearrangements, and interprocedural optimizations. It will operate on multiple levels of compiler intermediate representations that translate C/C++/Fortran, Message Passing Interface (MPI), Unified Parallel C, Co-Array Fortran, OpenMP, and Compute Unified Device Architecture (CUDA) programs to object code. In addition, HERCULES will provide reconfigurable cost models to allow the user to guide the optimization process and better quantify the effectiveness of transformations for the target system. We will investigate how to define a scripting language to specify code structures (patterns) and user-directed transformations to apply to the code. This information will be stored in a program repository and may be queried or reused within a single application or across applications. We envision HERCULES working with several production open-source compilers, the primary focus being the Open64 compiler.

Mission Relevance

Leadership-class computers at Department of Energy (DOE) laboratories deploy hundreds of thousands of compute cores with complex hardware to solve mission-critical science problems. Multiple programming models will likely be needed to exploit the power of such systems, making them complex to program. Currently, few code transformation tools exist to help the programmer navigate this complex environment and help the user manage the complexity of adapting their codes to new platforms, minimizing laborious code changes. The HERCULES system automates this process by allowing the programmer to specify code transformation patterns that can be applied repeatedly across a large code base, such as parallelization transformations or data structure changes. The system automates the process of applying transformations by using compiler technology to control the translation process of the codes. It also provides a separation of concerns between the science application and the platform-specific performance optimizations, by abstracting transformations and simplifying the code maintenance work flow.

Results and Accomplishments

We completed the following work during the year of the project. (1) We created an overall design of the tool and implemented an initial version of the transformation system that enables a complete workflow of the tool from pattern matching application code to querying of program analysis and applying source-to-source transformations and/or produce optimized object code. (2) We developed a pattern matching engine and a parser capable of detecting source code patterns using an underlying PROLOG technology that can match code on Department of Energy (DOE) applications [Denovo/3d Sweep, Community Atmosphere Model/Spectral Element (CAM/SE)] and High Performance Linpack (HPL) benchmark. These patterns, transformations, and application facts are stored in a persistent database that can be queried offline (post-translation) or online (during compilation process). (3) We developed a pattern-matching language that can be incrementally applied to existing applications written in C/C++/Fortran/OpenMP/MPI. The language is based on user-level directives with built-in functions and primitives to facilitate the pattern creation. In addition, advanced users of the tool can define patterns

using PROLOG directly or in terms of an object-oriented Application Programming Interface (API) that can generate PROLOG. (4) We implemented different transformations requested by the Oak Ridge Leadership Class Facility applications relevant to Denovo, CAM/SE, and the HPL benchmark. The transformations include loop unrolling, loop reversal, array scalarization (transforming certain array elements to scalars), tiling, user-driven specialization with constant propagation, loop tiling/blocking, insertion of OpenMP parallel regions, and user-driven instrumentation. We also explored other methods to construct patterns, and how to gather analysis to perform inter-procedural transformation including global data structure transformations, that is, array remappings and conversion of data structures of arrays to array of structures.

Information Shared

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05768

A Predictive Analysis Toolbox for Ultrascale Data Exploration

C.T. Symons, S.R. Sukumar, B.H. Park, M. Shankar, R.R. Vatsavai, R.K. Archibald, A.R. Ganguly, and S.J. Prowell

Project Description

The ability to produce ultrascale data far surpasses any current ability to understand it. There is no standard set of techniques or libraries that enables a domain scientist to effectively take advantage of the computational power necessary to analyze data at such scales. This project is relying on a novel, coordinated-learning framework that is specifically designed to take advantage of the availability of incredibly large amounts of data concerning a system under study. The approach is based on state-of-the-art machine learning techniques, and it allows incorporation of domain knowledge in a very simple and effective way, while not presuming the presence of any such knowledge. The core algorithms and application programming interfaces (APIs) of the toolbox are being developed in coordination with two diverse domain experts in an attempt to provide an accessible library that can serve a wide variety of potential users. The end result will be an ORNL-brand, ultrascale-data-analysis toolbox that enables a variety of scientists who are currently stymied by the scale of their data to effectively leverage the power of ultrascale computing platforms for knowledge discovery via predictive analysis.

Mission Relevance

The DOE Office of Science has initiatives for ultrascale computing and scientific discovery that requires high-performance computing. Because large-scale simulation-based approaches have demonstrated the value of high-performance computing to science, there has been less attention paid to the relative lack of extreme-scale analytical routines that are not based on simulation. Such approaches are necessary to support many forms of scientific discovery that are important to DOE and the nation in general. This

toolbox helps address that important gap by supporting discovery of important interactions through an integrated analysis of systems data in the form of extreme-scale, highly interdependent observation data. Since the project is developing new scientific exploratory capabilities for ultrascale datasets, it is directly aligned with some of DOE's core missions. Furthermore, the type of exploratory analysis for complex data supported by the project could provide substantial value to Department of Defense and other agencies that are overwhelmed with complex, interrelated data.

Results and Accomplishments

The main algorithmic core of the approach underlying the toolbox has been fully developed. Early tests demonstrate nearly linear scalability, which we expect to extend to huge scales based on algorithmic analysis. Successful examples of information discovery at moderate scales have been demonstrated, with the real power expected at extreme scales, where the assumptions of the algorithms are most accurate.

As part of the project, preprocessing algorithms and codes to convert relevant data into multiple learning tasks have been developed. The project currently incorporates a large set of learning algorithms that can be wrapped within the overall framework, depending on the characteristics of the data. For example, internal learners can be modified to accommodate data that is sequential (e.g., temporal), partially labeled, etc. Although the parallel nature of the framework itself is the critical aspect in terms of scalability, many of these core learners have been parallelized to enhance scalability even further. Existing open-source libraries have been investigated and leveraged in the development process, as appropriate.

Several domain experts have been consulted in order to formulate significant unsolved analysis problems to which the approach is applicable. As part of this process, preprocessed data has been obtained from several domains including climate, cyber security, sonar tracking, and manufacturing. Analysis has begun in order to demonstrate applicability to multiple problem spaces that deal with large, complexly interacting systems.

The work performed on this project has also resulted in an invention disclosure (Invention Disclosure Number: 201102611. Inventors: Christopher T. Symons, Sreenivas R. Sukumar, and Mallikarjun Shankar).

Information Shared

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05839

Motional Changes in Biomolecular Complexation

J.C. Smith

Project Description

The research is directed at understanding the dynamical changes on complexation in biological systems by combining computer simulation with experiments on the next-generation Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. Inelastic scattering experiments on ligand binding will be interpreted using analytical modeling and normal mode analysis, together with calculations on methyl group dynamical perturbations. Spin echo spectroscopic experiments will be performed on ligand-perturbed slow domain motions and corresponding software developed to interpret the experiments with molecular dynamics.

Mission Relevance

Recent DOE press releases, reports, R&D, and budget priorities indicate that this proposal is well-aligned with DOE's research focus for the next 5 years. The present proposal will begin to address the roadblocks in improvement of our understanding of the use of computer simulation in the analysis neutron scattering with computer simulation. The groundwork covered in the project will place ORNL in an advantageous position to secure funding from DOE, Office of Science (BER, BES, ASCR). DOE program managers are enthusiastic about this field of research.

Results and Accomplishments

In FY 2011 neutron scattering from hydrated lysozyme powder was calculated from molecular dynamics simulations and agreed quantitatively with the experimental data over a large frequency window (1 to 1000 GHz). The analysis showed that the hydration water performs sub-diffusive motion on the *ps* to *ns* timescale. In contrast, protein atoms in the same time window undergo confined motions, which were decomposed into localized diffusion, methyl group rotations, and jumps.

The change of protein vibrations on ligand binding is of functional and thermodynamic importance. In previous work we characterized the vibrational shift on ligand binding using inelastic neutron scattering. Neutron scattering experiments have demonstrated that binding of the cancer drug methotrexate softens the low-frequency vibrations of its target protein, dihydrofolate reductase (DHFR). The low-frequency region contains modes that tend to be strongly delocalized, collective vibrations. The magnitude of the shift indicated that the vibrational change contributes significantly to the total binding free energy. Here, this softening was fully reproduced using atomic detail normal-mode analysis. Decomposition of the vibrational density of states demonstrated that the largest contributions arise from structural elements of DHFR critical to stability and function. Analyzing the polarization of the modes (based on direction and size of atomic displacements) revealed a systematic type of motion characteristic of the modified modes. Mode-projection analysis revealed an increase of the breathing-like character of the affected vibrational modes, consistent with the experimentally observed increased adiabatic compressibility of the protein on complexation.

The increase of the vibrational flexibility observed using incoherent inelastic neutron scattering of DHFR, on binding of the ligand methotrexate, was *quantitatively* reproduced by our normal-mode analysis. In comparison, previous calculations were in only qualitative agreement. The success of our calculations is most likely due to the explicit hydration water taken into account in the NMA. However, the results cannot be generalized to other proteins and ligands since the effect depends on the strength of the

interactions involved. Furthermore, the analysis concentrates on the harmonic component of the dynamics. Anharmonic motions, which become significant for T > 200 K, can be restricted by ligand binding, and this is likely to be at the origin of the flexibility decrease observed by NMR and crystallography on binding small organic ligands to some proteins. The most significant softening of vibrational dynamics on complexation of DHFR with MTX is found in the loops of the protein containing the residues Gly-67, Gly-121, and Ala-145, which have been shown by mutagenesis to be crucial for the enzyme function. We observed the expansion of the dynamic domain boundary away from the binding site on ligand binding, which might be one of the factors causing the softening of the low-frequency modes. The low-frequency modes of the protein contain considerable radial (breathing) character, and these modes are affected by ligand binding. This demonstrates that the system becomes prone to deformation of the structure enabling change of the volume of the molecule, consistent with the adiabatic compressibility of complexed DHFR being higher than that of the holo form. Hence, the presence of breathing modes in globular proteins may make an important intrinsic contribution to protein compressibility.

A solid basis has now been established for the interpretation of inelastic and spin echo spectroscopy from globular protein complexes. This should provide the basis for future successful research proposals.

Information Shared

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06239

Scalable Connections for Diverse Information Stores: Knowledge Efficiencies for National Health Informatics Streamlining

A. Loebl, M. Shankar, W. McNair, E. Begoli, R. Patton, and C. Symons

Project Description

The American healthcare delivery system finds itself under great national scrutiny regarding its cost-to-care ratio. Pressing challenges facing public and private healthcare delivery infrastructures include (a) requirements for large-scale data analytics providing metrics to improve healthcare policy, (b) integration of multiple data sources (from claims to medical encounters) to minimize fraud, waste, and abuse, (c) scalable and flexible system infrastructure for Centers for Medicare and Medicaid (CMS) programs, and (d) stakeholder (beneficiaries, providers, payers, analysts) available services for performance and quality reporting. Here, we pilot a knowledge discovery infrastructure for the CMS instance of the above challenges. We take advantage of recent advances in large-scale data processing in the form of engineering advances pioneered by distributed commodity processing and non-relational (column oriented, document oriented, etc.) storage systems. To these advances, we introduce techniques to represent and connect data in a linked-data middleware—a unique design approach that can address the

adaptability and large-scale analytical requirements. We believe this approach will scale and also accommodate a proliferation of diverse data.

Mission Relevance

Economic security is a vital component of national security and stability. These two areas are keys to DOE and other federal agency priorities. Computational science lends itself not only to providing cycles for addressing the grand challenges of energy, materials, or security, but most important, it is a cornerstone of analyzing and presenting results in a manner that drives growth and operational improvements. Our approach is applicable to national data processing (storage, representation, and analysis) concerns where the ability to exchange, share, mine, and analyze volumes of data is hampered by the volume and location of data sets.

Federal agencies need a national-scale, extensible, real-time dynamic data linkage mechanism enabling local, state, and federal information sharing and dissemination. Providing a normative framework to enable this will significantly streamline agency costs. This need is applicable to energy grid, climate, and natural resource data in as much as it is healthcare.

Results and Accomplishments

We have created a systems blueprint with a layered framework consisting of Visualization, Analytics, and Architecture components that create flexible "verticals" to address CMS requirements.

- Our system architecture design constructs offer flexibility, scalability, and utility (cloud) large-scale computing as needed.
- We have piloted analytical pipelines that demonstrate analysis to expose structure embedded in the ways in which beneficiaries and providers interact for ~10^8 beneficiaries, ~10^6 providers, ~10^9 transactions in 1 year. Anomalous (in size, temporal behavior, and type) structures can expose potential fraud.
- We have piloted exploratory visualizations of national health indicators that reveal unexpected or hidden patterns. Addressing these patterns often leads to CMS policy guidance that can increase system efficiency.

CMS leadership favorably received the ORNL blueprint. A roadmap has been formulated for several vertical follow-on thrusts based on this LDRD with an expectation of strong follow-on funding.

Information Shared

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06240

Signals Solution Center Demonstration on HPC

M.A. Buckner, E.D. Farquhar, R.A. Kerekes, B.H. Park, T.S. Humble, and T.J. Naughton

Project Description

We propose to develop the Signals Solution Center (S2C) to address challenging signal mining problems in support of the Laboratory's Energy Security missions.

Signal mining problems include identifying structure in seemingly random signals, separating a single emitter from a sea of confounders, or identifying salient content in images. These sorts of problems have been identified as priorities in strategic planning documents and conversations with key personnel across major agencies within the US government.

Core ORNL capabilities to be leveraged by the S2C include (1) world-class sensor scientists and researchers; (2) world-class high-performance computing; (3) secure infrastructure and connectivity; and (4) leading-edge signal mining research and development capabilities.

The Learning-from-Signals (LFS) process is key to the S2C. Combined with ORNL's HPC resources, LFS offers ORNL a competitive advantage making the S2C an attractive location for sponsors looking solve their difficult signal mining science and technology challenges.

Mission Relevance

S2C and LFS are relevant to multiple DOE national security missions: Dynamic Spectrum Access (DSA) and secure, robust communications; enhanced wireless network security from specific device identification based on distinct native attributes or RF signatures; detection of unintentional signatures from devices at significant stand-off distances.

A comprehensive list of specific signal mining problems and associated program offices and budgets has been assembled. A quick review suggests that there is over $1billion of funding committed by federal agencies against these challenges.

Results and Accomplishments

The LFS engine code was successfully restructured, ported, parallelized, and tested on Frost. We first restructured the existing MATLAB implementation of the LFS engine to have a modular design, which allows easy reconfiguration and extensibility of the engine without modification to the engine code itself. We then ported the restructured MATLAB code to C++ and implemented a parallel code structure using Message Passing Interface (MPI). The Armadillo C++ Linear Algebra Library, which provides an efficient, optimized wrapper for the Basic Linear Algebra Subprograms (BLAS) and Linear Algebra PACKage (LAPACK) matrix libraries, was used to implement most of the matrix routines in the C++ code. Parallelism was achieved by dividing the test set among the available compute nodes. For every set of candidate model parameters received from the master node, each compute node calculates a set of error values and gradients for its assigned portion of the test. The master node gathers these results from the compute nodes, computes an aggregate error value for each model, and determines the next set of candidate model parameters. The C++ code was compiled and tested on Frost, an SGI Altix ICE cluster with 128 compute nodes. Initial tests using a 400-point, 60-dimensional dataset demonstrated a 90× speedup on 256 compute cores of Frost compared to the multi-threaded MATLAB implementation on a dual quad-core workstation. We expect to achieve even greater scalability with larger datasets. The

success of our HPC implementation will enable us to learn models on datasets of much greater size and complexity (>100,000 data points) and begin to solve more challenging signal mining problems.

Information Shared

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BIOMASS PRODUCTION AND CONVERSION FOR ENERGY AND MATERIALS

05201

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

J.G. Elkins, R. Jain, A.P. Borole, J.R. Mielenz, Z.K. Yang, Y. Yang, and B.H. Davison

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 2, depending on our results.

Mission Relevance

The work proposed here is 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

Progress was made toward expressing the necessary genes to produce fungible fuels (n-butanol) in a carbon monoxide utilizing host, *Rhodospirilum rubrum*. The 1-butanol pathway from *C. acetobutylicum*

was cloned into the broad-host-range vector, pBBR1MCS-5. The pathway consisted of genes for crotonase (*crt*), butyrl-CoA dehydrogenase (*bcd*), electron transfer flavoproteins A/B (*etfAB*), and hydroxybutyrl-CoA dehydrogenase (*hbd*). Quantitative PCR was used to verify transcription of each gene, which showed strong induction at the 5' end of the operon but weak induction of the downstream genes. The recombinant strain was grown in RRNCO medium in serum bottles with CO in the headspace. However, no 1-butanol was detected in samples analyzed by gas chromatography (GC/MS). The genomic GC-content of *C. acetobutylicum* is 30% as compared to 65% for *R. rubrum,* which likely leads to poor heterologous gene expression in these two distantly related organisms. Therefore, the crotonase (crt) gene was codon-optimized and produced in vitro using gene synthesis and cloned into the pBBR1MCS-2 vector. Expression of the synthetic gene yielded greater than a three-fold increase in enzyme activity in the recombinant *R. rubrum* strain. The entire 1- butanol pathway has now been synthesized for optimal codon usage in *R. rubrum*, and enzyme assays for each step in the pathway are in progress. The genes for 1-butanol production will be expressed from a CO inducible promoter that was developed for this project, and an invention disclosure has been filed. Activity of the ferrodoxin dependend- butyrl-CoA dehydrogenase (*bcd*) and electron transfer flavoprotein A/B (*etfAB*) complex was still undetectable in *R. rubrum* in cells grown in the light or dark on CO. Low activity of *bcd/etfAB* has also been observed in other Gram-negative expression hosts as well leading to low butanol yields. Therefore, we synthesized a new operon to replace both the *crt* and *bcd/EtfAB* genes consisting of a crotyonyl-CoA specific trans-enoyl-CoA reductase (Ter) gene from *Treponema denticola*. This alternative gene for enoyl-CoA reductase activity has led to markedly increased yields of n-butanol in other hosts such as *E. coli* and presumably will circumvent the roadblocks encountered with expression of the clostridial pathway in *R. rubrum*. In addition, a metabolic model was used to predict gene knockouts that may increase butanol production. As hypothesized, elimination of poly-beta-hydroxybutyrate (PHB) synthesis was predicted to increase yield; therefore, both alleles for PHB synthase were targeted for deletion.

Information Shared

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05221

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

M. Podar, R. Hettich, M. Keller, D. Myles, and J.C. 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 the 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 the 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, 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 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 the DOE Office of Biological and Environmental Science (BER) Genomic Science Program (formerly Genomics: _GTL) focus area and will be part of future ORNL Scientific Focus Areac 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 the National Science Foundation (NSF) programs, National Aeronautics and Space Administration (NASA)-–Astrobiology, and the National Institutes of Health (NIH) Microbiome program.

Results and Accomplishments

Objective 1. Genome sequencing of *Ignicoccus islandicus* and *I. pacificus*. We completed sequencing of the two genomes and are performing comparative analyses with the *I. hospitalis*.

Detection and isolation of novel nanoarchaea. We have completed analysis of *Nanoarchaea* in numerous terrestrial and marine samples and are preparing a publication. Ongoing efforts are directed towards isolation of novel *Nanoarchaea* in culture and using single-cell-genomics approaches.

Objective 2. Functional genomics of the *Ignicoccus–Nanoarchaeum* interaction. We have completed in-depth proteomic and microarray studies of cultures at various stages in the association. The first analysis has been published, and we are preparing additional publications.

Objective 3. Structural analysis and modeling of the *Ignicoccus–Nanoarchaeum* system. We have performed detailed structural modeling and molecular dynamics simulations of two major proteins identified by proteomics. One of the two proteins, Igni_1226, is particularly important as it forms pores in the outer membrane. Ongoing analyses are directed at understanding its potential role in metabolite exchange with *Nanoarchaeum,* as well as in the overall bioenergetic processes of *Ignicoccus*, and the results will be published as a stand-alone study. Several additional proteins have been cloned for expression and potential structural studies by X-ray and neutron scattering techniques.

Two grants have been funded that used scientific and technological developments achieved in this LDRD and which will allow continuation of these studies:

***From genomes to metabolomes: Understanding mechanisms of symbiosis and cell-cell signaling using the archaeal system* Ignicoccus-Nanoarchaeum**

Funding Agency: DOE-BER
Period: 04/01/11–3/31/14
M. Podar, Principal Investigator. Co-investigators: R. Hettich, ORNL, B. Bothner and V. Cpie, Montana State Univ.
Total request: $1,938,672.00
Total award to M. Podar at University of Tennessee: $632,672.
Total award to R. Hettich, ORNL: $675,000.

Enhancing expertise is archaeal taxonomy: Classical and molecular-based monographic research of the Nanoarchaeota.
Funding Agency: NSF
Period: 09/01/11–08/31/15
PD: A.L. Reysenbach, Portland State University)
Total award to M. Podar (Co-investigator) at University of Tennessee: $ 235,268

Information Shared

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05238

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

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External collaborators: Prof. J. Ghosh (UT-Austin), Prof. V. Kumar (U of Minnesota), Prof. D. Hui (HBCU faculty from Tennessee State University), R. Tetrault (USDA), P. Gowda (USDA), S. Johnson (Global Marketing Insights, Inc.), and B. Dorn (NASA)

Project Description

This project is addressing two key research challenges that are essential to realizing US 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 (1) efficiently monitoring croplands based on spectral, phenological, biogeophysical characteristics by reducing false positives (false changes); (2) drastically reducing the ground-truth data required to build models; (3) easily adapting models to diverse geographic settings with minimal retraining; and (4) automatically recognizing 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 by developing parallel algorithms on shared and distributed memory systems as well as 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 project 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 multitemporal biomass information, including crop types and their conditions. We expect that the 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

Through this research project, we developed several novel and innovative concepts, algorithms, and software prototypes. First, we developed a basic biomass monitoring framework that utilizes MODIS time series data for identifying changes in a continuous manner. The change detection is based on the extension of Gaussian Process (GP) learning. Experimental results have showed that the GP-based technique is not only more accurate than three other well-known approaches, but it is also capable of detecting changes in cropping patterns, which other techniques have failed to detect. However, the GP-based change detection technique is both computationally expensive ($O(n^3)$) and memory bound ($O(n^2)$). To address computational issues, we developed not only efficient techniques ($O(n^2)$) but also parallelized using shared memory (threads), distributed memory (MPI), and hybrid (MPI+threads) programming models. These results were presented at recent NASA conference on intelligent data understanding where it was rated as one of the best papers and recommended to be included in the *Statistical Analysis and Data Mining Journal* special issue. On the change characterization and classification front, we made significant contributions that addressed long-standing problems in the domain. More specifically, the contributions include (i) semi-supervised learning framework that address small sample problems in classification, (ii) adaptive spatial classification framework that addresses spatial heterogeneity and allows large area classification, and (iii) sub-class classification framework that extracts species-level information from aggregate classes. These algorithmic contributions were published by leading conferences and GeoInformatica journal. In addition, we developed techniques to extract phenological indices from the MODIS NDVI data, and compared it with the phenology indices derived from the AmeriFlux data. Experimental results showed a significant correlation (as high as 0.60) between the indices derived from these two different data sources. This study had demonstrated that data-driven methods could be effectively employed to provide realistic estimates of vegetation phenology indices using remote-sensing data. In addition to producing strong publications (more than 20, two best papers), this research has attracted the attention of academic community and as well as federal sponsors. The PI was invited to give talks and participate on various panels, including an NSF workshop (by invitation

only). In addition to feeding into several successful follow-on projects including UV-CDAT funded by DOE BER, the research has garnered funding from NGA for monitoring biomass in Afghanistan. In addition, the PI developed several workshops and tutorials on related topics and organized them with leading conferences, such as SC, IEEE ICDM, ACM SIGSPATIAL, and ACM KDD.

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05256

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

D.J. Weston, Y. Yang, R. Norby, S.D. Wullschleger, and C.W. 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 model plant 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 Solidago and Sphagnum, an important non-model species key to carbon cycling in a high-latitude ecosystem. 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. If successful, we believe that our efforts will contribute to the strategic goals of the DOE Office of Biological and Environmental Research (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

We investigated the consequences of warming on *Arabidopsis*, poplar and soybean using an integrated physiological, biochemical, and functional genomics approach analyzed within a network framework. Our results suggest that soybean has higher rates of photosynthesis under warmer temperature due to changes in the cellular antioxidant system and the expression of HSP17 gene family members. These biochemical mechanisms were regulated by a specific subnetwork.

To gain further insight into the conservation of this network and downstream biochemical events, we exposed the non-model organisms *Solidago* and *Sphagnum* to elevated temperatures. We found many orthologs of this network to be conserved in both sequence and expression. Furthermore, timing of this subnetwork is correlated to warming-induced photosynthetic decline, activity of the antioxidant system, and heat shock protein abundance. Our results indicate that there is a genomic subnetwork conserved among mosses, herbaceous annuals and woody perennials that is correlated to photosynthetic performance and thus carbon gain.

These findings will be useful as we begin to model species susceptibility to climatic change within an ecological context as well as modify bioenergy feedstocks to warm and arid regions. To date, results and research activities enabled by this project have assisted in the successful funding of (1) the Plant Microbe Interaction SFA (PI Doktycz, ORNL), (2) Kbase (PI Arkin, LBNL), (3) a JDRD project (PI Aimee Classen, University of Tennessee, Knoxville), (4) a successful Feedstocks Genomics proposal (PI Victyor Buscov, Michigan Technological University); invited talks and presentations include (5) the UCLA medical genomics group, (6) University of Missouri Integrative Biology Program, (7) iPlant Consortium, (8) Bowling Green State University, (9) the American Society of Plant Biologists, (10) a Gordon Research Conference and (11) one publication in press with two in review.

Information Shared

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05481

Novel Zeolitic Carbon Support for Catalytic Bioethanol Production

D.E. Jiang, S.-H. Chai, M. Kidder, Z. Wu, J.Y. Howe, S.H. Overbury, and S. Dai

Project Description

One of the key challenges in the thermochemical conversion of biomass to ethanol is controlling the catalytic transformation of biomass-derived syngas ($CO + H_2$) to obtain high ethanol selectivity with high CO conversion. The most promising catalysts for conversion of syngas to ethanol are based on Rh. Recently, it has been shown that confinement of the Rh catalyst inside carbon nanotubes greatly enhances yield and selectivity, although the origin of this enhancement is unclear. By understanding and controlling confinement effects, significant advances could be made in ethanol formation and other reactions such as Fischer-Tropsch synthesis and formation of longer chain alcohols. The overarching goal of this project is to understand and control the confinement effects on catalysis by transition-metal nanoclusters confined in porous supports. We will pursue three specific aims. First, how can we achieve and control the confinement where the monodisperse catalytic particles are confined in a well-defined porous environment? Second, how does the confinement by the porosity of the support affect activity and selectivity of the metal nanoclusters to catalytically convert syngas to ethanol? Third, how can we control the catalyst's performance to achieve desirable targets of activity and selectivity of syngas to ethanol? The knowledge generated from this project will help achieve high-yield ethanol formation from syngas and benefit other energy-relevant reactions, thereby attracting applied funding sources such as DOE-EERE Biomass Program and the joint DOE-USDA program on biofuels.

Mission Relevance

Catalysis is core to DOE's missions. The proof-of-principle study of this LDRD project could potentially attract future funding from DOE's highly successful catalysis program. The novel method to prepare the support and the confinement effect by the hybrid support will increase the knowledge base of heterogeneous catalysis for studying other energy-relevant reactions such as Fischer-Tropsch synthesis and formation of longer chain alcohols. Therefore, this project will position us to attract new funding from DOE such as the EERE office's Biomass Program. For example, President Barack Obama announced on May 5 that DOE plans to invest $786.5 million in Recovery Act Funds in biofuels, including $130 million in biofuels research and development. Moreover, several funding agencies have current and future programs to fund biofuels research. For example, USDA has a joint program with DOE to fund biofuels research (Biomass Research and Development Initiative, DE-PS36-09GO99016, Issued on 1/30/2009, Program funding: $25 million). The catalyst developed in this project is promising for the thermochemical route of converting biomass-derived syngas to ethanol, thereby benefiting this program.

Results and Accomplishments

In the past fiscal year (FY 2011), we investigated for the first time the graphitic mesoporous carbon (GMC), synthesized via a facile soft-templating route developed recently by our group, as the support of promoted Rh catalysts for ethanol production from synthesis gas ($CO + H_2$) conducted on a high-pressure flow reactor. A significant inhibition on the formation of undesired CH_4 and light hydrocarbons is observed over the GMC-supported catalyst in comparison to the conventional SiO_2-supported counterpart, while the formation rate of desired C_2H_5OH is maintained. The reaction-induced growth of active Rh nanoparticles over GMC is found much slower than that over SiO_2. In addition, GMC as support shows higher catalytic activity for C_2H_5OH formation than other carbon materials such as amorphous mesoporous carbon and non-porous carbon black. The preferable performance of GMC could be associated with unique electron structure of graphitic carbon providing a specific metal-support

interaction, as well as its featured nanochannels offering a confinement environment for metal particles. The surface modification of GMC by wet oxidation with HNO_3 can further enhance the catalytic activity for C_2H_5OH formation. Our discovery suggests a promising application of GMC as the support of nanostructured metals and metal oxides for not only CO hydrogenation to C_2H_5OH but also other catalytic reactions such as hydrodeoxygenation and hydrogenolysis of biomass-derived feedstock (e.g., polyols, cellulose, lignocellulose) to produce liquid fuels.

Information Shared

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05548

Catalytic Conversion of Lignin Feedstocks for Bioenergy Applications

W. Wang, T.J. Phelps, A.P. Borole, T.J. Tschaplinski, J.-W. Moon, and B. Gu

Project Description

Annual production of 60 billion gallons of biofuels results in the generation of about 200 billion kilograms of wet lignin residue of low value (~$0.01/kg), which mostly goes to boiler. Value from lignitic waste can benefit from metal-based nanoparticle catalytic depolymerization. We investigated photocatalytic approaches to transform lignin to value-added fuel or feedstocks. Our hypothesis was that lignin can provide value-added chemicals through photochemically catalyzed depolymerization using structurally modified TiO_2 nanocatalysts under visible light. While conventional methodologies use TiO_2 and UV light for complete oxidation of organics, novel transition metal–doped nanocatalysts with lowered bandgap energy were used for enhanced lignin conversion under sunlight. To further advance catalysis of lignin for value-added components, we also investigated mechanisms to reduce or displace light-mediated catalytic activation with alternatives such as electrochemical means to degrade lignin. Compared to conventional thermochemical processes, knowledge gained through this project from both experiments and mechanistic studies is expected to yield an effective pathway to convert lignin into value-added products at lower temperature, pressure, and lower energy input.

Mission Relevance

The goal of this project is to develop an efficient photocatalytic pathway to breakdown low-value biopolymers such as lignin into value-added chemicals or feedstocks and to obtain a fundamental understanding of the mechanisms of the photo-catalytic depolymerization processes. The project is directly relevant to the Biomass Program of the DOE Office of Energy Efficiency and Renewable Energy (EERE) Biomass Program aimed at transforming the nation's renewable and abundant biomass resources into cost-competitive, high-performance biofuels, bioproducts, and biopower. The research is also expected to benefit in the general area of renewable energy for developing new technologies for biomass (e.g., plant-derived material) conversion into valuable chemicals and fuels.

Results and Accomplishments

During the second year of this project with limited support ($112K), we have made progresses in the following two areas.

1. Refine TiO_2-based nanocatalysts to enhance photocatalytic efficiency
We have screened commercially available TiO_2 catalysts from different sources including Degussa P-25 TiO_2, Nanotek TiO_2, and Sigma-Aldrich products and compared their photocatalytic efficiencies with the synthesized TiO_2 with varying structures (rutile, anatase, and amorphous) and morphologies (nanoparticles, nanorods, nanotubes, and nanowires). However, results indicate that none of these pure TiO_2 catalysts could photodegradate lignin biopolymers under visible light irradiation. We thus developed methods to synthesize sutructurally modified TiO_2 nanoparticles with lowered band-gap energy and demonstrated photocatalytic capability of the TiO_2 catalysts under visible light. To further enhance the catalytic efficiency under visible light, we fabricated a series of TiO_2-based thin film catalysts and systematically studied correlations between catalyst structures and their photocatalytic responses.

We have successfully fabricated new TiO_2 nanostructural films through an anodization process in a mixture of dimethyl suloxide (DMSO) and HF electrolyte solution followed by annealing at different temperatures. A method was also developed to evaluate their photocatalytic responses by direct photocurrent measurements at varying irradiation wavelengths. The crystal structures and optical properties of these TiO_2 films were characterized by The UV-VIS-NIR reflectance spectroscopy, X-ray diffraction (XRD) and Raman spectroscopy. The results reveal that the color changes of the TiO_2 films result from visible light absorption at different wavelengths. The nanostructured TiO_2 films exhibit high photocurrent response under visible light, which is validated by the photo-degradation of organic dye compounds. To our knowledge, this is the first to demonstrate that a controlled fabrication and annealing process can be used to fabricate structured TiO_2 films with varying light absorption characteristics and photocurrent responses. The films show promise to be used for photocatalysis processes, including biopolymer lignin degradation, water splitting, and solar cell applications, etc.

2. Determine photocatalytic reactions and lignin degradation products
We have studied the photodegradation reaction of lignin (molecular weight ~ 60,000) in aqueous solution. It was observed that the water-soluble lignin could be photo-depolymerized in the presence of Cr-doped or Cr, N-codoped nanoparticle catalysts under visible light at depolymerization rate of about 0.1 g(lignin)/L/hr/g(catalyst). With the thin TiO_2 film catalysts, higher depolymerization rate was observed at 0.5 g(lignin)/L/hr/m^2(catalyst). It is the first time to demonstrate that lignin biopolymers could be depolymerized under visible light irradiation, although the depolymerization rate is still low for commercialization. UV-visible spectroscopic analysis showed formation of some new compounds in depolymerized lignin products, implying that lignin is not completed degraded to CO_2. Fourier transform infrared spectroscopy (FTIR) analysis revealed existence of some new aromatic structures in the end products. Gas chromatography–mass spectrometry (GC-MS) analysis confirmed that the depolymerized lignin products contain a series of small molecular fragments with molecular weight less than 200. These results demonstrate that lignin biopolymers can be converted to small molecules for value-added chemicals and fuel additives. This research opens up a new route for conversion of low-value lignin biopolymers to value-added monomers at a low energy input (e.g., under solar light).

Information Shared

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05551

Neutron Imaging of Fluids within Plant-Soil-Groundwater Systems

H.Z. Bilheux, E. Perfect, J. Horita, J. Warren, M. Kang, C. Cheng, S. Voisin, and K. Willis

Project Description

This project develops a collaborative science program to investigate and model the phase structure and flow dynamics of fluids (water, brines, air, CO_2) within plants, soils, and rocks using noninvasive, nondestructive neutron imaging techniques. The theoretical treatment of fluids in porous media has improved substantially over the last several decades; however, model validation using time-resolved (seconds to minutes), high-resolution (tens of microns) measurements of fluid distributions in heterogeneous natural systems has been a major obstacle. Neutron imaging provides high sensitivity to light elements in fluids (e.g., hydrogen) and deep penetration into plants and earth materials. The scientific objectives of this project are to (1) develop quantitative imaging techniques to accurately measure 3D phase structures and 2D fluid flow in porous media, (2) test and refine imaging/modeling capabilities using homogenous model systems, and (3) apply imaging/modeling capabilities to identify fluid pathways, rates of flow, and interactions between porous media, fluids, and plants under dynamic and complex environmental drivers.

Mission Relevance

Utilizing the High Flux Isotope Reactor (HFIR) R&D Cold Guide 1 (CG-1) and the National Institute of Standards and Technology (NIST) BT-2 beamlines, we have developed in situ measurement to investigate soil-plant-atmosphere water exchange dynamics, water retention, unsaturated flow and solute transport in the vadose zone and multi-phase flow and transport in groundwater systems.

Results and Accomplishments

To address several key questions regarding the distributions and dynamic flow of fluids (air, CO_2, water, brines) within plant–soil–groundwater systems, using 2D and 3D neutron imaging techniques, we have identified three main tasks for our project.

Measuring and quantifying the distribution of fluids in porous media evaluating water transport limitations in soil-plant systems assessment of analytical and numerical models for predicting fluid flow. We have made significant progress on many aspects of our project over the past 9–10 months and met our deliverables for the first year as summarized here. Measuring and quantifying the distribution of fluids in porous media. Typical 2D neutron images contain over 4 million pixels (2048 × 2048). A 3D reconstructed data set, in turn, usually consists of hundreds of 2D images, depending on the rotational increment selected (usually 0.5° or better). The boundary of a sample within a container is located in the image, and the thickness of water is calculated on a pixel-by-pixel basis using the Beer-Lambert equation: $I = I0 \exp(-\mu \cdot \Delta x)$, where I is the transmitted beam intensity, I0 is the incident beam intensity, μ is the attenuation coefficient, and Δx is the thickness of the sample. Two sets of very similar experiments were conducted at the imaging facility and HFIR CG-1D development beamline for imaging and quantifying the amount and distribution of water in a soil column as a function of water potential. The NIST BT-2 is at the only world-class neutron imaging facility in the United States, whereas the newly commissioned HFIR CG-1D instrument is a development beamline that is not designed for imaging measurements. Nevertheless, CG-1D has been successfully used for this Director's R&D Fund–Neutron Sciences project. Comparative experiments at the two imaging facilities have been performed. Flint #13 sand and Hanford soil were packed inside an aluminum cylinder with a 2.7 cm OD and initially saturated with water. Various water potentials (ψ) were applied to the bottom of the column using the hanging water column, and radiography (2D) images were taken at each equilibrium state during drying and wetting processes

with a 60 s exposure time. Three-dimensional images with a rotational increment of 0.25° were also acquired at about half way in the drying and wetting stages. The 2D images of the soil column using NIST BT-2 illustrate water movement into the soil during the wetting process. The average water content of Flint #13 sand (4 cm height) at each equilibrium state during the drying and wetting cycles was measured by two methods: (1) volumetric measurements from the hanging water column and (2) integration of pixel-based water contents using neutron imaging data. The two methods yielded very similar average water retention curves. Similar measurements were performed at HFIR CG-1, using two different samples, Hanford and Flint, respectively.

Evaluating water transport limitations in soil–plant systems. Switchgrass seeds were grown in pure silica sand within aluminum cylinders and subjected to low moisture conditions. Water was applied to the young seedlings through an injection port at the base of roots. A series of neutron images were taken every 2 min at HFIR CG-1D (exposure time was 120 s). After 18 min, there was little detectable change in the water content of the roots, albeit the plants were exposed to low light conditions which likely limited their uptake and transport of the injected water. Further work has utilized both D_2O and H_2O to enhance image contrast, addition of illumination treatments to enhance water flux, thin rectangular containers to improve root display, and longer intervals to track water flux. Maize seeds were germinated in silica sand and watered with D_2O. After several weeks, 9 mL of water was injected into the bottom of the container and water distribution was tracked through time. The analysis reveals areas of increased moisture (large deep root, root tips) and decreased moisture (darker shallow roots) that establish the utility of this technique to determine water transport limitations in situ, specifically dynamics of water content surrounding root tissue. The relative soil–root hydration surrounding a growing root can reveal rhizosphere hydration at 80 mm resolution through time, which will be assessed during periods of drying to determine loss of conductivity. Our 2D/3D neutron imaging data for water in roots and soil clearly demonstrate the potential of the technique for tracing the flow of water to roots and quantifying the spatial distribution of water in partially saturated soil. Our future research will focus on investigating (1) differences in point water retention curves estimated from conventional hanging water column experiments and those measured directly by neutron imaging; (2) comparison of forward numerical simulations with direct neutron-based measurements of water distribution; (3) reduction in hydraulic conductance of rhizosphere as soil dries under undisturbed conditions; and (4) fine-scale, 3D geometry of air–water interfaces using neutron tomography.

Assessment of analytical and numerical models for predicting fluid flow. We have extracted point water retention functions for Flint #13 sand by constructing the drying curve on a pixel-by-pixel basis and then averaging row-by-row across the cylinder. The range in point functions obtained from different heights in the column is quite small as expected for a relatively homogenous material like Flint sand. We are now in the process of modeling the average curves using TRUECELL to analytically predict the point function, which can be compared with the observed point functions obtained by neutron imaging. Inverse numerical modeling of the 2D water distributions using HYDRUS 2D is also under way. The degree to which the observed and predicted functions agree with each other can provide an objective evaluation of the assumptions inherent within the different models.

05557

Decision Support for Secure and Sustainable Bioenergy System

P. Leiby, R.U. Martinez, G. Oladosu, N. Thomas, C. Liu, and E. Webb

Project Description

Biofuels are hoped to advance environmental goals, improve energy security, and provide economic and social benefits in a sustainable manner. However, biofuels are facing strong challenges on grounds of potential land and water degradation, CO_2 emissions, and shocks to food supply and food security. It is now understood that the particular configuration of practices, processes, and technologies used in the biofuels system will strongly influence emissions, impacts, and the degree to which sustainability goals are attained. While it is not yet fully understood, the energy security component of sustainability also depends on the choice of bioenergy methods and technologies. Energy security depends on the ability to avoid, diminish, or adjust to shocks to the supply system and price. The comprehensive understanding of this aspect of security and how it relates to technologies used, infrastructure, and practice has not yet been systematically researched and modeled for bioenergy, or any other energy technologies. This project moves proactively to address that major research and analytical gap by formulating and developing a model for assessing risk, variability, vulnerability, and resilience in the biofuels system, and the implications for sustainability, with a particular focus on energy security. The resulting product will respond to the opportunity to create what could eventually become an open and accepted standard for bioenergy security analysis.

Mission Relevance

Sustainability and energy security in particular are key objectives of the US energy system. There are no known studies or systems analysis models addressing economic and energy security analysis for bioenergy. Formal systems analysis tools to measure and ensure the sustainability of bioenergy systems are of considerable relevance to the missions of the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE) and other DOE offices, the US Department of Agriculture (USDA), the Environmental Protection Agency (EPA) Office of Transportation and Air Quality (OTAQ), and other offices and to the Department of Transportation (DOT) and the Department of Defense (DOD) for biofuels. Basic energy security estimates have recently been incorporated in rulemakings on fuel economy (DOT) and renewable fuels and climate (EPA). The demand for more rigorous, defensible scientific assessments will necessarily grow as improved methods are developed and tools are available.

Results and Accomplishments

Model Development Progress The project established a rigorous quantitative framework for bioenergy sustainability assessment. After surveying related models and literature, the Decision Support (model) framework was designed, formally specified, and documented. The model implementation approach combines a dual long- and short-run perspective. A dynamic optimization of long-run biofuel (and petroleum fuel) system design with respect to costs is used to select long-lived infrastructure (biorefineries, retail stations, vehicles, etc.) annually through 2030. This is followed by short-run simulations of intra-year variations subject to important sources of volatility (e.g., droughts, floods, crop yields, and oil market shocks).

The current version of the long-run, nonlinear dynamic model depicts three US regions (Census Division 3, Census Division 4 and rest of the country), four feedstocks (corn, stover, switchgrass, and forest residues), and two possible logistics designs with a different number and sequences of operations in the feedstock's path from farm to biorefinery, enabling a detailed analysis of logistics related to feedstock transportation, preprocessing, and storage. Five biorefinery types are modeled representing different

process types (dry milling, biochemical conversion, thermochemical conversion) and degrees of feedstock flexibility. The model acknowledges the trade-off between biorefinery capital costs and transportation costs, which matters in choosing biorefinery size. It also keeps track of biorefinery vintage to account for slowly adjusting capital stock and the change in drawing radius that results from changes in feedstock density over time.

Grain and cellulosic ethanol shipments between and within regions connect biorefinery output to petroleum terminals where ethanol is stored (short term or long term) and blended with gasoline to produce E10 or E85 blends. Gasoline supply curves were generated through simulations with the AEO2011 Preliminary version of NEMS. Permanent shocks to light-duty vehicle travel demand ranging from –25% to +25% were simulated in increments/decrements of 5% relative to the baseline. The evolution of E85 retail infrastructure and its associated costs are evaluated in the model. E85 throughput increases can be achieved by increasing the number of retail stations offering E85, increasing the number of pumps offering E85 in stations that carry this blend or increasing the utilization factor at existing E85 pumps. Finally, a multinomial logit framework is used to model the choice between E10 and E85 consumption by flexible fuel vehicles (FFVs). As the price of gasoline and E10 increases relative to that of E85, sharing elasticities describe how the FFVs substitute E85 for E10. In turn, total fuel demand is also elastic for both conventional gasoline vehicles and FFVs. The objective function represents the net social surplus from the light-duty vehicle fuel market.

Coding/implementation is done with GAMS for optimization and Python for short-run simulation and linking utilities. Integration methods translate Polysys data to feedstock supply curves at flexible levels of aggregation. A separate GAMS subroutine solves for the optimal biorefinery sizes based on POLYSYS feedstock density information and transportation and capital cost data. Biomass Logistics Model (BLM) data are utilized for feedstock logistics representation and costs. Collaboration with the Hilliard LDRD project team will generate spatially derived biorefinery siting and transportation costs. HyTrans/PHEV code modules have been adapted to represent the fuel choice decision by FFVs and can be extended for evolution. The Knowledge Development Framework will be utilized for data archiving and result warehousing. An initial Web-based Input/Output module was developed for visual display of data and results.

Preliminary model tests highlight the value of biorefinery flexibility, and the importance of the market for coproducts, in promoting the economic and energy security of biofuels. Working and speculative stocks for biomass and ethanol are also key buffers that enhance fuel system resilience to short-term shocks and allow responsiveness to longer-term price signals.

The predominant conversion technology chosen in each region depends on its predominant feedstock. Flexible thermochemical processes appear as the most valuable in a large portion of the country, despite their capital cost being the highest. In part, this is due to higher yields obtained through that process for forest residues, which is the dominant cellulosic feedstock in that region at the beginning of the planning period. Moreover, thermochemical processes are able to switch across feedstocks as available volumes of agricultural residues and perennial grasses increase.

The overall system costs associated with the conventional and pioneer logistic designs are very close, even though they imply starkly different industry configurations. Migrating from a conventional design, characterized by transportation of bales to local biorefineries, to a pioneer design in which feedstock preprocessing creates a more homogeneous, flowable format which can be transported further and stored longer results in an increase in preprocessing and storage costs that offsets the savings in transportation and unit capital costs. The pioneer design requires enormous biorefineries to be successful (20 million dry tons/year for some feedstock-process-region combinations). The economic and sustainability trade-offs associated with each of those logistic approaches need to be further refined.

Refurbishing underutilized gasoline retail infrastructure is a much cheaper alternative to increase E85 availability than building new underground storage tanks and dispensers. However, retail capacity is not straightforward to define or measure and little data are available. The reference case of the long-run model provides an upper bound to the cost of building enough E85 capacity into the system, as it assumes that all capacity additions are new capital. The capital cost per gallon of E85 is large in the first few years, due to low utilization factors, but it stabilizes at approximately $0.1/gal during the second half of the planning horizon. Increasing E85 retail availability is one of two vital components (along with FFVs) to expand the size of the domestic ethanol market beyond the current blend wall. This modeling framework provides insights about the cost and benefits of different approaches to create a market that can absorb the biofuel production levels projected in the RFS-2.

Applications will allow the testing of alternative biofuel types (e.g., drop-in biofuels), technologies, and pathways (e.g., rail versus pipeline-based ethanol distribution) and alternative configurations of the biofuels system and thus provide measures of energy, economic, and environmental sustainability. Simulating short-term shocks to oil or biomass supply with and without each of the flexibility elements included in this decision support system (e.g., inventories, multifeedstock biorefineries, number of FFVs) will facilitate cost-benefit analysis and inform decisions about the priority with which each of those elements should be treated.

BRDI Grant: ORNL has been awarded a BRDI grant ($731,000 for FY 2011 to FY 2015), in partnership with seed developer CERES and chemical company Exelus, to apply this modeling framework to investigate the economic and environmental sustainability of a particular biofuel pathway characterized by improved yield, drought-resistant seed varieties of miscanthus developed by CERES and by a scalable thermochemical conversion process introduced by Exelus, which would produce drop-in biofuel rather than ethanol.

Expected DOE/OBP funding: Initial funding of $200K is anticipated in FY 2012 to begin utilization of this developed capability for "Biofuels National Strategic Benefits Analysis."

Information Shared

Publication: Two conference papers have been submitted as a result of this work. First, "Modeling Energy Security and Economic Sustainability Issues of the U.S. Biofuel Industry" will be presented at the 30th International Association for Energy Economics conference in October 2011. Second, "Over the Blend Wall: E85 Retailing Costs and Constraints" has been submitted for the 2012 TRB National conference and is in review for publication in the Transportation Research Record. A presentation, "Integrating Biofuels Supply-Demand Chain Modeling at Local and National Levels for Strategic Analysis" will be made summarizing the project at the Biofuels Supply Chain Workshop at NREL on Sept. 21, 2011, in Golden Colorado.

05594

Direct Catalytic Conversion of Ethanol to Hydrocarbons—A First-Principles Theoretical and Experimental Study

K.N. Chaitanya, B.H. Davison, and J.R. Mielenz

Project Description

The goal of this project is to explore direct catalytic conversion of ethanol to hydrocarbons for use as transportation fuel and as raw materials for the chemical industry. Our preliminary studies indicate that dilute ethanol streams can be catalytically converted to olefins. Guided by theoretical studies, we propose to develop catalysts that can selectively convert dilute aqueous ethanol streams and fermentation streams to hydrocarbons at low temperatures and pressure. The results of this project will lead to substantial intellectual property and publications that will establish the expertise of ORNL in the conversion of ethanol and other products such as bio-butanol to hydrocarbons. The results of this research will enable us to respond to the anticipated calls from DOE-OBP (Office of Biomass Program), DOD, and ARPA-E. Further investigation and optimization of catalytic process and process development for commercialization of technology will be carried out under follow-on funding from these offices.

Mission Relevance

The results of this project will demonstrate that it is possible to convert dilute ethanol streams to C2+ hydrocarbons. This work is very well aligned with the missions of DOE-OBP. DOD and ARPA-E offices are also interested in this topic. A successful demonstration of catalytic process to convert ethanol streams to C2+ hydrocarbons will enable us to work with program managers to secure funding for the optimization of the catalytic process that employs fermentation streams to produce C2+ hydrocarbon streams that can be used as renewable chemical feedstock and can also be mixed with fuel (diesel, gasoline, or JP-*) in any ratio for transportation or power generation.

Results and Accomplishments

We have successfully demonstrated that the dilute aqueous ethanol stream containing 5–10% ethanol can be converted to hydrocarbons over zeolite catalysts at 400C at LHSV (Liquid Hourly Space Velocity) of 12.5/h (temperature and LHSV not optimized) at atmospheric pressure. The product contains a distribution of aliphatic and aromatic hydrocarbons, and excess water does not appear to have an impact on hydrocarbon distribution but choice of catalyst can selectively favor aromatics over aliphatic hydrocarbons in the product stream. The ethanol conversion is complete and there is very little, if any, ethylene in the product stream. This observation and the presence of even and odd number carbon-containing hydrocarbons in the product stream suggest that ethanol conversion does not necessarily proceed via ethylene formation and its upgrading. Instead, the ethanol conversion might proceed via alkoxy intermediates as seen in methanol conversion to gasoline.

In our efforts to build a scientific basis for mechanistic understanding, we have undertaken DFT studies of zeolites and found that S1 and S2 type structure are indeed lowest energy structures where M2+ counters two skeletal aluminum atoms. We will initiate mechanistic studies of ethanol conversion on S2 type structure in the next fiscal year.

Information Shared

Invention Disclosure 2010-02414, DOE S-115,462, "Catalytic Conversion of Bioethanol to Hydrocarbons," Provisional Patent Application has been filed.

05641

Advanced Bioprocessing for Sustainable Biorefinery Technology Development

A.P. Borole, D. Pelletier, J.R. Mielenz, J.G. Elkins, A. Guss, and B.H. Davison

Project Description

Efficient production of fungible fuels and future bioproducts from mature biorefinery technologies will combine multiple biochemical and thermo-chemical processes. One such hybrid process includes biomass gasification to syngas, followed by a fermentative step to produce fungible fuels. Many limitations currently plague syngas transformation including mass transfer, biocatalyst issues and product recovery. We are proposing a novel system to transform production of fuels from syngas. This includes two components: Bioreactor development and pathway development. A bioreactor capable of high rates of mass transfer and conversion is described. A new and efficient pathway for incorporation of CO into fungible fuels via intermediate fermentation products is proposed. The performance of this bioreactor is expected to be significantly better than existing designs and will revolutionize the technology for conversion of syngas from biomass, which can be one of the most abundant, easily produced, and cheap energy source available today.

Mission Relevance

This LDRD seeks to develop solutions to two most pressing issues related to syngas conversion to biofuels and bioproducts. Demonstration of effective utilization of carbon monoxide can result in a major step forward in hybrid biochemical-thermochemical biorefinery process development. The reactor can potentially be used with other biocatalysts currently being used for ethanol/butanol production. The second component of this work, that is, pathway development, opens doors to higher throughput and increased rates of conversion for fuels and chemicals production. Potential sponsors for follow-on funding include ARPA-E (which recently had a solicitation for breakthrough concepts of this nature), DOE-USDA Biomass R&D Initiative (which is now seeking innovative integrated projects), EERE, as well as chemical companies like DuPont who are moving into the fuels market (DDCE JV). The results will be a drop-in fuel that meets the current infrastructure and vehicle requirements in this country.

Results and Accomplishments

- Assembled pathway genes into a 2 gene operon and demonstrated expression of both gene products from this construct.
- Biofuel intermediate production was demonstrated using extract obtained from the engineered clone.
- Control of CO conversion and microbial growth on key experimental parameters was also demonstrated.

Milestone status:

- Month 10. Demonstration of proof-of-principle linking CO conversion to experimental parameters (completed, 2 months in advance)
- Month 12. Expression of biosynthetic pathway (completed, 4 months in advance)

Information Shared

Patents

Bioreactor for syngas bioconversion, submitted 9/21/2011.

Biosynthetic pathway for generation of intermediates from pathway metabolites, invention disclosure in preparation.

Manuscripts in preparation

"A novel pathway for biofuel intermediates via heterologous expression of dehydrogenase," to be submitted to *Appl. Environ. Microbiol* (January 2012)

"Growth of *R. rubrum* on carbon monoxide under controlled conditions," to be submitted to *Biotechnol. & Bioeng* (February 2012)

Manuscript in review

"Electro-Active Biofilms: Current Status and Research Needs," Borole, AP; Reguera, G; Ringeisen, B; Wang, Z; Hong, BH; and Feng, A; review paper submitted to *Energy and Environmental Science*

05663

Nanoporous Inorganic Membranes for Selective Separations in High-Temperature Flow-through Recycle Pretreatment of Lignocellulosic Biomass

R.R Bhave

Project Description

We propose to investigate a new concept for pretreating cellulosic biomass to make it amenable to bioconversion. Flow-through Recycle (FTR) pretreatment will offer radical reductions in the cost of overcoming the recalcitrance of cellulosic biomass, the major technical obstacle to cost-effective production of fuels and chemicals from these feedstocks, while also providing a unique approach to biomass fractionation for value-added co-products. We propose to test FTR pretreatment on a variety of feedstocks, generating solid and liquid fractions that will be characterized with respect to composition and fermentability. Nanoporous inorganic membranes with pore diameters in the range of 1 to 10 nm will be evaluated to determine the separation performance on solubilized fractions (lignin, sugars, and protein) at pretreatment conditions including temperatures up to 250˚C and operating pressures up to 550 psi. Successful demonstration of FTR pretreatment would enhance ORNL leadership in materials and separation technologies in what has emerged as a strategic need for this country—biomass-derived fuels and chemicals.

Mission Relevance

Separations are one of the key focus areas of DOE-EERE/ITP. Our novel pretreatment research initiative in lignocellulosic biomass processing using membranes can reduce the cost of overcoming biomass recalcitrance and 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 programs resulting from this research that will focus on development of novel approaches in separation and purification to increase the bioconversion yield to ethanol and co-products.

Results and Accomplishments

We performed comprehensive evaluations of poplar and bagasse hydrolyzates prepared by high-temperature pretreatment process at temperatures in the range of 180–220°C. Glucan recovery of >95% was achieved for both poplar and bagasse feedstocks. Xylan recovery was >85% for all the conditions. Hydrolyzate characterization using GC-MS showed the major constituents as glucose, xylose, arabinose, syringaldehyde, phenolics and sinapyl alcohol. Nanoporous membranes were fabricated and evaluated for carbohydrate retention. These membranes showed >98% carbohydrate retention for both poplar and bagasse samples with reasonable flux (~25 liter/hr-m^2). Cleaning protocols were established for the efficient regeneration of fouled membranes. Flow-through pretreated solids reactivity was found to be 7 to 22% higher than batch pretreatment.

Information Shared

There are no publications for FY 2011 but a provisional patent application for IDSA#2406 is in process to file by October 31, 2011.

05801

Unraveling the Molecular and Biochemical Basis of Crassulacean Acid Metabolism (CAM) in Agave for Sustainable Biofuel Production

X. Yang, D.J. Weston, S.D. Wullschleger, and T.J. Tschaplinski

Project Description

As an emerging biofuel crop, *Agave* has high cellulose and sugar contents, along with high biomass yield. More importantly, it is one of the most water-use-efficient plants in the world due to its crassulacean acid metabolism (CAM). The goal of this project is to establish CAM expertise at ORNL and characterize genes regulating CAM physiology. CAM has four phases: phase I, CO_2 fixation catalyzed by phosphoenolpyruvate carboxylase (PEPC), and accumulation of malate at night with the stomata open; phase II, CO_2 fixation shifted from PEPC fixation to Rubisco fixation after dawn; phase III, Rubisco refixation of CO_2 released from malate decarboxylation with the stomata closed in the late morning; and phase IV, direct CO_2 fixation by Rubisco with limited stomatal opening in the late afternoon. Two dimensional aspects (diurnal 24 hour time course and developmental difference in CAM between young and mature leaves) will be explored using a systems biology approach integrating physiology, genomics, metabolomics, and computational biology. This research will discover the transcriptional and metabolic networks driving the four CAM phases, set the stage for genetic improvement of *Agave* to increase the magnitude of CAM expression, and consequently enhance biomass production.

Mission Relevance

Biofuel crops are currently envisioned to be generally planted on agricultural land. Yet for many locations around the world, marginal lands represent a valuable resource that could prove to be a viable option. Crops will need to be tailored to such water-limited and degraded regions, as current biomass production systems using C3 and C4 plants are poorly suited for biomass production on such lands without irrigation. With the CAM pathway, Agave uses water and soil resources very efficiently. Some Agave cultivars possess high sugar and cellulose content. Furthermore, Agave is adapted to growth on marginal lands making it an ideal feedstock by avoiding competition with food production. However, there is essentially no biochemical or genomics-based studies to inform improvement strategies for bioenergy purposes. The goal of the proposed research is to obtain a genomic and biochemical-based understanding of CAM in

Agave necessary for its consideration as a biofuel feedstock. This project will aid our long-term mission in bioenergy research and enable ORNL to be a world leader in Agave biofuel research.

Results and Accomplishments

We have met and exceeded the deliverables for the first year (FY 2011). Task 1 (Physiological study of CAM phase dynamics) has been completed. The acid titration and enzymatic assay data verified our hypothesis that CAM expression in Agave is induced developmentally, with the CAM pathway expressed in mature leaves and the C3 pathway expressed in the young leaves. To our knowledge, this is the first research revealing the C3 vs. CAM difference in Agave, laying a foundation for discovery of differential gene expression associated with CAM dynamics. In Task 2A, the long-read sequencing of transcriptome in *A. americana* 'Marginata' using Roche 454 platform has been completed. A total of 3,011,508 sequencing reads (ESTs) were obtained from 23 tissues. These ESTs were assembled into 105,893 transcription units (TUs), of which ~38,000 TUs encode for proteins having homologs in non-CAM plant species and the remaining ~67,000 TUs likely encode for novel proteins specific to CAM and Agave as well as non-coding RNAs that play regulatory roles and singletons with low homology to other known genes. In Task 2B, we have analyzed leaf samples of four Agave species using gas chromatography–mass spectrometry (GC-MS) and found interesting differences in soluble sugars and organic acids among these species. Furthermore, leaf samples of *A. americana* were collected at nine time points over a 24 h period, and analysis of soluble sugars and organic acids by GC-MS was completed. Additionally, we have made good progress in single-copy gene cloning and determination of ploidy level and homozygosity. This will facilitate the identification of Agave species for biofuel research.

Information Shared

Yang, X., Li, T., Weston, D., Karve, A., Labbe, J.L., Gunter, L.E., Sukumar, P., Borland, A., Chen, J.-G., Wullschleger, S.D., Tschaplinski, T.J., and Tuskan G.A. 2011. "Innovative biological solutions to challenges in sustainable biofuels production," in *Biofuel Production-Recent Developments and Prospects*, (ed. M.A.D.S. Bernardes), Intech, Rijeka (in press).

05833

Harnessing Nitrogen and Sulfur Cycles to Develop Microbial Consortia for Consolidated Bioprocessing

D.E. Graham

Project Description

Anaerobic digesters use microorganisms to convert complex carbohydrates from biomass into organic acids and alcohols (potential biofuels). While most studies focus on carbon flux in these digesters, understanding nitrogen and sulfur fluxes will be essential for maintaining cost-competitive microbial biocatalysts and processing fermentation wastes. After primary fermentation, both elements will be enriched in the residue, and subsequent combustion will produce NO_x and SO_2 gases. These gas emissions are regulated, so we want to recycle or deplete their precursors from waste. This project characterized nitrogen, sulfur, and vitamin requirements in cellulolytic systems and developed analytical techniques and biochemical reagents for monitoring enzymatic activity in monocultures and stable co-cultures of *Clostridium thermocellum* and *Caldicellulosiruptor bescii*. Metabolic models of cellulolytic bacteria were used to design batch cultures that demonstrated the feasibility of anaerobic, consolidated bioprocessing

using inexpensive sulfate as the sole sulfur source to ferment pretreated biomass, producing alcohol and mixed acids.

Mission Relevance

This LDRD project demonstrated systems of microbial co-cultures engineered for consolidated cellulose bioprocessing. The results, reagents, and methods developed here serve as preliminary data for future grant proposals in biofuel production, carbon cycling, bioprocessing waste reduction and bioconversion technology. These experiments produced the first systematic evaluation of sulfur and nitrogen requirements for consolidated bioprocessing through mass balance analyses. This project anticipates future funding initiatives from DOE BER and EERE, as it addresses two priority goals: develop biofuels as renewable, sustainable energy resources and determine the relationships between climate change and terrestrial nutrient cycling processes.

Results and Accomplishments

Defined minimal growth media were developed for batch cultures of *Clostridium thermocellum* ATCC 27405 and *Caldicellulosiruptor bescii*, two thermophilic cellulose-degrading bacteria. Both organisms are normally grown using expensive L-cysteine as a reducing agent and sulfur source. However, both *C. thermocellum* and *C. bescii* were shown to incorporate inexpensive sulfate as a sole sulfur source through assimilatory sulfate reduction, when an alternative reducing agent was supplied to maintain anoxic conditions. Reduced concentrations of either ammonium or urea were sufficient nitrogen sources for *C. thermocellum*, but only ammonium was sufficient for *C. bescii*. Acid-pretreated switchgrass or poplar could not support high bacterial growth rates without nitrogen or sulfur source supplementation. Minimal vitamin and cofactor requirements were identified by metabolic reconstruction from genome sequences and validated experimentally. A comprehensive analysis of fermentation products accounted for a substantial proportion of carbon and electron equivalents in the closed systems. The new defined growth medium for *C. thermocellum* efficiently supported ethanolic fermentation using crystalline cellulose and acid-pretreated switchgrass or poplar. Another defined minimal medium supported stable cocultures of *C. thermocellum* and *C. bescii*, simplifying fermentation product analysis. Polyclonal antibodies specific to *Caldicellulosiruptor* cells have been developed and validated, along with high-throughput, microplate-based fluorescence assays of glycosidase enzymatic activity to rapidly characterize microbial activities. This project demonstrated the potential to reduce fermentation costs and reduce waste in consolidated bioprocessing by manipulating growth conditions through metabolic model-directed experimentation.

Information Shared

Graham, D. E. 2010. "A new role for coenzyme F_{420} in aflatoxin reduction by soil mycobacteria," *Mol. Microbiol.* **78**:533–536.

Graham, D. E. 2011. "2-Oxoacid Metabolism in Methanogenic CoM and CoB Biosynthesis," pp. 301–326 in A. C. Rosenzweig and S. W. Ragsdale (ed.), *Methods Enzymol.*, vol. 494. Academic Press.

06232

Integrative Signaling Modules Guiding Plants Response to Environmental Stresses

J.-G. Chen

Project Description

As plants are sessile organisms that cannot relocate to escape biotic and abiotic stresses, they have evolved complicated yet precise mechanisms to respond to biological and environmental stimuli. An understanding of the associated signal transduction networks is critical for developing effective strategies for enhancing bioenergy sustainability and for crop improvement. Classical genetic screens have identified many components involved in signal transduction, but it remains unclear how these components interact with each other, how signals are integrated, how signal specificity and fidelity are achieved, and how the mechanism of signal transduction functions at the molecular level. In this project, molecular, cellular, genetic, biochemical, and bioinformatics approaches are being taken to address how the Receptor for Activated C Protein Kinase 1 (RACK1), a versatile scaffold protein, integrates input signals from diverse signal transduction pathways and facilitates the spatial and temporal regulation of signal transduction. The proposed research will develop signaling modules guiding plant response to environmental stresses. The platform established through the research will be an integral component of resources for facilitating the molecular and biochemical studies in model organisms and bioenergy crops.

Mission Relevance

This project is highly relevant to DOE missions. Tools and technologies of functional genomics are of critical importance to many areas of interest to the DOE, such as bioenergy, carbon sequestration, global climate change, and plant-microbe interactions. Study of plant response to the changing environment is one of the major themes in DOE's Biological and Environmental Research programs and is one of the primary focuses of DOE's Genomic Science Program. This project will also benefit other federal agencies, such as the US Department of Agriculture (USDA) and National Science Foundation (NSF). For example, study of the molecular mechanisms of plant stress responses is one of the primary focuses of USDA National Institute of Food and Agriculture Plant Sciences Program and of NSF Plant Genome Research Program. This project may also benefit the Energy for Sustainability Program recently launched by NSF.

Results and Accomplishments

In this reporting year, we have established both yeast two-hybrid (Y2H) and protoplast transient expression systems and identified and characterized a number of RACK interacting proteins. Firstly, we identified Eukaryotic Initiation Factor 6 (eIF6) as an interacting partner for RACK1. We demonstrated the interaction using Y2H and protoplast transient expression system-based bi-molecular fluorescence complementation (BiFC) assays. More importantly, we demonstrated that the action of RACK1-eIF6 complex in regulating ribosome assembly and biogenesis involves abscisic acid (ABA), the key plant stress hormone. The significance of our work is that we have discovered RACK1 signaling complex as a novel molecular link between ABA signaling and the regulation of protein translation initiation. Secondly, we identified With No lysine Kinases (WNK) as interacting partners for RACK1. Mammalian WNKs regulate ion homeostasis and other pathophysiological processes including cancer, hypertension, and renal ion transport, but the function of plant WNKs is poorly understood. We demonstrated that WNKs phosphorylate RACK1. These findings shed new insight into the molecular mechanism of action of RACK1 signaling complex in stress responses. Finally, we identified Universal Stress Proteins (USP) as interacting partners for RACK1. USPs were originally identified in bacteria as important mediators of

cell survival under a wide variety of stress conditions. The discovery of USPs as interacting partners for RACK1 provides an opportunity to dissect the molecular mechanisms of action of an evolutionarily conserved protein family in stress responses.

Information Shared

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06244

Demonstration of Electric Vehicle Dynamic On-Road Wireless Power Charging

J.M. Miller

Project Description

This project is focused on the development and refinement of key functional elements of wireless power transfer (WPT) for in-motion applications that now limit its introduction and commercialization. These include grid-side power conversion and regulation, coil-to-coil transfer efficiency, and bidirectional communication between the vehicle and the grid. The three most pressing challenges to be addressed involve coupling coil designs that have efficiency >97%, rectifier and filter designs that facilitate optimum grid-side power quality targets and low latency vehicle-to-infrastructure (V2I) communications. The ORNL system is unique in three aspects: (1) the coupling coil geometry is specific to dynamic in-motion charging (but compatible with stationary charging) and avoids the existing system "fountain" effect of charging field null zones; (2) grid side regulation of charging power that facilitates high rate charging of the vehicle battery pack, effectively dc fast charge rate, and (3) the implementation of novel, dynamic conjugate matching control strategy that manages vehicle receiver power quality.

The program also requires innovations for the sequential energizing of multiple transmit coil arrays necessary for dynamic on-road charging. Successful demonstration of dynamic on-road power charging promotes energy independence of the transportation sector and enhances vehicle electrification.

Mission Relevance

Wireless charging is now seen by DOE and many in the automotive field as the enabling technology if widespread implementation of electric vehicles is to occur. The ease of use is seen as the technology advance that will make battery or plug-in vehicles accepted by the average household. However, the game-changing potential for WPT can only be realized if in-motion technology is widely accepted. Pioneering work on high-efficiency and high-power coupling coil designs now under way in this LDRD project will facilitate faster progress on DOE Vehicle Technology Program–funded wireless power stationary charging. Novel coil geometry and conductor design now in progress will lay the foundation for stationary charging at standard 6.6 kW levels, but most importantly, for high rate dynamic charging at equivalent dc fast charge burst mode at 100 kW power level. When developed, this system will benefit not only DOE interests (super truck) but DOD interest for on-the-fly charging of base transportation systems as well as commercial deployment of hybridized heavy-duty vehicles such as port-to-rail drayage trucks.

Results and Accomplishments

This report covers FY 2011 pull-ahead funding of LDRD# 6021, "Demonstration of Electric Vehicle Dynamic On-Road Wireless Power Charging," for the reporting months of August–September 2011. For this period the team's accomplishments consist of design work, material and equipment procurement, and facility and mule vehicle identification. Design work is focused in five key areas: (1) the coupling coil geometry and conductor design (led by FED group); (2) power converter design and fabrication (NTRC led unit rated 15 kVA); (3) transmit cable design (inverter to road way transmit pad, FED led); (4) vehicle on-board-charger (OBC) modification to include the level 2 WPT dc input power port (NTRC led); and (5) the V2I dedicated short-range communications (DSRC) that is NTRC vehicle systems team led. Equipment procurement for WPT-specific laboratory power source and battery eliminator is needed for functional validation of the modified OBC, plus material procurement in support of power inverter and coupling coil designs. Facility conversion commenced in July at the NTRC power electronics and electric machines laboratory (L101) high bay that will be needed to house the laboratory equipment noted, plus development benches for OBC testing, power inverter development and testing, and DSRC communications testing. Floor space is also reserved for the mule vehicle and on-floor transmit pad. The mule vehicle must be compatible with a commercially available OBC that is also compliant with the OBC manufacturer access to vehicle controller area network (CAN) battery pack messages. The earlier LDRD-funded project hardware built for evanescent wave power coupling is being modified to include a second transmit coil to study transmit pad road way pitch and power coupling influence on the moving receiver coil.

Information Shared

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ELECTRIC GRID TECHNOLOGY

05469

The Eastern United States as a Test Bed for Smart Grid Technologies: A Virtual Power System Enabled by Ultrascale Computing

J.J. Nutaro, T. Kuruganti, K.S. Perumalla, A. Shankar, and J. Stovall

Project Description

Our goal is to develop and demonstrate a capability to simulate electric power systems that include large numbers of autonomous software and communication intensive elements. The focus of our research is on simultaneously enabling geographic scales and electro-mechanical dynamics necessary for modeling distributed control and monitoring applications in the Smart Grid. Specific applications of the new simulation capability include (1) the production of synthetic phasor measurement unit (PMU) data at a scale that is practical for the evaluation of sensor-based technologies; (2) analysis and design of mitigation strategies for coordinated computer-based attacks on dynamic control processes; and (3) the evaluation of distributed controls for frequency regulation, integration of renewable and distributed generation resources, and other wide-area control problems.

Mission Relevance

This research is directly aligned with the mission of the DOE Office of Electricity Delivery and Energy Reliability and, recently, the National Institute of Standards and Technology (NIST) to understand, develop, and promote smart grid technologies. The research undertaken in this project can support DOE and NIST as they develop technical standards and assess the impact of new technologies on power system reliability and security. The ability to conduct large-scale evaluations of proposed smart grid technologies is also of interest to electric power utilities such as the Tennessee Valley Authority as they build infrastructure to incorporate new sources of generation, load as a resource, and other smart-grid concepts.

Results and Accomplishments

Key accomplishments in the project's first year include (1) the development of a new, accurate, and robust method for calculating frequency at loads from state variables used in standard models of electromechanical dynamics in generation and transmission; (2) the implementation of a web-based system for the dynamic, geo-referenced visualization of frequency in large power systems; and (3) a proof-of-principle demonstration showing how high-performance computing resources can be applied effectively and incrementally to simulate distributed control in a smart electrical power system.

Accomplishments in the project's second and final year include the following. (1) Preparation and submission of papers to the IEEE Transactions on Power Systems and IEEE Transactions on Smart Grid are under way. The paper titled "Calculating Frequency at Loads in Simulations of Electro-Mechanical Transients" is in its second round of review following revisions, and the paper titled "Discrete sensing

and actuation in a simulation model of frequency responsive loads" is pending review. (2) An invitation was extended to present at a panel on open source software in the power industry held at the IEEE Power Engineering Society's annual meeting; we presented our paper entitled "Designing Power System Simulators for the Smart Grid: Combining Controls, Communications, and Electro-Mechanical Dynamics." (3) Development of a new method for solving large, sparse linear systems and demonstration of the new method in ORNL's THYME software for power system simulation was achieved.

Information Shared

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05470

Microelectromechanical Systems—Based Pyroelectric Thermal Energy Scavengers and Coolers

S.R. Hunter, P. Datskos, S. Rajic, and N.V. Lavrik

Project Description

The project focuses on developing a new type of high-efficiency, low-grade waste-heat energy converter that can be used to actively cool electronic devices, solar concentrator photovoltaic cells, computers, and larger waste-heat-producing systems, while generating electricity that can be used to power monitoring sensor systems or recycled to provide some of the electrical power for these computers and other electrical devices. The project objective is to demonstrate the feasibility of fabricating high-conversion-efficiency microelectromechanical-systems-based pyroelectric energy converters that can be fabricated into scalable arrays using well-known microscale fabrication techniques and materials. The specific goals of the project are to demonstrate that overall electrical energy conversion efficiencies in the range of 20–30% and efficiencies up to 80% of the Carnot efficiency limit, and that these efficiencies are achievable with arrays of up to 10^6 converter elements. These energy conversion efficiencies are greater than those previously demonstrated—or proposed—for any other type of waste-heat energy recovery technology. The widespread implementation of this technology will result in large reductions in waste-heat production (and subsequent cooling requirements) and the generation of high-quality electrical energy from a wide range of waste heat sources.

Mission Relevance

Energy scavenging and improved systems-level electrical efficiencies are of considerable interest to DOE and other federal agencies such as the Defense Advanced Research Projects Agency (DARPA), as well as industry. During the past year, our project development efforts focused on teaming with industrial partners (L3 and Lockheed Martin) that have already expressed interest in this technology and will help us secure funding from programs at DOE and at DARPA. The ORNL Technology Transfer Office has also decided to pursue patents of a fundamental nature in this technology, and the first patent application was submitted to the United States Patent and Trademark Office during FY 2011.

The DOE Office of Energy Efficiency and Renewable Energy offers significant funding opportunities in the Industrial Technologies Program for new energy efficiency approaches, and we plan to pursue funding from these sources. Commercial partners such as L3 (Dallas) that have considerable experience in ferroelectric materials have expressed interest in teaming with ORNL for future projects based on this technology. In addition, several programs at DARPA have energy scavenging components and, by teaming with defense contractors such as Lockheed Martin, we will pursue these opportunities in FY 2012.

Results and Accomplishments

Our efforts during the prior year focused on performing the following tasks: (1) designing, modeling, and optimizing the operation of resonating bimorph pyroelectric capacitor structures using COMSOL finite-element modeling software, (2) fabricating several different sizes of test cantilevers and pyroelectric capacitor structures, (3) fabricating a temperature-controlled vacuum test station to perform controlled temperature thermal conductance studies of self-resonating cantilever and pyroelectric structures, and (4) testing, characterizing, and optimizing the performance of several thin-film and cantilever-based self-resonators and fully integrated pyroelectric capacitive devices. A finite-element model of the self-resonating microcantilever structure was developed using the finite-element software, and the effect of varying thermal and mechanical properties of the microcantilever structure on the mechanical response and temperature cycling was studied. Optimum microcantilever design parameters were obtained, allowing maximum temperature cycling of the pyroelectric material in the microcantilever structure thermal energy harvesting. A modeled pyroelectric material embedded in the cantilever structure that would experience equivalent temperature cycling has been observed to have a temperature cycling frequency an order of magnitude greater than that reported for previous attempts in pyroelectric energy harvesting. Other modeling studies indicated that tip deflections of several tens of micrometers, with temperature differentials of 200°C, are possible with multilayer pyroelectric capacitive cantilever structures that are 1–3 mm in length with optimized thicknesses. Pyroelectric capacitors made from polyvinylidene fluoride–trifluoroethylene copolymer (PVDF-TrFE or copolymer) were fabricated and integrated into resonating cantilevers to form pyroelectric current generating devices. Self-resonating micro-cantilevers that produce appreciable (few μA) current when interfaced between a waste heat source and a heat sink are achievable with energy harvesters that show thermal responsivities of 5–10 μm/°C and shuttle between source and sink at 100 Hz–1 kHz frequencies. The devices are ultrasensitive to minor temperature fluctuations, and the Olsen or other thermal energy conversion cycles can be utilized to further improve the efficiency of thermal-to-electrical energy conversion. These devices show promise for quick integration with rechargeable energy storage devices.

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05556

Highly Efficient Refrigeration Systems Based on Advanced Magnetocaloric Materials

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Project Description

Air-conditioning and refrigeration cycles account for 31% of the energy consumed in the United States and 15% of energy consumed worldwide. In this project, we are exploring advanced materials for ultra-high-efficiency heating, ventilation, air-conditioning and refrigeration (HVACR) systems based on magnetocaloric (MC) refrigeration cycles. Magnetic cooling systems hold the potential for improvements of 60–100% in performance over conventional gas compression systems and do not require ozone-depleting gas refrigerants. Alloys with enhanced properties are needed to meet the demands of commercial HVACR systems. We hypothesize that the magnetically induced first-order structural phase changes in shape memory alloys such as Ni_2MnGa can be harnessed to produce MC materials with significantly improved properties through careful alloying. Nanostructured materials approaches will be used to create alloys of varying composition that may be quickly analyzed to determine which compositions yield the optimum cooling properties, and first-principles modeling techniques will be used to establish an improved understanding of the physical principles governing the magnitude and temperature dependence of the maganetocaloric effect (MCE). This project will establish a foundation in magnetic cooling technology using ORNL's unique capabilities through which practical, commercial magnetic cooling systems will be realized.

Mission Relevance

Forms of refrigeration including air-conditioning, chilling, and freezing are responsible for 40–60% of the energy used in US commercial buildings and 15% of total worldwide energy consumption. Magnetic refrigeration, which exploits the magnetocaloric effect, is a fluorocarbon-free technology that has the potential to offer energy efficiency improvements of 20–30% in excess of conventional gas-compression

refrigeration technology. Magnetic heating and cooling occur with the magnetization and demagnetization of MCE materials and can be incorporated into highly efficient heat pump cycles. This project directly supports DOE's Building Technologies Program High Priority R&D goal of "developing new, highly energy-efficient HVAC equipment" that will significantly reduce overall energy needs in new and existing commercial buildings.

Results and Accomplishments

This project uses an integrated computational and experimental approach. A computational model of the magnetocaloric effect in Ni_2MnGa based on ORNL's leading first-principles modeling code, Locally Self-consistent Multiple Scattering (LSMS), has been developed and run on 28,800 Jaguar processors using 200 Monte Carlo "walkers" for a 144 atom supercell. The results of this model are used to fit a Heisenburg model to generate the density of magnetic states. To enhance the ability to measure the properties of multiple materials, we have developed the capability for discovery of new magnetocaloric alloys using combinatorial sputtering.

Bulk samples of the Ni_2MnGa near and off-stoichiometry alloys were prepared for testing in experiments at the National High Magnetic Field Laboratory and in ORNL's 9 Tesla superconducting magnet. These alloys were suggested by both our computational modeling efforts, and some that have been widely investigated as standards for comparison and some of the Ni_2MnGa alloys included small amounts of Fe and/or Cu to examine the effects of these elements on the structural and magnetic transition temperature. These materials were characterized using differential scanning calorimeter (DSC) and superconducting quantum interference device (SQUID) techniques. The results of testing the bulk alloy materials demonstrated that it is possible to control the structural and magnetic transition temperatures using small amounts of Fe and Cu and that it is possible to manipulate the Curie temperature using these materials.

A system for preparing magnetic films with graded compositions has been commissioned in the Nanosciences Technology Laboratory (NSTL) in ORNL's Building 3500. Ni_2MnGa magnetocaloric films have been produced with graded compositions. These films have varying amounts of the dopant Fe and Cu that can be used to modify the Curie temperature of the material and based on our DSC measurements drives the structural and magnetic phase transformations to the same temperature. In order to determine the effects of composition on the magnetic properties of these materials, a magneto-optical Kerr effect measurement system has been assembled. This system uses polarized laser illumination to measure the relative magnetization (B-H) curves of localized areas on a magnetic film.

We have fabricated bulk samples of a new Fe-Ni-Co-Al alloy using high-magnetic-field casting at the National High Magnetic Field Laboratory. We have characterized the transition temperatures by making resistivity measurements at field and no field conditions using the 16 Tesla Bruker magnet at the Spallation Neutron Source. We have confirmed the magnetic and structural transitions using differential scanning calorimeter. The magnetic properties have been determined using a Quantum Design superconducting quantum interference device (SQUID). Metallography and microscopy imaging revealed very interesting microstructural features characteristic of a high-performance material. Further microstructural characterization was performed using electron backscatter diffraction.

In summary, we have performed a comprehensive analysis of the Ni_2MnGa shape memory alloy for magnetocaloric applications. We have shown that we can control the structural magnetic transition temperatures of this material by careful alloying. The facilities used for this project include the Center for Computational Sciences, the Spallation Neutron Source, and the High Temperature Materials Laboratory. Some researchers associated with this project are affiliated with the Building Technologies Research and Integration Center.

Information Shared

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Presentations

1st World Congress on Integrated Computational Materials Engineering (ICME) Conference Presentation, "First Principles Modeling of Shape Memory Alloy Magnetic Refrigeration Materials," July 10, 2011, Seven Springs, Pennsylvania.

05593

Power Flow Control Using Distributed Saturable Reactors

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Project Description

A series-connected reactor can be used to control power flow on a transmission line through a modification of its impedance. Dry-type reactors with constant reactance values (air core) have been used on a few occasions for power flow control. Another type of reactor that uses a saturable ferromagnetic core has been used for fault current limitation in superconductive circuits. This proposal combines these two concepts with new technology in one device that has the potential to revolutionize power systems operation. A saturable core, series reactor, with continuous reactance control that uses power electronics to provide and control the bias dc current is proposed. The goal is to create a simpler, more effective, reliable, and cheaper power flow control device that will enable power systems, for the first time since their inception a century ago, to operate not just in compliance with the laws of physics but also in a way that is market compatible and friendly, most economical, and most reliable.

Mission Relevance

The control of power flow in interconnected power systems is a major concern for utilities and system operators and has become more urgent with deregulation pushing market transactions. If not controlled, power flows due to these market transactions can lead to a number of issues in system operation. Some of the commonly encountered problems include

- overloading of lines and transformers;
- increased system losses;
- reduction in security margins;
- contractual violations concerning power import/export; and
- increased fault current levels beyond equipment ratings.

Thus far, full power flow control has been prohibitively expensive, requiring a large number of complicated and costly devices. Also, the reliability of these complex devices has been in question. Only a partial power flow control is exerted in contemporary power systems with relatively few strategically located controllers. As a result, power systems almost always operate in a suboptimal way in regards to

flows, losses, and economic power transport. The cost of such suboptimal operation is significant given the amount of investment in this infrastructure. As an example, this cost is estimated to be around $2 billion per year for the PJM (Pennsylvania, Jersey, Maryland) system only.

The cost of the new controller is estimated to be around two orders of magnitude lower than the current state-of-the-art solutions. Such cost-effectiveness of this new device will allow for system-wide deployment and distributed power flow control on a scale never implemented before. A number of these controllers placed in strategic locations and coordinated by the system operator can eliminate the common transmission system problems listed above and enable, cost-wise, truly optimal power system operation while satisfying technical, security, environmental, and other constraints.

Results and Accomplishments

In order to determine the appropriate value for the inductance of the saturable reactor prototype, a detailed analysis of the high-voltage (69 kV and above) transmission line parameters in the US power grid was performed. In total, 37590 lines were analyzed from the three US interconnections: Eastern Interconnection (EI), Western Electricity Coordinating Council (WECC), and Electric Reliability Council of Texas (ERCOT). Based on the average total line series impedances, representative line reactances at the main transmission voltage levels have been determined. These reactances are used as the reference for the appropriate inductance value of the series saturable reactor prototype. In consultation with Waukesha Electric Systems (WES), our industry partner, a targeted prototype has been determined for the subtransmission voltage levels, that is, 69–115 kV. At these voltages, the typical line reactance is somewhere around 5 Ω, and this value has been chosen as the basic design parameter. It corresponds to an inductance of 13.3 mH at 60 Hz. In a need of a larger reactance, two or more such reactor modules can be added together in series.

A novel magnetic core geometry for the controller has been designed that addresses the two main weaknesses found in the basic saturable reactor:

- magnetic coupling between the control and controlled circuits and the unwanted transformation effect in the dc circuit and
- asymmetry in the two half-cycles of the ac sinusoid.

Furthermore, the new core eliminates the difficulty of saturating a core that has air gaps. The air gaps have to be introduced in the path of the ac magnetic flux in order to achieve the desired value of inductance. However, this also makes the saturation by the bias dc winding much more difficult and will require a more powerful dc supply. The new design introduces the concept of "local saturation" that solves this problem effectively and eliminates the need for high power, typically a superconductive, bias dc winding.

05659

Real-Time Simulation of Power Grid Disruptions

S.J. Fernandez, O.A. Omitaomu, K.A. Spafford, J.J. Nutaro, A. Shankar, and S.R. Sukumar

Project Description

This project established the feasibility, defined the scientific issues, and designed potential solutions to important smart grid simulation problems only addressable within an exascale scientific computing application. This objective is accomplished by (1) using the existing frequency recorders on the national grid to establish a representative and scalable real-time data stream; (2) invoking newly developed signature identification algorithms; (3) modeling dynamically a representative region of the Eastern interconnect and measuring the scalability and computational benchmarks for a national capability; and (4) constructing a prototype simulation for the system's concept of smart grid deployment.

Mission Relevance

A consensus is developing within the Department of Energy that a ***qualitatively*** new problem that exascale applications could contribute to the evolution of the 21st Century power grid is the real-time ingestion of smart grid data into a platform to forecast those disruptions that invoke the system's self-healing function within a 2–4 second decision loop. DOE-OE and DOE-SC workshop selected the key power grid problem needing exascale computing as coupling of real-time data streams (1–2 TB per hour) as the data are ingested to dynamic models. DOE Office of Electricity has an important goal of understanding and responding to the status (observed and predicted) of the electric grid. The Office of Science has a goal of applying the next generation of scientific computing to significant power grid problems. This project will take ORNL's unique monitoring capability and process the data through the entire process chain to demonstrate the scale, simulation issues, and potential solutions that have limited these simulations to the present time and position us to capture a grid simulation center with a wide range of potential applications to DOE-OE and DOE-SC programs.

Results and Accomplishments

We developed and tested a database system to receive the real-time data from the ORNL/UT GRIDEYE system as a simulant for real-time smart grid data. This database was 1 TB in size containing generator trips embedded with noise, varying noise structure, and intermittently reporting sensors. From analysis of this dataset, an idealized Eastern Interconnection network of 83 stations was simulated and used to test signature extraction algorithms. These modeling results confirmed that a nation-wide capability would require collection of about 1TB of data per hour, and archiving 1 year of data would require approximately 8.7 PB. The data structure demonstrated capability of a pre-processing ingests speed of 1.2 GB per second while automatically trapping errors and inconsistencies in the data sets. We required new algorithmic approaches as well as parallel formulations to address this new coupling. These new algorithms were embedded in a code entitled GAEDA and copyright asserted. The feasibility of the interface has been demonstrated; however, two new concepts were required to meet the speed and efficiency requirements. A preliminary design was developed for the integrated detection system. First, the functionality of the GAEDA code will allow multiple event detection algorithms to operate simultaneously and "vote" on the detection of an event from precursor signals.

Program Development Accomplishments

1) Design requirements for the site selection of frequency disturbance requirements were transmitted to DOE-ISER to support procurement of future GridEye sensors.
2) A key program development objective is a continuing, close collaboration with General Electric's "Big Data Initiative" (BDI). BDI has as its objective the development of Advanced Computing Applications and technology to satisfy demand caused by implementation of Smart Grid technology. A proposal for a prototype demonstrator was requested by 11/15/2011.
3) A patent disclosure for the Real Time Simulation of Power Grid Disruptions was filed and used as the basis of UT-Battelle NDA No. 865IP with General Electric. A key meeting between laboratory management and GE BDI leadership occurred June 3 and a request for licensing information was received August 15.
4) The GPU Accelerated Event Detection Algorithm (GAEDA) code was documented to assert copyright supporting licensing discussions with Qado Energy to supporting their decision platform providing situation awareness for distribution utilities.
5) Four white papers were submitted in support of DoD calls for concepts.

Information Shared

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05971

Citizen Engagement for Energy Efficient Communities (CoNNECT)

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Project Description

Energy efficiency and renewable energy are two main strategies presently being promoted for achieving sustainable energy policy. Of these strategies, energy efficiency is relatively easier and cheaper to implement. As a result, there have been some programs that targeted the use of energy-efficient technologies and appliances in buildings. However, it is highly unlikely that these programs can scale up to achieve the projected energy saving because they are usually treated as one-time improvements that are not monitored and measured over time. Allowing consumers to easily analyze, share, and benchmark their own energy usage data can lead to an effective and sustainable way to achieve many of the Energy Efficiency and Renewable Energy (EERE) goals. We propose to develop an integrated multi-partner platform called **C**itizen e**N**gagement for e**N**ergy **E**fficient **C**ommuni**T**ies (CoNNECT) that will (i) establish a community-based network of stakeholders to facilitate consumer engagement for energy efficiency; (ii) provide a prototype internet-based decision support application to better inform and motivate consumers; and (iii) provide data analysis capabilities that will drive the decision support system for comparative visualization and identification of spatial consumption and carbon emission patterns. This platform will strongly position ORNL for future programmatic opportunities in large-scale utility data analytics and EERE programs.

Mission Relevance

The Department of Energy (DOE) Offices of Electricity (OE), EERE, Solar Program have emphasized the need for residential and commercial customers to curtail their energy consumption since they are responsible for about 40% of the electricity produced in the United States, as well as the need to increase renewable energy integration into electricity generation at the distribution level. Therefore, this project complements DOE missions in the area of energy efficiency and renewable energy integration. The methods, tools, and insights developed in this LDRD project will benefit developing programs within the United States DOE OE, EERE, and Solar Office. The results and capabilities developed during this project are being utilized in the development of proposals to various programs in pursuit of follow-on funding.

Results and Accomplishments

We have established an action network that includes utility companies as well as city and county governments for achieving energy-efficient communities. We currently have four utility companies, the city of Knoxville, and Knox County as members. We are in the process of extending the partnership to utilities in Oak Ridge and Lenoir City. The existing partnership has led to the ownership of facility-level data for developing capabilities to achieve energy-efficient communities. We have also developed a geodatabase that integrates monthly energy consumption data with property, planimetric, zoning, land use, and topographic data in a novel way that provides new insights about spatial and temporal patterns in energy consumption. This geodatabase is a unique data repository capability at ORNL. We have also developed a framework for engaging citizens for energy-efficient and sustainable communities. A feedback technology that implements the framework has also been developed. The technology uses consumer energy usage data to provide mechanisms with which users can monitor and compare behavior, and allow them to better evaluate their conservation performance over time. Even though the initial proposal is limited to the public, key findings show that the application is of equal value to the utilities. As a result, a modification of the framework has also been developed for a utility version of the feedback technology. The feedback technology is currently being tested by selected members of the public for initial assessment. The technology is planned to be rolled out to the utilities and public in the first quarter of FY 2012.

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GLOBAL SECURITY SCIENCE AND TECHNOLOGY

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/her location and bearing. ORNL has conceptually developed several novel radiolocation signal formats and mathematical data-fusion algorithms (US Patents 6,556,942; 7,394,381; and 7,626,544 issued plus six more patents pending) and is 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 the Department of Justice and of assets by DOE, the 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 US 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,

logistics), and the Department of Transportation/Federal Aviation Administration (reliable navigation and timing).

Results and Accomplishments

We have completed the proof-of-concept R&D of a new, patentable high-performance version of TPS, a terrestrially based RF backup for GPS, compatibly operating in the existing worldwide 90–110 kHz LORAN-C radio-navigation band. A new variant of the system developed under this project replaces the existing LORAN format (discontinued by the US government in February 2010) with a new specialized spread-spectrum signal that will greatly improve the accuracy, range, and robustness of the old LORAN protocol. The new signal's format design has been essentially completed, and detailed system performance simulations have been confirmed; a US patent disclosure is also currently in preparation. In addition to a first patent (US Patent 7,626,544, December 1, 2009), two more were issued on TPS during fiscal year 2011 (US Patents 7,859,464, December 28, 2010, and 7,876,267, January 25, 2011), and a fourth is close to allowance. Further, we continued 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 outperform current miniaturized INS units (based on optical and microelectromechanical 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 have demonstrated nearly a factor-of-100 improvement in phase drift over standard quartz oscillator units and radically better long-term overall stabilities. In addition, we have pioneered a novel dual-mode compensated oscillator architecture using a 5th-overtone crystal mode to correct for quartz temperature-induced resonance drifts; a further US Patent application (11/083,366) on the system ("ORIENT") was filed on April 8, 2011. We have also continued 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. Finally, five research papers on aspects of the overall research effort have been published, including two recently presented at the IEEE Milcom Conference in Baltimore, Maryland, in November 2011.

05437

Standoff Detection and Imaging of Chemicals

A. Passian and T. Thundat

Project Description

Development of novel standoff detection methods that can overcome the drawbacks of present techniques is essential in defeating the terrorist threat posed by the use of explosives and chemical/bio agents. Detection of chemicals using point sensors based on receptors suffers from disadvantages such as limited shelf life, use of reagents, or poor selectivity. Standoff detection of chemicals agents using techniques such as Raman and laser-induced breakdown spectroscopy use complex, bulky, and expensive equipment. Here we propose to develop a novel standoff detection technique based on reverse photoacoustic spectroscopy (RePAS) that can provide molecular signatures of chemicals with high specificity and sensitivity. The RePAS technique is based on the collection of scattered mid-infrared light from suspected objects illuminated with tunable quantum cascade lasers (QCL). The captured light is used for exciting photoacoustic (PAS) signals on a quartz oscillator. The proposed approach leads to the development of portable devices with high sensitivity and selectivity. This sensor paradigm allows standoff detection

covering distances up to 100 m using eye-safe QCL. RePAS also provides a path towards developing a broad area imaging system for chemical imaging of surfaces. We will develop a system that images surface contamination of a large area within seconds.

Mission Relevance

We are confident that success of this LDRD will result in follow-on funding from industry and many agencies including JIEDDO, US Air Force, Army, Navy, and DHS. Our JIEDDO program manager, Dr. Mike Rafailov, is extremely interested in our technology. Mr. David Lagandere and Maj. C.J. Maldonado have expressed very high interest in using our standoff imaging for health applications. Captain Mark Stoffel of ONR has been an enthusiastic supporter of our standoff technology. The MARS company is very interested in our standoff technology for detection of food pathogens. Dr. K.K. Law of China Lake visited us to form a teaming arrangement with Boeing Inc. for standoff imaging technique for US Navy. Other interested program managers who visited us include Dr. Mike Shepard of DHS and Dr. Richard Lareau of DHS/TSL. We have received licensing enquiries from companies such as Raytheon, Pranalytica, Inc., and Daylight Solutions, Inc., about commercial collaboration/licensing.

Results and Accomplishments

We introduced a new pump-probe photothermal spectroscopy (PTS) technique scalable to long distances where a QCL pump is integrated with a visible probe system positioned to detect the thermo-optically induced changes in a target surface that can be representative of the IR absorption spectra of the sample. Complex compounds such as cellulose, polystyrene, organophosphate pesticide, as well as common substances such as cosmetics and acrylic paint were evaluated. The results suggest that chemical identification of remote substances through interpretation of their pump-probe spectra is a viable approach to standoff detection. The key accomplishments to date are (1) demonstrated IR absorption-induced thermo-physical changes on target surfaces in a standoff fashion; (2) demonstrated pump-probe QCL-based photothermal Business Sensitive 1 spectroscopy without the use the expensive IR cameras, telescopes, or detectors; (3) investigated the effects of modulation frequency; (4) investigated the effects of laser power; (5) developed software for testing, calibration, and control of mechanical systems for rastered imaging; (6) developed scalable prototype hardware for standoff detection (using pump and probe lasers); (7) investigated several substances common but important from a standoff point of view (paint, latex, cellulose, wax, organophosphate pesticide) using standoff detection; (8) characterized the QCL beam profile using specially designed microcantilever sensors and commercial beam profilers; (9) for analyzing the integrity of the pump-probe spectra, FT-IR spectral comparisons were made and cross-correlation algorithms were developed; (10) characterized background spectra of different surfaces and materials, including silicon and aluminum.

Information Shared

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05477

Cyber Defensive Countermeasures

J.M. Beaver, X. Cui, C.T. Symons, M.G. Lindsey, C.A. Shue, E.M. Ferragut, and B.C. Jewell

Project Description

Unauthorized data exfiltration is a significant concern in both business and government and can have consequences ranging from commercial disadvantage to a complete breakdown of our national security. This project addresses the data exfiltration problem through the research and development of the following capabilities: (1) research and development of methods for detecting unauthorized data exfiltration events through mining computer host operational data to identify the patterns of exfiltration activities, (2) research and development of active response techniques such as dynamic honeypots to migrate malicious exfiltration processes to a quarantined environment for forensic evidence collection and countermeasure deployment, and (3) research and development of defensive countermeasures, such as redacted files, to aid investigators in analyzing attack vectors and determining attribution.

As seen at ORNL, the Pentagon, and other enterprise-scale computer networks, attackers that breach a system's defense have a distinct advantage because their presence is difficult to detect, they have a window into potentially sensitive data, and their true identity and location is hidden. This project seeks to mitigate the advantages attackers gain through intrusion by identifying malicious behaviors on each host computer. It is expected to provide the capability for an organization to detect and respond to unauthorized exfiltration attempts.

Mission Relevance

Data exfiltration is a pressing government and commercial concern. There are numerous publicly reported instances of sensitive data being stolen from both government and industry entities and either exposed publicly or funneled to groups that will maliciously exploit the data. Unlike other tools that focus on detection at the network perimeter, this work focuses on a host-based exfiltration detection system that analyzes behaviors of users and processes. It addresses a need for exfiltration detection within a targeted network, should an intruder successfully breach the perimeter defense. To date, there are no host-based tools that automate both the reliable detection of data exfiltration activities and the invocation of the dynamic honeypot response.

The successful completion of this research will position ORNL and DOE to become a leader in data loss prevention. The data exfiltration detection and dynamic honeypot elements of this work support the mission of the Cyber Security Protection Program in DOE's National Security Department, the Cyber Security Program Area of the Department of Homeland Security's Command, Control and Interoperability Division, as well as the newly formed US Cyber Command.

Results and Accomplishments

A focus was placed on refining and integrating the capabilities developed in the first year of work. The paragraphs below summarize the accomplishments.

- *Multiple sensors for exfiltration data collection.* Refinement continued on the system call sequence analyzer developed in the first year of work, with the addition of an active outlier model to detect anomalous sequence behaviors. We also created two new sensors: the first for a semi-Markov model of inter-arrival times of log entries and the second for system call time-series language modeling. Testing showed the second of these to be appropriate for the exfiltration analysis. Finally, a naive

Bayes model was developed and tested to classify exfiltration events. The naive Bayes model and the system call sensor were implemented as sensors for integration with the rest of the system.

- *Dynamic honeypots and honey tokens*. The focus for the active response element of this work was to develop the software infrastructure for performing real-time response actions. We implemented an integrated *dynamic honeypot* prototype that secures the organizational data by quarantining malicious user sessions through process migration. Actively running user processes are relocated to a virtual machine where they are insulated from the files they are attempting to steal. The dynamic honeypot was integrated with the exfiltration detection to provide an end-to-end data exfiltration detection/response capability. In order to deceive the attacker and maintain the illusion that they are working with the real target file system, we developed a prototype for automated file system mirroring that replicates the original file system structure and the mirrored files are altered to appear authentic. The altered files, called *honey tokens*, are adapted from the actual file system files but have been automatically redacted using a developed method for entity extraction/replacement.

- *Integrated exfiltration detection/response system*. Leveraging the previously developed detection/reponse capabilities, an information fusion pipeline was developed to acquire all information, make an automatic decision about a user's behavior, and migrate that user's processes if an unauthorized exfiltration is probable. The pipeline is centered on a key-value pair data representation called a *feature set* and includes three architectural components: data collectors that capture the raw feature data, derivers that compute additional features based on the raw data, and alerters that analyze the accumulated evidence and take action if it is warranted. The pipeline is the basis for the prototype implementation of the exfiltration detection/response system that incorporates the various data collectors, probabilistic models, and machine learners applied to the exfiltration problem.

Information Shared

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05487

Biological Signature Identification and Threat Evaluation System (BioSITES)

R.W. Cottingham, T.S. Brettin, S.D. Brown, and D.J. Quest

Project Description

The United States has a well-established and accomplished multiagency process dedicated to nuclear forensics; there is no parallel process for biological forensics, underpinned by state-of the-art science. BioWatch, the current standard in deployed biothreat detection, cannot detect genetically engineered threats. There is a pressing need for a new system leveraging recent scientific advances to improve threat detection. We propose a new system called BioSITES that will integrate systems biology knowledge repositories with new data collection technologies such as high-throughput sequencing. This will enable the construction of better detectors and provide a basis for mitigation, response, protection, and forensics and therefore a path for future development of BioSITES and biodefense.

Newly funded initiatives are establishing ORNL as a leader in knowledgebase development for systems biology research. Further, ORNL projects such as the BioEnergy Science Center were awarded in recognition of the resident expertise in systems biology research and management of such large-scale biological projects. This project leverages these core competencies toward the development of a new kind of biodefense system required to respond to upcoming threats of the 21st century. The BioSITES prototype will demonstrate capabilities that go beyond current deployed systems.

Mission Relevance

Implementation of the BioSITES prototype will provide the technological foundation that will allow our team to demonstrate capabilities to the Department of Defense (DOD) and the Department of Homeland Security (DHS) that will ultimately improve threat detection, reduce detection costs, and improve response times. This system would be useful for both homeland security and for defending American military personnel; therefore, funding could come from DHS and DoD [e.g., the Defense Threat Reduction Agency (DTRA)] to advance their existing deployed systems.

The investigators have been in contact with DTRA and DHS and have provided briefings on the concept to relevant program managers. These briefings have received a favorable response, but a working model of the system is needed to attract funding.

Results and Accomplishments

The concepts of Scenarios and Scenario Driven Development (SDD) from the first year of this LDRD project have been extended to a new concept developed in the second year called Scenario Driven Data Modeling (SDDM). SDDM builds on SDD and improves aspects related to the modeling of data that exists in a stream and modeling of data in catalogs. In SDDM all non-streaming data is modeled as a multi-relational graph (or Semantic Network). Real-time algorithms are used to compare data in the graph to data in the stream. These conceptual development methodologies enable rapid, accurate development of the software and system components and methods for integrating diverse sources of data and data streams in ways that support the real-time performance needed for BioSITES.

Significant improvements to the Ontology for Scenarios were made, and the capability to link concepts across ontologies was prototyped that enables leveraging the power of existing ontologies. These capabilities are highlighted in a manuscript on the SDDM process submitted to *BMC Bioinformatics* (see

publications). As a result of all of these developments, BioSITES is capable of implementing any scenario that involves screening biological sequence and relevant data, geographic location, and time.

This led to the development of a scenario based on the recent naturally occurring threat of the NDM-1 gene that confers resistance to multiple antibiotics. SDDM was used to fully refine this scenario into a Semantic Knowledgebase representing NDM-1 as a public health threat. As part of the development of this scenario, sensors were created that look for the NDM-1 gene in a stream of sequence data, and a new kind of detector was developed for streaming ProMED articles that extracts content from representative ProMED articles describing NDM-1 that are preprocessed into a semantic representation.

An application of BioSITES this past year was in furthering our relationship with LLNL by providing analytical capabilities. The taxonomic organization of DNA sequence data was used in analyzing complex metagenomics samples that contained *Bacillus anthracis* Ames as a "spiked-in" threat to test false positive and false negative rates of detection. This work resulted in two published reports (see publications) and is being included in a report to DHS and likely a future peer-reviewed publication.

Following on the NDM-1 work, more recently our focus has been on a demo scenario of a genetically engineered or synthetic biology based threat for DHS and DOD. This scenario considers the possibility of a threat engineered via orders to synthesis companies that are currently screening orders for category A agents. However in this scenario the orders are fragmented and sent to multiple synthesis companies to make them undetectable. This is being developed and will be the focus through the third year.

Information Shared

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05573

Rapid Radiochemistry Applications in Nuclear Forensics

H.L. Hall, J.R. Garrison, D. Hanson, and S.J. Jones

Project Description

We will develop fundamentally new capabilities 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 time frame in which nuclear forensics can provide quantitative data for interpretation, as well as develop 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 post-docs 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. These include DOE, through the National Nuclear Security Administration, the Department of Homeland Security, and the Department of Defense. Agencies such as the Department of State and the FBI are users of nuclear forensics data as well.

Results and Accomplishments

In this final year of the project, we have continued to explore the gas-phase chemistry approach, as this has the potential for much greater increases in the speed of analysis and we are elucidating new opportunities for further scientific research in this area. Our review of the relevant scientific literature for existing work on the applications of thermochromatography to radiochemical separations was published, and our efforts in modeling and simulation of the gas-phase species-wall interactions for the cases where the thermodynamic data are known was completed (initially in MatLab). We found MatLab to be too slow for effective use of the simulation beyond proof-of-principle work, and so we ported the model into a compiled language for speed. Using the model, we were able to reproduce existing experimental data across a range of metal-ligand complexes, and demonstrated via simulation the ability of the thermochromatographic method for separation of the entire lanthanide series in less than 60 minutes. Using our simulation code, we have also developed early designs for experimental configurations, and used these results to support a capital investment on at the University of Tennessee for the experimental phase of this work. Two graduate students at the UT completed their MS degree in nuclear engineering on this project, and a third student in the Center for Interdisciplinary Research and Graduate Education is working on the experimental design.

Information Shared

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05599

Potable Water Reclamation from Diesel Exhaust by Inorganic Membranes

M.M. DeBusk, J. Klett, B.L. Bischoff, and C.S. Daw

Project Description

The goal of our project is to develop and demonstrate enabling technologies for a small footprint, high-efficiency water-reclamation system. At present, water generated during fuel combustion, at a rate of 1 gallon per gallon of fuel consumed in vehicle engines or stationary generators, is discharged with exhaust. Water recovered from exhaust will help alleviate the military's logistical problem associated with water management in combat and national/global disaster areas. Fifty percent of the military's logistical burden is related to delivering water (predominately bottled water) to forward locations, increasing troop vulnerability and limiting tactical use, making it DOD's #2 priority for logistics solutions.

The primary enabling technology for our water-reclamation system is based on inorganic membranes and facilitates increased potable water recovery, while requiring less energy and space than conventional

condensation recovery methods. We plan to maximize both the overall system energy efficiency and the level of water recovery from vehicle/generator exhaust by tailoring and improving the properties of inorganic membranes (pore size, flux) and integrating the membrane with a small, lightweight advance cooling system.

Mission Relevance

This project aims to develop and demonstrate enabling technologies for a small-footprint, high-efficiency inorganic membrane-based water-reclamation system that can be used in diesel/JP8 engine exhaust applications. A device capable of reclaiming potable water at the point-of-use from currently wasted water vapor in engine exhaust will advance both our national and energy security. Producing water from available sources, such as diesel exhaust, will reduce the burdens associated with water transport in combat zones and is DoD's #2 priority for logistics solutions. Reducing the logistical burden will also reduce the military's current energy consumption associated with bottled water transport. The successful demonstration of this membrane reclamation system's potential will position us to request funds from the Army, Marine Corp., and other active branches of DoD for full-scale demonstration and testing.

Results and Accomplishments

Significant accomplishments have been achieved for this project, meeting the deliverables outlined in the original proposal, and positioning the project for completion of the remaining deliverables in the second year. Deliverables completed for the first year included Task I—Development, fabrication and characterization of four different pore size membranes; Task II—Design and construction of a membrane testing system, initiation of membrane efficiency evaluations under a set of standard test parameters; Task IV—Design of a CFD model that can be used to develop a system to control the temperature of the membrane module; Task V—Begin construction of an integrated system model for simulating the effect of the genset and the membrane module for water reclamation. The following describes some of the results obtained through completion of the project deliverables. Membranes falling into four pore sizes (ca. 4, 6, 8 and 10 nm) were prepared. All membranes were characterized for flow-weighted pore size distribution, gas permeance, water flux, and bubble point (water breakthrough pressure). The water reclamation efficiencies of the membranes were evaluated as a function of flow rate, membrane temperature control, inlet gas temperature, and feed-gas water-vapor content. Improvement in reclamation efficiency as a result of reducing the membrane pore size (9.5 to 8.2 nm) is apparent at cooling temperatures of 25 and 30°C; however, at 35°C, the improvement is less apparent. The CFD model is being employed to understand the actual temperature profiles at the membrane/gas interface so that graphite foam can be properly integrated into the membrane holder for better temperature control, which is crucial in maximizing efficiency. Preliminary simulations of the water extraction system as it would be integrated with a conventional military genset indicate that the energy penalties associated with membrane-based water extraction are likely to amount to only a few percent of the total genset power output.

Information Shared

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05623

Functionally Graded and Geometrically Ordered Titanium Composite Armor Materials

S.D. Nunn, R.R. Dehoff, and S. Simunovic

Project Description

Titanium and its alloys have many superior characteristics which make it desirable for use in defense systems. Among these are high strength, light weight, and corrosion resistance. Ti-6Al-4V provides more efficient ballistic protection than conventional steel armor, but it is far less efficient than state-of-the-art ceramic armor. The ceramics exhibit high compressive strength, very high hardness, and light weight. The increased availability of recently developed low-cost titanium powders to fabricate structural components using solid state powder metallurgy processing technology provides an unprecedented opportunity to engineer advanced composite armor structures which combine titanium and ceramic materials. This project will investigate two types of composites: (1) Functionally Graded Composites, which consist of two or more blended phases where the ratios can be continuously graded or locally varied and (2) Layered Hybrid Composites, which consist of discrete regions or strata of different materials. Throughout the project, computer modeling will be used to assist in the design of composite structures, choice of materials, and prediction of ballistic performance. The goal of this project is to design, fabricate, model, and test new composites of titanium and ceramics having unique properties and performance capabilities for use in critical defense applications. Demonstration of titanium-based composite materials with improved protective properties would generate immediate interest for further development and utilization of these materials over a broad range of land, air, and naval systems.

Mission Relevance

This project supports DOE's mission to develop new materials and new material processing methods that will benefit US government agencies in accomplishing their goals related to national security, energy conservation, and US competitiveness. The development of advanced titanium composite materials will enhance the performance of ballistic armor for both military and homeland security applications. Simultaneously, it has the potential to substantially reduce the weight of vehicles and systems, which will result in significant fuel savings. The processing methods being proposed utilize low-cost titanium materials and eliminate most of the manufacturing waste (often greater than 90%) that is typically associated with conventional processing, thus conserving a critical resource. Variations of the technology that focus on reduction in wear, friction, and galling between mating components will result in lower energy requirements, reduced maintenance, and conservation of vital raw materials in both government and civilian applications. The project benefits a broad spectrum of programs for DoD and DHS, and supports DOE's EERE program.

Results and Accomplishments

Several ceramic compounds were evaluated as candidates for forming graded composites with titanium by blending powders of the two materials. Chemical and thermodynamic stability of the composites was assessed, and fully dense (no porosity) samples of the composites were fabricated and evaluated. It was found that the addition of 20 vol % boron carbide (B_4C) to Ti-6Al-4V increased the hardness from Rockwell C 39 for the titanium alloy alone to 65 for the composite. This is higher than the hardness of many tool steels and could result in significant deformation of armor-piercing penetrators. Solid ceramics for forming hybrid composites with titanium were also evaluated. Either strong or weak interfacial bonding between the titanium and the ceramic could be produced, depending on the particular ceramic material. Testing showed that alumina (Al_2O_3) formed a very strong interfacial bond with titanium.

Processing methods were evaluated, and several approaches were demonstrated for producing titanium/ceramic composites with controlled geometric characteristics of varying complexity. The distribution of the ceramic in the titanium matrix can be controlled, as well as the topological complexity of the interfaces between materials. We have developed parametric three-dimensional Finite-Element Method (FEM) models for layered materials with different interface morphologies in order to assess the effect of relatively large length scale geometric features on stress wave propagation in various armor configurations. The modeled geometric features are based on a step-wise cubic representation similar to volumetric raster discretization on regular spatial grids. This approach provides a simple basis for parametric analysis of the effect of geometric features on the armor response. Other discretization approaches will be developed in the second year of the project to model features that do not conform well to this representation. We have also developed a new analytical formulation for modeling one-dimensional stress wave propagation involving systems with multiple interfaces. It constructs a tree structure (e.g., binary tree for 1-D approximation) that recursively generates new stress waves (branches) at each interface (tree node) and sums all stresses over a selected time interval. The binary tree approach overcomes some of the limitations of classical one-dimensional stress analysis using Lagrangian diagrams. We have also obtained a one-dimensional stress wave propagation program, SWAP-9, that incorporates non-linear material response and failure. The program will be used for parametric analysis of longer-term response in laminar structures.

NUCLEAR ENERGY SCIENCE AND TECHNOLOGY

05384

Scalable, Fully Implicit Algorithms for First-Principles Kinetic Simulations at the Ultrascale

L. Chacón, J.-G. Chen, and D.C. Barnes

Project Description

This project aims at developing a novel, scalable kinetic algorithmic strategy based on fully implicit nonlinear methods. The approach will be able to exploit ORNL's ultrascale computing capabilities to enable a first-of-a-kind future predictive thermonuclear plasma modeling capability. Plasmas in the regimes of interest for nuclear fusion feature extremely disparate time and length scales. Current first-principles kinetic algorithms are explicit, needing to resolve the fastest timescales and the smallest length scales in the model for numerical stability, and are therefore extremely inefficient. The fully implicit character of our approach will eliminate numerical stability constraints (thus enhancing efficiency possibly by orders of magnitude). Its nonlinear character will deliver enhanced accuracy and nonlinear stability. Our approach will be particle based and thus naturally suitable for parallel supercomputers. If successful, this research will enable simulations that are presently unattainable with current algorithms even with ultrascale computing and will have direct implications for first-tier DOE projects such as ITER.

Mission Relevance

The project has strong relevance to two DOE missions: energy security and scientific discovery and innovation. Relevance to energy security stems from this project's connection to magnetic fusion energy and the international fusion reactor, ITER (which if successful could help ensure the energy supply of humanity for centuries to come). By enabling a predictive capability, this project may have direct impact on the success of ITER and the US magnetic fusion program and may contribute to ensure a good scientific/technological return on US investment in such an experiment. Relevance to scientific discovery and innovation stems from the strong connection with two offices of the DOE Office of Science: the Office of Fusion Energy Science and the Office of Applied Scientific Computing Research. Success in this project will contribute to the core goals of both offices and will contribute to US scientific prominence in the world.

Results and Accomplishments

Our research in this project to date has confirmed its main premise, namely, that a fully implicit, nonlinear PIC kinetic algorithm is possible, which enables accurate and efficient kinetic simulations. Thus, after more than 20 years of research in implicit PIC methods, we have demonstrated the first fully implicit PIC algorithm that can take time steps much larger (and mesh resolutions much coarser) than explicit PIC in a stable, accurate manner. We have also made significant progress towards the implementation of our implicit PIC algorithm on GPU architectures, which is of particular relevance to ORNL's future ultrascale

computing facilities. There is ample evidence of the tremendous potential for GPU-vs-CPU speedup in explicit PIC simulations. Implicit PIC, however, presents different challenges on a GPU. On the one hand, the most expensive operation in our algorithm is the particle push, which must be performed for all particles once per nonlinear residual evaluation. However, the particle push is a segregated operation in our nonlinear residual computation, which can be independently computed on GPU hardware. This presents a clear, rapid-development path for implicit PIC to effectively exploit upcoming heterogeneous hardware architectures. On the other hand, the optimization of the particle push stage on GPU is complicated by its implicit, adaptive, and charge-conserving nature, and has required a tailored implementation. Nvidia Fermi GPU numerical experiments of the particle push stage (including moment accumulation and employing a large implicit time step) demonstrate excellent scalability up to 8000 threads, speedups of up to 300 (in single precision) vs a 3.3. Intel Xeon^{TM} CPU, and an overall GPU computational efficiency between 20 and 30% of the peak theoretical performance.

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05424

Revolutionary Radiation Transport for Next-Generation Predictive Multiphysics Modeling and Simulation

J.C. Wagner, T.M. Evans, S.W. Mosher, D.E. Peplow, and J.A. Turner

Project Description

Nuclear power is a viable and proven technology for carbon-free production of electricity. For some time, efforts have been under way to develop advanced nuclear energy systems that offer significant improvements with respect to cost, safety, and sustainability. However, the pace at which these new technologies can be developed and deployed into viable options and our ability to advance the state of the art for such systems are limited by inherent approximations in our aging computational tools and approach. There is a definite need for, and programmatic opportunities associated with, drastic, not incremental, improvements in our modeling and simulation (M&S) capabilities. Responding to this need, this project proposes to leverage our recently developed and unique hybrid (deterministic/Monte Carlo) radiation transport methods, codes, capabilities, and associated experience to establish a revolutionary change in radiation transport M&S and to ensure that ORNL remains at the forefront of this transition. We will develop a parallel, hybrid radiation transport M&S package that will be operable within a multiphysics framework and provide a distinguishing anchor for pursuing programmatic funding for further capability development. The work will emphasize fission reactor analysis, though it will provide an enabling, predictive M&S capability that could substantially advance the state of the art in many areas and support a leadership role in computational modeling for nuclear energy and national security applications.

Mission Relevance

The work is focused on developing an enabling, "game changing" radiation transport capability that will have direct applicability and benefits to addressing the nation's nuclear technology challenges, including (1) design of new nuclear power systems and support of safe, economical, and extended operation of existing fission-based reactors; (2) full-scale fuel cycle facility analyses for safety and safeguards; (3) national security applications; and (4) evaluation of risks associated with geologic disposal of defense and commercial nuclear waste. The proposed capability will have direct relevance to the following organizations: DOE Office of Nuclear Energy, related to large-scale reactors, fuels, waste disposal, shielding, and safeguards M&S; DOE Office of Science, Fusion Energy Science Program, related to M&S for ITER, the proposed Fusion Nuclear Science Facility, and hybrid fusion–fission concepts; Department of Homeland Security and Defense Threat Reduction Agency, related to M&S for applications such as detection of nuclear material and radiation dose from an improvised nuclear device in an urban environment; and NNSA, related to M&S to support nuclear nonproliferation and safeguards.

Results and Accomplishments

During the first year, the team developed ideas and methods for overcoming the two foremost technical challenges to enabling high-fidelity Monte Carlo–based radiation transport for reactor core simulations on high-performance computers (HPC). A new hybrid deterministic/Monte Carlo k-eigenvalue transport method (extension of FW-CADIS method) was developed that overcomes the major limitation of conventional Monte Carlo by distributing computational effort, and hence statistical precision, uniformly across the region of interest. Additionally, a novel multi-set overlapping region (MLOR) domain-decomposition algorithm was developed to exploit the computational power that HPC platforms (like Jaguar) provide. During the second year, the team focused on implementing and testing the ideas and methods developed during the first year. A new multi-decomposition parallel, combinatorial geometry Monte Carlo transport code named *Shift* has been developed and undergone initial verification, validation, and parallel performance testing. The *Shift* hybrid transport code is being developed within the Denovo transport toolkit to take full advantage of Denovo's existing massively parallel deterministic radiation transport capabilities. We have demonstrated the effectiveness of the FW-CADIS method for improving both source and flux convergence efficiency. We have developed and implemented a new, novel technique for estimating mesh tally variances in domain-decomposed problems. Additionally, we have conducted additional testing and evaluation of our hybrid and domain-decomposition approaches using challenging benchmark problems found in the literature. As of the writing of this summary, two other major activities are currently in progress: (1) integrating the hybrid methods into *Shift* and (2) implementing continuous-energy physics into the *Shift* code.

Information Shared

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05531

Plasma Heating to Enable Fusion Energy Plasma Material Interface Research

J.B. Caughman, T. Bigelow, S. Diem, R.H. Goulding, D.L. Hillis, M. Peng, D. Rasmussen, and J.B. Wilgen

Project Description

A recent report by the Fusion Energy Sciences Advisory Committee (FESAC) to DOE stated that issues related to plasma facing components and materials will require a major extrapolation from current state of knowledge and will need substantial development. The R&D program needed to address these issues will require new facilities to improve our understanding of the mechanisms underlying plasma-surface interactions and the design of plasma facing components (PFC) and radio frequency (RF) antennas. We anticipate that ORNL will propose a new facility for addressing these critical issues. The facility will require a large-area plasma (~100 cm^2) with reactor relevant heat flux (20 MW/m^2) and particle flux ($10^{23}/m^2s$). We plan to use a helicon plasma source to create the plasma. However, substantial additional plasma heating will be required to obtain the desired fluxes.

This project addresses the need to couple power to the plasma electrons using microwave power. The high-plasma density needed to obtain the desired plasma parameters for material and antenna testing requires the use of either electron Bernstein waves (EBW) or Whistler waves. Such an approach needs to be demonstrated with high magnetic fields (~1 Tesla) in a cylindrical magnetic mirror geometry. Diagnostics and modeling are needed to characterize plasma performance to determine electron temperature/density power scaling and wave-coupling mechanisms, while appropriate launchers for wave coupling in high-density plasmas need to be demonstrated.

Mission Relevance

The Office of Fusion Energy Sciences has recently conducted a series of Research Needs Workshops to determine the key research opportunities of the fusion energy program for the next 20 years to address the gaps and issues in demonstrating fusion energy as a power source. The plasma material interface, covering plasma surface interactions, plasma facing components, and RF antennas, is identified as a critical area of research. It is expected that high priority will be assigned to a new facility for studying the plasma-material interface at a high plasma flux, and also to a new facility for studying RF antenna physics. Both of these facilities will require a high-density plasma over a large area. Success of this project will position ORNL to take the lead in these research efforts and host the required facilities. The likely funding range for these facilities will be $50 million to $100 million each. We have submitted proposals in these areas and are continuing our efforts to build the research program.

Results and Accomplishments

The primary objectives of the project were to build an experimental device, demonstrate microwave power coupling to a high-density plasma using whistler waves and electron Bernstein waves, and to model the wave propagation in the plasma. Substantial progress was made in each of these areas.

The experimental device consists of a central vacuum chamber surrounded by two magnet pairs on either side. An 18 GHz klystron source was used to create the main plasma in the chamber using an O-mode launcher at power levels up to 8 kW, while a 6 GHz klystron source (2.5 kW) was used for whistler wave and EBW coupling. Peak plasma densities of ~$9\times10^{11}/cm^3$ were obtained with an electron temperature of 6–10 eV.

Microwave power coupling into an over-dense plasma was achieved, which was the main focus of this project. Whistler waves at 6 GHz were launched from the high-magnetic-field region towards the lower magnetic field region of the central chamber. Microwaves were able to couple to the over-dense plasma (density greater that the 6 GHz cutoff density of ~$4.5\times10^{11}/cm^3$), with the power mostly going to increased density production. Evidence of wave interaction with the resonance zone was observed, including a change in the plasma density profile and possibly the electron temperature. A launcher designed for EBW coupling was mounted to the central vacuum chamber. The launcher angle was variable from ± 8 degrees, since EBWs need to be launched at an optimized angle with respect to the magnetic field. Power coupling was observed in over-dense plasma conditions in a similar way as the Whistler waves, indicating strong resonant zone interactions. Evidence of a slight change in the electron temperature profile as a function of launch angle was also seen.

A spatially three-dimensional ray tracing code, GENRAY-C, has been developed to model Whistler wave and EBW propagation and absorption in our multiple-magnet geometry. The code was developed by CompX and was built using components from the GENRAY code, which has been used extensively to model microwave heating in a variety of toroidal devices. Full wave absorption was predicted for 6 GHz Whistler waves launched from the throat of the device, which is consistent with observed experimental results. An O-X-B mode conversion scheme was used to launch 3, 4, and 6 GHz EBW power in the central chamber, and full absorption was seen for all frequencies within 5 to 10 cm of the plasma edge. Both Whistler waves and EBWs seem feasible for over-dense plasma coupling.

05570

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

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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) measurement and optimization of performance characteristics during high power tests; (4) study of the effect of magnetic field geometry on performance; and (5) 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 high-flux helicon device was operated at power levels up to 28 kW, which was the maximum rf power available during the experiments. Performance was optimized by varying the gas flow and magnetic field strength (|B|), as well as optimizing the axial |B| profile. Maximum plasma densities in the source region of 4×10^{19} m^{-3} were achieved with He, and 2.6×10^{19} m^{-3} with H and D. These values were achieved at relatively low |B| under the antenna = 0.03–0.1 T. A peak He ion flux of $3.5 \times 10^{22}/m^2$-s was measured at the source exit, with the total particle production of ~ 2.4×10^{20}/s, corresponding to a gas utilization efficiency of 35%. The maximum source density achieved for the goal value of |B| = 0.5 T under the antenna was 1.4×10^{19} m^3 (using He). The densities, ion flux, and gas utilization achieved were, respectively, 100% (H, D, He), 70% (He), and 70% (He) of the project goals, with a maximum available rf power that was 30% of the design value. This power level was insufficient for achieving high-efficiency H and D production at |B| = 0.5 T. The goal for injected energy of 200 kJ per pulse was met (10 s duration at 20 kW). Heat fluxes profiles were measured on the aluminum nitride ceramic, with a maximum value of 40 kW/m^2 observed at an input power level of 16 kW. This is within the acceptable range for this input power level.

Information Shared

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05714

Advanced Alloy Development for the Next-Generation Liquid-Fluoride-Salt-Cooled Nuclear Reactor

G. Muralidharan, S. Dai, D.E. Holcomb, W. Ren, M.L. Santella, R.R. Unocic, and D.F. Wilson

Project Description

Development of a structural alloy tailored to the high-temperature creep strength and liquid-salt corrosion resistance needs of Fluoride-Salt-Cooled High-Temperature Reactors (FHRs), a reactor class being investigated by the DOE-NE Advanced Reactor Concepts program for production of electricity and high-temperature process heat, is necessary to increase FHR efficiency and component lifetime. The primary objective of the proposed project is to develop and demonstrate an effective computation-based design methodology for the development of alloys that combine good high-temperature creep strength with high-temperature liquid-salt compatibility. Work is being performed to understand the relationships between alloy compositions, microstructures, and the two critical material properties of interest over nontraditional compositional ranges. Based upon the developed relationships, computational thermodynamic models are being used to identify new candidate alloy compositions. An initial set of candidate alloys have been identified and are being experimentally assessed for their resistance to liquid-fluoride-salt attack and creep resistance in inert atmosphere. Measurements of their high-temperature creep behavior in liquid fluoride salt and their ease of fabrication are also planned. Experimental results will allow refinement of the predictive capability of the developed methodology, thus enabling future rapid, cost-effective alloy development at ORNL.

Mission Relevance

The FY 2012 DOE-NE advanced reactor concepts program plan identifies FHRs as one of its two primary supported advanced reactor concepts (the other being sodium-cooled reactor). Thus the next few years appear especially opportune to encourage programmatic growth. This project is aimed at initiating a larger DOE-NE-sponsored program on developing and fully qualifying an FHR tailored alloy (likely a $50 million + 10 year program). One of the major deterrents to DOE investment is the conventional wisdom that alloy development is an extremely protracted and a prohibitively expensive process. Successful development of an accelerated methodology to alloy development will increase DOE-NE's support of a much-needed alloy development program for this class of reactors. Also, increasing the efficiency of solar thermal power systems is critically dependent on increasing the temperature of the heat transport technology, and hence the knowledge developed in this project is readily applicable to the DOE-EERE solar thermal program.

Results and Accomplishments

In the first year of the project, the computational thermodynamic modeling tool, JMatPro, was used to calculate the equilibrium microstructure of alloys with particular reference to types and amounts of strengthening phases present in the alloys as a function of temperature and composition space (consisting of several alloying element additions and with minimum acceptable chromium levels). An initial set of model alloys with desirable microstructural strengthening characteristics (solid solution strengthening combined with carbide or gamma' strengthening) have been defined, successfully cast, and fabricated into small plates. High-temperature tensile testing of the alloys shows that some of these alloys have the potential to possess improved high-temperature creep properties. Characterization of the effect of isothermal exposure of selected alloys to FLiNaK with particular reference to metal dissolution and surface damage in sealed capsules is in progress. Creep properties of selected compositions are being evaluated in inert atmosphere to confirm the initial microstructure-based assessment of the potential for improved properties. Several alternative system designs to perform high-temperature creep resistance testing of candidate alloys in the presence of a molten salt in situ were considered and evaluated. A design in which the liquid is contained within a hollow cylindrical specimen was selected because it offered the maximum flexibility with minimum complexity. With the help of data obtained in this work and existing literature data, the preferred precipitation strengthening avenues will be established over the next year, along with the preferred ranges for alloying element additions.

Information Shared

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05740

Material Degradation Phenomena and Mitigation for Nuclear Energy Systems

Z. Feng, Z. Yu, K. An, X.-L. Wang, W. Zhang, and R.E. Stoller

Project Description

This LDRD project aims at advancing our knowledge on the fundamentals of defect transport and damage mechanisms under the extreme temperature, stress, and radiation conditions relevant to current and future generation nuclear energy systems. We propose to develop and demonstrate a unique neutron experiment approach—the coupled simultaneous small-angle neutron scattering (SANS) and wide-angle neutron diffraction (WAND)—for in situ and time-resolved interrogation of the nanoscale and the macroscopic material damage phenomena, and most intriguingly, the dynamic interactions between the two length scales under combined high-temperature, stress, and radiation conditions. A multi-scale modeling framework will also be developed to collaborate with the SANS/WAND experiment results to connect the nano-scale damage process with the macroscopic material deformation and failure behavior under the extreme environment.

The proposed project is motivated by the specific materials challenges for life extension of existing nuclear reactors, and for future nuclear energy systems operated at much higher temperature and irradiation doses. The successful development and demonstration of the neutron experimental capability

and multi-scale model would attract future research programs from DOE/NE, NNSA, NRC, and the nuclear industry related to life extension and next-generation nuclear reactor materials, two areas of anticipated significant growth of R&D for ORNL.

Mission Relevance

This LDRD project aims at advancing our knowledge on the fundamentals of defect transport and damage mechanisms under the extreme temperature, stress, and radiation conditions relevant to current and future generation nuclear energy systems. It supports the missions of the DOE Offices of Fusion Energy Sciences and Nuclear Energy, the Nuclear Regulatory Commission, and the commercial nuclear power industry. Specifically, the results may be relevant to the interests of the DOE/NE LWR Sustainability Program (LWRSP) and EPRI's Long-Term Operation Program in weld repair of irradiated materials. Results on stress effects on He bubble evolution are also likely to stimulate interest from DOE/OFES.

Results and Accomplishments

In FY 2011, the first year of the project, the R&D efforts have been primarily on the development of individual neutron diffraction experiments (systems, approaches and techniques), as well as materials degradation/damage models at different length scales. Considerable progress has been made in the first year, and the project is on schedule to complete all its major milestones. On the in situ WAND measurement, we have successfully solved the challenge of achieving sufficient time resolution while ensuring a relative uniform temperature in the gage volume under fast heating and cooling rates (up to 30°C/sec, 20–1000°C). This was achieved by means of (1) a purposely built heating device and optimization of the specimen geometry and dimensions based on heating rate and other sample conditions and (2) the asynchronous stroboscopic neutron diffraction experiment and data analysis procedure. A time resolution of 0.1 second was achieved for the gage volume suitable for the planned material degradation study for nuclear energy systems. The in situ WAND experiment approach was used to study the phase transformation of high-strength steels under far-from-equilibrium conditions. Very rich information on phase transformations was obtained and is being further analyzed, including the phase stability of different phases under non-equilibrium heating and cooling conditions. Already, two industry partners, General Motors and Alcoa, have expressed their interest in follow-on work to study the phase transformation kinetics of advanced high-strength steels and Al alloys using the newly developed neutron diffraction experiment techniques. On the multi-scale modeling of material damage processes, we focused on the new capability to handle the effects of combined stress and temperature on the kinetics of nano-cavity growth and its influence on the material damage behavior.

05767

Study of Gas-Phase Separations for Closed and Modified Open Used Nuclear Fuel Reprocessing

J. Johnson, B. Spencer, R. Jubin, and G. Del Cul

Project Description

The objective of the proposed work is to establish ORNL as a leader in the investigation of high-temperature reactions of used nuclear fuel with gaseous species. The topic is relevant to science-based development of dry processes for future nuclear fuel cycles and to safe storage of used fuel. Voloxidation is a dry process in which used nuclear fuel is oxidized to release volatile and semi-volatile components. While experimental studies have been performed to demonstrate the process or investigate specific aspects, there are currently significant gaps in the understanding of the process fundamentals, with little predictive capability. The knowledge gaps are greater for the related technologies presently under consideration, such as halide volatility or dry nitration processes. Experimental studies and the development of predictive models are needed to meet the DOE Office of Nuclear Energy's near-term goal to define and analyze fuel cycle technologies for developing options that increase the sustainability and availability of nuclear energy. This work is aimed at closing the gaps by developing phenomenological models of gas-solid thermal processing of used fuel and establishing a unique experimental facility for data collection and model validation. By creating a capability to develop comprehensive understanding of new and original gas-phase separations processes through coupled theory and experimentation, this project will appropriately position ORNL as a leader in the development of methods for the study of modified open fuel cycle technology. It will also provide a vital research capability for examining factors in safe storage of used nuclear fuel, which is gaining increasing attention in light of the activities of the Blue Ribbon Commission on America's Nuclear Future and the recent Fukushima Daiichi Nuclear Power Plant disaster.

Mission Relevance

The capability to perform coupled experimentation and model development aligns with the Office of Nuclear Energy's goal for science-based research and development to define and analyze fuel cycle technologies for developing options that increase the sustainability and availability of nuclear energy. With the current emphasis in the research being placed on a modified open cycle, gas treatment processes will be an important starting point from which other processes will be developed. The Separations and Waste Forms Technical Area of the Nuclear Energy Fuel Cycle Technologies Program has identified gas treatment separations as key processes for which better understanding and modeling is greatly needed. This work will help to close this gap in knowledge.

Results and Accomplishments

Efforts through the first 8 months of the project have focused on the two main objectives for the first year: (1) establishing experimental capability for the investigation of the phenomena controlling the rate of UO_2 oxidation within cladding pieces at high temperatures under a reactive atmosphere and (2) initial development and validation of an overall reaction model. Excellent progress has been made toward the goals set for the first year. Significant accomplishments made to date include the following: (1) a method for cladding sintered depleted UO_2 pellets has been established, enabling fundamental experimentation with representative surrogates; (2) a dual-scale Thermal Gravimetric Analysis (TGA) unit was established to enable spalling rate measurements with used fuel; (3) measurements of spalling rate of depleted UO_2 pellets have been made at various temperatures; (4) experiments to determine the conditions under which

the formation of oxidation product layers limits diffusion of gaseous reactants have been initiated; (5) an initial reaction rate model has been developed.

The experiments performed thus far have provided new insight into the phenomena occurring during the oxidation of oxide fuel in cladding, which is essential for the development of an accurate predictive model for segmented fuel-gas reactions. Based on the initial results, it is clear that a combination of diffusive and kinetic resistances control the rate of reaction.

05840

Closing Technology Gaps with the Development of Advanced Fusion Experimental Facilities

A. Lumsdaine

Project Description

The realization of commercially viable fusion power would essentially end the current societal problems of energy supply (greenhouse gas emission, release of other pollutants, fuel importation from hostile societies, nonrenewable supply, storage of long-term radioactive waste, risk of runaway reaction or meltdown, risk of proliferation of nuclear materials, etc.). The continued international support for research in fusion energy is a testimony to its remarkable possibilities. The ITER international experimental reactor will begin operation in the next decade and will subsequently generate relatively long-pulse burning plasmas, producing up to 10 times the energy required for operation. This will be a substantial initial step towards the realization of a fusion power plant. The purpose of this project is to develop a world-class fusion technology program at ORNL that builds on existing areas of strength within the lab and addresses technology gaps in fusion engineering, particularly in the area of materials for fusion applications. This is done by providing high-end multiphysics computational analysis, mechanical design, and project engineering to participate in the development of critical experimental facilities and projects that will bridge the gaps between ITER and commercially viable fusion power.

Mission Relevance

This project is specifically relevant to the energy resources mission of DOE. When the objectives of the project are realized, ORNL will have developed capabilities that will enable technologies for closing some of the technology gaps that currently stand in the way of realizing commercial power through magnetically confined fusion energy. Particularly, progress will be made towards the planning and construction of facilities (such as a Fusion Nuclear Science Facility, a Plasma Materials Test Stand, a Test Blanket Module, or collaboration on a compact Stellarator) for solving plasma material interface issues, which are among the most critical for the development of a fusion power plant.

Results and Accomplishments

The linkage of the VisualDOC commercial optimization code with ANSYS APDL, ANSYS CFX, and ANSYS Workbench was accomplished. Design optimization of three-dimensional complex systems in multiphysics environments can be performed with any ANSYS component, and can easily be integrated with any analysis code. CFD modeling of fluid flow and heat transfer for the Fusion Nuclear Science Facility (FNSF) centerpost was accomplished. Multiphysics analysis (thermal and structural) of the FNSF centerpost was also completed. A preliminary study on irradiation effects on a copper alloy has been performed to analyze the suitability for the FNSF centerpost. Flow profiles and thermal transfer for

helium flow through roughened pipes for a Dual Cooled Lead Lithium (DCLL) test blanket have been completed using the computational fluid dynamics capability of the ANSYS multiphysics code, and these results have been validated with published empirical results. The ANSYS multiphysics code has been used to perform structural and modal analysis on stellarator design components. In addition, a two-dimensional design optimization study has been completed on the cooling channel design for the FNSF centerpost. Structural analysis was performed for a tokamak port diagnostic under plasma disruption conditions. Electromagnetic loading was computed analytically, while stress analysis was done using ANSYS. Computational fluid dynamics studies were performed on cooling tubes with internal twisted tape for high heat flux divertor components. The specific element analyzed is to be placed in the Wendelstein 7-X divertor in Greifswald, Germany, but the analysis would also be pertinent to ITER and future fusion reactors.

Information Shared

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06237

An Approach for Linking Glass Composition and Structure to Long-Term Performance

E.M. Pierce

Research Plan

The objective of the research outlined in this LDRD proposal is to develop a mechanistic understanding of the processes that control the long-term corrosion of nuclear waste glass, specifically alumino-borosilicate glass. The specific aim is to improve our understanding of the processes that control the formation and conversion of an amorphous hydrated-surface layer (e.g., gel-layer) to a structurally order crypto-crystalline or crystalline alteration product during the glass-water reaction. The gel-layer (e.g., three-dimensional hydrated surface-layer) forms when network bonds in the glass are hydrolyzed by water and relatively insoluble elements contain in the glass (e.g., Al, Fe, Si) condense at the glass-water interface. Upon completion of this project, the tools and knowledge gained through this research will provide the fundamental understanding required to develop the sub-continuum scale models needed to demonstrate that nuclear waste immobilized from reprocessing schemes (specifically modified open and full recycling) can be disposed of in a responsible manner. The technical challenge of improving the technical basis for glass weathering represents one key aspect that must be addressed in order to develop a sustainable nuclear fuel cycle as an option to address the looming energy and potential CO_2 emission crisis expected to result from future increases in energy consumption.

Mission Relevance

A promising option to the looming energy and potential CO_2 emission crisis is to increase the amount of electricity being generated through the use of nuclear power (*Nature* 2006 and *Science* 2005). In order to realize the full potential of a nuclear energy renaissance, the Department of Energy's (DOE's) Office of Nuclear Energy (NE) has been focused on research, development, and demonstration activities that will ensure nuclear power remains a viable option for the US energy portfolio (NE 2010). A major objective for NE is the development of sustainable nuclear fuel cycles with the goal of developing a suite of options that will enable future decision makers to make informed choices about how to best manage the used fuel from reactors. Each of the existing fuel cycle options—once-through, modified open cycle, and full recycling—that are being considered as part of this effort presents unique scientific challenges as it relates to the disposal of nuclear waste. Two of the three fuel cycle options—modified open and full recycling—contain a reprocessing scheme that is expected to produce borosilicate glass as a candidate waste forms.

Results and Accomplishments

In the first year (FY 2011) of this late start LDRD, the major achievements included (1) design of two new reactors that will allow for in situ characterization of glass surfaces during corrosion, (2) composition and structural analysis of weathered sodium alumino-borosilicate glass samples, and (3) the addition of new features to the existing Monte Carlo model being developed to simulate the glass corrosion and surface layer development processes. Based on these results, our next year's work will focus on obtaining in situ measurements of surface layer formation and incorporating these observed features into an update of the existing Monte Carlo model.

06243

Establishment of Welding Capability for Irradiated Materials

J.T. Busby, Z. Feng, R.G. Miller, and W. Zhang

Project Description

ORNL will design and develop a capability for the use of advanced welding techniques inside a hot cell. This prototype facility will bring to ORNL a one-of-a-kind capability in the world for welding technology development for irradiated materials. This proposal will support design, procurement, and fabrication of key elements of this facility. When complete, this capability will also complement other facilities and capabilities at ORNL to provide a "one-stop" facility in support of the nuclear power industry. It is planned to design, manufacture, and install the remote welding facility in hot cell C of Building 7930.

The unique hot cell welding facility will house the state-of-the-art, portable friction stir welding, laser welding, arc welding, and automation equipment. The present proposal will cover the design and fabrication of base infrastructure in the hot cell such as the manipulator and worktable. The state-of-the-art welding equipment will be acquired as part of the ongoing synergetic activities and the potential follow-on funding.

Mission Relevance

There are over 100 nuclear power plants operating in the United States which generate approximately 20% of the nation's electricity. These plants range from 15 to 40 years old. Extending the service lives of the current fleet of nuclear power plants beyond 60 years (even beyond 80 years) is imperative to allow for the environmentally responsible energy infrastructures (including construction of new nuclear power

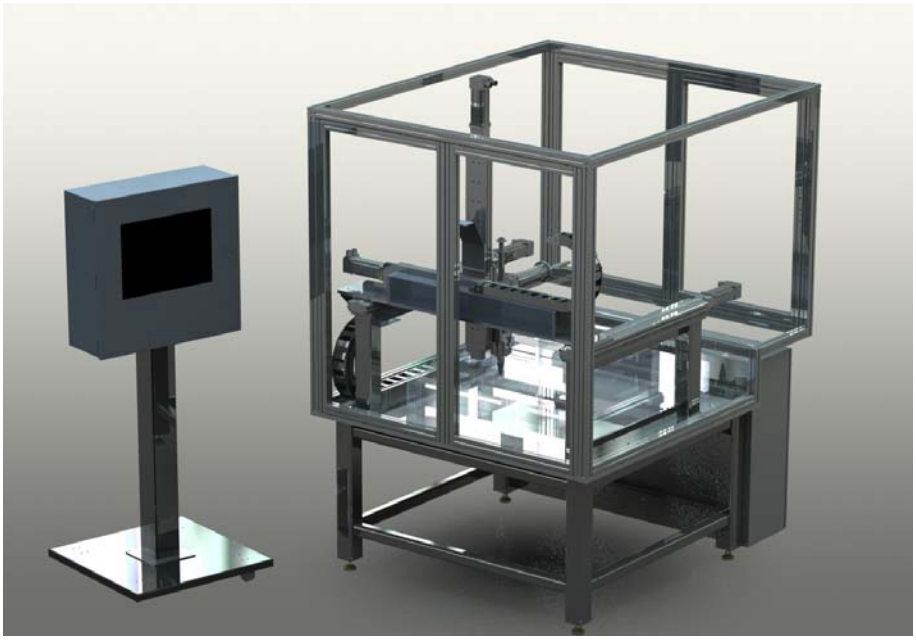
plants) being developed and matured. Such critical needs are well recognized by both the industry and the US government (DOE/NE and NRC). Degradation of structural materials in this environment can lead to reduced performance, and in some cases, sudden failure. Material repair and improvement technologies based on welding are a cost-effective way to mitigate the structural material degradation, as the replacement of components can be extremely expensive and time-consuming.

Results and Accomplishments

The proposed hot cell welding facility will be a crucial enabler for developing and validating the scientific and technological basis for solving the specific materials challenges for life-extension of existing nuclear reactors, and for future nuclear energy systems operated at much higher temperature.

In FY 2011, the first year of the project, we have completed the preliminary conceptual design of the welding hot cell. Inputs from the personnel in charge of Building 7930 where the welding hot cell is physically located regarding the operation of machinery in hot cell environment, and the safety regulations dealing with radioactive materials, were taken into consideration in the concept design of the welding hot cell, and subsequent detailed design, engineering, and construction. Subcontractors were identified for the detailed design, engineering, and eventual construction of the welding hot cell housing facility. Bill of Materials and estimated costs of various welding-related equipment were developed and verified with potential equipment suppliers.

A design for a key welding component (the laser welding unit) is shown below.



Schematic of laser system for use in welding of irradiated materials.

UNDERSTANDING CLIMATE CHANGE IMPACTS

05212

Uncertainty Assessment and Reduction for Climate Extremes and Climate Change Impacts

A.R. Ganguly, M.L. Branstetter, D.J. Erickson III, S.-C. Kao, E.A. Kodra, E.S. Parish, N. Singh, K.J.K. Steinhaeuser, N. Chawla, S. Ghosh, V. Kumar, M. Steinbach (all no-cost academic collaborators), and P. 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.

This LDRD project has generated papers in interdisciplinary journals like *Proceedings of the National Academy of Sciences* (PNAS) with a recent one in advanced review at the journal *Nature Climate Change*. The project has also generated highlights in the journals *Nature*, PNAS and *Nature Climate Change* based on published papers in *Geophysical Research Letters* and PNAS. A recently accepted paper in *Journal of Geophysical Research* has generated initial interest in *Science* magazine. The deliverables from this LDRD have been used for projects funded by the DOE (Office of Science projects) and the DOD (Office of the Secretary of Defense led Quadrennial Defense review), as well as opened pathways to other agencies (e.g., Nuclear Regulatory Commission, NASA, Centers for Disease Control, National Science Foundation, NOAA, EPA). The new funding received and capabilities developed promise significant funding even under difficult funding situations for climate, environment, and related areas.

In addition to papers in top interdisciplinary venues and climate science journals, the computational components have led to papers and invited talks in top computer science conferences such as ICDM and ICML. We have also initiated a new workshop in IEEE ICDM to develop recognition for brand ORNL in the computational climate and sustainability communities. The new insights from this project have been reported in the national media like USA Today and MSNBC as well as widely in the international media (e.g., La Scienza in Italy and The Hindu in India), besides being cited in reports of the United Nations, U.S. Navy, and the National Academies, as well as other agencies and organizations including by fellow scientists and sponsoring agencies in their papers and presentations.

While some of the work is still in various stages of publication, 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, Massachusetts Institute of Technology, 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. The PI chaired two sessions at the 2010 Fall Meeting of the American Geophysical Union (AGU) in December, one on climate-related extremes and another on uncertainty quantification for climate. The PI has been invited for two talks at the 2011 AGU, and was invited for a workshop on global challenges of the International Conference on Machine Learning, as well as a recent Climate Informatics workshop organized by the New York Academy of Sciences. The project has improved the recognition of ORNL in the area of climate extremes and climate data mining or machine learning. The contributors to this LDRD hail from three ORNL divisions, specifically, CSED, ESD, and CSMD, who have worked together without regard to divisional barriers.

Information Shared

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05528

Enhancing Climate Impact Integrated Assessment for Water through Climate Informatics

W.C. Lenhardt, M.L. Branstetter, A.W. King, L. Pouchard, K. Shih-Chieh, and D. Wang

Project Description

Our objective is to demonstrate that climate informatics is a viable method to enable the analysis of the impact of climate change on water, such as hydrology and watersheds. Both, in turn, influence power infrastructure and agriculture. End-to-end analysis is needed for policy makers to achieve an understanding of the global impacts of compartmentalized decisions on the country's infrastructure. This kind of analysis is difficult because of the cross-disciplinary nature of the expertise involved and the fact that needed datasets are owned and stored in different archives at various agencies. Data and process descriptions for the transformation of datasets are unavailable, hidden in the software, or abstracted in the scientists' minds. Climate informatics will provide a solution to the data and metadata challenges, thus enabling rigorous and reproducible impact analysis based upon higher spatial and temporal resolution observational data and traceable processes. We will create a climate informatics capability at ORNL consisting of a data repository, informatics tools, and potential integration with Earth System Grid that the DOE Office of Biological and Environmental Research will find attractive for its projected program growth in this area. Simultaneously, the creation of a data archive and associated tools for water-related observational and modeling data will fill a gap in the national landscape: this effort has the potential for putting ORNL at the forefront of climate change impact studies, water dataset collections, and climate informatics.

Mission Relevance

Numerous high-profile reports, including reports from DOE Office of Science, the National Science Foundation, and the National Academies, have highlighted three issues salient to this research: (1) contemporary science cannot be successful without informatics and cyberinfrastructure; (2) particularly in the area of climate change science and given the challenges of integrating model data with observational data, climate informatics is a necessary complement to high-performance computing and domain science; and (3) climate science and the application of climate science to areas such as impacts, adaptation, and vulnerability analysis and decision support will need the type of science translation/knowledge capture encapsulated by our project. In addition, we chose water as a substantive focus due to its relevance to various energy-related issues of interest to DOE.

Results and Accomplishments

Work during the first quarter of FY 2011 focused on finalizing the system architecture, work on integrating the user tagging system with the proposed data system, preparing for the various reviews, and developing a paper for submission to a relevant journal as well as submitting and presenting a poster on the project at the Fall 2010 AGU meeting in San Francisco.

This project was reviewed in January 2011, and based on the results of the review, the project was discontinued.

Information Shared

AGU Fall 2010 Poster, "An Observational and Computational Variable-Tagging System for Climate Change Informatics" Line C Pouchard, Andrew Runciman, Marcia Branstetter, W. Christopher Lenhardt, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Paper submitted but not accepted for publication. Submitted to a special issue of IEEE Software that explored the challenges in developing the software infrastructure for understanding and responding to climate change. "Climate Informatics: Bridging Theory and Experiment to Advance Climate Change Sciences," Dali Wang, W. Christopher Lenhardt, Anthony Wayne King, Marcia L. Branstetter, Shih-Chieh Kao, Line Catherine Pouchard

05606

Characterization and Modeling of Permafrost Microbial Community Diversity and Metabolism during Simulated Global Warming

D.A. Elias, D.E. Graham, T.J. Phelps, and P.E. Thornton

Project Description

Carbon cycle models suggest that permafrost soils contain massive reservoirs of organic carbon, whose mineralization would substantially increase greenhouse gas (GHG) levels. Models simulating current GHG production and transport do not address permafrost thawing due to global warming, or the subsequent microbial mineralization of buried carbon. This project has measured GHG emissions from permafrost cores during controlled warming, and we have produced fundamental data for single point source models of GHG emissions. We are also developing a systems biology approach toward aiding in the development of more discreet and locally accurate models for predicting CH_4 and CO_2 generation and emissions from the release of trapped GHG due to enhanced microbial metabolism of buried nutrients. Current and recent microcosm experiments at ORNL are characterizing perturbations in microbial metabolism and GHG production, and these data will help to focus future long-term studies on specific controlling factors. This integrated effort continues to support the Earth System Modeling and Carbon Cycle Science thrust areas within the Climate Change Science Institute.

Mission Relevance

The US DOE has identified GHG release as the "non-linear tipping point" for global warming. Efforts are under way within the Climate & Environmental Sciences Division of OBER towards better understanding of these processes for more accurate predictive capabilities, and funding is expected to increase in the near term. Current GHG emission models estimate active layer gas release, and often underestimate biogenic CH_4 while assuming litter pools exist in upper soil layers. Decomposition rates are calculated from the soil top 40 cm, but it is spatially varied throughout the permafrost layer. Carbon distribution is not modeled, but the Climate Land Model (CLM4) does include soil temperature, moisture, and freeze/thaw status to >3 m depths. There are also no parameters for discreet depth discrimination (i.e., surface, active or permafrost) nor is there a component for the effect of a changing pH. The work performed on this project is aimed at accentuating the models predictive capabilities by providing environmentally relevant biogeochemical data derived from microbial community metabolism of warmed permafrost core material.

Results and Accomplishments

Year 1 deliverables were met within 8 months of funding or are on track, with the team poised to exceed deliverables by month 12. This project is also on track for all Year 2 deliverables. For Aim 1, we obtained four frozen core samples from Fairbanks, AK, to a depth of approximately 3 m. Sediment samples from three of the cores were removed from different depths and analyzed for pH, total nitrogen, and organic carbon, which all increased with depth. Organic carbon was >83% of the total carbon in all cases. Sediment microcosms were constructed from samples of the surface, active and permafrost layers of the Fairbanks cores, and incubated for 3 months at –2°C, +3°C, and +5°C. Surface microcosms began aerobic, while all others were constructed in an anaerobic glove bag. While all frozen samples thawed during incubation, increased warming (–2°C to +5°C) did not significantly increase CO_2 or CH_4 generation and emission. Carbon dioxide increased to 14% (v/v) headspace gas in the surface sediments and up to 3% in the active and permafrost incubations. Methane was absent in the surface layers, up to 0.2% in the active sediments and highest in the permafrost incubations at 0.5%. The highest rates of CO_2 generation in the surface incubations (0.120 μmol/g sediment/month) were approximately 20 times faster than the highest CH_4 generation rates in the permafrost incubations (0.006 μmol/g sediment/month). These results indicate that anoxic conditions, more neutral pH, high water, and organic carbon contents of the thawed permafrost samples were most conducive to methanogenesis. After 6 months incubation, the pH of almost all sediments dropped to below 5.8. At this acidic pH, CH_4 production declines substantially, and dissolved CO_2 will be volatilized, further increasing the CO_2 emission rates and yields. DNA extraction and phylotyping experiments are under way to identify changes in the microbial population that corresponded to organic matter mineralization and acidification during the microcosms' incubation. We have also provided samples to collaborators at LBNL-JGI for DNA extraction and metagenome sequencing.

For Aim 2, we have compared the effects of water saturation in microcosms, and determined that high water content is secondary to anaerobiosis in controlling CH_4 and CO_2 emission profiles. We also established Fairbanks sediment microcosms in the presence of pH buffers to identify pH-dependent effects on organic matter mineralization during FY 2012.

For Aim 3, we have hired a new post-doctoral researcher and begun engaging him in parameterizing land models using the organic matter mineralization and GHG production rates we determined in the sample microcosms. This modeling effort is on track for FY 2012.

Information Shared

At present, one publication is planned that will incorporate the above datasets along with (1) changes in the microbial community between the original sediments and those at the end of 6 month incubation using 16S rRNA gene pyrosequencing and (2) a revised model prediction using the above data. This work will also be presented at the 2011 Fall American Geophysical Union meeting in San Francisco.

- "Characterization and Modeling of Microbial Carbon Metabolism in Thawing Permafrost," Dwayne A. Elias, Tommy J. Phelps, Peter E. Thornton, and David E. Graham.

05685

Modeling Long-Term Population Resettlement under Climate Change Scenarios

B.L. Bhaduri, J. Santos-Hernandez, B.L. Preston, X. Cui, J. Schryver, and R. Medina

Project Description

Changes in climate are expected to challenge the capacity of human settlements to adapt to a changing environment. Some of the predicted impacts include increase in the duration of wildfires, increase in the likelihood of flooding, more severe and longer heat waves, more intense hurricanes, desertification, increase in snowstorms, and an increase in foodborne, airborne, and waterborne diseases, among others. The goal of this project is to develop a conceptual model of population dynamics covering displacement, migration, and resettlement as an interactive consequence of vulnerability to climate change and its impacts on social arrangements, political stability, economic prosperity, water resources, land cover, and land use. The climate-induced population dynamics conceptual model is unconventional and innovative in that it is not just a theoretical exercise to identify factors or variables that operate and interact in human and environmental systems. In contrast, we present an alternative dialectical approach that models human life as interactions among adaptive agents who influence one another in response to the influence they receive (a breakthrough in the social sciences and disaster studies). ORNL and our group of researchers are strategically positioned to develop this spatio-temporal dialectic simulation of climate-induced population dynamics for the analysis of geopolitical and security analysis.

Mission Relevance

Changes in climate patterns and extremes are increasingly a source of concern across the government. As it has been exemplified by events such as the Dust Bowl in the 1930s, Hurricane Katrina in 2005, and Hurricane Irene more recently, climate events can disrupt the daily routine of households in the affected areas, resulting in thousands of people displaced. The primary goal of this project is to develop an integrated model, and subsequently a software agent–based simulation, that would allow us to examine how environmental factors affect migratory patterns; specifically, what households are likely to stay in their current location, what households are likely to relocate, what households are likely to have members who are migrants and where do these migrants go, whether they will return to their country of origin, and if so, the length of their displacement. We are currently working on the development of a software agent–based simulation of reactive adaptation to climate change that allows us to model behavioral intentions regarding household relocation. This LDRD project is expected to develop new understanding of climate change–induced human migration and resettlement that has tremendous implications for the future of natural resources and geopolitical stability. It seeks to improve scientific knowledge of the potential consequences of climatic change. This project is relevant to both the Office of Advanced Scientific Computing Research and the Office of Biological and Environmental Research, because of (1) the novel computational requirements of the proposed modeling effort, which include the representation of complex systems via high-performance computing and (2) the potential applications in the context of integrated assessment modeling, respectively. This project is also relevant to other federal agencies including the Department of Defense and United States Agency for International Development (USAID) due to the potential applications of the research with respect to identifying vulnerable populations and communities that may be adversely affected by climate change in the decades ahead, prompting humanitarian and/or security crises to which US agencies may need to respond. In this context, this project can assist in preparedness and contingency planning for federal agencies.

Results and Accomplishments

Our research builds on the social vulnerability approach and adapts the reactive adaptation to climate change (RACC) and the multi-alternative decision field theory (MDFT) frameworks to integrate push-and-pull factors into a single quantitative model that conceptualizes migration decisions as a non-linear process. We have focused on developing a conceptual framework that allow us to better understand how households adapt and how their decisions are influenced not only by others but also by multi-level social forces that structure human and environmental systems. Development of an integrated conceptual framework of climate-induced population dynamics has been completed and is continually refined. This conceptual framework development has utilized current scientific knowledge through the review of close to 200 research articles on social impacts of climate change, social vulnerability, migration decision making, disasters and population displacement, forced migration, internal migration, transnational social networks, hazards and disasters in Bangladesh, hazards and disasters in the West Sahel region, and human adaptation to climate change. Using demographic and socioeconomic data, a scenario-based platform made of households nested in a social system is being developed to model agent decision intentions as a function of attitudes generated through interaction with others, subjective norms that are partially conditioned by demographic and socioeconomic characteristics, and of the perceived capacity of the social unit for adaption. An interactive visualization platform is being developed to present the framework, describe the elements in each dimension, provide scientific references, and evaluate the availability of data for each element. In addition, an analysis of demographic and socioeconomic characteristics by country within each climate zone is ongoing. Accomplishments to this date include the following.

- The completion of an integrated conceptual framework of climate-induced population dynamics (currently being reviewed and refined)
- An extensive review of the scientific literature on the relationship between climate, disasters, and human migration is near completion.
- A collection of sub-national survey, demographic, and socioeconomic data for Bangladesh, Senegal, Mauritania, Mali, Niger, Nigeria, and Burkina Faso
- Developing and benchmarking an agent-based modeling prototype to assess the computational requirements for scaling the simulation

Information Shared

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Bhaduri, B., Cui, X., Liu, C., Santos-Hernandez, J., Preston, B., Schryver, J., Nutaro, J., Hadley, S., Medina, R., and Kim, H. 2011. "Knowledge Discovery for Exploring the Relations between Climate Change and Population Dynamics," *Geocomputation* 2011. London, United Kingdom.

Santos-Hernández, J., Bhaduri, B., Preston, P., Cui, X., and Schryver, J. "From vulnerability profiles to vulnerable agents: Conceptualizing social vulnerability to population displacement in Bangladesh," in preparation and to be submitted to the journal *Nature Climate Change*.

05893

Quantifying Economic Losses Associated with Climate Extremes under Conditions of Climatic and Socioeconomic Change

B.L. Preston, W. Shem, E.S. Parish, and M. Maloney

Project Description

The economic costs of extreme weather events have increased markedly in recent decades, largely as a result of socioeconomic processes and trends. Yet, quantitative understanding of the interactions between climatic and socioeconomic change on economic damages from climatic extremes is lacking. The parallel application of "top down" and "bottom up" analytical methods will be applied within a GIS environment to address this knowledge gap. The Hazards U.S. Multi-Hazard Model (HAZUS-MH) will be parameterized for a cross section of US case study communities as part of a "bottom up" comparison of economic damages in response to simulated extreme events. Model sensitivity will be tested using a range of hazard event return periods and observed and synthetic development patterns. NCEP reanalysis products as well global and regional climate modeling will be used to quantify changes in the spatiotemporal distribution of climatic extremes given anthropogenic climate change. To generalize simulation results across a range of spatial scales, empirical models of hazard losses will be developed based upon US county, state, and national data for historical losses as well as data for extreme event frequencies and socioeconomic conditions. These top down models will then be perturbed with climate model projections of extremes and socioeconomic scenarios to estimate future economic losses.

Mission Relevance

The project seeks to improve the scientific basis for assessing the potential consequences of climatic change by linking global and regional modeling of climatic extremes to hazard models for the estimation of economic impacts. The proposed project also seeks to contribute to the development of more integrated assessment tools for estimating future impacts with a particular emphasis on integrating scenarios of alternative demographic and economic futures with information on climate variability and climate change. This work is most relevant to the Office of Biological and Environmental Research, particularly with respect to the development of methods for accounting for the costs of extreme weather events within integrated assessment models.

Results and Accomplishments

Over the course of FY 2011, the project has achieved a number of milestones. Principle among these achievements has been the development of a metric (referred to as "potential socioeconomic exposure" or PSE) that reflects the spatial and temporal distribution of societal exposure to climatic extremes across the United States at the county level. Through the development of a stochastic component cohort model as well as multiple scenarios of future economic development, this metric has been projected into the future (in annual time steps) out to the year 2054. Our metric of PSE is also being used to examine the implications of changes in socioeconomic exposure to specific climatic extremes. To examine other metrics of socioeconomic vulnerability to natural hazards and climate change, our project has begun focusing on the US coastal zone including the analysis of various historical land cover data sets to estimate changes in urbanization in areas exposed to coastal hazards. Our project has also made progress in regional climate modeling efforts. A series of simulations with the Weather and Research Forecasting Model (WRF) have been conducted to evaluate the model's performance at reproducing a historical extreme rainfall event that occurred in the metropolitan Atlanta, Georgia, area in September of 2009. In addition, the sensitivity of simulations to different land use scenarios (focused on urbanization in the Atlanta area) was also evaluated.

Information Shared

Preston, B.L., Danese, C., and Yuen, E.J. 2011. "Embedding Climate Change Risk Assessment in a Governance Context," Colorado Conference on Earth System Governance, 17–20 May, 2011, Fort Collins, CO.

Preston, B.L. 2011. "Committed Climate Vulnerability and Its Implications for Adaptation Demand," *Global Environmental Change*, in preparation.

Preston, B.L., and Maloney, M. 2011. "U.S. Socioeconomic Exposure to Climate Extremes: Past, Present, and Future." *Sustainability Science*, in preparation.

Preston, B.L., Shem, W., Parish, E., and Maloney, M. 2011. "Exploring Drivers of Vulnerability to Climate Extremes in Dynamic Urban Environments: A Case Study," *Regional Environmental Change*, in preparation.

Shem, W., Parish, E., Preston, B.L. and Maloney, M. 2011. "Using WRF to Assess the Sensitivity of an Extreme Rainfall Event to Land Use Change," *Climate Research*, in preparation.

SCIENTIFIC DISCOVERY AND INNOVATION

05501

Enabling Plant Systems Biology Investigations for Carbon Cycling and Biosequestration Research

U. Kalluri, H.Z. Bilheux, S. Gleason, and G. Fann

Project Description

New insights into molecular controls of partitioning, transport, and fate of carbon fixed by photosynthesis in plants and its correlation with other measured plant system properties can be gained by undertaking a systems biology approach of using sophisticated system profiling techniques and modeling. Towards enabling such an approach, we propose to (1) develop, adapt, and apply adapt x-ray micro-CT and neutron imaging technologies to studying plant systems, (2) generate experimental data using in vivo as well as ex situ molecular and phenotype profiling methods, and (3) develop an initial modeling framework to assess, correlate, and predict as to which spatiotemporal changes in system dynamics are key to predicting emergent properties of system.

Mission Relevance

The project will demonstrate a new investigative approach that has also been recently advocated in the recent National Academy of Sciences report on "New Biology." The proposed efforts are envisioned to help position ORNL as a leader in in vivo plant imaging and modeling efforts to study plant growth and responses. The measurement and modeling approaches developed here are directly applicable in sustainability assessments of bioenergy feedstock plant materials modified in cell wall chemistry. Proposed efforts are expected to complement and further strengthen ORNL's position to pursue future funding opportunities related to the declared grand research challenges within the DOE Biological and Environmental Research programs, the Climate Change, Feedstock Genomics and Plant-Microbe Science areas.

Results and Accomplishments

Through this project, salient progress towards developing a CT-imaging technique to study live plants included optimization of sample generation with specified container, achieving resolution of ~ 50–100 micron without system calibration, successful live whole-plant scanning at 512 × 512 × 512 voxels in under 30 minutes, and whole-plant reconstruction, refining the image output using suitable algorithms to filter noise. Also, salient progress in developing the neutron imaging technique included optimization plant growth using aluminum containers and sand, successful demonstration of neutron imaging capabilities at CG1D, although CG1 is not an imaging beamline, achievement of ~70 micron resolution, increased understanding of conducting dynamic studies, acquisition of data from water phantom samples that could quantitatively inform water uptake in plants, performed neutron CT. The labeling, growth, delivery, and imaging experiments (boron-labeled sucrose transport and water transport in auxin mutants)

were undertaken successfully, and imaging data obtained from ~4 hr measurements are being analyzed and drafted into a cross-disciplinary manuscript. From the same set of plants used for neutron imaging, a pair of auxin mutant and control Poplar plants was used for xCT imaging and histochemical studies, to look at structure at the cellular level for use in the modeling effort. We have implemented a coupled partial differential equation model (one equation for the water movement in the soil and another for water movement in the plant roots) in MADNESS (a 2011 R&D winner), a high-level environment for the solution of integral and differential equations using adaptive, fast methods.

Information Shared

Paquit, Vincent C., Shaun S. Gleason, and Udaya C. Kalluri, "Monitoring plant growth using high resolution micro-CT images," Proceedings of Image Processing: Machine Vision Applications IV (SPIE Electronic Imaging Symposium), 7877–33, January 2011.

Gleason, S. G., Paquit, V.C., Bilheux, H. Z., Willis, K. J., Deleon, A. M., McNutt, W. M., and Kalluri, U. C. "X-ray and Neutron Imaging for Plant Systems Biology Investigations," IEEE Proceedings (Future of Instrumentation International Workshop) 2011.

05565

Engineered Chemical Nanomanufacturing of Quantum Dot Nanocrystals—Meeting the Energy Technology Demands

M.Z. Hu, D.W. DePaoli, and G.E. Jellison, Jr.

Project Description

The objective of this project is to develop a core chemical nanomanufacturing capability that can fulfill the large-quantity demands of high-quality, molecularly tailored quantum dots (QDs) for energy applications. ORNL and DOE have been strategically investing in scientific studies of QDs because of great potential in several important energy applications such as solid-state lighting, solar cells, and photoelectrochemical devices for water splitting. However, current methods for producing QDs are primarily suitable for small-quantity R&D samples and for medical and biological labeling and imaging. We plan to use our recent breakthrough in chemical synthesis of QD nanocrystals by a newly discovered thermodynamically driven noninjection process (TD-NIP) to develop industrially viable QD production methods. This approach is well suited to process scale-up because of its simplicity and its potential for high reproducibility of produced QDs between batches. This effort will collect necessary engineering data on thermodynamic equilibria, chemical reaction kinetics, and nanocrystal nucleation and growth to understand the process parameters for tailored production of QDs in various compositions and demonstrate a scalable and reproducible process. Successful development of this innovative technology will enable ORNL efforts focused on specific energy applications of a new class of nanocrystals.

Mission Relevance

The project is directly relevant to the mission of the Industrial Technologies Program (ITP) of the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE). The nanomanufacturing initiative of ITP is focused on the scale-up and commercialization of nanotechnologies related to energy. The project is also applicable to other DOE EERE missions, including solid-state lighting and solar programs. The capability of producing QDs in large scale may also be applicable to programs in other federal agencies, such as the Department of Defense and the Department of Homeland Security.

Results and Accomplishments

Our discovery of a thermodynamic equilibrium-driven mechanism, via a non-injection process approach, has achieved the very first-time demonstration of using microwave processing to produce a new class of nanocrystals, that is, magic-size/molecular-species quantum dots (MSQDs). With well-defined molecular features, MSQDs are drastically different from conventional, regular quantum dots (RQDs) in terms of their formation mechanism, particle characteristics, and properties. Microwave synthesis has been developed as an engineering scale-up methodology to produce nanocrystals in significant quantities with the high quality (i.e., with essentially identical size and precisely controlled numbers of atoms in each nanocrystal). The new scientific MSQD-formation phenomenon, so far achieved with Cd-containing systems (CdSe, CdS, CdTe, or CdSeTe), could be further developed as an innovative green process technology for creating various new environmental friendly material systems (such as CuInS2, CuInSe2, PbSe) with high impacts on energy and many other applications.

During the past year we have successfully met project goals and have made new discoveries that we expect to lead to significant opportunities for future funding. Highlights of past progress include the following.

- Developed a microwave-processing methodology for engineering development
  - Demonstrated for the first time that MSQDs can be produced via microwave processing
  - In contrast to the conventional heating, microwave synthesis has produced nanocrystals of lower defects with tailorable trap emission
  - Determined condition regimes of cluster (gel) formation and nanocrystal formation
  - Identified the need of co-solvent to tailor the microwave absorption efficiency
  - Conducted small-angle neutron scattering (SANS) experiment using HFIR
  - Analysis of SANS data, using a unified model, for microwave-synthesized MSQDs has revealed the existence of two-dimension levels of object
  - SANS study clarified the controversial scientific issue regarding MSQD morphology by supporting the existence of nanosheet structure in colloidal solutions.
- Developed a potential pathway for producing MSQD of targeted composition (such CIS, CISe, PbSe) for energy applications and engineering methodology for next-year process technology development on large-throughput continuous synthesis.

Beyond the currently studied model CdSe system, the microwave-aided MSQD-forming phenomenon could be utilized for other targeted compositions of practical significance to energy and opto/electronics applications. Future considerations for engineering scale-up are also discussed, including the need of co-solvent addition to improve microwave absorption efficiency and continuous flow mode to reduce reactor volume while allowing large throughput production of nanocrystals.

Information Shared

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05684

Towards Full First-Principles Simulations of Correlated Electron Materials

T.A. Maier, G. Alvarez, M.S. Summers, and T.C. Schulthess

Project Description

The goal of this project is to develop a capability for material specific and predictive simulations of correlated electron materials. Two immediate aims will guide our research: (1) the development of many-body methods and simulation tools that will enable the computation of emergent properties of material specific models, which are generated from first principles by electronic structure techniques; (2) the integration of these many-body methods with state-of-the-art electronic structure techniques to form a robust and parameter-free first-principles framework for simulations of correlated electron systems. Our effort will be guided by the objective to develop robust procedures and simulation tools with predictive power, which can make use of future exascale computing architectures. As a proof of principle, we will use these tools to perform material-specific simulations of cuprate high-temperature superconductors. In particular we will focus on solving one of the most important questions at the forefront of condensed matter physics, the link between differences in the chemical composition and the critical temperature between different compounds. The concepts, procedures, and tools we will develop in this project will be applicable to a range of new materials and will allow the intelligent design of new complex materials with optimized properties.

Mission Relevance

This project is relevant to several DOE initiatives. The development of advanced computer algorithms and fast codes to treat many-particle systems and, in particular, the development of predictive models for the discovery of new materials with targeted properties are important aspects of the mission of the Division of Materials Sciences and Engineering in the Office of Basic Energy Sciences. The new tools that will be developed in this project will also be beneficial to the CNMS by providing a new capability that will enable growth of the CNMS user community, an important goal of the CNMS. Furthermore, the project is also in line with the vision for computational science at the exascale at DOE/ASCR.

Results and Accomplishments

Our work in FY 2011 has been focused on developing effective low-energy models for single-layer cuprate superconductors using a full potential linear augmented plane wave (FP-LAPW) framework,

implementing a state-of-the-art continuous-time auxiliary field quantum Monte Carlo (CT-QMC) solver for multi-orbital models within the dynamic cluster approximation DCA++ framework, and applying this methodology to calculate the superconducting transition temperature of a number of single-layer cuprate materials. Our scientific/technical accomplishments during the first 9 months of this project can be summarized as follows. (1) We have applied an FP-LAPW framework combined with a random-phase approximation (RPA) to generate low-energy effective multi-band models of a selected set of single-layer cuprate superconductors. (2) We have extended the DCA++ framework to interface with the output of the FP-LAPW calculations and to support models with multiple orbitals. (3) We have developed a robust implementation of a state-of-the-art continuous time auxiliary field solver for the DCA++ cluster problem for multi-orbital Hubbard models. (4) We have started to develop a new solver based on the density matrix renormalization group (DMRG) approach to enable the direct calculation of dynamic quantities such as magnetic structure factors to support comparisons with neutron scattering experiments.

These developments have allowed us to start applying the integrated FP-LAPW—RPA—DCA framework to calculate the superconducting transition temperature of a set of selected single-layer cuprate superconductors.

05698

Quantum Lightwave Circuits

P.G. Evans, R.S. Bennink, D.D. Earl, W.P. Grice, T.S. Humble, and R.C. Pooser

Project Description

Quantum Information Science (QIS) is an innovative and enormously promising new field comprising the creation, storage, manipulation, secure transfer, and use of information encoded in the quantum states of particles or light. Applications of QIS relevant to global security include secure communications, quantum sensing, and quantum computing. Of the many physical implementations of QIS, the photonic approach is the most mature, yet deployment of photonic QIS systems outside of the laboratory has been hampered by scaling, power requirements, and stability issues. We propose development of integrated quantum lightwave circuits to advance the capabilities, and accelerate the transfer, of this nascent technology from research to the applications domain. Our approach will take advantage of new techniques for fabricating polarization manipulating and phase modulating circuit elements on silicon-on-insulator (SOI) waveguide platforms. Our goal is to demonstrate dynamic, multi-photon integrated quantum lightwave circuits that outperform their bulky and delicate lab brethren in terms of size, stability, and tunability. In addition, the ability to integrate quantum lightwave circuitry with ORNL's existing telecom-band multi-photon entangled sources will provide ORNL with a unique capability that highlights excellent fundamental science-to-global security applications in a highly flexible, reproducible, and affordable package.

Mission Relevance

Quantum information science will continue to shape the global security landscape in the next decade. Global security areas that benefit under QIS development include completely secure communications; quantum sensing for nuclear safeguards and nonproliferation; and quantum computing for advanced materials simulation and support to our intelligence community.

To date, QIS proof-of-principle demonstrations have mostly been lab based, in which bulk optical equipment is precisely aligned on large tables in environmentally stable laboratories. This approach does

not lend itself favorably to being deployed on a naval vessel, on a surveillance satellite, in a soldier's backpack, or even on a computer user's desk. Advances in technology and engineering are required to take QIS out of the lab and bridge it to real-life global security problems. We propose the quantum lightwave circuit—a quantum optical equivalent to the electronic integrated circuit—as an enabling technology to fill this need.

The DOE is likely to benefit both directly through the NA-22 program with quantum sensors and indirectly through Work for Others programs with DARPA, DHS, ARO, and the intelligence community.

Results and Accomplishments

All basic optical circuit elements have been designed and modeled, and exceed initial performance metrics. A user proposal to fabricate QLCs at the Center for Nanophase Materials Science (CNMS) nanofabrication facility was granted with positive external reviewer comments. Fabrication work has begun and we anticipate the demonstration of functional QLCs by the end of FY 2011. Designs for two- and four-photon QLCs have been created. Other opportunities have arisen to develop scalable QLCs containing many beam-splitting elements for quantum information and imaging applications.

Additional accomplishments include development of reconfigurable beam-splitting element and methods to allow the incorporation of third-order optical nonlinearities in QLCs. Simulations show that a typical beam splitter, when packaged with a resistive heating element, is capable of being tuned to provide a splitting ratio from 50/50 to 70/30. Third-order ($\chi^{(3)}$) optical nonlinearities will enable such technologically important tasks as four-wave mixing and cross-phase modulation between co-propagating beams. Together, these two developments lead to the possibility of creating flexible and user-reconfigurable quantum lightwave circuits.

Information Shared

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A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, US Department of Energy.

05699

Incorporating Molecular-Scale Mechanisms Stabilizing Soil Organic Carbon into Terrestrial Carbon Cycle Models

M. Mayes, W.M. Post III, H. Ambaye, L. Petridis, and S. Jagadamma

Project Description

The top meter of soil contains 1500 Pg of carbon (C), and contemporary models often simulate C dynamics by determining pool sizes and turnover rates post hoc. Consequently, soil C response to climate change is inadequately predicted in many circumstances. Our project produces a mechanistic model of cycling of organic C (OC) in soils. We hypothesize that attachment at the interface with soil minerals will determine the bioavailability of C to microbes, and thereby exert control over soil OC turnover. The relationship between attachment and stabilization for common OC compounds (lignin, lipid, sugars, starch) will be determined in batch sorption and long-term incubation experiments using a global suite of

soils. The mechanisms of attachment will be determined using a coupled application of neutron reflectometry and molecular dynamics simulation. The turnover of the OC compounds as they cycle through measurable pools (dissolved, mineral OC, particulate OC, and microbial biomass) will be modeled through the mechanism of enzyme-facilitated microbial degradation. The model framework will be developed and validated using published data, followed by application using our coupled sorption and degradation measurements on global soils. The ultimate outcome is a validated, realistic, globally relevant soil C model that is linkable into widely used global circulation models.

Mission Relevance

We seek to build a program providing a new theoretical and quantitative framework for systematic, mechanistically based terrestrial C cycling models. Our program will enhance the Energy and Environmental Sciences Directorate's existing strengths in ecological response to climate change, modeling global and terrestrial C, and in using molecular-scale techniques to study interfacial processes between contaminants, soils, and aquifer materials. We are directly lobbying the Climate and Environmental Sciences Division of Biological and Environmental Research (BER) for future funding to be redirected from the Climate Mitigation Science Focus Area (SFA) to the Terrestrial Ecosystem SFA. Our model can be used in the new ORNL-led Next Generation Ecosystem Experiment (NGEE) project on C cycling in the Arctic. Finally, new techniques developed through interdivisional collaborations using neutron reflectometry and supercomputer modeling will interrogate interfacial, molecular-scale adsorption processes in soils and subsurface media. These techniques will be applicable to the Subsurface Biogeochemical Research program at BER and many other areas.

Results and Accomplishments

This research will provide comprehensive data and validated modeling to represent the turnover of major organic compounds found in a global suite of soils. We are on or ahead of schedule for all deliverables. In Objective 1, we determine relationships between attachment and stabilization for common OC compounds (lignin, lipid, sugars, starch), added in batch sorption and long-term incubation experiments to soils obtained from artic, tropical, and temperate climates. We completed most sorption experiments and observed the mineral fraction of surface soils having greater sorption than subsurface soils. Since surface soils are thought to have lower capacity for OC, this could suggest more effective degradation. In Year 2, we will determine the influence of microbial degradation. For Objective 2, we determine the mechanisms of sorption and its influence on C stabilization using a novel, coupled application of neutron reflectometry (NR) and molecular dynamics (MD) simulation. We conducted NR experiments at the Spallation Neutron Source (SNS) using OC-mineral systems prepared at Center for Nanophase Materials Sciences (CNMS). We observed the formation of stacked layers of OC that was dependent upon the chemical character. We are establishing the technical framework to combine investigations of the organic–inorganic interface using MD simulation and NR measurements. Objective 3 developed a new model of the turnover of OC compounds through measurable soil pools via enzyme-facilitated microbial degradation. We have completed a literature review of over 100 publications to determine parameter values and have coded and tested a simulation model for OC cycling in soils.

Information Shared

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05770

Quantum Imaging by Compressive Sampling for Enhanced Surveillance and Real Time Monitoring

R.C. Pooser, P.G. Evans, W.P. Grice, T.S. Humble, D.D. Earl, and R.S. Bennink

Project Description

Quantum imaging, which involves manipulation of images stored in quantum mechanical systems, is a rapidly growing field that promises increases in the information capacity of images. This increase in information capacity yields improvement in image resolution and information content that is expected to subsequently impact the performance of many imaging applications. Remote sensing, pattern recognition, position measurements, image amplification, and surveillance are a few specific applications that can benefit from quantum imaging methods. Current efforts in quantum imaging require expensive CCD cameras, however, and they are based on designs limited to detecting very low light levels. Consequently, these quantum imaging methods are limited by long integration times, a need to reduce the incoming photon number, and a significant post-processing requirement for image recovery. We propose a method of quantum imaging whereby the CCD camera is replaced with a more economical compressive measurement apparatus that eliminates the post-processing requirement. The proposed method allows for more efficient detectors to acquire the images and reduces overall integration time. This fundamental speed up in quantum imaging acquisition time would enable applications of "quantum monitoring" or "quantum surveillance," where changing quantum images are monitored in real time. We propose to develop and demonstrate a system that is capable of producing and measuring real-time changes in quantum images by using multiple-spatial-mode quantum optics alongside the theory of compressive sampling. This will allow us to perform experiments that advance the state of the art in quantum imaging and enable the development of new quantum imaging applications. This proposal leverages existing ORNL expertise to design and demonstrate the first real-time quantum imaging device.

Mission Relevance

This project is important to ORNL because it would be a first for quantum information science. Quantum information science is part of ORNL's cyber security program, and thus the project supports ORNL's and DOE's broader mission of information security. While most of the research proposed here is fundamental science, it will still lead to a new capability at ORNL: "compressive quantum imaging." DARPA has shown interest in compressive sampling due to the potential to increase the speed of communications in both classical and quantum contexts, specifically citing quantum imaging in the BAA for its "InPho" program. The ability to do real-time quantum imaging would also attract the attention of agencies like DTRA, and anyone else interested in covert, high-sensitivity monitoring in low light levels. The results of

this project would also be a likely candidate to include in an NA-22 proposal targeted at remote sensing for nonproliferation.

Results and Accomplishments

We have fully achieved our 10 month milestones. We have designed and built a nonlinear optics system based on four wave mixing in rubidium. The system is aligned and amplifies approximately 100 spatial modes. We observe 4.1 decibels (dB) of quantum noise reduction (~10 dB inferred), making it state of the art. Our spatial light modulator (SLM) imaging apparatus is implemented and can imprint images onto our probe beam for use in image amplification and quantum imaging. We use a computer program to upload intensity images to the SLM, followed by imaging optics in order to record the resulting images. Currently we are able to view twin quantum images output by our quantum imaging system when the SLM is used as an input to the four wave mixing system. We plan to improve the image quality further by increasing the number of amplified spatial modes. Our compressive imaging detector also successfully runs compressive imaging algorithms. We use a digital mirror display device that we can control via software and implement compressive sampling algorithms therein. We have adopted a popular collection of convex optimization algorithms for reconstruction. These algorithms use interior point methods (primal-dual algorithm) for solving the L1-minimization problem under various constraints.

Information Shared

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05977

Bacterial Iron and Uranium Redox Cycling in the Contaminated Subsurface

F.E. Loeffler

Project Description

The incomplete understanding of the microbial processes affecting uranium (U) flux in subsurface environments is a major shortcoming to meaningfully predict long-term radionuclide mobility and fate. The proposed work will advance scientific understanding towards DOE goals by (1) determining the environmental conditions that favor U(VI) reduction versus U(IV) oxidation, (2) obtaining U(VI)-respiring bacterial isolates from contaminated DOE sites, and (3) performing comparative analyses of U(VI)-reducing bacteria to determine differences in reduction rates, mechanisms, growth yields, and response to fluctuating redox conditions. These efforts will provide relevant new information for monitoring and predicting the contributions of indigenous microbes for the long-term stability and the fate of radionuclides.

Mission Relevance

Subsurface uranium (U) contamination presents a major remediation challenge at DOE sites. Traditional site remedies are expensive, often without meeting cleanup criteria, and innovative, economically feasible technologies are needed. Bioremediation is a promising approach to provide cost-effective corrective solutions for addressing radionuclide subsurface contamination. With increased knowledge of the microbial controls on U mobility, the long-term fate of U can be predicted with less uncertainty, and

resource allocation can be directed towards sites where natural processes are insufficient to prevent U plumes from breaching compliance boundaries. At sites that require intervention, the new information generated will allow site management based on scientific principles rather than empirical practices. The study of microbial metal cycling is a focus area of DOE's Subsurface Biogeochemical Research Program, and this project anticipates future funding initiatives from DOE BER.

Results and Accomplishments

Microcosms have been established with soils collected from uranium (U)-impacted DOE sites, including the 300 Area at the Pacific Northwest National Laboratory and the Oak Ridge IFRC sites. Sequential transfers yielded metal- and radionuclide-reducing enrichment cultures. Distinct bacterial isolates including a *Desulfovibrio* sp., several *Anaeromyxobacter* sp., and two *Geobacter* sp. were obtained and are being characterized. *Anaeromyxobacter* spp. reduce U(VI), and we demonstrated previously that *Anaeromyxobacter dehalogenans* strain 2CP-C grows with U(VI) as electron acceptor. Oxic-anoxic transition zones are hot spots for redox reactions controlling U mobility, and understanding the activity of metal-reducing and metal-oxidizing bacteria adapted to life in redox transition zones is crucial. Studies with *Anaeromyxobacter dehalogenans* strain 2CP-C suggested that these bacteria are microaerophiles that detoxify oxygen at high oxygen partial pressures but switch their metabolism to oxygen respiration at oxygen partial pressures at and below 0.18 atm. Further, strain 2CP-C reduces Fe(III) to Fe(II) or oxidizes Fe(II) to Fe(III), depending on the prevailing redox conditions. These features indicate that *Anaeromyxobacter* spp. are uniquely adapted to conditions at oxic-anoxic interfaces where they affect metal redox chemistry, and hence U mobility. Additional experiments with *Desulfitobacterium* spp., which are commonly found in soil and subsurface environments, demonstrated that these bacteria reduce U(VI) to mononuclear U, rather than the commonly described uraninite. These efforts to characterize U(VI)-reducing bacteria, especially those active in oxic-anoxic transition zones, generate new information about the microbiology and their activities controlling of U mobility in the contaminated subsurface.

Information Shared

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SUMMARIES OF PROJECTS SUPPORTED THROUGH THE SEED MONEY FUND

BIOSCIENCES DIVISION

05879

White Light Produced by a Scalable Biosynthesized Zinc Gallate Mixture

J.-W. Moon, T.J. Phelps, C.E. Duty, P.C. Joshi, G.D. Jia, G.E. Jellison, Jr., and L.J. Love

Project Description

We are pursuing a new approach to generating white light using scalable and economical microbial production of zinc gallate phosphors which can emit red, green, and blue (RGB) colors for use in energy-efficient solid state lighting (SSL). Improvement over current SSL technology requires advances in several areas: (1) improved reactions to produce appropriate phosphors, (2) less complicated fabrication, (3) better control over stoichiometry during mass production, and (4) ways to eliminate or cope with unexpected secondary phases. NanoFermentation™, which employs microbes to produce high-quality nanoparticles, can provide (1) consistent, nanoscale particle size without energy-intensive milling; (2) ease of stoichiometric control; (3) reproducibility; and (4) a low-temperature, scalable, and economical process. The scientific focus of this program is entirely innovative and complements the biomineralization principle in which nucleation is initiated by reduced elements accepting dumped electrons. Instead metal reduction is not required for nucleation of the nanoparticles. This research will give ORNL a competitive advantage in biomineralization research and relevant funding opportunities. In this project, we explore the unprecedented use of NanoFermentation to produce controllably doped zinc gallate nanoparticles that emit red, green and blue light, and then combine these single-color particles to produce white light.

Mission Relevance

DOE has identified no other lighting technology that offers as much potential to save energy and enhance the quality of our building environments, contributing to our nation's energy and climate change solutions as SSL. Our goal is “white light” via mixtures of zinc gallates, which emit red, green, and blue, to meet the desires of the R&D program within the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE) and to demonstrate a biofacilitated white light–emitting diode. Through inexpensive microbiological production, cheap fabrication, and ease of mixing similar zinc gallates, we can acquire a useful white light source with low energy input, implying a green solution for white light in both manufacturing and application aspects.

Low temperature and scalable production of bio zinc gallate is of benefit not only as a green energy process that saves energy resources but also for incorporating nanomaterials into devices. Project results will affect white light research itself as well as support basic knowledge to produce a spinel-type precipitate in which there are no reducible metals in the biologically mediated system. Therefore, successful white light production using NanoFermentation will give us a chance to obtain future funding

from the DOE EERE Industrial Technologies Program (ITP), the DOE Environmental Security Technology Certification Program, and the Department of Defense. Results of the project will be shared with Defense Advanced Research Projects Agency to advance pending funds relevant to NanoFermentation.

Results and Accomplishments

Selected bacteria were incubated with ionic metal precursors such as zinc, gallium, and various range of doping elements, such as Mn, Cr, Eu, and Co with consideration given to the molar fraction and time of incubation. Final products of various pure and metal-doped zinc gallates were successfully produced in batch sizes scaled from 10 mL in pressure tubes to 1 L in culture bottles. Subsamples were processed through centrifugation, washing, and stored by mixing with methanol and were characterized for phase purity using X-ray powder diffraction. Some fractions were freeze dried for post-treatment (sintering), emission measurement, and/or blending for white light. Some fraction of the cleaned wet samples underwent 10% hydrogen peroxide treatment or was directly deposited on fused silica plates.

Research has concentrated on the metal-doped zinc gallate formation under the adjusted pH-Eh micro-environment mediated by microbial activity without reducible metal or non-metal components in the system. All synthesized pure and metal-doped zinc gallates crystallized with the spinel structure. In some cases, where the dopant level was too high, the microbial activity ceased due to high toxicity. After sintering for a short amount of time, the metal-doped zinc gallates exhibited relevant emission colors, depending on the dopant. Undoped and cobalt-doped zinc gallates produced blue light; manganese-doped zinc gallates where the manganese replaced either the zinc or gallim in nominal mole fraction in precursor composition produced green light; and chromium- and europium-doped zinc gallates where the dopant replaced the gallium produced produced red light. Simple blending of cobalt for blue, manganese for green, and chromium for red resulted in doped zinc gallates that produced white light.

Currently, without any further optimization, production is approximately 1.8g/L/month compared to solid state synthesis that can produce zinc gallate batches up to hundreds of grams and cannot exceed 1 kg of homogeneous final products. NanoFermentation shows great possibility of scale-up. Based on the emission of RGB and blended white light, future work includes enhancing emission intensity, adapting long wavelength for excitation, balancing belnding ratio, and scale-up. However, the research performed in this study confirmed the white light from simple blending of zinc gallates emitting each RGB color.

Follow-on Funding

DOE EERE ITP has great interest in funding our work on the massive production of solid state lighting material using economic and scalable microbial manufacturing to lessen resource demand and climate change.

Information Shared

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05897

Non-Destructive Biofuel Initiative

A. Vass, M. Wise, E. Greenbaum, D.J. Weston, and B.R. Evans

Project Description

Common tactics to produce ethanolic biofuels include either the growth of a biological matrix (corn, switchgrass, etc.) with subsequent destruction and fermentation of the material or genetic engineering of material (algae, yeast, etc.) to enhance its ability to produce and tolerate increased levels of ethanol in their environment. The purpose of this proposal is to explore a different approach—one that does not require difficult, expensive genetic manipulation of the biological system or the destruction and costly fermentation of the biological matrix. The concept is to capitalize on, and scientifically understand, the natural ethanol off-gassing of desert plants.

In order to evaluate the true potential of these plants as a viable source of ethanol, it will be necessary to accurately determine the rate of ethanol production and begin to understand the basic mechanism of ethanol production of these plants. In particular, it will be important to experimentally establish whether or not ethanol is produced by a mechanism that is directly or closely coupled to photosynthesis or whether it is a decoupled reaction related to plant stress, environmental factors, or microbes.

Mission Relevance

This work falls within the leadership agenda areas of climate change science, systems biology, and environmental sustainability—experimental capabilities addressing sustainable bioenergy generation. It meets the overarching goals of the LDRD Biomass Production and Conversion for Energy and Materials call. ORNL has a strong program in plant research, and the data collected through this work could be incorporated into larger proposals to DOE programs funded through several offices including the Office of Science Biological and Environmental Research (BER) and Basic Energy Sciences (BES) programs and the Office of Energy Efficiency and Renewable Energy (EERE). It is also noted that decreasing the volatile organics in these plants would be of interest to agencies concerned with wildfires. Plant genome sequencing projects may also be initiated through this work with the Joint Genome Institute. The potential for plant-microbe interactions is also timely and of interest to the DOE Genomes to Life program. Additionally, these plants would not compete for valuable agricultural land or land destined for housing needs, are not important food crops, would not interfere with food production, and require little water and low nutrients.

Results and Accomplishments

Using desert plants that naturally off-gas ethanol, thereby not consuming the biomass for energy harvesting, would be an attractive strategy for year-round bio-ethanol production. The plants would continue to grow and sequester carbon, would not compete for valuable agricultural land or land destined for housing needs, and are not important food crops and therefore would not interfere with food production. Additionally, costs associated with continual replanting, harvesting and fermentation of the product would not increase the expense of the final product. The transpired ethanol could be harvested by simple vapor condensation and collection by modification of sheeting plastic tents such as those used for temporary protection of field crops.

A key goal of this project was to test the correlation of the rate of ethanol production with real-time exposure to light. If such a correlation exists, it will be a novel observation where carbon dioxide is directly converted into a small fuel molecule. Leaf photosynthetic activity was determined using a Walz ED-P700 spectrofluorimeter to measure P700, a LI-COR LI-2652 meter to measure CO_2, and a Clark

electrode to measure O_2. Rabbitbrush and sagebrush maintained in a greenhouse both had P700 activity. Rabbitbrush showed high O_2 evolution rates comparable to C3 and CAM controls. Sagebrush showed low O_2 evolution rates similar to C4 controls but carried out CO_2 fixation from 689 ppm CO_2 in air. Rabbitbrush cultivated indoors under window illumination had P700 activity and O_2 evolution comparable to earlier greenhouse specimens. Treatment with an antibiotic-antifungal solution had no adverse effects on rabbitbrush photosynthesis. While experiments are still under way, it does not appear that ethanol production is linked to the photosynthetic pathway.

Rabbitbrush exhibits a number of adaptations for surviving in a cold, arid environment. One of these is that leaves and stems are covered with a felt-like layer of trichomes that insulates the plant and reduces transpiration. It was from this material that a fungus was isolated that was found to produce significant amounts of ethanol (as well as other interesting products) on a variety of sole carbon sources including cellulose, xylan, pectin, cellobiose and terpenes. Additional studies, such as verifying fermentation of biomass-derived pentose sugars and determining ethanol production from sucrose as a sole carbon source (i.e., sugar cane) will help determine the role of this fungus in the production of ethanolic biofuels.

Information Shared

No publications will be submitted until an invention disclosure is filed.

06249

Toward Biological Upgrading of Ethanol to C6 and C8 Ethyl Esters

J.G. Elkins and T.J. Phelps

Project Description

This proposal aims to determine the productivity and yield for 4-carbon (C4) and 6-carbon (C6) fatty acids from *Clostridium kluyveri* growing on ethanol and acetate as carbon and energy sources. The second goal is to characterize the growth and fatty acid production of *C. kluyveri* both in spent media from *Saccharomyces cerevisiae* and in combination with yeast as a co-culture. The experimental plan includes growing both organisms in a defined medium and measuring substrate utilization and end-product formation via high-performance liquid chromatography (HPLC) and gas chromatography (GC). The results will be used to assess the potential of this system for generating fatty acid ethyl esters for use as advanced biofuel additives.

Mission Relevance

The Energy Independence and Security Act (EISA) of 2007 mandates that by 2022 over 857 million barrels of fuel per year must be produced from renewable sources. In addition, over 58% of that fuel must be non-ethanol, advanced biofuel (Public Law 110–140). However, few bioprocesses are as productive, robust, and time tested as the anaerobic fermentation of glucose to ethanol by yeast, specifically *Saccharomyces cerevisiae*. Currently the demand for gasoline in the United States is 9 million barrels per day. Ethanol production from starch is the only bioprocess capable of supplying the motor fuel market with about 1 million barrels of product per day. Ethanol is currently the primary oxygenate added to fuels replacing MTBE, but its chemical properties prohibit pipeline transport as well as blends at high ratios. The EPA recently raised the blend wall from 10% to 15% ethanol for use in gasoline. As cellulosic and syngas-derived ethanol become more technologically feasible, the demand for ethanol may still be capped due to the limitation of blending with gasoline as well as the electrification of the personal vehicle fleet. The economics of ethanol production also relies heavily on the value of co-products such as dried

distillers grains with solubles (DDGS) for animal feed. A diversification of product streams that included alternative fuel additives as co-products would strengthen process economics since excess ethanol could be "upgraded" to other molecules via a secondary fermentation step.

Results and Accomplishments

This project began just prior to the close of FY 2011. *C. kluyveri* has been cultivated in a defined minimal medium containing only acetate and ethanol as the carbon source. Time course experiments have been completed to track production of butyric and hexanoic acid during growth. HPLC analysis confirmed the stoichiometric conversion of ethanol to C4 and C6 fatty acids, with 50 mM ethanol being completely consumed within a 72 hr growth period. Surprisingly, little acetate was consumed relative to ethanol, which is a favorable result. Additional experiments are now in progress to determine the optimal acetate-to-ethanol ratio that still allows maximal growth and conversion of alcohol to longer chain fatty acids.

CENTER FOR NANOPHASE MATERIALS SCIENCES

05876

Probing Photovoltaic Processes at the Single-Interface Level

A.-P. Li, K. Bevan, G. Eres, T. Kim, and H.N. Lee

Project Description

The project addresses the problems of studying photovoltaic energy conversion processes at an individual interface level. Asymmetric interfaces play a key role in applications that involve renewable energy conversion processes. The experimental study of interfacial energy conversion and transfer processes has so far largely relied on bulk characterization of materials averaged over multiple interfaces across large length scales. This approach lacks a direct link with the local interfacial electronic and structural properties. The need to control and understand photovoltaic (PV) energy conversion at the single-interface level is particularly pressing with inorganic materials. Here we leverage the unique scanning probe microscopy and materials expertise at ORNL to develop a new interfacial probing technique to address this critical scientific challenge. Specifically, the local electrostatic potentiometry is to be implemented in the ORNL four-probe scanning tunneling microscope to provide the first-ever measurement of PV and its correlations with interfacial properties at the single-interface level under active photocarrier generation conditions.

Mission Relevance

The objective of this project is to develop a tool that reveals the correlation between the PV process and the local interfacial properties at the single-interface level. The results of this research can provide understanding of the solar energy conversion processes in unprecedented detail, which will provide a key component to future DOE programs that focus on development of renewable energy from environmentally friendly sources such as solar power, whose performance relies on an atomistic understanding and control of interfacial processes. As such, this project upholds DOE's commitment to drive basic scientific discovery in order to drive economic competitiveness. The new capabilities developed in this project are providing another unique tool to address interfacial issues in energy materials, solar energy conversion, energy storage, solid-state lighting, and related technologies, complementing efforts in materials synthesis and single molecular imaging programs. It also aligns well with the Tennessee Solar Initiative by establishing another visible ORNL basic scientific initiative. Programs of the Defense Advanced Research Projects Agency will also benefit from understanding these interfacial processes in developing devices for practical applications.

Results and Accomplishments

In a typical solar cell, a hetero-interface is formed by joining two distinct materials to form a semiconductor p-n junction or a metal/semiconductor Schottky junction. Photo-generated electron-hole pairs are most able to separate before recombining when they are excited within the interfacial built-in

electric field. Thus the interfacial electronic and atomic structure properties will have a deterministic role in characterizing the photocurrent, open circuit voltage, and internal quantum efficiency.

To address the interfacial properties in atomic resolution, we have carried out extensive studies with scanning probe microscopy techniques on the cross-sectional surfaces of several different types of heterojunctions relevant to PV processes. A surprising discovery was made that revealed a nanoscale periodic modulation pattern on the surface of sodium chloride, one of the most common platforms for catalysts, thin-film growth, and atmospheric aerosols. We associate the formation of the pattern with a strong electrostatic charging on the cleavage surface. Calculation of the electrostatic energy shows that a surface reconstruction is energetically metastable in the presence of a strong surface charge, and reproduces well the observed periodic pattern.

To probe the interfacial transport properties, we have implemented the scanning tunneling potentiometry capability in a four-probe scanning tunneling microscope system. The scattering effects of grain boundaries and step edges on the electrochemical potential have been examined with nanoscopic resolution. A direct comparison between macroscopy transport, local electronic properties, and local transport will provide an unprecedented opportunity to separate surface effects from bulk effect, and allow us to compare spatially topography, spectroscopy, and local potential.

With the newly developed interfacial scanning probe microscopy and tunneling potentiometry techniques, we have studied the silicon nanowire photovoltaic p-i-n junctions in order to elucidate the intrinsic characteristics and limits of nano-enabled solar cells. Using an axial nanowire building block, we have examined the structural and electronic properties with atomic resolution, which revealed the important role of surface electronic states in the photovoltaic processes.

Information Shared

Clark, Kendal W., Shengyong Qin, X.-G. Zhang, John F. Wendelken, and An-Ping Li. Submitted. "Nanoscale Periodic Modulations on Sodium Chloride Induced by Surface Charges," *ACS Nano*.

05963

Addressable Nanopore Array: Multiscale Fluidic Interface to Cell Culture

C.P. Collier, S.T. Retterer, and T.E. McKnight

Project Description

Developing a real-time spatiotemporal map of molecular events that unfold during cell–cell and cell–matrix interactions is critical to understanding the biochemical drivers and consequences of phenotypic changes in individual cells and tissues. However, decoding these complex signaling cascades within a living organism can be extremely cumbersome. Relevant *in vitro* tissue models and cell culture provide tractable and informative alternatives. The focus of this proposal is to develop and validate a fluid interface to facilitate control and sampling of the local micro-environment surrounding cultured cells. The interface will be comprised of an addressable nanopore array (ANA) etched into an ensemble of surface micromachined fluid channels, which will enable the local delivery of dosing molecules to cultured cells and facilitate the capture of dilute response biomarkers secreted from cell culture into discrete water-in-oil droplets.

Mission Relevance

Successful completion of the work proposed here will result in a technological platform for probing tissue samples in cell culture and for drug screening, disease detection, tissue engineering, and directed differentiation of cells, with improved sensitivity and specificity compared to conventional methods. Results may thus be directly applicable to targeted DOE Biological and Environmental Research (BER) initiatives such as 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 environmental quality and national security.

Results and Accomplishments

We have successfully completed Task 1: Optimization of water-in-oil plug formation in surface micromachined channels. Specifically, we have developed and integrated a flow-focusing junction to generate water-in-oil plugs in sampling surface micromachined channels (SMCs), upstream of the addressable nanopore interface with cell culture. Previously, oil from the sampling SMCs would leak into the cell culture space through the addressable nanopore interface; Task 1 was designed to prevent this oil leakage. To do this, we apply a vacuum to the sampling SMC downstream of the addressable pore while keeping a positive pressure on the other side of the pore to minimize oil infiltration. Movie sequences of device operation show reproducible water-in-oil plug formation in the SMC without oil leaking into the cell culture space through the addressable pore. Task 2 will demonstrate controlled dosing via steady-state or pulsed concentration gradients from “dosing” pore openings, and Task 3 will detect the capture of fluorescent molecules leaked from cell culture into water-in-oil plugs through “sampling” pore openings. Task 2 will be satisfied first; dosing will involve applying positive pressure to both ends of a SMC loaded with an aqueous fluorescent solution, forcing material through the nanopore that will be located near the cells of interest. In Task 3, we will detect fluorescent molecules captured from highly dilute aqueous solution from the cell culture area and entrained in ultrasmall water-in-oil droplets in the SMCs developed in Task 1.

05965

Thermopower at the Atomic Scale

P. Maksymovych

Project Description

This proposal seeks to develop a nanoscale measurement of thermopower, a critically important variable in thermoelectric energy conversion. The past decade has witnessed numerous theoretical and experimental proposals aimed at significant improvement of thermoelectric figure of merit through nanoscale modifications. However, today there exists a tremendous gap between our ability to implement such modifications and to evaluate thermoelectric performance at the commensurate length scale. In this project, we will develop a unique approach for measuring thermopower down to the atomic scale based on scanning probe microscopy. We will be able to measure electronic and thermoelectronic properties simultaneously and correlate thermoelectric effects on well-defined semiconductor surfaces with the respective behavior in the bulk.

Mission Relevance

Thermoelectrics has the potential to convert waste heat to useful power, thereby generating tremendous energy savings. Our development will link atomic-scale heterogeneity with thermoelectric performance,

allowing us to study nanostructured and unconventionally doped materials with unprecedented spatial resolution, and prospectively uncover new thermoelectric properties. These topics are the focus of several programs in the Department of Energy (DOE), the Army Research Office (ARO), and the Defense Advanced Research Projects Agency (DARPA). On a broader note, linking nano and macro performance is a grand challenge for any functional material, and its resolve for thermoelectrics is only in its infancy. In the future, developments resulting from this proposal can lead to a new atomic-scale probe of complex behavior and phase transitions in a broad range of material systems, including problems in solid state electrochemistry, phase transitions, and correlated electron behavior.

Results and Accomplishments

Local thermovoltage has been successfully measured with sub-nm spatial resolution and ~20 μV sensitivity through the modification of electronics and development of new algorithms for a scanning probe microscope. Applying new methodologies to a test metal surface has revealed for the first time that local thermovoltage is strongly dependent on the geometry and electronic structure of the tip-surface junction in a scanning probe microscope. Specifically, satisfactory agreement with earlier quantum mechanical models can be achieved only for certain electronic structures of the probe tip. More importantly, ignoring this fact (as in a number of prior papers) may lead to wrong conclusions about the magnitude of thermopower and type of carriers in the surface. Subsequent systematic measurements on the origin of the chemical contrast suggested that the material-specific thermoelectronic behavior can be decoupled from the junction properties, paving the way to the primary goal of the project of relating nanoscopic and macroscopic thermoelectric measurements. Altogether, we have accomplished critically enabling steps to reveal the full potential of local thermoelectric characterization for addressing the energy-harvesting performance of nanoscale and nanostructured materials.

Information Shared

Maksymovych, P. In preparation. “Systematic thermoelectric microscopy with sub-nm resolution.” *Phys. Rev. B.*

05968

Probing Oxygen Reduction/Evolution Reactions on the Nanoscale: Towards Viable Lithium-Air Batteries

S. Jesse and S.V. Kalinin

Project Description

This project will use advanced atomic force microscopy techniques to study local ion diffusion and electrochemical activity on the active surfaces of model lithium-air battery systems. The overarching goal of this proposal is to (a) demonstrate proof-of principle studies of oxygen reduction and evolution and ion diffusion on the nanoscale by dynamic electrochemical strain microscopy, (b) validate this on model systems on lithium-conductors carrying aspects of the functionality of full air cathodes, and (c) explore the local electrochemistry of oxygen reduction and evolution on ionic conductor surface modified with catalysts. Specific effort is oriented towards the development of scanning probe microscopy (SPM)–based methods for probing irreversible and partially reversible electrochemical reactions, common for lithium-air systems.

Mission Relevance

The "development of the new microscopic and spectroscopic techniques spanning the atomic and mesoscopic scales…is critical to achieving the ability to design electrical energy storage (EES) systems rationally, including materials and novel architectures that exhibit optimal performance," as stated in the report of the Basic Energy Sciences (BES) Workshop on EES. Dynamic electrochemical strain microscopy will allow quantifying thermodynamics and kinetics of electrochemical reactions on the nanoscale in lithium-air systems, opening the pathway towards understanding electrocatalysis in these systems. As such, it will directly benefit DOE, BES, and the Office of Energy Efficiency and Renewable Energy (EERE) missions. Beyond DOE, high-density, high-lifetime systems are critical to virtually all federal programs, ranging from NIH (implantable devices) to DoD (remote sensors, military equipment) and Homeland Security. Furthermore, irreversible electrochemical processes are an inseparable part of areas such as CO_2 sequestration, electroresistive electronics, etc., and hence development of tools for their local probing will have an impact well beyond the scope of original work.

Results and Accomplishments

In the FY 2011, we have suggested and developed a scanning probe microscopy approach for mapping local *irreversible* electrochemical processes in nanoscale volumes based on the detection of bias-induced frequency shifts of cantilevers in contact with an electrochemically active surface. Using this method, we explore local electrochemical reactivity in lithium-ion conductive glass ceramic developed for applications as an electrolyte in lithium-air and lithium-water batteries. Near-unity transference numbers for ionic transport are demonstrated, and detection limits for current-based and strain-based detection are established. The tip-induced electrochemical process is shown to be a first-order transformation, and nucleation potential is found to be close to the lithium-metal reduction potential. Spatial variability of the nucleation bias is explored and linked to the local phase composition. These studies provide both insight into nanoscale ionic phenomena in practical lithium-ion electrolyte and open pathways for probing *irreversible* electrochemical, bias-induced, and thermal transformations in nanoscale systems. These studies complete both the instrumental framework and proof-of-concept imaging of lithium-ion conductive material and lay the foundation for exploring the role of individual catalyst particles on lithium electrochemical activity.

Information Shared

Arruda, T. M., A. Kumar, S. V. Kalinin, and S. Jesse. In print. "Mapping Irreversible Electrochemical Processes on the Nanoscale: Ionic Phenomena in Li-ion Conductive Glass Ceramics," *Nano Lett.*

Jess, Stephen, Thomas Arruda, Amit Kumar, and Sergei V. Kalinin, "Method of Probing Irreversible Electrochemical Reactions and Bias- and Temperature-Induced Transformations," patent disclosure IDSA 2607.

Microscopy Today Innovation Award in 2011 for "Electrochemical Strain Microscopy" (partially).

CHEMICAL SCIENCES DIVISION

05860

PAMAM Dendrimers with Regularly Alternating Functionalization as Potential Carriers for Imaging and Therapeutic Agents for Biomedical Applications

P.V. Bonnesen, K. Hong, J. Yang, and S.M. Kilbey II

Project Description

Biocompatible poly(amidoamine) PAMAM dendrimers of generation 4 (G4) or greater are receiving increasing attention as nanocarriers for bioactive molecules (or "ligands") that can be delivered to the surfaces of cells. The surface of a G4 PAMAM dendrimer can be derivatized with up to 64 ligands, which can be the same or different. These multivalent ligand–dendrimer conjugates can potentially display different pharmacological properties depending on how the different ligands are spatially arranged on the dendrimer surface and their relative abundance. In this project our objectives are to (a) demonstrate that we can synthesize and fully characterize a novel PAMAM dendrimer with a topographic architecture wherein the peripheral branches regularly alternate between two differently functionalized end groups in a well-defined manner; (b) prepare from this dendrimer a series of multivalent ligand–dendrimer conjugates in which two different bioactive molecules have been attached to the alternating end groups; and (c) compare the biological activity of these dendrimer conjugates with analogous PAMAM dendrimer conjugates possessing the same bioactive molecules attached in an uncontrolled, random spatial arrangement [via suitable bioassays through a no-cost collaboration with colleagues at the National Institutes of Health (NIH)].

Mission Relevance

This project aims to increase understanding of how the ability to tailor the functional display of chemical motifs at the nanoscale impacts functionality. These materials are primarily of interest as therapeutic agents, but there is also potential relevance to sensors for chemical and biological compounds, and to catalysis. It is our intention to further expand into architecturally designed dendrimer nanoparticles for biomedical applications. Results generated and capabilities enabled through this project will support proposals to relevant programs within either the NIH or the National Cancer Institute (NCI). There could be significant benefits in the areas of drug delivery for therapy and imaging (e.g., cancer), which would support NIH goals of conducting and supporting research "in the causes, diagnosis, prevention, and cure of human diseases" (from NIH website), and NCI goals "with respect to the cause, diagnosis, prevention, and treatment of cancer" (NCI website).

Results and Accomplishments

We had previously evaluated and refined the underlying chemistry for attaching a precursor arm to a PAMAM dendrimer surface, from which we could then attach a second branch. Each branch will later be functionalized with a different bioactive molecule using orthogonal chemistries. However, the success of the project hinged upon the development of a novel series of linkers in high purity. This linker permitted only a single reaction at the primary amine terminus of the dendrimer, such that a second different reaction could then be performed on the secondary amine to generate the second branch. Obtaining this new type of linker in high purity proved to be a significant challenge. Not only is high purity needed for efficiency in subsequent reactions (and to minimize side reactions), but medical (therapeutic) applications require high-purity compounds, as impurities are usually problematic. We were able to prepare impure batches, and we were able to demonstrate proof-of-principle on the linking chemistry (to the dendrimer) with this impure linker, but the derivatized PAMAM dendrimers produced contained too many impurities to continue on to the subsequent steps. It became apparent that for this project to be successful we needed to develop a new, viable synthetic approach to linkers of higher purity, especially because these dendrimers were to be used for biomedical applications. Accordingly we turned or attention to other routes to prepare these linkers, and we have made some progress in that endeavor, including successful synthetic routes to some precursors to the linkers that are or could be of general use to the organic community but that had no synthetic route described in the literature. We plan to complete the revised syntheses of the linkers and test the chemistry on PAMAM dendrimers by the end of FY 2011.

Information Shared

None to date, though a publication is planned on the synthesis of the linker molecules and associated chemistry.

05875

Electrolytic Hydrogen Production: A New Materials and Structural Approach

E. Greenbaum, I.I. Kravchenko, C.A. Sanders, and B.R. Evans

Project Description

The focus of this proposal is a new materials and structural approach to the science and technology of electrolytic hydrogen production. The goal of the work is measurement of threshold currents for cross-migration of oxygen into the hydrogen compartment as a function of electrode and compartment geometry, including the ion channels that connect the compartments. A measure of success was defined as production of a >99% H_2 stream with <1% O_2 content. This was achieved. Another measure of success was the utilization of abundant and inexpensive materials such as silicon and carbon-based polymers for the primary construction materials of the electrolytic units. This also has been achieved using silicon wafers with etched micropores and microporous polyethylene sheeting. Polyethylene sheeting is a substrate to which photolithographed nickel electrodes firmly adhere.

Mission Relevance

The scientific/technical problem that this proposal addresses is the economical production of carbon-neutral hydrogen and oxygen via the electrolysis of water. Our proposed solution is the use of readily available materials, microfabrication technology, and bidirectional wireless information transfer to produce electrolyzer units that have the potential for practical high-volume scale-up. The objective is

significant because it addresses one of DOE's core missions: "Promoting America's energy security through reliable, clean, and affordable energy." The results of this ORNL seed money project support the mission with proof-of-principle demonstration and a new materials and structural design that can lead to economical domestic production of carbon-neutral hydrogen and oxygen.

Results and Accomplishments

The key objective of this project has been achieved: proof-of-principle demonstration that laminar streaming of hydrogen and oxygen bubbles on opposite sides of vertically oriented planar wafers can produce a hydrogen stream of greater than 99% purity without the use of proton-conducting polymers. Using modern lithographic techniques, wafer barriers were fabricated at the ORNL Center for Nanophase Materials Sciences (CNMS) that served as both proton-conducting wafers and electrode surface supports. Silicon and porous plastic wafers, which are abundant, relatively inexpensive, and available from commercial sources, can be patterned with pores and nickel electrodes. Minimal diffusive cross-migration of product gases across the wafer barrier was achieved by using electrolysis currents of less than 1 mA per electrode pair. The final experiments that were performed on this project used a ~30 cm tall tower that can approximate a prototype design of a real-world system. Because of limitations of the commercially available porous plastic, we mimicked lithographed electrodes with 100 μm nickel wires. We used 100 mM phosphate buffer at pH 7 as the electrolyte. The main accomplishment of this work is that we have developed a new materials and structural approach to electrolytic hydrogen production that can be integrated with solar, wind, and nuclear energy.

Information Shared

US Patent Application 12/963,857, "Apparatus and Method for the Electrolysis of Water," filed December 9, 2010.

05880

Nuclear Materials FTIR

L.A. Lewis, R. Moyers, and D. Schuh

Project Description

Fourier transform infrared spectroscopy (FTIR) hyperspectral imaging could potentially facilitate the identification of chemical species peculiar to nuclear materials and their processing for close-range measurements (up to 25 m) of trace residues or for long-range applications (up to 5 km) of major contaminants. The goal of this project is to analyze the long-wavelength (thermal) signature of targeted uranium-based solids, such as UO_3, U_3O_8, and UO_2F_2, using a single-point (passive) FTIR system and assess the merits of performance and limits of detection utilizing this technique to acquire FTIR imaging data to identify areas of contamination from either close-range or standoff distances. If successful, the technique could be utilized in nuclear proliferation, contamination, and characterization applications.

Mission Relevance

The identification of nuclear materials is important in preventing the proliferation of nuclear weapons and also preventing the use of nuclear materials in dirty bombs. It is possible that the high-resolution chemical identification capabilities of FTIR hyperspectral thermal imaging can be applied to imaging surface contaminants and airborne emissions related to nuclear material processing at substantial standoff distances. FTIR hyperspectral imaging creates false-color images of chemicals from interferograms (i.e.,

signals measured from the superposition of waves that have been split and phase shifted) which, when superimposed on optical images, yield intuitive, visible presentations of measured materials.

The search for and identification of nuclear materials traditionally have been conducted by detecting characteristic ionizing photons or neutrons emitted during nuclear transitions of the subject material. The use of radiation-based detection methods to sense and identify the presence of radioisotopes is only a partial solution to preventing the proliferation of nuclear material. Key fundamental detection issues remain, including the relative ease with which nuclear materials can be shielded, geometric limitations (detector sizes and source-to-detector operating ranges), and potentially long counting times. Additional sensing approaches may complement or supplement measured radiation observations. For some applications, these approaches could potentially support nuclear materials production processing and control; in other cases, they may help reveal the presence of contraband materials or the occurrence of undeclared activities.

Results and Accomplishments

The FTIR spectrometer used to collect spectral data was a modified Bomem MR254 with a ZnSe beamsplitter. The instrument was configured with two detectors: an indium antimony (InSb) detector responsive to mid-wave infrared (MWIR) radiation and a mercury cadmium telluride (MCT) detector responsive to the long-wave infrared (LWIR) radiation (cm^{-1}). Data were acquired on UO_3 (yellow and red), UO_2F_2, U_3O_8, UO_2, UO_3, UF_4, and NH_4NO_3 and collected under both direct and indirect lighting conditions. Spectra that exhibited a noticeable difference between lamp/no-lamp data were then checked against spectra acquired from an empty petri dish to determine if the features were caused by the materials being tested or reflections from the petri dish itself.

LWIR: There is virtually no difference between LWIR spectra with the lamp on or off, and the only absorption features visible are due to atmospheric water vapor. Post-test checks on the spectrometer showed the LWIR detector bias on the preamp was too low, which affected the detector sensitivity, and is probably the reason no useful data were collected in the LWIR.

MWIR: MWIR data shows definite differences between data collected with lamp on versus data acquired with the lamp off, indicating the MWIR detector was working properly. However, comparison of data acquired from most samples to that acquired from the empty dish with the lamp on indicate that most of the spectral features were due to the petri dish. The one possible exception is in the spectrum acquired from UO_2F_2, which may exhibit a weak absorption features around 4700 and 5200 wavenumbers.

05895

Carbon Quantum Dots: Potential Eco-Friendly Light Harvesters for Solar Cells

G.A. Baker and R. Dabestani

Project Description

Photovoltaic (PV) technologies delivering high power efficiency with long-term stability at low consumer cost will form an integral and growing component of independent, sustainable energy infrastructures globally. We have proposed proof-of-principle studies of newly discovered carbon nano-dots (C-dots; surface-passivated nanoscale carbon particles) as novel, tunable, inexpensive, and renewable light-harvesting elements for PV solar cells.

C-dots are cheap, highly photostable, and nontoxic, in contrast with other light-harvesting candidates [i.e., quantum dots, (QDs), conducting polymers, organic dyes]. Most importantly, they exhibit tunable quantum confinement optical properties, suggesting profound potential in solar cells. Although C-dots have manifold potential advantages over existing PV materials, they have not been utilized in PV applications. We seek to investigate the potential of utilizing C-dots for PV application demonstrating proof-of-concept to lay the groundwork for establishing a completely new class of solar cell. Clearly, novel photo-harvesting materials lie at the forefront of solar cell technology, and if successful, this research would represent a critical breakthrough in PV with clear intellectual property, ushering in an unheralded field in green solar cell technology.

Mission Relevance

This work has excellent potential to attract immediate follow-on funding from numerous agencies including the DOE Office of Energy Efficiency and Renewable Energy (EERE), the Office of Science Basic Energy Sciences (BES), and the Advanced Research Projects Agency–Energy (ARPA-E). The current National Solar Technology Roadmap on sensitized solar cells published by the EERE program specifically calls out the urgent need to develop next-generation sensitizers with improved efficiency/stability and a deeper understanding of the fundamentals to realize the real potential of this technology. Additionally in winter 2010, EERE's Solar Technology Program plans to have funding opportunities for applications that have a high impact on innovative evolutionary improvements that can be supplied across the industry at high volumes and lower costs than conventional technology today. If successful, C-dots would provide such a low-cost, high-volume, and additionally nontoxic (thereby lowering recycling and associated costs) component and be a potentially disruptive technology for sensitized solar cells. In addition, the H.R. 3585 Solar Technology Roadmap Act recently passed in the House would authorize appropriations totaling $2.25 billion over the 2011–2015 period for DOE to support various programs related to solar energy technology.

Results and Accomplishments

The principal investigator (Gary Baker) accepted an academic position a few months after the funding of this proposal. Unfortunately, none of the C-dots proposed were synthesized or characterized spectroscopically to determine the feasibility of this class of compounds as a new generation for solar energy. As a result, no useful data or information was obtained to examine the suitability of C-dots for solar energy application.

05964

Microwave Activation for Advanced Catalytic Conversion of Biomass to Hydrocarbon Fuels and Chemical Feedstocks

W.L. Griffith and L.A. Berry

Project Description

We propose to develop proof-of-principle for a revolutionary new technology for selective microwave activation of catalysts for production of hydrocarbon fuels and chemical feedstocks. This process could convert a number of low-valued by-product biomaterials—lignin monomers, cutin waxes, and fatty acids—to high-valued hydrocarbons and aromatics. Microwave-activated catalysis meets national needs for renewable fuels and greenhouse gas reductions. Process advantages may include (1) reduced temperature operation (150°C less than conventional processes), (2) no added solvents, (3) no hydrogen

requirement, (4) high concentrations of a limited number of key target products, and (5) production of aromatics and cyclics needed in "drop-in" fuels. Successful proof-of-principle could meet the needs of the Department of Energy (DOE), Department of Defense (DoD), and industry for directly usable, infrastructure-compatible petrochemicals and fuel replacements from biomass. Tasks to demonstrate proof-of-principle comprise catalysis, microwave application, and analytical studies to demonstrate the potential utility of advanced microwave-assisted catalytic conversion. Computer models of the system that could serve as a basis for the "full commercial system" extrapolations and estimates needed in downstream technology development proposals are also planned.

Mission Relevance

Successful completion of this project will enable new R&D activities in these DOE Office of Energy Efficiency and Renewable Energy (EERE) areas: (1) Office of the Advanced Materials Program (AM, formerly ITP), energy efficient production of solvents and feedstocks for industrial chemicals from biomaterials, and (2) Biomass Program (BP), lignin and cutin-based coproducts, infrastructure compatible fuels. Timing of this research is expected to permit targeting of the early stages of these developing efforts: sustainable manufacturing and infrastructure compatible fuels. In these agencies, multiagency biofuels (DoD-Navy, DOE, USDA), successful proof-of-principle results could provide the capability to generate required aromatics and naphthenics for military fuels that cannot now be derived from biomass. These DoD components currently fund biofuels programs with (1) the Navy, with the U.S. Department of Agriculture; (2) Defense Advanced Research Projects Agency (DARPA), 100% bioderived JP-8 fuel); (3) Air Force (green jet fuel); and (4) Marines (emerging, primarily diesel). Mass and energy balance data is critical to completing formalized energy and feasibility assessments in proposals.

Results and Accomplishments

Data that provide a basis for estimating feasibility, energy, and emissions of industrial-scale processes is required in proposals of targetted funders and will be developed. In order to accomplish this, we have completed, evaluated, and verified improvements to an existing small-sample microwave system that provides separate control of microwave application and sample temperature. These accomplishments include (1) added solid-state, low-voltage, variable-frequency microwave amplifier system; (2) added computer-controlled, solid-state, high-speed switching to pulse power; (3) added fast response system to monitor power at sample chamber; (4) added computer fine-tuning of the microwave system to minimize reflected power as a function of temperature; (5) integrated these improvements into a LabView control and data acquisition system; and (6) acquired access to a Comsol multiphysics simulation system to support interpretation of the data and estimate scaleup. These improvements establish a testing platform to provide the data required to both establish proof-of-principle and to estimate feasibility and energy for industrial-scale processes as required in proposals of targetted funders. The larger sample size (5 ml) possible with this system will greatly improve our ability to evaluate products and mass balances for samples. In the next year, the improved microwave system will be used to develop proof-of-principle for microwave-activated catalytic conversion of C8-C25 fatty acids, C18-C25 alcohols, lignin model compounds, and lignins to corresponding hydrocarbons and aromatics.

06248

Polar Perovskite Oxides with Local-Bond Frustration

C.A. Bridges

Project Description

The goal of this project is to provide experimental confirmation for a novel concept in which chemical disorder can be manipulated to produce enhanced polar behavior in the perovskite structure, and to thereby provide a new, rational approach to the design of polar materials with giant dielectric responses. If successful, it will be possible to predict strategies and even specific compositions for bulk polar oxides with unprecedented properties such as high polarization and giant piezoelectricity. Therefore, this proposal aims to demonstrate an important paradigm in condensed matter sciences: *a rational approach to materials discovery in which compounds with exceptional properties will be discovered and synthesized on the basis of first-principles calculations.* The focus will be the effect on dielectric properties of bismuth substitution into the high dielectric permittivity material $Sr(Zn_{1/3}Nb_{2/3})O_3$, based upon the results of recent computational studies that suggest a large enhancement in dielectric response with doping.

Mission Relevance

The ability to create materials by design has been highlighted as a Grand Challenge in the National Research Council (NRC) report *Frontiers in Crystalline Matter*, and the control over and understanding of emergent phenomena is one of the five Grand Challenges of Basic Energy Sciences in the *Directing Matter and Energy* report. A close relationship between theory and experiment is critical to meeting these challenges, as this will enable the optimization of the materials design process by limiting the parameter space for predictive calculations. This project will address these challenges by demonstrating directly that first-principles calculations can be used to provide new materials with enhanced dielectric properties. Furthermore, the development of ferroelectric and piezoelectric polar materials is of interest to the Department of Defense for piezoelectric energy generation, sensors, and fuel injectors.

Results and Accomplishments

The high dielectric permittivity parent compound $Sr(Zn_{1/3}Nb_{2/3})O_3$ has been prepared and has been confirmed to be phase pure. Synthesis of the x = 0.1 bismuth-doped compound $(Bi_{0.1}Sr_{0.9})(Zn_{11/30}\ Nb_{19/30}\ O_3)$ has been initiated, and the material requires refining to obtain phase purity. Funding was granted at the end of the first year, and thus synthesis and dielectric property measurements will be completed in the second year.

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

05870

Qualitative System Identification for Tumor Modeling: Knowledge Discovery from Observations of In Vivo Tumors

J.J. Nutaro

Project Description

The goal of this project is to build and demonstrate an inductive reasoning engine for discovering models of tumor growth from features in time series images of mouse models of human breast cancer. Our approach integrates (1) fuzzy inductive reasoning, (2) genetic algorithms, and (3) high performance computing to enable the construction of dynamic models directly from imaging characteristics that correlate with disease outcome. The effectiveness of the approach is demonstrated by its application to data provided by our collaborators at the Vanderbilt University Institute of Imaging Science (VUIIS). This approach to cancer modeling is new to the field of cancer biology, and the demonstration is the first instance of qualitative system identification being applied to imaging characteristics to understand fundamental aspects of tumor response to therapy.

Mission Relevance

The project directly supports the DOE Office of Advanced Scientific Computing Research mission of providing computational capabilities for answering critical questions that range from the function of living cells to the power of fusion energy. Our goal is to fill a crucial gap between the growing volume of data obtained from observations of complex systems and the construction of theories to explain observed behaviors. By advancing the state of the art in system identification, it will become possible to extract directly from data the rules governing complex systems; rules that exist in available data sets but remain invisible to the unaided eye.

Results and Accomplishments

ORNL has built a state-of-the-art tool for inductive modeling and demonstrated the principles of its operation using test data from cellular automata and from tumors simulated with Vanderbilt's advanced models. Preliminary test results are very encouraging, showing a better than 90% accurate prediction rate for a single time step for the simulated data.

05881

Thwarting Online Deception and Phishing with Honeypots and DNS Analysis

C.A. Shue

Project Description

Criminals impersonate legitimate institutions and defraud users through the Internet. In phishing attacks, criminals send deceptive emails that encourage users to follow a link to a fraudulent Web site and provide sensitive information. In 2007, such attacks led to financial losses exceeding $3billion.

Phishers must obtain email addresses for potential victims before they can launch an attack. Phishers harvest addresses through Web crawling, yet little is known about which sites they crawl or whether their crawlers exhibit atypical DNS access patterns. With extensive real-time data from trap email addresses (or honeypots) at external sites and ORNL, combined with ORNL server logs, we are examining phishing Web crawler access patterns. This will enable us to (1) prevent crawlers from harvesting our users' email addresses, (2) block spam from the crawlers' networks, and (3) determine whether a campaign is Internet-wide or targeting the DOE.

Mission Relevance

Phishing has serious implications for organizations, including ORNL. In a June 2009 phishing test of the lab staff, ORNL Cyber Security found that over 20% of our users were deceived, including 14.86% of our technically savvy users authorized to administer their own machines. These phishing attacks can lead to infected machines, the loss of sensitive information, and a tarnished reputation for the organization. By protecting our users from phishing attacks, we can avoid these risks for ORNL and the DOE.

Our approach has broad implications for other federal agencies, including the DOD, DHS, and FBI. This work can deter financial crimes, help limit infiltrations into federal computers, and avoid the loss of sensitive data.

Results and Accomplishments

We have created the honeypot systems for distributing trap email accounts and for receiving phishing messages. We have been advertising the device to attract more phisher attention so that we can study their behavior. We have also obtained DNS server logs and network connection information from ITSD. We have analyzed these logs to determine the timing difference between a DNS resolver's query and the Web/mail client access attempt. In doing so, we have found some atypical behavior with DNS caching that seems to be common among attackers: attackers tend to cache DNS responses long past when the records have expired. These caching violations can be a warning sign for automated malicious activity. However, some clients that have not been blacklisted also violate DNS cache limits. These clients may have been false negatives in blacklisting or automated visitors that are not malicious. We have additionally detected an instance of misconfiguration with an ISP resolver.

These results may allow us to detect automated visitor behavior early in the connection and allow us to take appropriate action, such as filtering email messages or adjusting the information we release to these visitors.

In our second year, we have shown that our system can automatically protect servers by changing the IP addresses associated with these machines, providing a level of access control that would prevent outside

adversaries from attacking. This system can be implemented without substantial overheads at the protection system.

Information Shared

Shue, C.A., and Kalafut, A.J. 2011. "Using DNS Interactions to Detect and Thwart Malicious Clients." Under submission.

Shue, C.A., Kalafut, A.J., Taylor, C.R., and Allman, M. 2011. "On Building Programmatic Capabilities for O(Free)," under submission.

Taylor, C.R., and Shue, C.A. 2011. "Using the Domain Name System to Thwart Automated Client-Based Attacks." ORNL/TM-2011/289, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

05884

Drag Reduction with Superhydrophobic Surfaces

C. Barbier and B. D'Urso

Project Description

Superhydrophobic surfaces such as leaves of a lotus plant consist of a hydrophobic surface combined with microstructures or protrusions. These surfaces are extremely difficult to wet, and recently they have been shown to reduce drag in water flow. However, their drag reduction has been investigated mainly in the laminar region (small objects, small velocity), and few data are available in the turbulent regime (larger objects, larger velocity), where most practical applications are.

We will fabricate a new generation of superhydrophobic material that will combine both microscale and macroscale features for optimizing drag reduction in the turbulent regime. These materials will be tested in the Center for Nanophase Materials Sciences (CNMS) with a cone-plate rheometer. In parallel, numerical tools will be developed and validated on these measurements. They will be then used to demonstrate the capabilities of these materials for practical applications such as pipelines or seafaring vessels.

Mission Relevance

The scope of this work is consistent with DOE's commitment to nanotechnology research and development as well as to advanced computational methods. This research expands the application of superhydrophobic surfaces for drag reduction in pipelines, on ships, and in many other contexts. In so doing, it creates the potential for substantial energy savings in the wide range of applications where drag creates energy losses. Thus, it is well aligned with DOE objectives.

An efficient drag reduction technology will be particularly useful to the Department of Defense or Office of Naval Research for their vessels, and the Department of Agriculture for irrigation applications.

Results and Accomplishments

The slip boundary condition was implemented in OpenFOAM and was validated with theory. A series of calculations was run for two different slip lengths (25 and 50 μm) for a cone-and-plate geometry and a range of rotational speeds varying from 25 to 1,000 rpm. Convergence of the calculations was improved by writing an application that maps the fields from one case to another by multiplying the pressure and

velocity fields with an appropriate factor. The simulations were mainly used to determine the slip length in the turbulent regime.

The superhydrophobic samples began with annealed 99.9995% pure aluminum discs, which were cut flat by single point diamond turning. For grooved samples, a series of concentric grooves (or riblets) were cut into the sample with a 90 degree dead sharp diamond tool. The surface structures were formed on the surface by a series of anodizing steps in citric acid with alternating etching steps in 2% tetra methyl ammonium hydroxide. The anodizing steps created aluminum oxide pores that grow into the aluminum substrate, while the etching widens the pore at each step. The combined effect was to create flared aluminum oxide pores that intersect each other, leaving a pattern of sharp surface features. Finally, the samples were spin-coated with a sub-micron-thick layer of Hyflon AD60, a hydrophobic polymer, which leaves the surface superhydrophobic.

Samples with 10, 100, and 1,000 μm deep grooves were tested at CNMS with a commercial rheometer (AR 2000, TA Instruments) with an angular velocity between 2 and 150 rad/s. A stainless steel cone of 60 mm in diameter, 2 degrees in cone angle, and 51 μm in truncation was used. A sample holder was built in order to test the samples at rotational speed above 80 rad/s. At low Reynolds number, drag reduction varying from 10 to 30% is observed. As the rotational speed increased, the drag reductions decreased but remain above 10% for the surfaces with 100 and 1,000 μm grooves. Based on the simulations, the slip length of the grooved superhydrophobic surfaces was of the order of 100 μm, which is two times larger than the slip length found in the literature in the turbulent regime.

COMPUTER SCIENCE AND MATHEMATICS DIVISION

05877

Novel Standoff Sensing Method for Explosives with Rydberg State Spectroscopy and Radar Detection

F. Rudakov

Project Description

Standoff trace chemical sensing is of paramount importance for national and homeland security, nonproliferation control, and environmental monitoring. Currently, most techniques for standoff detection are based on remotely probing vibrational spectra of the target molecules using infrared (IR) or Raman spectroscopies. Yet, the complexity of vibrational spectra scales very quickly with the molecular size, making detection of large organic molecules in complex environments very challenging. We propose a novel approach to standoff trace chemical sensing. The basis for our technique is Rydberg Fingerprint Spectroscopy followed by microwave-based detection. The target molecules are first excited to the 3*s* Rydberg state and then pass through the higher lying Rydberg states when probed by two-photon ionization. Transitions between the Rydberg states reveal a highly resolved and purely electronic spectrum that is characteristic of the molecular structure. This spectrum is subsequently recovered by probing the remotely generated photoinduced plasma with microwave radiation. Scattering of the microwaves from the photoinduced plasma reveals the underlying Rydberg spectrum and the "molecular fingerprint." Complexity of the Rydberg spectrum does not scale with the molecular size, making the technique well suited for detection of large organic molecules such as those of explosives and chemical warfare agents. The technique is completely orthogonal to well-established techniques such as IR, Raman, and laser-induced breakdown (LIB) spectroscopies.

Mission Relevance

The proposed technique for standoff detection is scientifically novel and may find multiple applications. For example, because of its high sensitivity, the proposed design can be used for detection of airborne chemicals (i.e., for pollution monitoring). Rydberg spectroscopy is insensitive to molecular vibrational motion. Therefore, the proposed design may be applicable for studying combustion reactions. Besides, since the complexity of the Rydberg spectra does not scale with the size of the molecule, the technique is well applicable for characterization of large biomolecules organic molecules and clusters. The proposed design may also find applications in nuclear cycle monitoring and nonproliferation control.

Results and Accomplishments

We designed and built an experimental setup consisting of Nd:YAG pumped OPO coupled with a microwave homodyne transceiver detection system. We demonstrated feasibility of the technique by acquiring Rydberg spectrum of 1,4-diazobicyclooctane (DABCO). Transitions between the 3*s* Rydberg state and higher lying Rydberg states were probed using two-color photoionization with 266 nm photons

and photons in the range 460–2400 nm. The laser-induced plasma was probed with 11 GHz microwave radiation. Highly resolved Rydberg spectra were acquired in vacuum and in air.

The proposed technique is orthogonal to well-established standoff detection techniques and thus can complement them. It is not confined to reflection geometries and can be used for trace chemical sensing in open air. Other applications of the proposed design may also be suggested. For example, because of the insensitivity of Rydberg spectra to the vibrational motion of the molecule (unlike IR and Raman spectroscopies), the technique can be applied for in situ detection of combustion radicals and intermediates.

Information Shared

F. Rudakov and Z. Zhang, "Standoff Detection of Large Organic Molecules Using Rydberg Fingerprint Spectroscopy and Coherent Microwave Rayleigh Scattering," *Optics Letters*, accepted for publication.
F. Rudakov and P.M. Weber, "Ultrafast structural dynamics and isomerization in Rydberg-exited Quadricyclane-Norbornadiene System," submitted to *Journal of American Chemical Society*, preprint available.

05905

Asynchronous Algorithms for Exascale Computations

R. Deiterding and J. Barhen

Project Description

Harnessing the compute power of the upcoming generation of exascale super-computers is a daunting task. Exascale machines will consist of millions of parallel computing elements thereby mandating changes in the present computational algorithms. One of the most promising paths forward builds upon the concept of concurrently asynchronous algorithms. This involves a methodology that implements concurrent tasks in a parallel solver, built on a fixed-point iteration scheme, without explicit waiting at synchronization points. While the theoretical conditions for convergence of numerous asynchronous iterative methods are well established, almost no practical results are available for the current generation of distributed memory high-performance computing systems. The objective of this project is to quantify the benefit of asynchronous iteration for prototypical, yet representative, parallel linear algebra solvers. To obtain results of general practical interest, we are concentrating on the two most important classes of iterative methods for sparse linear problems, as they typically arise in the solution of large-scale problems of partial differential equations (PDE): multigrid algorithms and Krylov subspace methods. In particular, we are investigating the benefit of asynchronous communication in the smoothing iterations of a grid-based geometric multiplicative multigrid implementation and in the solving iterations of a conjugate gradient method.

Mission Relevance

Linear iterative methods are among the most crucial components for obtaining good scale-up of simulation software on exascale systems. Numerous application codes, for instance, in fusion or combustion simulation, engineering, or astrophysics, require implicit discretizations on computational meshes, thereby leading to large sparse linear problems. The DOE Office of Advanced Computing Research has a fundamental interest in exploring new classes of linear iterative algorithms for sparse problems that can effectively use exascale systems. The effective utilization of exascale systems is also of

great interest to numerous other federal agencies, including the Department of Defense, the National Aeronautics and Space Administration, and the Missile Defense Agency, which carry out large-scale simulations of (partial) differential equations using linear iterative methods.

Results and Accomplishments

We have implemented a prototypical iterative grid-based (i.e., matrix-free) PDE solver for the two-dimensional Poisson equation. This solver uses a generic MPI-based communication module, built on nonblocking communication routines, that allows both synchronous and asynchronous data exchange (using MPI testsome() on the receiver side) at processor boundaries. While the employed Red-Black Gauss-Seidel iteration method could be confirmed to be amenable to asynchronous iteration, the required operation count of $O(N^2)$, where N denotes the number of unknowns, still makes for an uncompetitive solution approach. To improve overall performance, a geometric multiplicative multigrid method was implemented, which uses Red-Black Gauss-Seidel iteration as a smoother. Our present prototype allows asynchronous smoothing iterations, and after verifying the implementation in serial and for synchronous parallel communication, successful preliminary test runs on moderate core counts on OLCF's IBM BG/P Eugene have been conducted.

While multigrid has principally optimal algorithmic complexity of $O(N)$, its convergence can be limited for poorly conditioned problems. We are therefore investigating Krylov-subspace-type methods on a hybrid CPU/GPU system. Potential methods for implementing concurrently asynchronous algorithms (e.g., asynchronously parallel matrix-vector kernels) have been explored, and we are developing the prototype of a conjugate gradient method that is parallelized using CUDA. We have successfully carried out computations that involved overlap of concurrent GPU kernels, data transfers (with page-locked memory), and host computations, within the framework of CUDA streams. That allowed a major reduction of idle times between processors, and better exploitation of the hundreds of cores on a GPU device.

05956

Increase Power Conversion Efficiency of Broad-Area Laser Diode Array Coherent Beam Combining

B. Liu and Y. Braiman

Project Description

Coherent arrays of high power semiconductor lasers may have an extensive variety of applications such as directed energy, free-space optical communication, nonlinear optics processes such as high-efficiency blue-green light generation, and others. One of the major obstacles limiting applications of coherently combined semiconductor laser arrays is relatively low power conversion efficiency (PCE), currently in the range of 10%. We propose an effective approach to increase the PCE of the coherent beam combining of a broad-area laser diode array to the level of ~40% using custom-designed low-loss broad-area laser diodes or to the level of 30–35% with low cost commercial laser diodes by optimizing the external cavity design and broad-area laser diode configuration. Achieving 30% PCE will make semiconductor lasers much more attractive than fiber lasers for numerous applications, as semiconductor lasers are much more compact, less expensive, and provide much broader wavelength choice for many commercial and defense applications.

Mission Relevance

Development of high-conversion-efficiency semiconductor laser array coherent beam combining technology will be beneficial for variety of DOE and national security missions, including cost-efficient energy sources for manufacturing and ultra-fast computer data networking.

Our project seeks to improve the technology for coherent combination of laser beams, specifically by improving power conversion efficiency, reducing footprint, and reducing cost. Applications of this technology to directed-energy systems and communications will support the interests of the Department of Homeland Security, NASA, and several Department of Defense organizations: the Joint Technology Office, the Space and Missile Defense Center, and the Office of Naval Research.

Results and Accomplishments

Based on results of our numerical simulations, we ordered laser diode arrays and implemented experimental design as proposed. We experimentally demonstrated 20% power conversion efficiency from the V-shape external cavity system, an almost two times increase compared to our previous experimental results. This result was achieved by optimizing the external cavity design, and there is still room for additional optimization and increase in power conversion efficiency. Doubling the power conversion efficiency will significantly help follow-up funding efforts in FY 2012.

06255

Scalable Algorithms for Structure Identification on Tree-like Complex Networks

B.D. Sullivan and M. Mahoney

Project Description

Large-scale, complex networks naturally represent relationships in a variety of settings such as social relationships, computer/communication networks, and genomic sequences. Efficient analysis of these networks is an outstanding issue important to numerous sponsors, including DOE/Advanced Scientific Computing Research (ASCR), as analysis can reveal important details about social hierarchy, computational bottlenecks, etc. We propose to advance the state of the art in complex network analysis by investigating and characterizing relationships between two notions of “tree-like-ness” for large-scale complex networks.

Although there is a large body of work suggesting that such networks have tree-like properties, existing algorithmic/statistical tools for identifying tree-like structure were developed for more structured applications, limiting their usefulness. The two notions we focus on are hyperbolicity, a geometric notion describing the maximum deviation of shortest path distance from a tree metric, and tree-width, a combinatorial quantity from structural graph theory measuring the scale of the subgraphs which must be collapsed in order to see an underlying tree. To date, there is little research elucidating and exploiting the relationships between them. Establishing theoretical connections, bounds, and heuristics will have implications for algorithms in areas including compact routing, sparse spanners, and community detection. This project will establish the proof-of-principle evidence connecting hyperbolicity and tree-width needed for future proposals to pre-identified sponsors.

Mission Relevance

The project supports the DOE mission by laying the groundwork for new methodologies for understanding petascale data and complex networks, both areas where we have strong indications of future calls and investment through the ASCR Applied Mathematics program. Specifically, our methods will help elucidate the "intermediate structure" of complex networks—salient characteristics and structural properties that are not captured by local metrics (e.g., clustering coefficient) or global ones (e.g., degree distribution). This intermediate structure plays a critical role in the dynamic evolution of the network and the behavior of diffusion processes on it, two problems identified as critical in DOE workshops.

Results and Accomplishments

In the 30 days since the project was funded in September 2011, we have already established our first theoretical results, giving a tight min/max condition on the hyperbolicity in terms of tree width and the size of the largest induced cycle in the graph. We expect submission of a paper detailing these results before the end of 2011.

The principal investigator (Blair Sullivan) has also participated in two invitation-only workshops: "Large Graphs: Modeling, Algorithms, and Applications" at the Institute for Mathematics and Applications and "Geometry of Large Networks" at the American Institute of Mathematics, where she has given talks on the subject area and discovered a promising future collaborator in the area.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

05873

Computational Simulation of Catalytic Biomass Pyrolysis

C.S. Daw, C.E.A. Finney, and S. Pannala

Project Description

This project is targeted at developing and demonstrating unique computational tools for simulating catalytic pyrolysis of woody biomass with sufficient chemistry, kinetics, and multiphase hydrodynamics to interpret laboratory- and pilot-scale reactor data and evaluate potential barriers to commercial scale-up. Addition of catalytic materials to biomass pyrolyzers has been recognized as a promising step to reducing problematic tar products, but to date there has been no development of models to interpret experiments or to aid in scale-up of reactor designs. This project will utilize two computational codes to simulate catalytic biomass pyrolyzers: MFIX (Multiphase Flow with Interphase eXchanges), a DOE-FE sponsored code for general multiphase flow simulation, and FBCSIM, an ORNL-developed steady-state code for fluidized-bed combustion of coal. Both codes are being adapted for biomass chemistry, physical properties, and pyrolysis operating conditions and then compared with appropriate experimental data for validation. In addition, laboratory experiments with simulated biomass particles are being used to develop improved models of biomass particle mixing in fluidized-bed reactors.

Mission Relevance

Catalytic biomass pyrolysis has been recently identified by the DOE Office of Biomass Programs (OBP) Thermochemical Platform as one of the most promising research areas leading toward the development of alternative, non-petroleum transportation fuels from biomass. Computational simulation capabilities for these reactors currently available to industry are relatively limited, and additional tools are needed to aid in the interpretation of laboratory experiments with candidate catalysts as well as guide the evaluation of candidate biomass feedstocks, reactor designs, and pyrolysis conditions. ORNL has unique prior experience and expertise in computational fluidized-bed simulation and applied catalysis as well as world-class computational facilities that can be directed toward this effort. Making full use of these capabilities can be of benefit to both the DOE-OBP Thermochemical Platform and the Integrated Biorefinery Program in accelerating development of commercially viable processes for biofuels production.

Results and Accomplishments

In FY 2011 we continued to update our steady-state fluidized-bed reactor code (FBC), including the addition of biomass-specific heat and mass transfer correlations reported in the literature to account for biomass particle heat up and devolatilization. We also added a statistical model that accounts for biomass particle dispersion from different injection points and the tendency of the biomass particles to segregate from the rest of the solid bed material. The latter model was developed in collaboration with Jack Halow,

a professor at Waynesburg University in Pennsylvania, and three undergraduate students under his direction. This work has also resulted in the development of a novel experimental technique for measuring particle mixing in fluidized-bed reactors based on the use of a magnetic particle tracking system. The details of this technique were published earlier this year in *Industrial and Engineering Chemistry Research* (see reference below). An additional journal manuscript on the statistical model resulting from experimental studies with simulated biomass particles is in progress.

Our work with the MFIX code was also supported for several months by Sudharshan Renganathan, an ORISE Post-Master's Fellow from Georgia Institute of Technology. The MFIX work with Renganathan has led to the development of improved methods for extracting statistical correlations for bubble dynamics and gas-solids mixing from MFIX output that can be used for more rapidly interpreting experimental trends and as a basis for improving mixing and circulation estimates in FBC. We are now summarizing these results in another journal article and incorporating them into FBC subroutines. In the future we expect that use of these correlations will allow closer synchronization between MFIX and FBC.

We have continued limited interactions with collaborators at NREL, who have provided additional data on biomass particle devolatilization that is being incorporated in both MFIX and FBC. As time and future funding permit, we plan to continue collaborating with NREL on comparisons of the biomass mixing predictions made by different computational models of pyrolysis reactors. This year we have also had limited interactions with the Korea Institute of Science and Technology (KIST) and the École Polytechnique in Montreal, but we have had to reduce priorities in these directions because of limited funding and the need to devote more effort toward completing journal papers on our modeling results and analysis of the magnetic tracer experiments. A joint presentation with our partners at Waynesburg University has been scheduled for the National AIChE Meeting this fall in Minneapolis.

Information Shared

E. Patterson, J. Halow, and S. Daw, "Innovative Method Using Magnetic Particle Tracking to Measure Solids Circulation in a Spouted Fluidized Bed," *Ind. Eng. Chem. Res.* 2010, *49,* 5037–5043.

C.S. Daw, J.S. Halow, and C.E.A. Finney, "Modeling spatio-temporal trajectories of individual segregating particles in bubbling fluidized beds," Manuscript in preparation.

S. Renganathan, S. Pannala, C.E.A. Finney, and C.S. Daw, "Extraction of bubble statistics from CFD simulations of bubbling fluidized beds," Manuscript in preparation.

J.S. Halow, B. Crawshaw, C.S. Daw, and C.E.A. Finney, "Mixing and Segregation of Biomass Particles in a Bubbling Bed," Presentation at the 2011 Annual Meeting of the American Institute of Chemical Engineers, Minneapolis, MN, October 16–21, 2011.

05896

Emissions Adsorption at Cold Start: An Energy-Efficient Emission-Control Strategy for Hybrid Electric Vehicles and Plug-in Hybrid Electric Vehicles

Z. Gao, M.-Y. Kim, J.-S. Choi, C.S. Daw, and J.E. Parks, II

Project Description

This project aims to reduce the emissions during cold starting of vehicles by utilizing the unique capabilities of low-cost adsorbers for hydrocarbons (HC) and nitrogen oxides (NOx) pollutants as emitted from hybrid electric and plug-in hybrid electric vehicles. Cold start emissions account for the majority of

emissions from modern vehicles during the transient drive cycles that form the basis for emission compliance. The low-cost adsorbers include Ag-zeolites and Fe-Mn-based transition metal oxides. The combination of these adsorbers is able to adsorb HC and NOx at low temperature. At higher temperature, these emissions can be desorbed and subsequently oxidized in a downstream-placed conventional catalytic converter. The proposed work evaluates the feasibility of HC and NOx emissions control based on using these low-cost adsorbers during the cold start of leading-edge hybrid vehicles. The proposed tasks included (1) identifying materials for low-cost adsorbers and utilizing microreactor experiments to characterize removal of HC and NO_x emissions simultaneously under reaction conditions relevant to cold-starting and (2) developing a low-order physically consistent computational model simulating an aftertreatment monolith with the trap materials and estimating the removal of cold-starting HC and NOx under realistic steady-state and transient vehicle operation.

Mission Relevance

Leading-edge hybrid electric and plug-in hybrid electric vehicles demonstrate high fuel efficiency in light-duty vehicles. However, the cold start or multi-cold-start events in HEVs and PHEVs force these modern vehicles to sacrifice fuel economy in order to reduce HC and NOx emissions, for example, by managing the engine under suboptimal conditions with respect to fuel efficiency. This project utilizes the unique capabilities of low-cost adsorbers for HC and NOx emissions to reduce these emissions without causing any fuel penalty during cold starting of vehicles. The technology could largely promote the nation's energy security against importing foreign petroleum and protect the environment by providing a low-cost solution. Thus, the project directly supports the mission of various DOE programs; especially Energy Efficiency and Renewable Energy's Vehicle Technologies Program (VTP) can benefit from the proposed emission control strategy in their research of advanced energy efficient and clean transportation technologies. The results also support the US Department of Transportation (DOT) and the US Environmental Protection Agency (EPA) in their mission to address energy security and global climate change. We have made significant progress in securing funding from the DOE Office of Vehicle Technologies to support our emission control and vehicle simulations in FY 2012.

Results and Accomplishments

We have completed the two major project tasks outlined in the project description. First, the kinetic mechanism of Ag-zeolites and Fe-Mn-Zr oxides for HC and NOx adsorption at ambient and related desorption at high temperature has been identified by utilizing microreactor experiments. Then a physically consistent passive hydrocarbon and NO_x adsorber model has been developed by fitting the experimental lab measurements. We numerically evaluated the potential of the passive hydrocarbon and NO_x adsorber in reducing HC and NO_x emissions under transient vehicle operation. The results show that the device can contribute an extra 68–80% HC emissions removal and an extra 27–35% NO_x emissions reduction in a PHEV. For a HEV, the extra emissions removals are 43–47% in HC and 26–32% in NO_x, respectively. The results also demonstrate that these extra emission removals neither cause any fuel penalty or require engine operating change and configuration modification. The material cost is much less than the precious metal. Consequently, this passive hydrocarbon and NO_x adsorber technology is both technologically practical and low cost.

05962

$CuInS_2$/ZnS Core-Shell Nanocrystals—A Designer Red Emitter to Revolutionize Solid-State Lighting Technology

M.Z. Hu, Q. Dai, I. Ivanov, and C.E. Duty

Project Description

This project investigates a unique integrated surface/defect engineering approach (via nanocrystal surface shell growth, molecular ligand passivation, plus pulsed thermal annealing) to achieving high photoluminescence (PL) efficiency and stability in a novel $CuInS_2$/ZnS nanomaterial for use as a designer red emitter in solid-state white lighting technologies. An environmentally benign, non-injection chemical synthesis process will be studied. Such a designer material has high potential to replace the currently used red emitters in industry, which face issues in efficiency and toxicity. We will verify and evaluate the proposed approach regarding individual/combined effectiveness in reducing the defect level and thus enhancing the quantum efficiency of red emission. This effort will attract collaboration and sponsorship from industrial and government sponsors, and the development of such emitters could provide the means to meet DOE's need for safe, efficient light sources.

Mission Relevance

This project is directly relevant to the mission in energy efficiency and clean energy. We expect relevant upcoming opportunities for advanced material/process development and application in energy technologies with the Solid-State Lighting program of the EERE Building Technologies Program, the ITP nanomanufacturing program, and the Solar Energy Technologies program. It could also benefit DOD/DARPA and NIH.

Results and Accomplishments

The project focuses on demonstrating an integrated surface/defect engineering approach to achieving high efficiency and stability in the proposed nontoxic nanomaterials. A possibly reproducible and scalable green chemistry process, engineered by surface shell and ligands and annealed thermally, is used to synthesize the nanomaterials. The resulting designer red emitter should have a significant impact on solid-state lighting applications. We have planned to collect essential data on emission efficiency, stability, reproducibility, and process scalability.

This project began in February 2011. During the last 7 months, we have established the chemical synthesis procedures and completed time-course kinetic studies for both the nanocrystal $CuInS_2$ core and the ZnS shell. We have verified the reproducibility of the core-shell nanocrystal synthesis. We have achieved demonstration of near two orders-of-magnitude drastic enhancement of photoluminescence emission intensity in the desirable red emission range. This proves that the low lattice mismatch (2–3%) between $CuInS_2$ and ZnS indeed helps the low-defect growth of shells to enhance the PL emission efficiency. Preliminary stability data were also collected, indicating that shell protection has significantly improved the stability. FY 2012 effort with the residual $60,000 will be on the refined core-shell synthesis strategy, further proof of principle on efficiency enhancement by pulsed thermal annealing reduction of defect levels, and process scalability using a microwave-assisted process.

Information Shared

Michael Z. Hu, Invited Keynote Lecture, "Engineering of Chemical Processes and Nanomaterials for Energy Applications," 2011 Kentucky Statewide Workshop: Renewable Energy & Energy Efficiency, March 13–15, 2011. (Results from this Seed project were partially presented.)

Michael Z. Hu, Invited Talk, "Engineering of NanoMaterials for Clean Energy Applications," 2011 International Conference on Small Sciences (ICSS2011), August 15–18, 2011, Sydney, Australia. (Results from this Seed project were partially presented.)
Steven M. Klase and Michael Z. Hu, SULI poster presentation, "Chemical Synthesis of $CuInS_2$ Quantum Dots Nanocrystals for Clean Energy Applications," August 12, 2011, ORNL.

05966

Enhancement of Ion Transport in Carbon Electrodes Using Low-Amplitude, High-Frequency Electrical Signals

C. Tsouris, S. Dai, D.W. DePaoli, and S. Yiacoumi

Project Description

During recent tests of desalination of saline water by capacitive deionization, we measured a significant increase in the transport rates of ions in charged mesoporous-carbon electrodes when a low-amplitude alternate-current (ac) signal was superimposed on the applied direct-current (dc) potential used to charge the electrodes. In this short Seed Money project, we further investigated this discovery, which could have broad impact on (1) ion sorption/desorption in capacitive deionization processes used for water desalination, (2) faster charging of supercapacitors and batteries used for energy storage, and (3) novel membrane separations. The phenomenon is attributed to the electrostatic image force between charged particles (ions) and the conductive wall (carbon). This force is attractive and slows down the diffusion of ions in the pores of mesoporous carbon. An ac signal superimposed on the dc signal that is used to charge the carbon electrodes lessens the effect of the attractive image force, thus increasing the diffusion rate of ions. Experiments focused on better understanding the phenomenon were conducted using mesoporous carbon membranes and neutron imaging.

Mission Relevance

This work could lead to an improved capacitive deionization process for water desalination. Energy security is strongly linked to the availability of water. Water is needed for cooling in nuclear energy production, hydrofracturing in the recovery of natural gas from shale, and developing geothermal energy, among several other energy-related applications. Furthermore, produced water generated from oil and gas operations can be treated by capacitive deionization for reuse. Treating and reusing water is therefore important for our energy security. This project is expected to lead to more effective and energy-efficient water treatment. Development of improved water desalination methods, such as capacitive deionization, is important to a number of sectors including agriculture, urban development, industrial development, and defense. The results of this work could also lead to better energy storage devices, such as supercapacitors.

Results and Accomplishments

Capacitive deionization experiments performed with a flow-through cell with a pair of graphite plates coated with mesoporous carbon, synthesized at ORNL, showed higher electrosorption and regeneration rates for Instant Ocean solutions of concentrations 10,000 and 20,000 ppm when an ac signal was superimposed on the dc signal. The rates of increase for electrosorption were 23% for the 10,000 ppm experiment and 46% for the 20,000 ppm experiment. For regeneration, the rates of increase were 220% for the 10,000 ppm experiment and 520% for the 20,000 ppm experiment. The ac effect was stronger during regeneration because the dc potential was turned off for desorption to occur. Neutron imaging experiments using a specially designed capacitive deionization cell with ORNL mesoporous carbon

electrodes that could operate in the neutron beam at the ORNL High-Flux Isotope Reactor Neutron Imaging Facility demonstrated greater transport rates of ions between electrodes upon addition of an ac signal superimposed on a dc potential. Permeation experiments of rhodamine B using an electrochemical cell with two chambers separated by a mesoporous carbon membrane showed higher transport rates when an ac signal was applied between the membrane and a platinum counter electrode submerged in the receiver solution. These results demonstrated that an ac signal superimposed on a dc potential during capacitive deionization or other electrochemical processes enhances the ion transport rates and could have applications in transport-limited electrochemical processes.

05967

Transition-Metal Carbides as Ingredients for Active and Stable Bio-Oil Upgrading Catalysts

J.-S. Choi, V. Schwartz, and S.A. Lewis

Project Description

This project addresses a critical technical challenge in developing pyrolysis-based processes to produce infrastructure-compatible hydrocarbon fuels from lignocellulosic biomass: to design active and stable catalysts for pyrolysis oil (bio-oil) upgrading with minimal use of precious metals. We will demonstrate a novel class of catalysts by incorporating molybdenum carbides as substitutes for platinum-group metals, a key component of the best known catalysts in bio-oil upgrading. The precious-metal-like surface reactivity as well as refractory character of carbides could lead to active and stable catalysts in the upgrading of water-, oxygen- and acid-rich bio-oils. To achieve desired catalytic performance, surface properties of molybdenum carbides such as hydrogen activation and hydrophilicity-hydrophobicity balance will be controlled with nanosynthesis and microscale characterization capabilities. Catalytic performance will be evaluated in laboratory reactors using model compounds representing different fractions of bio-oils to broadly assess the upgrading potential of carbide-based catalysts. The study of the catalyst durability aspect will be particularly emphasized.

Mission Relevance

With DOE's move away from biomass conversion technologies for producing ethanol to those for producing drop-in biofuels, thermochemical technologies are receiving much greater emphasis. Pyrolysis is a particularly promising technology. However, bio-oils produced from pyrolysis are not suitable for direct application in internal combustion engines without further upgrading. To enable pyrolysis-based processes, effective catalyst technologies need to be developed. Conventional catalysts developed for the petroleum industry have proven inadequate for bio-oils. This project aims to address this challenge by developing novel catalysts, which can strengthen DOE biofuel programs (Office of Biomass Program, Vehicle Technologies Program). Catalytic technologies enabling biofuels production should benefit the USDA and DOD as well; these agencies are increasingly promoting production of advanced biofuels from renewable sources. In particular, the USDA supports research projects to accelerate the development of a commercial advanced biofuels industry based on non-food, non-feed biomass crops.

Results and Accomplishments

Our efforts in FY 2011 were first focused on establishing procedures needed for carbide synthesis, characterization, reactor evaluation, and analytical chemistry. Significant progress has been made in all of these areas, which allowed us to obtain initial results indicating the potential of molybdenum carbides as

bio-oil upgrading catalysts. A series of bulk molybdenum carbides were prepared and characterized with x-ray diffraction, BET, and CO chemisorption to determine structural changes as a function of synthesis parameters. Properties relevant to catalytic performance such as surface area and number of active sites proved especially sensitive to the nature of oxide precursor and carburization temperature. With a laboratory batch reactor, carbides were evaluated in the hydrodeoxygenation of guaiacol in the presence of a large amount of water. The reactor feed was chosen as a model representing the lignin fraction of real bio-oils. Carbides showed lower activity than a commercial carbon-supported ruthenium catalyst, which could be explained in part by significantly lower surface areas of bulk carbides. Molybdenum carbides showed unique product selectivity and good stability in the harsh upgrading conditions employed in this study: high temperature and water content. Therefore, further increasing surface area could improve activity and make molybdenum carbides a cost-effective catalyst for bio-oil upgrading. Developing methods to increase the surface area and the number of active sites will be a major task in FY 2012 along with reactor study with other types of model compounds.

ENVIRONMENTAL SCIENCES DIVISION

05854

Hydrogel-Encapsulated Solids for In Vivo Contaminant Availability Testing During Ingestion by Large Vertebrates

M.S. Greeley and S.C. Brooks

Project Description

Current methodology at the Environmental Protection Agency (EPA) to assess the bioavailability of environmental contaminants from ingested solids (e.g., sediment, paint, food, fly ash) is difficult and expensive because it requires measurement of contaminant uptake by tissue (e.g., blood, bone, liver) in dosed bioreceptors. This project takes a simpler, novel, and alternative approach that encapsulates contaminated solids within water- and solute-permeable hydrogels in small configurations which could be recovered intact after passing through the gastrointestinal tract of vertebrate organisms. Using X-ray fluorescence (XRF) analysis, the in vivo solubilization of a model contaminant, lead, is measured in test solids before and after gut passage in a model fish bioreceptor. Given proof of principle that hydrogel specimens can pass through the vertebrate gut, that residual contaminants can be recovered and quantified, and that solubilized contaminants can be absorbed, the established approach for in vivo contaminant availability testing could be supplemented or replaced by a relatively noninvasive alternative procedure that significantly decreases testing time and effort and greatly reduces cost.

Mission Relevance

The proposed method for evaluating the bioavailability of environmental contaminants could significantly simplify and lower the costs for environmental testing and assessments of DOE-contaminated soils and sediments. Advancing such innovative environmental testing technology directly supports the EM-22 (Environmental Restoration) and the DOE Office of Science by providing new analytical tools to support the environmental restoration mission. Development of this novel approach for assessing contaminant bioavailability also directly supports the EPA mission to assess the health risks associated with the management and selection of remediation alternatives at hazardous waste sites. The results could also benefit Department of Defense (DOD) programs responsible for the management and remediation of DOD hazardous waste sites.

Results and Accomplishments

Appropriate hydrogel configurations and the specific experimental procedures required for successfully passing hydrogels encapsulating contaminated soils intact through the gastrointestinal tracts of two model vertebrate bioreceptors, largemouth bass and channel catfish, were developed and tested without causing apparent harm to initial test subjects. A range of known lead concentrations were added to the hydrogels, and the responses of the XRF analyzer to the geometry and matrix of the encapsulated solids were evaluated to document the accuracy and precision of this nondestructive assay method. Using hydrogels

containing lead-contaminated soils, we were able to measure lead concentrations in test solids before and after gut passage by noninvasive XRF analysis. In support of the in vivo studies, the kinetics of in vitro lead diffusion and leaching from hydrogels were also characterized for both aquarium water and simulated gastric solutions.

The potential of this innovative approach to assess the bioavailability of metals in soil has been demonstrated by the successful passage through the GI tract of a majority of the tested hydrogels and a proven ability to nondestructively measure lead in the hydrogels before and after passage. However, significant complications with this approach were encountered: (1) loss or breakage during GI tract passage of hydrogels encapsulating certain soils; (2) the unexplained death of several fish test subjects in later studies during or immediately after the passage of hydrogels; (3) magnification of lead from either water or the fish GI tract in hydrogels encapsulating certain soils; and (4) leaching of soluble lead into aquarium water after GI tract passage but before hydrogel recovery. To minimize challenges posed by an aquatic test system (e.g., adsorption of lead into soil-encapsulating hydrogels from aquarium water), further development and refinement of this approach should be pursued with a terrestrial model organism.

05871

Plasmonic Effects for Improved Photocarrier Generation in Thin-Film Solar Energy Materials

S.K. Seal, X. Xu, M.C. Troparevsky, Y. Li, Z. Zhang, and B. Gu

Project Description

A fundamental constraint that governs the quantum efficiency of solar energy materials is the efficacy with which the solar spectrum is utilized towards photocarrier generation. Conventional approaches to mitigating this issue use various processing technologies to manage optical and electrical losses, but solar cell efficiencies have leveled off at around 18%. The new concept of nanoplasmonics offers exciting possibilities for getting around the bandgap limitation and coupling a wider spectral range of light into the photovoltaic active layer with the potential to dramatically increase the efficacy of the current generation of solar cells. We proposed a novel approach for increasing the efficiency of photocarrier generation in thin film solar cells by tailoring the spectral response of metal nanostructures to couple super-bandgap light into fluorescent emitters such as quantum dots and fluorescent dyes. A substantial gain in efficiency of up to 15% over existing values may be possible.

Mission Relevance

This project incorporates fundamental research in the fields of photovoltaics, energy conversion, and plasmonics research and is thus directly relevant to the DOE's renewable energy program, specifically the Solar Energy Technologies Program. The research is also expected to benefit in the general area of renewable energy as well as in the context of plasmonic interactions research.

Results and Accomplishments

We have synthesized semicontinuous gold films of varying thicknesses on quartz substrates by thermal evaporation. The average gold nanoparticle size is ~20 nm. Extinction spectra recorded with a CARY 5000 spectrophotometer show a broad absorption curve over the visible and near-IR range. We also have succeeded in modifying the absorption spectrum in a controllable manner through laser irradiation with a Nd:YAG second harmonic pumped dye laser. The modification process involves using power thresholds

sufficiently high so as to "burn" a spectral hole (transmission peak) in the otherwise broad absorption curve at the wavelength of irradiation. Thus, we have demonstrated the use of this process to engineer a film that absorbs at short wavelengths and transmits at higher ones.

The modified films have been coated with a spacer layer of SiO_2 (to prevent fluorescence quenching). A layer of CTe quantum dots in an aqueous solution was then deposited on the sample. The fluorescence intensity from the sample was then measured, as a function of angle in, with an angle-resolved spectrometer setup specially developed for the purpose at an excitation wavelength of 543 nm. There was clear evidence of reshaping of the fluorescent spectrum while comparing the photomodified spectra with the unmodified spectra. The reshaping is polarization sensitive. While a clear enhancement was not observed for the spacer layer thickness used, this can easily be improved by using an appropriate spacer layer thickness and does not detract from the main result of being able to reshape the fluorescence spectrum by tailoring the optical response of the metal nanostructure. The amount of reshaping was found to depend on the metal nanostructure geometry. The fluorescent emission was also found to be anisotropic; that is, directionality was observed and also found to be sensitive to the metal nanostructure. Both phenomena in conjunction lead to a large increase in fluorescent downshifting efficiencies, demonstrating the advantages of using plasmonic nanostructures towards augmenting downshifting yields. Individually, the two phenomena have potential applications as biomarkers, chemical sensing, and light sources.

Information Shared

Presentation: SPIE Optics and Photonics 2011, "Reshaping the fluorescence spectrum with random metal dielectric films."

05898

Air Stable Fe-C Nanocomposite for Degradation of Chlorinated Solvents

J. Gao, W. Wang, L. Liang, A.J. Rondinone, and F. He

Project Description

Removal of chlorinated hydrocarbons in groundwater and soils represents a challenging environmental issue. Nanoscale zerovalent iron (NZVI) is a promising material for remediation of these contaminated sites. However, with more than a decade of development, current NZVI technology still suffers from high material cost, instant aggregation in water, and inability to target hydrophobic contaminants [i.e., dense non-aqueous-phase liquids (DNAPLs)] in source zones. We tackled these problems by developing a novel and inexpensive iron-carbon (Fe-C) nanocomposite through ball milling of microscale iron with activated carbon powder. In our next step, we will coat this nanocomposite with surfactants to enable its delivery in subsurface and active attack of DNAPL phase. Through physical characterization, trichloroethene (TCE) degradation tests, and air and water oxidation stability tests, we will establish the proof of principle that this novel material cannot only efficiently degrade contaminants but also can maintain its reactivity.

Mission Relevance

Chlorinated solvents are among the most widely detected contaminants in soil and groundwater at thousands of DOE and DOD contaminated sites. We aim to develop and demonstrate this novel material for application in rapid and in situ remediation of source zone in contaminated federal (including DOE),

industrial, and private sites. This project has direct relevance to ongoing site remediation efforts of DOE and other federal agencies (e.g., DOD and USEPA) including DOE EM-30 (Office of Engineering and Technology), DOD Strategic Environmental Restoration and Development Program (SERDP), Environmental Security Technology Certification Program (ESTCP), and National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program.

Results and Accomplishments

Our ultimate goal is to develop a novel Fe-C nanocomposite material and utilize it for effective degradation of chlorinated hydrocarbon contaminants. During FY 2011 (January–September), our efforts focused on three primary tasks.

Task 1—Synthesis and characterization of the Fe-C nanocomposite (completed). We synthesized the Fe-C nanocomposite by ball milling microscale iron and activated carbon powder using propylene glycol as a lubricant. The resultant products were characterized using Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy-Electron energy loss spectroscopy (TEM-EELS). The TEM and SEM results showed that Fe nanoparticles are probably imbedded in the activated carbon support although this structure needs to be further confirmed by other techniques such as X-ray photoelectron spectroscopy. DLS results showed that when the particles are dispersed in water, the hydrodynamic diameter is consistent with that obtained by TEM.

Task 2—Testing the bare NZVI and Fe-C nanocomposite for dechlorination (partially finished). We have conducted the dechlorination experiment on a model contaminant, trichloethene (TCE), using the prepared Fe-C nanocomposite and bare NZVI. The results showed that Fe-C nanocomposite material instantaneously removed more than 90% of trichloroethene (TCE) from contaminated solution majorly through sorption. The monitoring of reaction intermediates further showed that TCE is continuously degraded after the rapid sorption period. In comparison, the bare NZVI degraded TCE at a much slower rate may be due to the aggregation of bare NZVI during reaction.

Task 3—Dispersing Fe-C nanocomposite in water: Stability, mobility, and partitioning characteristics (partially finished). We have successfully dispersed the nanomaterial in water using carboxymethyl cellulose (CMC) as a stabilizer. During FY 2012, we plan to add propylene glycol soluble polymer especially amphiphilic block copolymers into the lubricant to provide the in situ stabilization of the milled Fe-C nanocomposite and increase the hydrophobicity of the nanocomposite to allow its dispersion in DNAPL phase. At the same time, we will test the water and air oxidation of the Fe-C nanocomposite to assess its stability in air and lifetime in groundwater.

Information Shared

Gao, J., Wang, W., Liang, L., Rondinone, A. J., and He, F. “Green synthesis of Fe-C nanocomposite material and its application in degradation of chlorinated hydrocarbons,” 243rd ACS National Meeting & Exposition, March 25–29, 2012, San Diego, California, abstract submitted.

He, F., Wang, W., and Liang, L. “Air stable Fe-C core-shell nanocomposite.” Invention disclosure, submitted to ORNL Legal, number 201002453.

GLOBAL NUCLEAR SECURITY AND TECHNOLOGY DIVISION

05850

Liquid-Medium Position-Sensitive Thermal-Neutron Ionization Chamber

G.W. Wright, T.L. Van Vuure, Z.W. Bell, and J.P. Hayward

Project Description

All instruments at the Spallation Neutron Source are limited to some extent by the flux that their detectors are able to handle. A new detection principle is needed to significantly increase event rate capability.

BNL and ORNL have succeeded in increasing the event rate capability of detectors by running in ionization mode, whereas all previous position-sensitive detectors used proportional mode. This opens up a possible next step in development by finding a suitable liquid medium containing ^{10}B, rather than the scarce, low-density ^{3}He, that exhibits the characteristics required for use as a thermal neutron detection medium in ionization mode. If a suitable molecule can be found, the opportunities for neutron scattering science are enormous; orders of magnitude can be gained in global count rate and spatial resolution, time resolution and efficiency can be improved, while the stability and gamma rejection of ^{3}He detectors can be matched.

Mission Relevance

Neutron scattering is an important tool in many fields, notably those related to energy research such as high temperature superconductors, hydrogen storage, fuel cells, and advanced construction materials. The effort expended on the facilities for generating more neutrons is not matched by a development effort in detection technology. As a result, all instruments currently operational, under construction, or being designed at the Spallation Neutron Source are limited in some measure by the available detectors. This project focused on the basic science underlying a new detector type capable of meeting the requirements of these instruments.

Results and Accomplishments

Dr. Van Vuure (the original PI) compared the potential liquids and concluded that borazene was the best candidate because of its high boron content and nonpolar nature. The high boron content is needed for high neutron capture efficiency and the lack of polarity is needed to drift electric charge through the liquid without recombination. A purchase order was then placed with Boroscience International for 25 g of borazene. Unfortunately this borazene vendor was unable to manufacture the chemical, and after trying for a few months, asked to be let out of the contract. The order was cancelled and a search for another supplier was not successful.

The use of borazene is complicated by the fact that it is hazardous. Dr. Van Vuure addressed this issue by consulting lab safety professionals and also by designing a detector prototype that would be safe. It was concluded that a detector made from a glass container, with internal carbon electrodes, would meet the safety requirements, and one was fabricated. Arrangements were made to borrow detector hardware and electronic components from the Neutron Sciences detector and data acquisition groups.

Dr. Van Vuure left ORNL on short notice, and the project was transferred to Gomez Wright. He continued the search for a borazene vendor and worked on resolution of the safety issues for work with this chemical. The work activities were to occur in the Advanced Nuclear Measurements Laboratory in Building 3500, where access to a fume hood and other appropriate chemical hygiene requirements are available for work with this hazardous material. However, a substantial amount of time and funding are required to implement and review safety procedures and obtain modification and/or approval of an appropriate Research Safety Summary (RSS) for conducting chemical handling operations with this material.

It was decided that the challenges associated with the research, in addition to the scheduling and funding issues, did not allow for the effort that would have been required to put all of the safety systems and paperwork in place to make the measurement.

Because of the difficulty in identifying a supplier of borazene and the significant safety issues of working with it, coupled with the unexpected setback of the sudden departure of the original PI, work on the project was terminated and unspent funds were returned to the LDRD pool.

05899

Novel Gas Scintillation Counters for Neutron Detection

J.S. Neal, M.J. Harrison, L.A. Boatner, and Z.W. Bell

Project Description

Recent testing of conventional non-^{3}He gas-based proportional counter neutron detectors indicates a need for significantly improved neutron detection efficiency and gamma-ray discrimination. Specifically, the need to create stable and symmetric electric fields to promote uniform gas multiplication and charge collection over the sensitive volume imposes limits on the geometrical design and the amount of neutron converter materials in conventional gas proportional detectors. Consequently, we are investigating new options for developing efficient thermal neutron detectors based on gas scintillation rather than charge collection. These new options include, first, investigations of both inorganic and organic gas scintillators and, second, investigations of both the direct conventional scintillation counter mode and the scintillating proportional counter mode, in which an applied electric field accelerates electrons and ions to the point that collisions between them and the gas produce scintillation light. Gas scintillator systems will exhibit the desired low gamma-ray sensitivity while bringing more neutron-sensitive converter material to bear, since this approach removes the severe requirements associated with creating the uniform or symmetric electric fields optimized for charge collection in conventional proportional counters.

Mission Relevance

The ^{3}He supply crisis is now the highest priority for the global radiation detection communities—including homeland security, nuclear nonproliferation, defense, and the neutron research community (with serious implications for the Spallation Neutron Source facility at ORNL). We have recently

developed new concepts for the detection of thermal neutrons that would eliminate completely the use of ^{3}He, and we proposed to carry out research in order to the demonstrate proof of principle for our new concepts. The resolution of this issue is crucial to the DOE nuclear nonproliferation (i.e., NA-22) and neutron science programs.

A successful proof of principle of gas scintillators for thermal neutron detection is of great interest to the homeland security, nuclear nonproliferation, treaty verification, and defense communities, as well as to neutron science users. Potential homeland security/nuclear nonproliferation users include all organizations interested in the detection of thermal neutrons with high detection efficiencies and outstanding gamma-ray neutron discrimination. Potential funding agencies for these applications include the Domestic Nuclear Detection Office of the Department of Homeland Security and the Department of Defense Defense Threat Reduction Agency.

We currently have a proposal pending with National Nuclear Security Administration/NA-22 for a new 3 year effort on the development of new gas scintillators, including the use of both inorganic and organic gases, at a funding level in excess of $1.5 million.

Results and Accomplishments

A testing station was designed and constructed to investigate various gases and combinations thereof for scintillation performance. The test station consisted of a fast, low-noise, near-ultraviolet–sensitive Photonis XP2020 photomultiplier tube mounted to a vacuum chamber. The chamber was constructed such that various gases and gas combinations could be introduced at 10 psig or 1 atm pressure levels. Additionally, a secondary chamber was mounted to the main scintillation chamber from which volatile liquids and solids could be evaporated. This setup allowed for a screening-type investigation of the effects that the addition of small partial pressures of organic liquids and solids had on the properties of known scintillating gases.

The test station was utilized to measure the practical scintillation performance of several gases, combinations of gases, organic vapors, and combinations of organic vapors with gases. The gases evaluated for practical scintillation performance included CF_4, H_2, N_2, Ne, Ar, Kr, and Xe. The evaluated organic compounds in liquid or solid form included furan, acetylene, naphthalene, and ethane. From these gases and organic liquid-solid compounds, several combinations were studied and showed varying degrees of utility.

Pure CF_4 gas provided the best practical scintillation response at the pressure levels investigated. The addition of furan, acetylene, ethane, or naphthalene to any of the gases effectively quenched the scintillation performance observed for the pure forms of the gases. Unfortunately, the limited pressure controls of the test station prevented a detailed investigation of the combinations at reduced pressures and did not provide the capability to vary the concentrations of the organic compound admixtures. This limitation in the test station hindered the investigation because the high pressures of the organic compounds likely affected the scintillation due to excessive collisional losses. It was therefore determined that further investigation will be necessary at lower partial pressures to achieve an improvement in practical scintillation performance.

A separate test chamber was constructed for the evaluation of various noble gases. These measurements were conducted to investigate near-infrared emissions from noble gases when operated in either a direct or proportional scintillation mode. Results from measurement to measurement were, however, not reproducible—probably due to an unstable photomultiplier-voltage divider combination as well as thermionic emissions within the photomultiplier.

A new test station is presently under construction to achieve the functionality necessary for further investigations. This new test station will include a cooled photomultiplier assembly to significantly reduce dark noise contributions to the signal and to support the testing of both organic and noble gases across the ultraviolet–near-infrared spectrum.

05969

Authenticated Radio Frequency Identification

B.J. Stinson, M.J. Kuhn, and N.C. Rowe

Project Description

Analysis, simulation and laboratory experiments are being conducted to verify the validity of a novel wireless authentication method suitable for radio frequency identification (RFID) tags. The work will verify that short pulse [i.e., ultra-wideband (UWB)] radio systems and time-of-flight (ToF) measurements can be used to implement a location and device authentication protocol in practical RFID applications. This protocol simultaneously provides device authentication and location authentication, both of which are critical for implementing RFID in high security tagging, tracking, and secure wireless data transmission applications.

This research has direct application in the use of RFID for high value asset tracking, tagging, locating, and tamper indicating, specifically in the nuclear safeguards industry. DOE/NNSA and the IAEA often desire to use RFID for standoff verification of an item's location or seal status. These applications are long-term deployments with inventory and monitoring subsystems that rely (often intrinsically) on the ability to trust the data and location of the transmitting RFID tag. However, tags are not commercially available which provide this level of trust; namely, tags are not available that provide device and location authentication. Opportunities therefore clearly exist to further develop this technology beyond the research and proof-of-principle stages.

Mission Relevance

Radio frequency identification (RFID) provides clear advantages in many applications ranging from commercial "everyday" products such as contactless credit cards to high-value asset tracking and monitoring. NNSA, IAEA, DOD, and other agencies have the desire to use RFID for tagging/tracking applications. However, all of the agencies have a need for *authenticated* RFID, which provides assurance that the tag and reader system are trusted entities and have not been spoofed. In a radio frequency (RF) system, spoofing can occur in two ways: either the tag can be replicated and/or the tag can be physically removed and replaced with a repeater system. To mitigate the former requires that the device use an authentication method such that it is exceedingly difficult to replicate the tag. The latter requires that the device's *location* be authenticated.

The inadequacies of both device and location authentication in commercial (and known research) systems continue to keep RFID from being a viable solution in high security environments. In general, the commercial RFID industry is focused on tracking low-cost commodities and has directed product research and development to meet those needs. In addition, we anticipate that the future will continue to bring RFID to more secure sectors of the commercial market, including contactless credit cards, passports, medical data, and more. Government agencies will continue to have needs for tracking valuable or sensitive assets with considerably different priorities than commercial entities.

The research efforts proposed will provide validity to the conceptual design of an active RFID system based on UWB radios. The researchers believe that two-way active UWB communication is the most robust and complete technology on which to build a location authentication framework. If successful, this system will combine both device and location authentication by performing a challenge-response authentication protocol simultaneously with ToF measurements. The ToF measurements provide the ability to bound the known location of the tag to within a small region. Success of this concept in the proof-of-principle stage will lead to the development of valuable IP, with a high potential for government and commercial customers and licensees.

Results and Accomplishments

A two-way active UWB wireless communication and location system has been simulated, and all of the main blocks for the transmitter and receiver have been identified and designed. This includes use of an on-off keying (OOK) transmitted reference technique to transmit digital data via UWB radios, and a noncoherent latched comparator to convert UWB pulses into digital signals.

Current analysis and simulation show that the propagation delay (fixed delay) of our critical path from the time a UWB pulse is received to the time that another UWB pulse is transmitted will be around 10 ns. More simulation and experimental work is needed to verify with what uncertainty we can calculate the return time of flight. The 10 ns fixed propagation delay is within our expectations as the requirement for this system is to have as small a latency as possible for the tag response during the reader-tag bit-wise challenge response sequence.

We are currently fabricating and assembling microwave circuits to be used in our proof of concept experiments. We anticipate having all circuits fabricated and assembled by the end of FY 2011. The proof-of-concept experiments will be used to verify the critical path propagation delay and also will provide us with an understanding of the uncertainty in calculating the return time of flight at the reader for the actual distance bounding measurement.

MATERIALS SCIENCE AND TECHNOLOGY DIVISION

05856

Spin Excitations and Multiferroic State of Doped $CuFeO_2$

R. Fishman, F. Ye, and J. Fernandez-Baca

Description of Project

Because of strong coupling between electric polarization and magnetization, multiferroic materials hold tremendous technological promise in the magnetic storage industry based on the ability to manipulate magnetic bits with electric currents. This project utilizes ORNL's unique strengths in computation, theory, and neutron sciences by combining theoretical modeling with elastic and inelastic neutron-scattering measurements to study the multiferroic phase of a typical ferroelectric material. Comparing the observed spin excitations with theoretical predictions will allow us to characterize the multiferroic state and the microscopic interactions responsible for the ferroelectric behavior. This proposal will demonstrate that, because of the unique coupling between the neutron and electron spins, neutron scattering provides an indispensible tool in the search for new multiferroic materials. The successful completion of this project will lay the foundation for a combined modeling and neutron-based program on multiferroic materials that will attract funding from both scientific and user-based agencies.

Mission Relevance

This research bears directly on the strengths at ORNL in computation and neutron sciences. As a national center for neutron scattering, ORNL can make an immediate impact in the experimental characterization of multiferroic behavior.

Results and Accomplishments

We have evaluated the magnetic ground state and spin dynamics of a Ga-doped $CuFeO_2$ compound (3.5% Ga doping) in its multiferroic phase. We also measured the excitation spectrum of this material using the neutron-scattering facilities at ORNL. This work was published in a Rapid Communications article in *Physical Review B* [**82**, 020404 (2010)] and received the prestigious "Editor's Choice" designation. A separate paper on the modeling technique was published in *Physical Review B* [**82**, 14441 (2010)]. The agreement between the model and the experiment was excellent and allowed us to identify the complex spin structure that exhibits multiferroic behavior. Thus, we have shown that the excitation spectrum of a multiferroic material can be used as a dynamical "fingerprint" of the spin state. Feng Ye gave two invited talks about this work: one during the June 2010 meeting of the American Neutron Scattering Society in Ottawa and another during the March 2011 meeting of the American Physical Society in Dallas. Randy Fishman gave an invited talk about this work at the 2011 Telluride Workshop on Complex Materials.

Information Shared

Haraldsen, J. T., Ye, F., Fishman, R. S., Fernandez-Baca, J. A., Yamaguchi, Y., Kimura, K., and Kimura, T., 2010. "The Multiferroic Phase of Doped $CuFeO_2$ Identified using Inelastic Neutron Scattering," *Physical Review B, Rapid Communications*, **82**, 020404.

Haraldsen, J. T., and Fishman, R. S., 2010. "Effect of Interlayer Interactions and Lattice Distortions on the Magnetic Ground State and Spin Dynamics of a Geometrically Frustrated Triangular-Lattice Antiferromagnet," *Physical Review B*, **82**, 144441.

05861

High-Throughput Synthesis and Chemical Modification of Graphene Materials for High-Capacity Supercapacitors

N.C. Gallego, V.V. Bhat, and C.I. Contescu

Project Description

The goal of this project is to prove the concept that energy storage capacity of graphene-based supercapacitors can be enhanced via chemical modification. We synthesize graphene materials using a high throughput chemical method and modify them in a way that would (1) lead to an increase in electrical double-layer (EDL) capacitance and (2) introduce pseudocapacitance in the material. To achieve this objective, the graphene materials will be modified by a controlled thermochemical method. Modified graphenes will have more edge sites, where the amount of energy stored is ~10 times higher than that on the basal planes. A simple calculation shows that a more than 200% increase in the energy storage capacity for graphenes with 50 vol % holes compared to unmodified ones could potentially be achieved. The challenge of this task is to chemically modify the surface of graphene materials while maintaining high surface area and preventing the collapse of the exfoliated structures in dry state. Preparing materials with high surface area and porosity will ensure adequate electrolyte access to internal surfaces and will fully use the intrinsic capacitance of graphene materials. Thermochemical treatment will selectively introduce quinone-type surface groups that will add pseudocapacitance contributions to the total charge storage.

Mission Relevance

Electrochemical energy storage is one of the key challenges that DOE is addressing to harness renewable energy. EDL capacitors are electrical energy storage devices that bridge the gap between conventional capacitors and batteries in terms of power and energy density. With their fast charge/discharge rates and long life cycles, EDL capacitors complement batteries for transportation and grid applications. The project can help improve the energy storage efficiency of EDL capacitors.

The success of the project will also benefit the Defense Advanced Research Projects Agency. An efficient EDL capacitor can help to store energy for advanced defense equipment and vehicles that need high power and fast charging.

Results and Accomplishments

We have synthesized large amounts of graphene materials using a colloidal chemistry method based on oxidation and exfoliation of graphite powder, followed by liquid phase reduction of graphite oxide. The reduced graphite oxide (RGO) material has BET surface area of 370 m^2/g and is composed of wrinkled and curled sheets of a few layers of graphenes visible by electron microscopy. The available porosity is

contained in micropores (0.4 cm^3/g) and mesopores (0.8 cm^3/g). Further characterization indicated the presence of 1.3-nm-thick particles (3–4 graphene layers) with local graphitic order. The RGO material contains oxygen, which is released by thermal treatment as CO and CO_2 and leaves behind more exposed carbon atoms. By treating RGO up to 1000°C, we prepared a series of modified graphene materials, which were further characterized in 5 *M* H_2SO_4 by cyclic voltammetry, galvanostatic charge-discharge, and impedance spectroscopy. The gravimetric capacitance varies between 70 F/g (initial RGO) and 90 F/g (RGO treated at 400°C). These values are lower than those of high-surface-area carbons used in supercapacitors. However, area-normalized capacitance values of graphene materials (19–21 $\mu F/cm^2$ for unmodified RGO and RGO treated at 400°C) are higher than those of most high-surface-area carbons (7–12 $\mu F/cm^2$), approaching the limit for graphite edge planes (25–30 $\mu F/cm^2$) allowed by the size of electrolyte ions in water. Limitations arise from insufficient utilization of graphene surface because of van der Waals aggregation. Adding dispersants or nanosized spacers might improve the gravimetric capacitance of graphene materials.

Information Shared

Bhat, V. V., N. C. Gallego, and C. I. Contescu. 2010. "Modified multilayer graphenes for supercapacitors." *Proceedings of the Carbon 2010 Annual World Conference,* Clemson, SC, July 11–16.

05865

Vertically Aligned Cu-Si Core-Shell Nanowire Array as a High-Performance Anode Material for Energy Storage

J. Qu, H. Luo, N.J. Dudney, D. Ma

Project Description

Current graphite anodes of Li-ion batteries capacity have a low theoretical charge capacity (372 mAh/g). Silicon has the highest theoretical charge capacity (4,200 mAh/g), but it tends to pulverize due to the huge volume change upon Li^+ insertion/extraction. Silicon nanowires have been reported to withstand pulverization well because of high surface tension. However, high-aspect-ratio nanowires have long electron transport paths (high electrical resistivity) and are vulnerable to separation (capacity loss). Common techniques for synthesizing silicon nanowires require high temperature and vacuum (costly). This project will develop a highly aligned copper-silicon core-shell nanowire array as a high-performance anode. This unique nanostructured anode is expected to possess high capacity, have good capacity retention, and provide efficient charge transport. Fabrication is low cost and scalable.

Mission Relevance

DOE is strongly promoting transportation electrification, which is critical for reducing the nation's dependence on oil and reducing emissions. The future of electric vehicles largely depends upon the development of battery technologies. Lithium-ion batteries have shown the best potential, but their energy and power densities are far from adequate; therefore, technical breakthroughs are urgently needed. This project will develop novel silicon micro/nanowires-based anode materials that, if successfully developed, are expected to significantly increase the capacity and power density for lithium-ion batteries.

The technology, if successful, will potentially increase the charge capacity and power density for lithium-ion batteries and benefit other federal agencies such as the Department of Transportation and the

Department of Defense, including Army, Navy, Air Force, Defense Advanced Research Projects Agency, and Defense Threat Reduction Agency.

Results and Accomplishments

This study developed a new self-aligned Cu-Si core-shell nanowire array as a novel anode for lithium-ion batteries using a low-temperature, catalyst-free process. The silicon shell is amorphous as synthesized and accommodates Li ions without phase transformation. The copper core functions as a built-in current collector to provide very short (nanometer) electron transport pathways as well as a backbone to improve mechanical strength. Initial half-cell testing has demonstrated high Coulombic efficiency (97–100% after the first cycle) and good capacity retention at a charge-discharge rate 2 C or lower. No wire fracture or core-shell separation was observed after cycling. Based on the successful proof-of-concept results, a U.S. patent application has been filed, and a journal paper was submitted as well. The Partnerships Directorate and Technology 2020's Center have elected this Cu-Si core-shell nanowires anode as one of the six top potential ORNL technologies for "Bridging the Gap 2011" for Entrepreneurial Growth. Further research and development are needed to explore and realize the full potential of this unique nanostructured material. To seek follow-on research, a proposal has been submitted to Defense Threat Reduction Agency to compete the FY 2012 Strategic Exploratory and Emerging Discoveries investments, and another proposal is being prepared to respond to a DOE EERE new solicitation DE-FOA-0000560.

Information Shared

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05872

Can Neutrons Do It: Probing Performance of Li-Ion Batteries In Situ

Z. Feng, L. Cai, X.-L. Wang, K. An, S.E. Nagler, W. Zhang, C. Daniel, and N.J. Dudney

Project Description

High power Li-ion batteries need a cycle life of over 6,000 and a calendar life of 15 years or longer to achieve economic viability in battery-powered vehicles and in the future electricity infrastructure. This is about one order of magnitude higher than current technology provides and is a tremendous challenge because their capacity fades from internal degradation. Factors contributing to the performance of Li-ion batteries are very complex and vary significantly with the electrode materials, battery manufacturing processes, as well as charging/discharging rates, temperature, and other operating conditions. There is a paramount need to directly probe *inside* a "real-world" battery cell as it operates, to understand the fundamental processes and mechanisms of lithiation and de-lithiation, lithium transport, and the buildup of internal stress and temperature that contribute to the performance of the battery. Addressing this need, the project aims to develop an innovative in situ neutron diffraction experiment approach to probe Li-ion battery performance and degradation. Specifically, we will map the three-dimensional distribution of internal temperature, stress, the lithium intercalation processes and the state-of-charge (SOC) conditions of representative batteries used in electric vehicles—the capability of comprehensive nondestructive diagnostics of "real" battery/battery package performance under realistic operating conditions. It will

establish a capability for battery performance and battery materials R&D, a critically important subject in electrical energy storage.

Mission Relevance

The in situ neutron diffraction capability developed in this project will support DOE's major initiatives on high-power batteries for automotive applications and electric storage infrastructure. Specifically, it offers the unique capability to "see" *inside* a large format prismatic battery cell in a nondestructive way to understand and quantify the chemical, thermal, and mechanical processes and how these might affect the overall cell durability and performance of degradation-resistant electrode materials and manufacturing/packaging technologies. The research will benefit the Energy Storage Technologies of the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program. It will also benefit the DOE Office of Electricity Delivery and Energy Reliability, as well as the Wind and Solar Energy Programs.

Results and Accomplishments

We have successfully completed in FY 2011 on the VULCAN beamline more experiments on three different types of large format batteries from different battery original equipment manufacturers (OEMs) and suppliers. The batteries had different chemistries and were tested at different charging and discharging rates. We were able to determine the local state of charge (SOC) inside the battery by means of our novel neutron diffraction approach developed in this research. This novel approach also reduced the data collection time to about 2–3 min, which is sufficiently fast for in situ measurement of the transient behavior of batteries during charging-discharging cycles. Very rich information about the SOC of batteries was obtained and analyzed. For example, the experimental results show that during a rapid charge cycle (1 C, full charge in an hour), the graphite anode undergoes a disorder-to-order transition as Li ions are incorporated between the graphene layers, forming $Li_{12}C$ and Li_6C intercalation phases at fully charged condition. In contrast, the discharge follows the staging sequence of $Li_6C \geq Li_{12}C \geq Li_{24}C$, before the anode returns to the graphite phase. A lattice dilation as large as 4% was observed during a charge-discharge cycle. Our work demonstrates the potential of in situ neutron diffraction measurements for study of the dynamic chemical and structural changes in "real-world batteries" under rapid, realistic cycling conditions and for providing insights on degradation and other outstanding issues in energy storage materials. The project received strong interest and support from a major auto OEM and a battery manufacturer who donated to the project large format Li-ion batteries representative of those used in hybrid electric vehicles. We are continuing to work with them in FY 2012 on further studies of real-world batteries.

Information Shared

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05874

High-Efficiency and Low-Cost Photovoltaic Cell Wafers via Plasma Arc Lamp Processing of High-Purity Silicon Powder

A.A. Wereszczak, C.E. Duty, H.-T. Lin, and G.E. Jellison, Jr.

Project Description

The proposed research will demonstrate a revolutionary approach for the low-cost and rapid production of high efficiency silicon solar cells with high yield. It combines the use of ORNL's unique plasma arc lamp processing facility with two patents involving slurry casting and densification of high-purity, safely milled silicon powder. As a consequence, the yield of net-shape multicrystalline silicon (mc-Si) wafers could increase to 90–95% (only 10–30% currently), and per-wafer cost will decrease because the amount of time and labor to produce each wafer will decrease substantially. Furthermore, it may be possible to approach competitive solar cell efficiencies for mc-Si (15–18%). These game-changing advancements will reduce the cost of solar energy capture and accelerate the widespread exploitation of solar power generation. Lastly, this work will help establish unique mc-Si processing expertise at ORNL, thus creating opportunities to attract new funding.

Mission Relevance

The prospects that would arise from this project's successfully demonstrated proof of principle would be directly relevant to the mission and goals of the Energy Efficiency and Renewable Energy (DOE/EERE) Solar Technology Program. Those goals consist of reducing the cost of solar energy, being competitive with conventional energy sources, and bringing solar technology to a level of market penetration that enables a sustainable solar industry. Besides DOE/EERE (Solar Technology Program), other agencies involved with solar R&D (e.g., TVA) would eventually benefit from this project's work.

Results and Accomplishments

The proof of principle that silicon powder could be processed with plasma arc heating to melt and solidify a silicon component was demonstrated in early FY 2011. Electrical and optical property measurements (complex dielectric constant, absorption coefficient, and carrier concentration) were made, p-type semiconductive behavior was produced, and the melting and solidification produced a columnar structure of grains whose diameters were in excess of 200 μm. The measurements included the identification of semiconductor type (n- or p-type; this first sample was a p-type). For the remaining portion of FY 2011, the wetting behavior of molten silicon against a variety of mold materials was investigated. These included monolithic silicon carbide, silicon nitride, aluminum nitride, boron nitride, and graphite, all serving as molds (i.e., containers). It was observed that the melting characteristics of the silicon powder were very sensitive to the mold or container material in which it was heated while being subjected to plasma arc heating. If oxygen were available during plasma arc heating, then silicon powder would scavenge it, oxidize, and often not melt. Available oxygen was sourced from either the ambient environment or from those mold materials themselves. Therefore it was concluded that the availability of oxygen must be suppressed if net-shape silicon wafers are to be successfully made by plasma arc heating.

Information Shared

Portions of this work were included in a poster entitled "Net Shape Wafer Growth for C-Si Wafering," J. Carberry, A. Wereszczak, and A. Skumanich, given at 26th European Photovoltaic Solar Energy Conference and Exposition, Hamburg, Germany, 5–9 September 2011.

05882

Using Small-Angle Neutron Scattering (SANS) to Determine Gas Hydrate Pore-Scale Distribution

C.J. Rawn, G. Rother, K.C. Littrell, T.J. Phelps, and W.F. Waite

Project Summary

Understanding the pore-scale distribution of methane hydrate formed within sediment is crucial to safe energy extraction. The laboratory synthesis of sediment samples containing methane hydrate that closely mimic those found in nature is a key challenge to furthering scientific understanding of how methane is geologically accommodated. Hydrate in nature is likely to occur as pore fill, in contrast to laboratory samples, where hydrate more commonly cements sediment grains together. These differing distribution scenarios result in vastly different mechanical properties. We hypothesize that small-angle neutron scattering (SANS) experiments on gas hydrate and sediment mixtures can be used to accurately determine the distribution of gas hydrate and sediment. These experiments are challenging to conduct in situ because of the pressure, temperature, and time requirements needed for hydrate formation, thus requiring a proof of principle prior to proposing a full study for the anticipated DOE Office of Science initiative in gas hydrate research.

Mission Relevance

Gas hydrates are solid, crystalline structures in which water molecules arrange to form polyhedral cages large enough to hold low-molecular-weight molecules. These low-temperature, modest-pressure compounds occur in continental margin and terrestrial permafrost sediments where there are adequate sources of H_2O and hydrate-forming molecules (usually alkanes and, most commonly, methane). Gas hydrates are of interest from both economic and environmental standpoints, first as a potential source of natural gas and second as a reservoir of greenhouse gases (methane and carbon dioxide). Understanding the pore-scale distribution of methane hydrate formed within sediment is a variable crucial to the safe energy extraction and prediction of greenhouse gas releases resulting from climate changes.

The U.S. Geological Survey (USGS) is also a major player in the area of gas hydrates research. USGS scientists as well as scientists in academia, the gas and oil industry, and other national laboratories will use our results.

Results and Accomplishments

The existing SANS pressure/temperature cell has been used to form methane hydrate in sand. The general procedure was to evacuate the cell containing sand and then to pressurize with methane followed by adding a H_2O/D_2O mixture. The temperature of the cell was controlled by a circulating refrigerated water bath combined with a cooling jacket. A small camera visually tracked changes in the cell contents. Four SANS experiments were conducted on the CG2 SANS beamline at the High Flux Isotope Reactor (HFIR). During the first two experiments, no hydrate was formed. During the third experiment, hydrate was formed on the basis of a drop in the pressure data and visual observations; however, no conclusive results could be discerned from the analysis of the SANS data, most likely due to the fact that instead of a H_2O/D_2O mixture, only H_2O was used in the experiment. During the fourth experiment, the cell was pressurized with D_2O. Again, pressure data and visual observations suggest that hydrate was formed. The data for the fourth experiment have not been analyzed because new corrections need to be incorporated into the data reduction software.

05883

Synthesis of Ultrastrong Three-Dimensional Networks from sp^2 Carbon Using Low-Energy Molecular Transformations

G. Eres

Project Description

In this project we propose to demonstrate a promising path to new carbon structures that combine the properties of both nanotubes and graphene in a single material. The sp^2 bond is the strongest chemical bond in nature, imparting extraordinary mechanical strength, and remarkable electrical and thermal conductivity to nanotubes and graphene. Also, the nanoscale dimensionality gives these materials special properties that are attractive for a variety of applications. These same superior properties are extremely desirable in a bulk form. It is a serious drawback of currently used high energy synthesis methods that they are unable to convert carbon nanotubes and graphene into macroscale sp^2 carbon. Various attempts to overcome this problem by using physical methods such as compacting, weaving, or compressing augmented by chemical functionalization to form composites have produced material with inferior performance. We propose to use direct growth or low energy molecular transformations to make three-dimensional sp^2 carbon networks from known one- and two-dimensional forms (nanotubes and graphene) of sp^2 carbon. By solving the fundamental problem of sp^2 bonding between already existing carbon nanomaterials, this project has a potential to remove current obstacles and create totally new applications for sp^2 carbon materials.

Mission Relevance

Stronger and lighter materials made out of carbon are of great interest to DOE programs in advanced energy technologies such as transparent organic electronics for photovoltaics and flexible displays and functional electro optics, as well as conventional applications where substitution of lightweight materials reduces energy consumption. The combination of graphene and nanotubes has a potential to produce smart membranes with externally controllable transmission capabilities. A proposal titled “Integrated power electronics based on microswitches for solar power” is under consideration by ARPA-E for using graphene as a component in MEMS switch contacts.

Results and Accomplishments

The key result of the project is the demonstration of simultaneous growth of graphene and carbon nanotubes (CNTs). The Raman spectroscopy data show that both graphene and CNTs are present on the sample. The scanning electron microscopy (SEM) images clearly show the vertically aligned CNT forest surrounding the graphene edges. An interesting finding is that the graphene is extremely robust and remains to block the surface where the CNT catalyst resides even in strongly oxidizing environments. We are currently preparing samples for high resolution imaging by scanning transmission electron microscopy (STEM) to study the type of connection between the graphene and the CNTs. This project resulted in two journal publications and one conference presentation.

Information Shared

Authored articles

Ivan Vlassiouk, Murari Regmi, Pasquale Fulvio, Sheng Dai, Panos Datskos, Gyula Eres, and Sergei Smirnov, 2011. “Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene,” *ACS Nano* 5(7) 6069.

Murari Regmi, Matthew F. Chisholm, and Gyula Eres, “The Effect of Growth Parameters on the Intrinsic Properties of Large-Area Single Layer Graphene Grown by Chemical Vapor Deposition on Cu,” *Carbon*, accepted for publication.

Presentation

Gyula Eres, "Factors Affecting Epitaxial Growth of Graphene on Metal Surfaces." Diamond 2010—21st European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, and Nitrides, September 5–9, Budapest, Hungary.

Invention disclosure

Gyula Eres and Murari Regmi, "The growth of single layer graphene by molecular jet chemical vapor deposition."

05902

Design of Coaxial TiO_2 Nanotube Arrays for Solar Energy Utilization

M. Chi, X. Qiu, Z. Bi, M.P. Paranthaman, and I. Ivanov

Project Description

The goal of this proposal is to introduce a new concept for combining band structural and morphological engineering towards a novel design of co-axial p-n junction nanotubes for solar energy utilizations. TiO_2 nanotubes will be used as a model system for the proof-of-principle purpose. This co-axial nanostructured TiO_2 could lead to a significant improvement in the cost efficiency of current solar energy utilization techniques, such as photovoltaics, photocatalysis (solar fuel production), carbon capture, etc. The research is motivated by the fact that high-conversion-efficiency solar energy utilization can be realized by using nanostructured semiconductors arranged in unique configurations. This is accomplished by means of altering and enhancing the absorptive and carrier-generating properties of semiconductors in dramatic and specific ways. The proposed design incorporates a radial p-n junction inside TiO_2 nanotubes through a cost-efficient nitrogen doping approach. TiO_2 nanotubes with such a unique architecture are expected to have significantly enhanced light-capture efficiency, the capability of covering a wide range of the solar spectrum, and improved carrier collection efficiency. With this proposal, we seek to verify this design both theoretically and experimentally. The proposed concept can eventually not only enable cost-effective scalable solar energy utilization approaches, but also provide a new nanoscale test bed for future designs of novel nanostructured materials for photoinduced nanoelectronic devices and diverse nanosystems.

Mission Relevance

Federal funding agencies such as the DOE Office Basic Energy Science (BES) and Energy Efficiency and Renewable Energy (EERE) are focused on discovering novel materials and advancing fundamental understanding of the physical mechanisms associated with the conversion of solar energy into electricity. For example, the DOE Solar Energy Technologies Program (SETP) has various activities and funding opportunities for research programs directed towards cost-effective, long-lasting, highly efficient solar energy conversion and utilization. The work undertaken here has the opportunity for world leadership in nanomaterials for low-cost, high-efficiency PV applications. Furthermore, other federal agencies such as the Defense Advanced Research Projects Agency (DARPA) and the Industrial Technology Program (ITP) are increasing their support of solar energy technologies, as evidenced by numerous specific initiatives and ongoing calls for solar energy use related research.

Results and Accomplishments

Guided by our initial theoretical calculations, we have successfully realized that control of site-selective doping of nitrogen inside TiO_2 (anatase) nanotubes (i.e., nitrogen) enters the inner wall of the nanotubes preferentially, which results in radial doping along the axial direction inside the nanotubes. Highly ordered TiO_2 nanotube arrays, having varying nanotube diameters, lengths, and interpore distances, were

prepared by modifying experimental variables (e.g., voltage, electrolyte concentration, and temperature). Controlled N-doping was performed by carefully controlling ammonia gas atmospheres and temperatures. It was observed that the nanotubes, which were prepared at 40 V and post-annealed in ammonia at 550°C for 45 min, gave the best N-substitutional concentration and selective distribution. This sample also showed the best absorption at the visible light region as expected. EELS was performed to differentiate the interstitial and substitutional doping locally. Our microscopy experiments confirmed the selective N-doping inside single nanotubes. In addition, we have developed a unique sample preparation method, the combination of FIB and microtome, in order to study the microstructure and dopant distribution in the cross section of single nanotubes in TEMs. A series of characterization techniques have been optimized particularly for this research, for example, light absorption, band-gap estimation, and microscopy. The above results demonstrate that we are now able to tailor and optimize nanotube size and doping conditions, which provides the essential knowledge for developing and optimizing the internal p-n junction within single nanotubes.

Information Shared

Xiaofeng Qiu, Miaofang Chi, M. Parans Paranthaman, Ilia N. Ivanov, and Zhenyu Zhang, "Array of Titanium Dioxide Nanostructures for Solar Energy Utilization," Case No. 13489-166, 2011. Patent application filed.

05904

Effective Containment of Carbon Nanotubes for Oil Recovery Boom Products

P.A. Menchhofer and G.R. Romanoski

Project Description

This project focused on investigating the feasibility of utilizing carbon nanotubes (CNTs) as a sorbent media for oil remediation (while maintaining CNT containment) within readily available, low-cost or "traditional" material boom fabrics/media. The initiative for this effort came as a response to the recent Gulf oil spill crisis, and the calls for new and innovative remedial technologies for oil recovery. Successful demonstration of this concept could open new avenues for rapid cleanup of oil and other nonaqueous fluids and solvents while mitigating the environmental damage caused by man-made disasters. To establish the proof of principle for the project, loose (not contained) ORNL-made CNTs have been employed to very quickly (only minutes) capture up to 170 times their mass of used diesel engine motor oil (280 times their volume) in laboratory tests, thus demonstrating their great potential for oil recovery. This project, however, focused on the concept of combining simple principles and low-cost materials to achieve containment methods that could safely utilize CNTs to capture oil while minimizing their loss and introduction or escape into the environment.

Mission Relevance

Numerous agencies have issued calls for proposals for new sorbents and remediation technologies, including the Coast Guard, EPA, and NSF. Melt-spun polypropylene (MSPP) is the dominant material used currently for sorbent media in booms; however, MSPP is limited (in our test experiments) in with the capacity to absorb up to 17 times its mass of oil. At ratios of 170 times by mass (280:1 by volume), the utilization of CNTs for oil absorption represents a significant leap forward in efficiency; the

demonstration of their effective use and containment could move the concept closer to reality and provide an initial understanding of their potential deployment for this critical technology.

Results and Accomplishments

The experimental tasks utilized single- and multi-layered booms of nylon stocking material for CNT containment. A two-layer regime used MSPP boom sock material (Absorbent Care, Inc.) as an outer layer that surrounded an inner CNT-filled nylon stocking. The nylon tube stockings (96% nylon, 4% spandex) were either used as received or were first coated with "Rain X" (SOPUS Products, Houston, TX) to enhance the hydrophobic nature of the nylon, and were then loaded with ORNL-made CNTs. The MSPP outer containment socks provided a robust casing (good for protection) but impeded the absorption rates as compared to booms with only multiple layers of nylon. The experimental booms were able to absorb up to 170:1 (by mass) of the oil for the single nylon layer test, and up to 140:1 for the two-layer nylon/MSPP regime. Samples of post-treatment water sample filter materials were examined via Environmental SEM to determine the presence of CNTs. Although a single nylon layer was insufficient for *complete* containment (as trace amounts of CNTs were found in the post-treated water sample oil globules), by using two or more layers of nylon covered with an outer shell of MSPP, the CNT arrays (agglomerates) were effectively contained; that is, there was no visible loss or microscopic detection in the post-treated water samples, thus demonstrating excellent potential for oil spill mitigation technologies.

A follow-on study would build on the concepts of this initial Seed project, and attempt to develop "one-way" barrier layers that could potentially achieve further improvements.

Cost Benefit

From an approximate cost/benefit perspective, based on a current estimate for CNTs @ $1.00/g (with current techniques), the use of CNTs would increase costs over MSPP boom products by a factor of 5–10 times. For example, if constructing and employing a MSPP round boom (with a diameter of 7.62 cm), and by projecting a basis for maximum oil absorbency of 170:1 (by wt), approximately 16.4 g of CNTs would be needed per meter to absorb up to 4.6 liters of oil/m. Thus, at $1.00/g basis for the CNTs, the additional cost would add approximately $16.40/m. With the current cost for a conventional MSPP boom of the same size at only $3.28/m, this represents a fivefold increase. The demonstrated efficiency of CNTs to out-perform other state-of-the-art sorbents by up to tenfold combined with the urgency to mitigate some spill situations may justify these additional costs, although the development of boom reprocessing and re-use of the CNTs could offset their higher initial costs. Additionally, there may be substantial benefit when considering the increased efficiency and reduced time necessary to mitigate a sensitive ecological crisis (such as the recent oil spill into the Yellowstone River). If the technology developed by ORNL for CNT production could be further scaled for large production, it is expected that CNT costs could drop even lower, providing a potentially cost-effective high performance sorbent alternative.

05944

Turning Chalcopyrite into Dilute Magnetic Topological Insulators (DMTI) via Magnetic Doping

D. Xiao, W. Zhu, and G.M. Stocks

Project Description

The recent discovery of topological insulators has generated widespread research activity in the condensed matter and materials science communities. These materials are expected to display a variety of unconventional spintronics effects and could lead to entirely new device paradigms critical to basic energy research. A prerequisite for these practical applications is that ferromagnetism must be introduced alongside topological orders in these materials. We propose to theoretically investigate the possibility of establishing robust bulk ferromagnetism in topological insulators via magnetic doping a strong correlation effect, and their consequent effects on the topological properties of the host material. Successful execution of this research will lay the fundamental basis for developing energy-efficient spintronic devices based on the unique properties of topological insulators. This work will provide a foundation to open a new direction in current ORNL BES work on low-dimensional materials and grow funding opportunities.

Mission Relevance

As part of the energy strategy for the future, there is a basic research need for understanding the emergent topological phenomena in complex materials. The interplay between magnetism and the unusual metallic surfaces of these insulators may result in new spintronic or magnetoelectric devices, which are critically important in basic energy research because of their potential in energy-efficient applications. Our proposed work also addresses some of challenges identified in the 2007 report from the BESAC—"to discover how remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and to control these properties."

Successful execution of the proposed research will lay the fundamental basis towards developing energy-efficient spintronic devices based on the unique properties of topological insulators. It will place ORNL in an excellent position to propose new work in response to anticipated calls from DARPA (spin transport electronics)—both as originators as well as partners with other institutions who will need our expertise in theoretical understanding of magnetism in topological insulators.

Results and Accomplishments

In this project we start out to investigate the interplay between magnetism and band topology. Our main accomplishments are summarized here.

On the methodology front, we have developed a highly efficient first-principles method to evaluate the two most important topological invariants, the Z2 index for time-reversal invariant systems and the Chern number for broken time-reversal systems, based on the bulk band structure with the full-potential linearized augmented plane wave (FP-LAPW) formalism. This allows us to accurately determine the topological classification of the materials of interest and provides the necessary tool for further study of topological effects.

On the materials prediction front, we have shown that a variety of novel topological phases, including the quantum spin Hall state (nonmagnetic), as well integer and fractional quantum Hall states (magnetic order due to correlation effects), can be realized in oxide heterostructures. In particular, based on first-principles

calculations we have shown that $LaAuO_3$ (111) bilayers sandwiched between $LaAlO_3$ substrate could be a room-temperature quantum spin Hall insulator.

Information Shared

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05957

Separation of Carbon Dioxide from Flue Gases

B.L. Bischoff and C.K. Narula

Project Description

The goal of this project is to demonstrate the feasibility of supported liquid membranes for the separation of CO_2 from flue gas. At present, the state-of-the-art method relies on selective absorption of CO_2 in aqueous amines at source and release at collection point to separate CO_2 from emissions. The inherent inefficiencies resulting from low chemical efficiency of the process, energy needs, and evaporation and decomposition of aqueous amines make this process energetically and economically expensive. Our proposed liquid membrane based CO_2 separation process overcomes the problems associated with traditional aqueous amine process because it operates at a constant temperature, which decreases energy penalties, evaporative losses, and decomposition of the amine solution.

The proof-of-principle experiments will demonstrate that our thin inorganic based liquid amine membranes can produce a high purity CO_2 stream on a continuous basis with high flux. We estimate the footprint of the CO_2 separation plant, based on our liquid membrane process, to be 1/10 the size of aqueous amine process. The successful completion of the project will place ORNL in a competitive position to respond to anticipated calls from DOE Offices of FE and EERE for follow-on funding.

Mission Relevance

DOE Secretary Chu, in his letter to *Science*, stated that "overwhelming scientific evidence shows that CO_2 emissions from fossil fuels have caused the climate to change and that a dramatic reduction of these emissions is essential to reduce the risk of future devastating effects." Clearly, DOE is placing high priority to CO_2 separation, capture, and sequestration. In the United States, the majority of current emissions come from the production of electricity, primarily from coal-fired power plants. Existing coal-fired power plants account for over 30% of the CO_2 emissions in the United States. As such, DOE has set a post-combustion CO_2 capture target of 90% CO_2 capture at less than 20% increase in the cost of energy.

Results and Accomplishments

A series of nanoporous membranes, to be used as supports for the liquid amine membranes, was fabricated. The membranes were made by first forming tubular supports from 316L stainless steel and applying a thin (less than 5 μm thick) aluminum oxide separative layer to the inside surface. The supports have a pore size of approximately 4 μm. The average pore size of the aluminum oxide layer ranges from less than 5 nm up to 8 nm. A membrane with an average pore size of 4.7 nm was impregnated with a solution of 50% monoethanolamine in water. A test system was set up to evaluate the membranes at

temperatures up to 300°C. Preliminary results of this first membrane showed no detectable flow of either nitrogen or carbon dioxide at room temperature. Tests at 90°C showed an initial selectivity of 5.3 that increased to over 10 after an hour of operation. Extrapolation of the selectivity over long term operation indicates that a selectivity of 50 or even higher may be achievable. Long-term evaluations will be conducted in FY 2012 to confirm the higher selectivities over time. Finally, the preliminary tests showed good stability of the membranes. There was no evidence of a major loss of amines after a week of tests at temperatures ranging from room temperature to 90°C.

05959

Direct Imaging of Energy Generation and Collection in Photovoltaic Nanomaterials: EBIC in the STEM

B.S. Guiton, D.N. Leonard, and S.J. Pennycook

Project Description

Electron-beam-induced current (EBIC) measurements are being implemented in the aberration-corrected scanning transmission electron microscope (STEM). Electron-hole pairs formed by the beam—which acts analogously to a tiny ray of light—are collected and used to form an image, essentially mapping the energy conversion efficiency of the photovoltaic material in question. This will enable us to identify recombination centers and structures conducive to successful charge carrier collection. The highly intense and focused electron beam of the aberration-corrected microscope allows signal collection from much smaller regions than previously possible, permitting the characterization of cutting-edge photovoltaic materials on the scale of a single active nanostructure. This proof-of-principle study comprises a systematic test of a range of single axial p-n junction-containing nanowire devices with varying radii. Future research is anticipated on several cutting-edge inorganic nanomaterial photovoltaic systems, including radial-junction nanowires, hybrid structures, and nano-ink thin films. This represents the first viable method to directly image successful light-harvesting structures for nano-photovoltaics.

Mission Relevance

We anticipate that proof of this technique—the necessary characterization step to engineer nanostructured photvoltaics of useful efficiency—will be of mounting importance as U.S. energy security comes to rely increasingly on renewable energy sources. This research is highly applicable to the Basic Energy Sciences (BES) Divisions of Materials Sciences and Engineering, and Chemical Sciences. It is also highly supportive of the mission of the Office of Energy Efficiency and Renewable Energy's Solar Energy Technologies program. This project is highly applicable to several programs of the National Science Foundation, including the programs in Ceramics, Solid State and Materials Chemistry, Condensed Matter Physics, and Electronic and Photonic Materials; to the Solar Energy Initiative; and the Energy for Sustainability program. In addition, energy research, particularly solar energy technology development, is a key priority for the Department of Defense and for the missions of the National Aeronautics and Space Administration.

Results and Accomplishments

Significant progress has been made towards the goal of preparing single nanowire devices compatible with our TEM electrical feed-through holder, characterizing the electronic properties of these prototype devices, and to eliminate noise during collection of an EBIC measurement of such a device. Several devices have been made using micromanipulation in the focused ion beam (FIB) instrument: p-n junction

nanowires on the as-grown substrate are picked up and placed over a hole in an electron transparent silicon nitride membrane, and connected to the feed-through bonding pads using ion beam induced deposition (IBID). I-V curves have been collected from these devices, using the Protochips electrical-biasing holder ex situ to the microscope, allowing us to identify wires that contain p-n junctions (those which show rectifying as opposed to ohmic behavior). Limitations in the FIB micromanipulation approach have been identified and have led us to pursue two alternate device fabrication pathways. For these new fabrication approaches, wires are deposited onto the device substrate in an initial step, followed by lead fabrication using either IBID in the FIB, or electron-beam lithography; both of these methods are currently ongoing and show great promise. Initial EBIC measurements attempted with prototype devices have allowed us to identify and troubleshoot several sources of noise—a crucial first step to the successful collection of these low noise measurements.

05960

Tuning the Chemical Reactivity of Metal Nanoparticle Aggregates by Actively Controlling Their Electronic Coupling

G.M. Veith, D.E. Jiang, A.R. Lupini, and M.C. Troporevsky

Project Description

A fundamental challenge in the field of nanotechnology is tuning the properties of nanoparticles, in particular, the chemical reactivity and catalytic properties of metal nanoparticle aggregates. We propose adjusting the electronic coupling between nanoparticles to tune the chemical reactivity of metal nanoparticle aggregates. We believe this can be achieved by applying an electric field to the system, thus providing a novel way of actively controlling a chemical reaction. Recent theoretical studies on the electronic coupling between metal nanoparticles support our hypothesis. Utilizing the electronic coupling as a new tuning variable offers the paramount advantage of being able to tune the catalytic activity of metal nanoparticles in real time during the course of a reaction.

Mission Relevance

This project intends to establish a strong ORNL presence in the rapidly expanding field of tunable nanoparticles for clean energy production, nanomanufacturing, storage, and utilization. The importance of catalysis for energy production and utilization is extensively covered in the 2008 DOE report “Basic Research Needs: Catalysis for Energy,” which highlights DOE’s financial support for research in catalysis. The results of this study will be very relevant to DOE’s catalysis programs in the Office of Science and Energy Efficiency and Renewable Energy (EERE), both of which focus on investigating more efficient energy production from several domestic sources.

The tunability of the binding energies of molecular species could be used to control the capture and release of molecules such as CO_2. The demonstration of our concept will have an important impact to agencies such as ARPA-E or DOE Fossil Energy programs to pursue sequestration of CO_2.

Results and Accomplishments

To date we have successfully completed the synthesis of protected silver particles. These particles are protected with various functional groups which provide a way to adjust the spacings between the particles. These particles have been characterized by scanning transmission electron microscopy. In parallel, first principles density functional theory calculations of the binding of the CO on the Ag particles

have been completed, providing theoretical guidance for the separation required to develop electronic coupling between the silver particles. Cells have been constructed and tested to test the absorption and desorption of carbon monoxide on the silver particles as a function of potential.

In addition, we have discovered the new precious metal nanoparticles Pt_6N and Pd_5N. These 1–2 nm particles, grown on flat substrates and high-surface-area powders, are being investigated for catalytic activity.

Information Shared

May 2011—ID 201102612, "Method to prepare precious metal nitride films."
May 2011—ID 201102613, "Method to prepare precious metal nitride nanoparticles."

05961

Boosting Organic Solar Cell Efficiency Using Magnetism and Ferroelectricity

X. Xu

Project Description

Organic solar cells are highly attractive for energy production because of their low cost, light weight, mechanical flexibility, and environmental benignity. However, they are currently limited by low efficiency. Here, we propose a novel approach that combines both magnetism and ferroelectricity to significantly improve the power conversion efficiency (PCE) of organic solar cells. This unprecedented approach aims at simultaneously improving the diffusion of excitons and charge collection, two critical factors governing the PCE of organic solar cells. Specifically, we will merge the following two steps into one solar cell system: (1) chemically attaching molecular magnets in organic conjugated photovoltaic (PV) polymers, and (2) introducing a ferroelectric dipolar interface to enhance PV response. In step one, the locally spin-polarized transport induced by molecular magnets increases the population of longer lifetime triplet excitons, effectively improving the efficiency of exciton diffusion. In step two, the built-in electric field added by the permanent dipolar (ferroelectrics) interface enhances the net driving force inside PV materials, improving the charge collection efficiency. Combining these two approaches, we expect a dramatic enhancement of organic solar cells' PCE. This initiative is conceptually sound and holds great promise to advance the development of organic solar cells as the next generation in low-cost, environmentally friendly solar devices. With this initiative, ORNL will be placed in a strong position to attract follow-on funds to develop organic solar cells with high PCE.

Mission Relevance

This innovation brings together the expertise of ORNL in polymer chemistry and nanotechnology to address the efficiency issues, which are crucial for application and central to the "Science for Clean Energy" vision. It will place ORNL in a strong and unique position in the development of organic solar cells as the next generation in portable, flexible, and low-cost solar devices and to attract follow-on funds.

Results and Accomplishments

As proposed, we aim to use molecular magnets to increase the population of the long lifetime triplet excitons. The key step is to chemically attach the molecular magnets [Mn_{12}-acetate, or $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4$] to the polymer [P3HT or poly (3-hexylthiophene)] chain. This has been achieved through successful wet-chemical reaction between the P3HT and Mn_{12}-acetate. The next step is the test this material as the donor in a solar cell structure.

Along the other line, we try to use ferroelectric layers to improve the charge collection efficiency. We started with the spin valve structure to study the energy band shift caused by the ferroelectric layers. The $La_{0.7}Sr_{0.3}MnO_3/Pb_xZr_{1-x}TiO_3$/Alq3/Co/Au heterostructure shows strong anisotropy in the current-voltage relation and more importantly in the magnetoresistance, indicating strong energy band shift, in stark contrast with the heterostructure without the ferroelectric layer. More importantly, by applying a pulse of relatively higher voltage, the dependence of magnetoresistance on bias can be shifted. This shift is reversible, as the switching of the ferroelectric polarization. This active control of the energy level alignment will also be tested in the solar cell geometry to enhance the charge collection.

Information Shared

Enhanced dipole moments in photo-excited TTF–TCNQ dimmers. Mina Yoon, Yoshiyuki Miyamoto, and Matthias Scheffler. *New Journal of Physics* 13, 073039 (2011).

MEASUREMENT SCIENCE AND SYSTEMS ENGINEERING DIVISION

00525

Nonlinear Plasmonic Nanocircuit for Data Communications

A. 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 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 this work is to provide a proof of concept for an opto-thermo-plasmonic nanocircuit for data modulations and communications. This work in part entails an understanding of linear and nonlinear small-scale thermal processes and heat transport resulting from 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 this technology. Furthermore, the project involves optoelectronics and nanotechnology, which the National Institutes of Health considers will play important roles in cancer research.

Results and Accomplishments

After procuring necessary materials, planning experiments, and designing apparatus, the investigations, based on experiments and theoretical modeling of a single-nanoparticle optically excited plasmonic device (nanosystem), began to produce preliminary results. The theoretical modeling has required close examination of the connections between the various geometries for plasmonic systems [1]. Pre-experimental calculations were carried out to determine the thickness (in cases where comparison to thin continuous films were needed), particle size, and particle distribution of the proposed nanosystem to be fabricated, as well as polarization, wavelength, and power of the excitation source and the detection system. The experimental work has been 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 have been experimentally and theoretically studied. The results show that thermoplasmonics can be a viable approach to achieve modulation. The results clearly show that thermoplasmonic effect cannot be

neglected even if the ultimate desired outcome of the project work envisioned, i.e., high frequency modulation based on the direct plasmonic effect [2–4], can be achieved. Post-experimental calculations have been started in order to interpret the experimental results and optimize the performance of the nanosystem. The theoretical modeling using the finite difference time domain (FDTD) [5,6] supports the acquired experimental data. Apart from two invited talks and two poster presentations, thus far the five papers cited below have been published or accepted for publication. One of the invited talks [6], scheduled for October 7, 2011, is intended to solely focus on thermoplasmonics.

Information Shared

[1] A. Passian, S. Koucheckian, S. B. Yakubovich, and T. Thundat, "Properties of index transforms in modeling of nanostructures and plasmonic systems," *J. Math. Phys.* 51, 023518 (2010).
[2] A. Passian, L. Tetard, R. Farahi, B. Davison, A. Lereu, T. Thundat, S. Gleason, and K. Tobin, "Trends in high spatial high spectral resolution material characterization," Accepted, IEEE proceedings, *Future of Instrumentation* (2010).
[3] A. L. Lereu, Ph. Dumas, A. Passian, L. Tetard, R. Farahi, N. van Hulst, and M. Garcia Parajo, "Trends in high spatial high spectral resolution material characterization," Accepted, IEEE proceedings, *Future of Instrumentation* (2010).
[4] A. Passian, R. Farahi, L. Tetard, A. L. Lereu, and S. Gleason "Nanoplasmonics in energy and biomedical research," Accepted, IEEE proceedings, *Future of Instrumentation* (2011).
[5] A. L. Lereu, A. Passian, R. H. Farahi, L. Abel-Tiberini, L. Tetard, and T. Thundat "Polarimetric imaging and spectroscopy of arrays of optical nanoantennae," In review, *Nanotechnology* (2011).
[6] A. L. Lereu, A. Passian, and Ph. Dumas, "Near field optical microscopy: a brief review," In Press, *International Journal of Nanotechnology* (2011). http://www.fresnel.fr/ssop2/.

05859

Multimodal Biometric Recognition of Noncooperative Subjects at a Distance

C.B. Boehnen and R.A. Kerekes

Project Description

This project will create a proof-of-concept multibiometric system to capture data from noncooperative subjects at a distance. The proposed iris capture at a distance method is unique, and when combined with a previously successful ORNL off-angle iris recognition effort, it will significantly expand the applicability of iris recognition in uncontrolled settings. By capturing multiple biometrics and combining them to achieve identification, we can overcome a failure to capture or recognize any one specific biometric. The project is technically innovative and challenging but fundamentally achievable.

Mission Relevance

The project improves fundamental security of facilities and identification of individuals. As such, it is applicable to securing all DOE facilities as well as contributing to the national security programs of numerous other government agencies. The project improves biometric technology needs for the Department of Homeland Security, Department of Defense (DOD), Department of Justice, and others. Proof of this relevance can be seen in the follow-on funding we have received from a Biometrics Identity Management Agency (BIMA) BAA, where our prospoal was one of 4 selected from over 60 initial submissions. Work on the follow-on funding has just begun.

Results and Accomplishments

We successfully designed the device, built the device, captured a test dataset, and performed a multimodal biometric experiment to prove the viability of the system. On our small test dataset we were able to achieve perfect recognition performance as shown in the table. This table also demonstrates the importance of multimodal, multi-sample data collection which is one of aims of the project. Without both multi-gallery datasets and multimodal datasets, we would not have been able to achieve perfect recognition.

	Number of Gallery Images		
	1	2	3
Face	71.5884	84.596	98.2609
Left Iris	76.2864	86.6162	99.4203
Right Iris	76.0626	86.6162	99.1304
Combined	77.1812	87.1212	100

Even before we were able to produce these results, we applied for and received $674,000 in follow-on funding from the DOD Biometric Identity Management Agency (BIMA). Our proposal was one of 4 selected for funding from over 60 submissions. We plan to apply for additional funding in their coming BAA, which we anticipate being released in the coming weeks (it was delayed this year because of the CR problems). Additionally, two companies have expressed an interest in potentially commercializing some of the technology in the project. Talks are preliminary.

05878

Neutron Imaging for the Determination of Tumor Margins

T.L. Nichols, H.Z. Bilheux, P.R. Bingham, J.S. Brenizer, Jr., G.W. Kabalka, A.K. LeBlanc, A.M. Legendre, R.L. Donnell, M. Cekanova, A.S. Tremsin, K.L. Watkin, and L.M. Nodit

Project Description

The project was designed as a proof of principle that a low-energy neutron imaging system with 10–15 μm spatial resolution and boronated tissue stains will result in a clear delineation of normal and malignant cells that cannot be seen with standard optical approaches. This research explores the application of neutron imaging to enhance medical pathological specimen analysis using the cold guide (CG-1) beam at the High Flux Isotope Reactor (HFIR). Neutron images were obtained with a resolution of ~50 μm by collimating the beam with a pinhole neutron collimator. Malignant specimens of a skin tumor and melanoma were examined to evaluate the efficacy of neutron radiography as a tool for the determination of tumor margins. While previous research has indicated that neutron radiography may provide additional contrast as compared to the traditional methods, the spatial resolution of neutron radiography systems has only recently reached a level that would provide an image suitable for determination of tumor margins.

Normal cell sizes vary considerably depending upon the tissue but are typically on the order of 10–20 μm in diameter with nuclei of 5–8 μm. Malignant cells are typically 2–5 μm larger than the normal counterpart from the same original tissue type. A common method to improve contrast for radiographic studies is to incorporate a contrast agent into the sample for improved delineation between areas of interest. One novel aspect of this effort was to use boron and deuterated water to improve contrast between healthy and tumor tissue. Specially prepared histochemical stains were prepared by boronation with ^{10}B to improve the neutron image contrast and with deuterated water or alcohol as fixatives to

decrease neutron scattering. Since tumor cells have a different biochemical milieu (environment) than surrounding normal cells of origin, they were expected to demonstrate a contrast difference that can be exploited in addition to the boronated stains.

Mission Relevance

This project melds two of ORNL's primary mission foci: neutron science and systems biology. Using neutrons to image malignant tumor margins is both novel and innovative. It requires extending the field of neutron imaging to higher resolution images and incorporates boronated stains to increase the contrast between normal and malignant tissues. The neutron images are likely to distinguish the small differences in biochemical milieu that exist between normal and abnormal cells. The improved delineation of tumor margins will have significant impact on the major public health problem of cancer through systems biological application of the results of neutron imaging of these biological materials.

Results and Accomplishments

Work on this project started with discussions with colleagues on how best to perform the experiments at the CG-1 beam at HFIR. There were technical issues to address in order to improve the resolution to 10–15 μm or perhaps down to 1–2 μm. These were pursued with calculations and simulations. The best resolution available was at best 50 μm and on some images was in the 50–80 μm range. Several different fixation techniques were employed as well as staining procedures. The fixatives employed were alcohol, deuterated alcohol, and formalin.

The formalin caused the images to be dark from the introduction of more hydrogen. The deuterated alcohol provided the best images, but the plain alcohol fixed specimens were nearly as good. Since deuterated alcohol is so expensive and decreased the attenuation of the neutron beam by only a few percent, it was determined that alcohol was the best fixative. The reason to use a fixative is to render the tissue harmless but destroying all biological activity. The project allowed for fresh tissue imaging, and that was performed in conjunction with another project. The results were not significantly different from those fixed with alcohol, but the specimens shrank considerably as they dried with resulting changes in contrast. So going forward, all specimens were fixed with alcohol.

The aspect was to increase the contrast in the images. Tissues are routinely stained with eosin and hematoxylin for histopathological evaluation. Since these stains are what a pathologist expects to see, they were chosen as the most appropriate method to deliver a contrast agent if it were possible to boronate. Gadolinium was considered, but since it does not stay complexed to the molecule unless ensconced in a large molecular cage that would likely change the staining characteristics, it was not pursued. The hematoxylin stains nuclei a dark blue color, whereas eosin stains the cytoplasm a red color. The chemists were able to produce several boronated eosin compounds by adding a carboranyl group. All the boronated eosin stains reproduced well the staining characteristics of commercially available eosin. The stain that contained the most boron, which is two boron atoms per molecule, was used going forward. Attempts to boronate hematoxylin were not successful, and time did not allow the building of the molecule from smaller molecules. So the tissues were stained with the most boron containing compound of eosin and commercially available hematoxylin.

Many tumor-containing specimens were studied, and in all cases the tumor appeared darker on the images than the surrounding normal tissue. The resolution of the microchannel pore (MCP) detector proved to be a limiting factor. The MCP allowed rapid image attainment (5 minutes for a good quality image with adequate statistics in all pixels). However, the maximal resolution of 50 mm proved to be inadequate to definitively demonstrate that the technique can delineate malignant from normal tissue.

The requisite approvals for bringing and handling these biological materials have been obtained prior to beginning any work. Since the tissue cannot be placed in paraffin, as is customary, a meat cutter such as used in a deli was tried to cut the thin tissue specimens. This was needed because the very thin specimens that are cut by microtomes were too thin. If the specimen is too thin, the attenuation will not be large enough to overcome the background signal, and either no image will be seen or it will have a large amount of noise. If the specimen is too thick, there will be too few neutrons reaching the detector and many of the neutrons that reach the detector will have undergone multiple scatters, which will lose the image information and serves to further degrade the image. The best method was eventually determined to be accomplished by using a piece of plastic of the desired thickness (1–5 mm).

Several specimens have been made using ethanol, deuterated alcohol, and formalin. At this point, the attention in the project was turned to improving the resolution obtainable. The MCP that had been anticipated to have 10 μm resolution (being developed independently of this project) was not ready for use at HFIR in time for this project. So alternative methods were sought that could obtain resolution in the sub 5 μm range. The best solution to the problem was determined to be a film technique. Mounting high resolution film next to a specimen with a thin gadolinium film in between was felt the best solution. The Gd emits an electron when a neutron interacts with the nucleus. The electrons will travel a very short distance before exposing the film (they are physically next to one another, so the travel is into the film matrix), which leads to a potential resolution of 1–2 μm. This would allow the cell nuclei to be seen.

An assembly was designed and constructed to hold the film, Gd plate, and specimen between two aluminum plates held together by a vacuum supplied by a roughing pump. The film selected was an ultra-high-resolution holographic film. Despite many attempts, the holographic film never worked. Beyond the time of the current project, a member was successful by using reconnaissance film, which appears to have a resolution of better than 10 μm and may be as good as 3 μm. It is hoped that this research can be continued until a clear proof of principle has been obtained.

05903

Decoder-Assisted Frame Synchronization for Orthogonal Frequency Division Multiplexing (OFDM) Based Data Communications Systems

M.K. Howlader and M.A. Buckner

Project Description

Emerging Internet protocol–based systems transmit their data in packets, and a subsequent loss of synchronization reduces the data rate due to the required retransmissions. We are taking a novel approach for the rapid acquisition and detection of packet transmissions by buffering the entire packet. This approach is expected to reduce complexity over current synchronization approaches, which achieve synchronization by using a longer header, by eliminating the separation of packet processing stages and improving the acquisition time by basing decisions on all data in the packet rather than just a few header bits. Removing the longer header will increase the data rate. Not only will acquisition and detection be accomplished in a single step, but the acquisition process will be greatly enhanced through the application of all available information. Earlier results from our research on traditional non-OFDM-based systems indicate that the probability of a false acquisition of packets can be reduced by several orders of magnitude with this approach. Our intent now is to expand the research to OFDM-based communications systems. This research will explore code structures and hybrid decision matrices for the decoder to support joint frame synchronization and detection for OFDM-based systems.

Mission Relevance

The proposed research is based on a novel technique for frame synchronization. This technique offers unique contributions to the field of synchronization for communication systems. However, existing research results are not detailed enough to be considered for practical systems. There is a legitimate gap between the basic concept and the challenges for its application to practical systems. This proof-of-principle research will bridge this gap by showing that the frame synchronization scheme can be applied to practical OFDM systems.

The Industrial Wireless Program of the DOE Office of Energy Efficiency and Renewable Energy has shown interest in robust, fast, energy-efficient wireless communications systems, as has the Smart Grid Program of the DOE Office of Electricity Delivery and Energy Reliability. Other potential sponsors for the developed technology include DOD (ARL, NRL, AFRL, DARPA, etc.), DHS, and NASA. Interest in robust, fast, energy-efficient communications is of interest throughout the government sector, as well as in the commercial sector. OFDM-based communication systems are already planned for many military, space, homeland security, and commercial applications.

Results and Accomplishments

We developed a theoretical basis of a noncoherent decoder-assisted (NDA) frame synchronizer, a two-stage synchronization scheme based on the list-synchronization principle, for the serially concatenated coded differential modulation (SCCD) system in a burst OFDM transmission. For the coarse synchronization in the time domain, we adopted the conventional minimum mean square estimation (MMSE) rule based on the supplementary guard interval to provide a list of potential frame starting positions. For fine synchronization in the frequency domain, we used decoder-assisted methods to obtain more reliable final synchronization decisions. Here, we developed a new sync method by fully exploiting a combination of different decoder information. We used the Matlab program for our simulation results. We achieved the main goals of the project: develop a decoder-assisted frame synchronization technique for OFDM systems, select the proper sync word and derive the required cost function, and develop a method for decision making at the second stage of the synchronization (various optimizations of the decision matrix are needed). We also achieved results for joint frame synchronization and channel estimation. Moreover, we used the synchronization information of the OFDM system for a vehicle lane positioning technique based on a joint frequency difference of arrival (FDOA) and time difference of arrival (TDOA) principle by measuring Doppler frequency.

Information Shared

P. Vallance and M. Howlader, “Automotive Geolocation Using Wireless Infrastructure in a GPS Denied Environment,” Virginia Tech Wireless Symposium, June 2011.

05984

Development of Vacuum Micro/Nano Electronic Devices Using Glass Fiber Drawing Methods

K. Korsah, R. Kisner, A. Melin, J. Simpson, and I. Ivanov

Project Description

This seed money project was for the development of a new, cross-cutting technology applicable to advanced electronics and computer processors. The unique characteristics of the type of electronics proposed are operation at high frequencies (beyond that of semiconductors), high temperatures (500°C), and in high-radiation environments (no doped semiconductors). We envision such devices to thus find wide application in several scientific fields including: (1) supercomputers (requiring less cooling that run at clock speeds 100 times faster than current technology); and (2) hardened electronics for space, military, and advanced nuclear power applications (high radiation, high temperature, and/or small payload). Fabrication of these enabling devices employs a novel approach similar to optical fiber drawing, which lends itself to mass production comparable to photolithography.

Mission Relevance

This project could result in a technological breakthrough that is applicable to several DOE missions. Nuclear energy will benefit from electronics that can operate in high temperature and high radiation environments. The technological breakthrough will lead to increased clock speeds in high-performance computing. Specific programs in DOE/NE, for example, will benefit such as the Nuclear Energy Enabling Technologies program, Small Modular Reactor program, and Fuel Cycle Research and Development program. Benefits will extend beyond DOE and include defense programs. For example, interest has been expressed by the Air Force Research Laboratory. DARPA also can apply this technology for creating ultrafast computing engines.

Our Seed money projected ended in September 2011, and we have since approached DARPA for potential ongoing funding. Our initial contacts have been very encouraging, and it is hoped that we will eventually be successful in securing funding from DARPA.

Results and Accomplishments

We performed modeling and simulation of our vacuum field emission micro-triode concept. This helped to determine the geometry, configuration, and device structure necessary for a workable device. Vacuum diode structures were successfully fabricated using modified glass fiber drawing methods. For compatibility with current solid-state technologies, low operating voltages are needed for micro-triode-populated circuits. Current CMOS operating voltages range from about 3 volts to 15 volts. This voltage range should, therefore, be a target for the micro-triode. We set out, in the preliminary work of this seed money, to demonstrate device functionality rather than determine a lower operating voltage limit.

The field emission turn-on voltage (which establishes a lower operating voltage) is a function of cathode tip dimensions (curvature), spacing, and effective surface work function of the material. Because of equipment limitations, we were only able to fabricate tungsten tips of about 0.2 μm. With this tip dimension, we measured turn-on voltages of about 140 volts. Our calculations have indicated that, for a one-volt turn-on voltage, a radius of 17 nm is required. Part of ongoing work is to construct a control apparatus that can consistently form tips in the 10 nm range.

The diode structures we fabricated have been used in real circuits to demonstrate rectification. We also fabricated triode structures but were not able to characterize them within the project period. Funding continues to be sought for continued work in this area. The next step in the development of this class of vacuum micro/nano devices is to use triode structures in circuits to demonstrate amplification.

06250

Precision Long-Range Projectile Tracking

S. Rajic and P. Datskos

Project Description

The project entails proof-of-principle experiments and analysis to examine a novel optically based projectile tracking approach. The concept to be demonstrated is the basic feasibility of using the rotation of the projectile as the periodic source for a synchronous detection based tracking approach. The projectile itself will be completely passive in this approach and thus will contain no emitter, batteries, or electronics of any kind. This type of approach can provide covert projectile precision location information even in daylight hours that is presently not achievable. The successful completion of this project, along with additional follow-on funding, could lead to the elimination of a human spotter. Additionally, the information derived from such technology could be used to compensate the sight reticle to always be coincident with the projectile point of impact under any environmental conditions. Having detailed knowledge of a projectile's location over a long range can also be useful in determining the environmental condition along that path. That information can be beneficial in several additional applications beyond projectile tracking.

Mission Relevance

The feasibility demonstration of this approach will support the DOE national security mission in many ways, such as providing a substantial capability increase to DOE special courier teams. The primary funding source, and beneficiary, for this technology would ultimately be the DOD. Projectile tracking is of great concern to all of the military services.

Results and Accomplishments

Since the mid August project start date, we have procured several components and already performed reflectivity measurement on these components. We are in the process of analysis to determine a theoretical signal-to-ratio with these initial commercial reflectors. The majority of the results for this project will not be evident until next fiscal year.

PHYSICS DIVISION

05851

Solar-Wind Heavy Ion Sputtering of Lunar Regolith

F.W. Meyer, H.M. Meyer, III, N.F. Barghouty, and J.H. Adams, Jr.

Project Description

This project seeks to demonstrate the feasibility and proof of principle of laboratory measurements of sputtering by solar-wind highly charged ions of actual and simulated lunar soil samples. Actual lunar soil samples as well as lunar soil simulant material will be provided by Marshall Space Flight Center. These samples will be formed into self-supporting targets for use in a surface scattering chamber located at the ORNL Multicharged Ion Research Facility (MIRF), into which beams of solar-wind-relevant ion species, charge states, and energies can be directed. A quadrupole mass spectrometry based technique will be evaluated for use in comparing the sputtering efficiencies of solar-wind highly charged ions and protons.

Mission Relevance

This project is relevant to the DOE Office of Basic Energy Sciences mission to understand fundamental interactions of highly charged ions with electrons, atoms, molecules, and surfaces; to the DOE Office of Fusion Energy applied plasma science mission to understand and characterize atomic interactions occurring in plasma environments where highly charged plasma impurity ions may impact and do damage to vessel walls; and to NASA in support of its Lunar Advanced Science and Exploration Research (LASER) program.

Results and Accomplishments

In FY 2010 we performed preliminary measurements of lunar regolith simulant sputtering by protons and solar-wind-relevant multicharged ions using a quadrupole mass spectrometry approach. These measurements demonstrated significant sample charging problems due to the insulating nature of the lunar regolith simulant powder, which was prepared by pressing the powder into an ~1-cm-deep sample holder. An alternative sample preparation method was then devised in which a very thin layer of the powder was pressed onto double-sided C tape. X-ray induced photoelectron spectroscopy (XPS) analysis showed acceptably small C signals from this substrate, and subsequent beam exposure tests demonstrated an absence of charging effects. In addition, a time-of-flight mass analysis system and new data acquisition system were installed.

In FY 2011 improved measurements of kinetic and potential sputtering by protons and multicharged Ar ions were carried at the MIRF using the C-tape method to compare mass-resolved sputtering in the range 2–20 amu by 375eV/amu protons and same velocity Ar^{+}, Ar^{6+}, and Ar^{9+} ions. The Ar^{6+} and Ar^{9+} ions were used as proxies for solar-wind multicharged ions having neutralization energies in the range 300–1000 eV. To simulate the effect of the H loading of the surface due to the dominant H constituent of the

solar wind, prior to each of the Ar beam exposures, the sample was exposed to a high fluence (~10^{18}/cm^2) of 375 eV protons.

In these measurements mass spectra produced by different incident projectile species and charge states were acquired and normalized to the respective particle currents. Normalized mass spectra for all three investigated species are shown in Fig. 1. Ratios were taken of peak intensities of sputtered species for the different incident charge states which reflect ratios of the respective sputtering yields. In this manner, mass-resolved sputtering yield enhancements as a function of projectile charge and/or projectile mass could be identified. A factor of 80 enhancement of oxygen kinetic sputtering by Ar^+ over same-velocity protons was measured and an additional factor of two increase for Ar^{9+} over same-velocity Ar^+ was demonstrated, giving a clear indication of the importance of potential sputtering by multicharged ions.

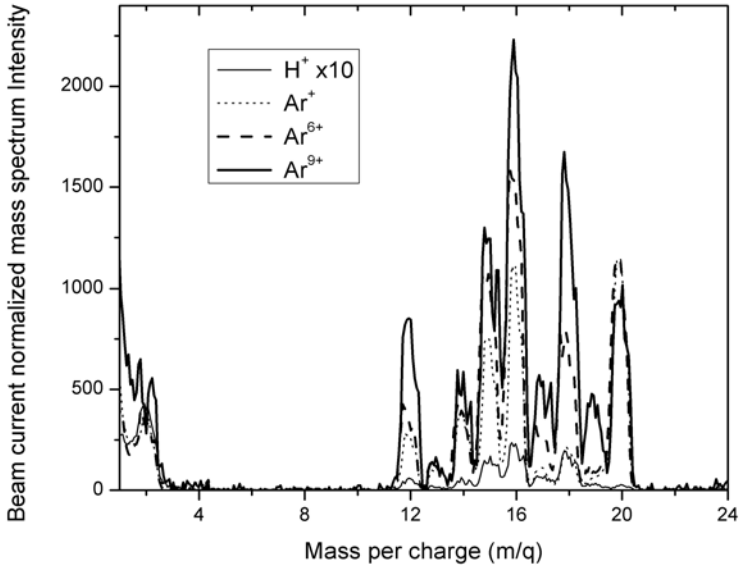

Fig. 1. Mass distribution of sputtered species and beam species reemission in the range 2–24 amu, normalized to the respective beam particle currents for protons, Ar^+, Ar^{6+}, and Ar^{9+} incident on room temperature lunar regolith simulant at 375 eV/amu. The mass-20 peaks are due to the incident Ar beams, and their similar peak heights support the beam current normalization used.

In addition, XPS measurements of beam-induced surface modification were carried out, in order to determine if the significant O sputtering observed in the QMS measurements could be correlated with changes in chemical states of metallic species in the various oxide constituents. As illustrated in Fig. 2, strong evidence of Fe reduction was found in the Fe 2*p*3/2 iron spectral region for those target areas that had been exposed to high fluence Ar^+ and Ar^{8+} beams. Using the scanning feature of the XPS system, target maps of reduced Fe were constructed. As can be seen from Fig. 3, the regions of reduced Fe were found exclusively in those target regions irradiated by the ion beams. Further, preferential oxidation of the beam exposed regions during transfer to the XPS system was found to result in enhanced O concentrations in the beam exposure regions.

On the basis of these very promising preliminary results, a proposal was prepared and submitted in response to the 2010 NASA-LASER (Lunar Advanced Science and Exploration Research) program call NNH10ZDA001N-LASER with submission deadline on Feb. 24, 2011. To strengthen the proposal, research collaboration was initiated with the deputy project scientist of the Lunar Reconnaissance Orbiter mission.

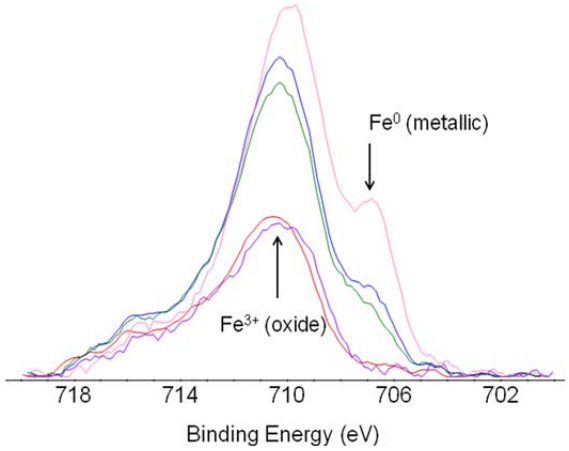

Fig. 2. Background subtracted Fe $2p_{3/2}$ spectra for beam exposed and unexposed target areas. The upper three traces were taken at beam-exposed spots and show reduced (i.e., metallic) forms of Fe. The lower two traces were taken in target regions that had not seen beam exposures and show Fe in the oxidized 3+ state.

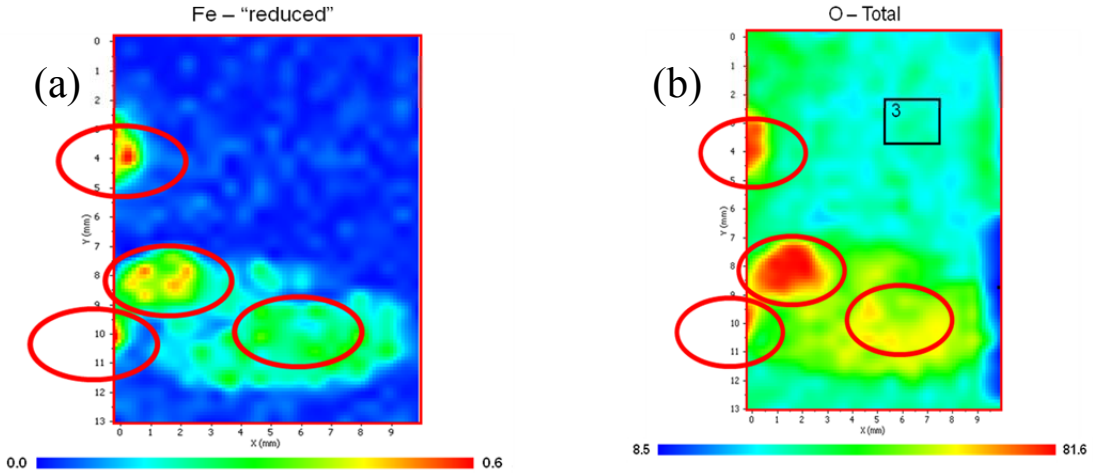

Fig. 3. (a) Reduced Fe (Fe0) is highest in the areas that were Ar-ion exposed (red circles); (b) after removing the sample from vacuum after ion beam exposure, the reduced Fe picked up some oxygen causing re-oxidation of the exposed areas. 3—background area where lower two scans in Fig. 2 were measured.

Information Shared

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A.F. Barghouty, F.W. Meyer, P.R. Harris, and J.H. Adams Jr., "Solar-wind Protons and Heavy Ions sputtering of Lunar Surface Materials." *Nucl. Instrum. Phys. Res. B*, **269**, 1310 (2011).

Proposals submitted

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05868

Irradiation Effects in Graphene-Based Electronics

P.S. Krstic

Project Description

The objective of the project is to conduct theoretical research to further fundamental understanding of the mechanisms of radiation interaction with graphene and graphene-based electronic. We study (1) the microstructural evolution, chemical composition, and electronic structure variation of freestanding graphene (monolayer or multilayer graphite) upon irradiation, (2) electronic and electrical properties variation of graphene-based devices under irradiation, and (3) defect behaviors and their effects on structural and electrical properties and device performance. The defects induced by irradiation are studied by methods of classical molecular dynamics by defining the chemical and structural changes of graphene for various kinds of impact particles (H, H_2, C, CH_4 and isotopes) and various ranges of impact energies (1–1000 eV). The change of electronic and band structure, in particular the conductance as a function of the radiation damage, are quantified by the quantum methods of electron transport.

Mission Relevance

Understanding radiation interaction with graphene and graphene-based electronic devices will lay the scientific foundation to develop radiation-tolerant graphene devices, which is of interest to space and missile systems and nuclear security applications. If successful, this research will open the opportunity to transfer unique electronic structure information on a graphene layer upon irradiation into its unique conductance signatures, toward application in an ultrasensitive single-particle or few-particles detector. The control and manipulation of molecules is one of the primary missions of the DOE Office of Basic Energy Sciences (BES). This research will lay the scientific foundation for the development of radiation-tolerant graphene devices, which is of interest in space and Department of Defense (DOD) missile systems, as well as to the National Aeronautics and Space Administration (NASA).

Results and Accomplishments

The microstructural evolution, chemical composition, and electronic structure variation of a freestanding single graphene sheet upon irradiation if H, D, T (hydrogen isotopes) and H_2 (hydrogen molecule), in the energy range 1–1000 eV, for normal and grazing angles of impact particle incidence, and for various vibrational excited H_2 molecules have been analyzed. The graphene sheet size was 3 nm × 3 nm. The simulation was performed by the classical molecular dynamics, using currently the most advanced hydrocarbon long-range potential (AIREBO), with characteristics improved recently by us. Instrumental in the calculations was also the summer (SULY) student from Middle Tennessee State University, Robert Ehemann.

Statistical analysis of these simulations, for thousand of impacts per a point in parametric space (energy, angle, particle, particle state), has led to the yields of the various dynamic processes, like reflection, transmission, sputtering, and sticking. In addition, the potential of graphene was mapped across the surface and the yields obtained were explained.

It was concluded that the results obtained by the standard hydrocarbon classical MD potentials, REBO and AEREBO, do not provide satisfactory data for the hydrogen chemistry with graphene, as well as for the transmission and reflection probabilities (due to the existence of unrealistic barriers in these potentials).

Using tight-binding Density Functional Theory (DFTB), the new potentials of H-graphene were developed, and applied quantum-classical molecular dynamics to calculate new data for H-sticking, H reflection, and transmission, as well as changes of the graphene HOMO-LUMO graph due to the H-imact (0.1–200 eV), indicate significant changes in the graphene conductivity and its ability to sensitively respond to the particle energy and type (chemistry). These important results are being prepared for publication.

05869

Modeling of the Plasma-Material Interface

P.S. Krstic and P.R. Kent

Project Description

This project will develop an innovative theoretical-computational capability for simulations of processes at the Plasma Material Interface (PMI) to help guide research on present and future linear and toroidal PMI experiments. We envision development of a capability to build and validate predictive models for both ion-beam-surface interactions and more complex plasma-surface interactions. The leading component of the proposed research will be development of classical molecular dynamics interatomic potentials for fusion-relevant composite surfaces (Li, C, H) and (W, C, H, He) and their validation with the available experimental beam-surface interaction data. However, in the case of Li-H-C (ionic solids), the quantum-classical approach is attempted (based on the tight-binding Density Functional Theory) to describe chemistry in the surface. In the transition to plasma irradiation studies, we will validate the models using the existing data from the plasma PMI machines, like PISCES B (UCSD), NSTX (PPPL), and beam surface experiments (Purdue).The work will provide a foundation for predictive science of the PMI and will integrate theory with available plasma surface and beam surface measurements to validate models for surface phenomena.

Mission Relevance

The walls of magnetic fusion reactors must sustain large particle and heat fluxes, which present a major challenge to achieving controlled fusion power. A recent panel report to the Fusion Energy Sciences Advisory Committee (FESAC07) found that of the top five critical knowledge gaps for fusion, four involve the PMI. Fusion community REsearch NEeds Workshops (RENEW09) in 2009 have recommended new PMI research programs and facilities to advance the science and technology of plasma-surface interactions. A valid simulation of the plasma-material interface in the big fusion reactors (ITER, DEMO) can save billions of dollars in the long term through a predictive scientific approach.

Understanding the effects of energetic particles on materials is of great relevance to the Department of Defense (DOD), the National Aeronautics and Space Administration (NASA), and the Nuclear Regulatory Commission (NRC).

Results and Accomplishments

Although the project has been active less than 6 months in FY 2010, great progress has been made on the task for the first period, “Development and validation of potentials for the systems containing (Li, C, H).” The principal challenge for mixed materials with lithium is strong polarization (because of the low electronegativity of lithium in comparison to carbon and hydrogen), which in addition to the short-range covalent bonds creates nonbonding, long-range Coulomb interactions between atoms. We have applied the Electronegativity Equalization Method (EEM) to develop a code and successfully apply it to a number

(27) of small Li-C-H-type molecules, whose energies, bonding distances, and Hessians were calculated by a computational chemistry method. In addition, a fitting procedure was developed at hydrocarbons, and generalized to Li-C-H mixtures, to obtain bond order (BO) parameterization of the covalent bonding for the problem. The efforts are now focused toward setting a common procedure for EEM and BO parameterization, followed by a test on the dynamics of Li-C-H (sputtering, reflection). Contributing to these development efforts were Jonny Dadras, a UTK graduate student supported by this project, and U. Z. Yang, a summer student from Purdue University.

However, the biggest achievement in this period is "conquering" a quantum-classical approach, using TBDFT, parameterized by K. Morokuma (Emory and Kyoto Universities); instrumental in the development was J. Jakowski (NICS, UTK). Our calculations of the dynamics of deuterium impact of a lithiated amorphous carbon has shown an excellent (qualitative) agreement with the experiments at Purdue and NSTX (PPPL) and also led to explanation of the contraintuitive retention of D at Li-C sites.

In collaboration with K. Morokuma, DFTB parameters for the Li-C-H-O system are developed, validated with experiments of Purdue University and NSTX (PPPL) (publications below), and the findings published. In addition, a new collaboration was established with H. Witek of Taiwan University, and UTK graduate student Jonny Dadraws was fully engaged in the project and spent 1 month in the Witek's group developing the parameterization for the W-H-He-C system, which provides to us a new capability to treat the collision chemistry of the fusion important tungsten surface system. Also, U.Z. Yang of Purdue helped us develop a verified EEM method for charges of the Li-C-H-O system, which attached to the classical (short range) potential developed in the previous year by Dadras and Kent enable treatment of the cumulative bombardment of the lithiated/oxydyzed carbon in NSTX experiments.

Information Shared

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Predrag S. Krstic, Jean Paul Allain, Alain Allouche, Jacek Jakowski, Jonny Dadras, and Chase N. Taylor, "Dynamics of Deuterium Retention and Sputtering of Li-C-O Surfaces," *Fusion Engineering and Design* (2011), online: doi:10.1016/j.fusengdes.2011.07.009.

A. Allouche and P.S. Krstic, Atomic hydrogen adsorption on lithium-doped graphite surfaces, *Carbon* (2011) online: doi:10.1016/j.carbon.2011.09.006.

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Stotler, D., Skinner, C. H., Blanchard, W., Kugel, H., Schneider, H., Zakharov, L. E., and Krstic, Predrag S, "Simulations of Diffusive Lithium Evaporation on onto the NSTX Vessel Walls," *J. of Nuclear Mat.* (2011), doi:10.1016/j.jnucmat.2010.11.070.

05906

Development of a Novel Electron Dynamics Simulation

C.O. Reinhold

Project Description

We have developed a considerable fraction of a multiple electron dynamics simulation that can add explicit electronic phenomena like multiple charge transfer, ionization, and Auger processes to the widely used method of molecular dynamics simulation. As a proof of principle, we started applications of this method to treat the dynamics of all electrons in C_{60} interacting with a multiply charged ion. The theoretical approach will provide a new computational tool to study ion–grain interactions. It will also open up the possibility for other follow-on work to integrate electronic and molecular dynamics for applications such as description of dusty plasmas, intense X-ray or laser interaction with molecules, and nano-patterning of surfaces by highly charged ions.

Mission Relevance

This work is of interest to the DOE Office of Fusion Energy Sciences because of the growing importance of understanding the formation and interaction of dust in fusion and other laboratory plasmas. Interest from the DOE Office of Basic Energy Sciences is likely in simulation of the coupled dynamics of electrons and ions following irradiation of molecules by intense pulses at the new Linac Coherent Light Source or from laboratory-based ultra-intense lasers. Of broader interest, an electronic and molecular dynamics simulation would impact science that requires more explicit treatment of electrons than is currently possible involving electron transfer among molecules, electron-driven reactions, and electron ejection. The work is directly applicable for seeking follow-on funding from NASA because of the need for ion–grain modeling for an important component of the cosmic rays entering our solar system, the creation of the building blocks of planets, and the kinetic chemistry of pre-stellar clouds.

Results and Accomplishments

In the second year, the project was active only briefly because of the departure from ORNL of David Schultz, the original PI, by the end of FY 2010 and Carlos Reinhold in December 2011. During this final stage of funding, we put a few finishing touches on the computer code that was started during the first year. Work was focused on the development of a prototype electron dynamics code that could be tested against a comprehensive set of experimental data for the simplest interacting systems. As a proof of principle, we started applications to treat the dynamics of 360 simultaneous active electrons in C_{60} interacting with multiply charged ions for which several recent experiment for distant collisions and penetrating collisions are available. These data provide a much more strenuous test of the simulation than those initially envisioned for the project.

REACTOR AND NUCLEAR SYSTEMS DIVISION

06256

Development of a Thermal-Hydraulics Simulation Tool for High-Fidelity Analysis of Transients in Small Modular Reactors

E.L. Popov, P.K. Jain, and P.P. Mukherjee

Project Description

The aim of this seed money project is to develop a parallel, 3D, Lattice Boltzmann Method (LBM)-based turbulent flow simulation code capable of handling Computer Aided Design (CAD)-based geometries and simple boundary conditions (e.g., flow inlets and pressure outlets) and to demonstrate its applicability for realistic nuclear applications. Software developments are specifically targeted towards establishing a proof of principle of LBM for nuclear applications to attract sponsors for further investments in this approach. LBM code will use the time-explicit, multirelaxation LBM scheme (MRT-LBM) to simulate the turbulent flows and will be designed to support the ultimate goal of developing a parallel coupled multiphysics solver (i.e., by possibly coupling it with ORNL's Denovo deterministic neutron transport code and AMP fuel performance code) in the future. The deliverable of this project will be a parallel "production-style" code that is able to simulate time-dependent turbulent/laminar flows in 3D CAD geometries, and an application model for ORNL's Small Advanced High Temperature Reactor design to demonstrate the LBM's applicability for small modular reactors (SMRs). It should be noted that by "production-style" we mean a code that can be used for multiple reactor concepts, is a general-purpose parallel 3D solver, and can support different computational domain shapes. It does not indicate that the code development will be finished at the end of this project and the delivered demonstrative solver would be ready to perform any production or qualified analyses.

Mission Relevance

The successful completion of this project will provide ORNL with a key and fundamental capability to support advanced R&D related to SMRs as well as future needs of key sponsors. In particular, it will put ORNL in a position to develop multiphysics simulation activities for SMRs using novel state-of-the-art methods. Once the proposed capability is successfully demonstrated, additional funds are expected to become available from sponsors to support specific programmatic interests and needs of several different agencies. The primary sponsors for near-term future developments would be the DOE-NE NEAMS and SMR/ARC program. Proposed simulation framework for SMRs would be directly relevant and applicable to the DOE-NE mission and would potentially benefit from the above programs. In addition, successful demonstration of an advanced nuclear simulation capability will also attract potential industrial collaborations, especially from the leading SMR vendors, such as Babcock and Wilcox (mPower), Westinghouse, and General Electric (Prism), which could provide funding through cooperative research arrangements.

Results and Accomplishments

The project was planned to begin in FY 2012; however, because of the availability of funds, it started just 2 weeks before the closing of FY 2011 and is therefore in its very early stages.

During this time, progress has been made by assembling together several LBM code modules and subroutines (developed by Dr. Jain for his Ph.D. dissertation). The assembled 2D code was able to meet preliminary consistency tests and was able to run on a parallel cluster. The tests were performed on NICS's Kraken machine and utilized 64 compute cores.

Work has also started on integrating VisIt with the assembled 2D code. VisIt is a free parallel visualization software developed at the Lawrence Livermore National Laboratory for visualizing and analyzing large simulation datasets (available at http://www.llnl.gov/visit). VisIt can access several different types of data set formats, including Silo, PDB, HDF5, VTK, etc., in scalar, vector, or tensor formats. In addition, literature survey has started to assess the most suitable and robust formulations of mesoscopic boundary conditions in the MRT-LBM framework.

SUMMARIES OF PROJECTS SUPPORTED THROUGH LABORATORY-WIDE FELLOWSHIPS

WEINBERG FELLOWSHIP

05919

Investigation of Quinone-Containing Organic Molecules as Lithium Cathodes

W. Tenhaeff

Project Description

With anthropogenic climate change at the forefront of public awareness, the impetus to develop energy storage systems to enable plug-in electric vehicles has never been greater. Lithium ion batteries, due to their high gravimetric and volumetric energy densities, are being developed for this application. State-of-the-art cathode materials receiving the most research attention are based on inorganic compounds containing transition metal elements. The limited abundance and cost of some of these transition metals has hindered their commercial implementation. Even for cathodes composed of abundant elements, such as $LiFePO_4$, the cost and pollution associated with high-temperature synthesis must be mitigated. Replacing inorganic cathode materials with organic species may significantly reduce material and manufacturing costs. Moreover, these organic species have the potential of being synthesized from renewable resources. Previously studied organic materials have not materialized into practical cathode materials due to their low-energy capacities. Only recently have organic materials with greater densities of electroactive functionalities, such as quinone species, received greater research interest. In order to understand how the microstructures within organic cathodes influence electrochemical performance, techniques to vapor deposit quinone species into well-defined cathode layers will be developed. The kinetics and thermodynamics of lithium incorporation into these materials will be investigated by integrating them into complete battery cells. The electrochemical, thermal, and mechanical stabilities of the materials will also be elucidated by electrochemical cycling.

Mission Relevance

This project will investigate the technical potential of utilizing organic materials as cathodes in lithium ion batteries. Energy storage is recognized as a critical need for transportation applications and electricity generation by renewable techniques (wind and solar). The DOE offices of Basic Energy Sciences and Energy Efficiency and Renewable Energy (EERE) are investing in battery research and development. In FY 2011, the Batteries for Advanced Transportation Technologies program of the Office of Vehicle Transportation will fund research on novel cathode materials. This project, which seeks to investigate environmentally friendly, low-cost sources for cathodes, is directly relevant.

Results and Accomplishments

In FY 2010, a thermal evaporation technique was developed to synthesize organic thin-film cathodes of 9,10-anthraquinone (9,10-AQ). A significant effort was the optimization of the reactor equipment and vacuum deposition process to yield continuous thin films. Unfortunately, the “as-deposited” films showed

an acicular morphology, which consequently precluded electrochemical characterization due to large grain boundary resistances. In FY 2011, film processing methods were developed to reduce these resistances. The fabrication procedures required to integrate these films into solid state thin-film batteries, which will enable fundamental characterization of electrochemical processes, were also investigated. A pressurized annealing process was developed to densify the deposited 9,10-AQ films and coarsen the acicular crystallites. X-ray diffraction and scanning electron microscopy revealed greater alignmnent of the crystallites parallel to the substrate. The incorporation of the annealed films into thin-film batteries required the sputter deposition of lithium phosphate oxynitride (Lipon) electrolyte directly onto the 9,10-AQ film, followed by thermal evaporation of lithium metal onto Lipon. The fabrication of these two films was successfully achieved, and a reasonable open-circuit voltage was measured. Fourier transform infrared spectroscopy of the Lipon-coated 9,10-AQ films showed that the chemical functionality of the film was retained during the deposition process. However, galavanostatic cycling of the completed thin-film batteries revealed limited capacity of the 9,10-AQ films. It is suspected that the grain boundaries remain too resistive, leading to poor electronic transport. Further efforts are required to control microstructure of these deposited organic films. However, the project was successful in demonstrating that organic cathode films can be integrated with established thin-film battery fabrication techniques. This approach should provide future opportunities to develop fundamental understandings of the electrochemical processes within these films.

05921

An Investigation into the Synthesis and Annealing of Iron-Based Superconductors under High Magnetic Fields

O. Rios, A. Safa-Sefat, G.M. Ludtka, and M.A. McGuire

Project Description

The state of the art in synthesis and processing of class II superconductors has recently made significant advances; however, there have been limited yet promising studies on processing of these materials under extreme conditions, specifically high magnetic fields. The current study investigates the structure, microstructure, and interrelated electrical properties of iron-based superconductors, reaction sintered and/or annealed, under high magnetic fields with the aim of increasing the critical current density at or below the critical transition temperature. It has been well established that magnetic ordering is deeply rooted in the underlying mechanism behind high-temperature superconductivity; therefore, it is expected that the synergistic action of the high magnetic fields and thermal energy will facilitate the growth of crystals that exhibit improved magnetic order below the critical temperature T_c (for superconductors) or Neel temperature (for antiferromagnets). Of the known high-temperature superconductors, the iron-based pnictide class of materials should most strongly respond to magnetic processing due to the strong magnetic properties of the iron atoms electronic structure.

Mission Relevance

Historically, superconductors are key energy materials that are important to the DOE mission and national security. A fundamental understanding of the underlying mechanisms behind superconductivity and how the material properties are affected by the synthesis and processing conditions is vital to the design of the next generation of materials. The current study investigates a relatively unexplored process variable (magnetic fields) that is state of the art in industrially transferable technologies. The results of this study are expected to help establish ORNL's expertise in the advanced high-magnetic field processing and synthesis of superconductors, thus better positioning ORNL in the soliciting future industry participation

and technology transfer through the DOE Office of Energy Efficiency and Renewable Energy Industrial Technologies Program (EERE-ITP) and future Office of Basic Energy Sciences (BES) initiatives.

Results and Accomplishments

We developed the methods and apparatus as well as designed and conducted elevated-temperature high-magnetic-field experiments that resulted in superconductors exhibiting up to a 59% increase in diamagnetic shielding. A high-frequency induction furnace capable of processing iron-based superconductors (SC) under high magnetic fields was designed and integrated into the ORNL 9T superconducting magnet, providing a unique capability at ORNL. Thus far we have magnetically annealed several iron-based superconductors with promising results indicated by magnetic susceptibility measurements. Initially, reaction-sintered samples of $LaFeAsO_{0.90}F_{0.10}$ and $CeFeAsO_{0.88}F_{0.12}$ were annealed at 1300°C under a 9T field in an inert atmosphere. The magnetic susceptibility in both these samples decreased from –0.75 to –0.85 ($4\pi\chi$) (13% decrease) and –0.85 to –1.0 ($4\pi\chi$) (18% decrease), respectively. These results indicate that the advanced processing yields materials that are more "perfectly" diamagnetic. Additionally, synthesis was performed on two pressed pellets of constituents of $NdFeAsO_{0.88}F_{0.12}$. In order to establish a controlled baseline, both samples were pressed from the same batch of components and then reaction sintered either with or without a magnetic field. The orientations of the pellets within the superconducting solenoid magnet were held constant throughout the experiment. The Meissner effect below the critical temperature was enhanced in both the parallel and orthogonal to the field directions, and reductions in susceptibility from –0.17 to –0.27 (emu/g) or a 59% improvement were found in the parallel direction. A modified magnetic synthesis experiment was performed on the $NdFeAsO_{0.88}F_{0.12}$ superconductor based on the promising results found in FY 2010. This experiment included controlled rapid cooling rates to kinetically limit the formation of lower temperature structures during slow cooling. The Meissner effect during the superconducting transition was slightly improved, and the transformation temperature was consistent. X-ray diffraction revealed that the quality of the crystal was improved, and there was no detectable diffraction from impurity phases remnant from the unreached precursors. Susceptibility measurements under a 1000G field revealed two distinct magnetic transitions. This study has led to the submission of an invention disclosure.

The FY 2012 plan consists of additional physical property measurements to investigate the two distinct magnetic transitions found in the $NdFeAsO_{0.88}F_{0.12}$ materials that were synthesized under high magnetic fields. Additionally, the microstructure will be investigated by SEM and limited EF-TEM. The goal is to link the modified electronic and magnetic properties with the crystal structure, microstructure, and morphology. A request for beam time to conduct inelastic neutron scattering experiments at the SNS or HFIR will be submitted in FY 2012. The results of this study should be published in FY 2012. The results of this study are expected to help establish ORNL's expertise in the advanced magnetic processing and synthesis of iron-based superconductors. Research will be supported by ORNL's Shared Research Equipment (SHaRE) User Facility, which is sponsored by the Office of Basic Energy Sciences, US Department of Energy.

05935

First-Principles Calculations and Computational Thermodynamic Modeling of Zn-S and Sn-S to Support Identifying Thermal Decomposition Pathways for Fabricating a New Photovoltaic Material, Cu_2ZnSnS_4

D. Shin

Project Description

Cu_2ZnSnS_4 (CZTS) has recently gained great interest as an inexpensive candidate photovoltaic material; however, the complex chemistry of Cu-Zn-Sn-S makes the optimization of a high-efficiency CZTS synthesis process difficult. Computational thermodynamic modeling of Cu-In-Ga-Se played an important role in identifying thermodynamic decomposition pathways for the $Cu(In,Ga)Se_2$-based photovoltaic devices production, and similar benefits are expected for CZTS. Current thermodynamic modeling for Cu-Zn-Sn-S is limited to Cu-Zn-Sn and Cu-S, but due to the high sulfur content of CZTS, thermodynamic modeling of Zn-S and Sn-S are necessary. Thermochemical measurements, such as heat capacities and formation enthalpies, directly affect the thermodynamic modeling quality and are thus preferred, but available data for Zn-S and Sn-S is only limited to phase equilibrium data. Evaluating thermodynamic parameters only with the phase boundary data may satisfy the relative Gibbs free energy among the phases to reproduce experimental phase boundaries, but they may be completely incorrect and hamper reliably extrapolating their energies to the higher order systems. First-principles calculations in this regard can provide thermochemical properties of sulfides to supplement scarce experimental data, and I propose a hybrid computational thermodynamic investigation, that is, a thermodynamic modeling and first-principles study on Zn-S and Sn-S.

Mission Relevance

Currently available photovoltaic materials are chalcogenide based, and their usage of toxic (cadmium) or expensive (indium and tellurium) elements is projected to restrict the production of these solar cells. Thermodynamic modeling of Zn-S and Sn-S will eventually provide insight into the production of non-toxic and inexpensive new photovoltaic materials based on CZTS and will help garner new funding opportunities from DOE, such as EERE's focus on solar energy technologies program.

Results and Accomplishments

The primary FY 2011 effort focused on the thermodynamic modeling of the binary sulfide phases in the Sn-S system. Available Gibbs free energy descriptions for the solid phases in Sn-S, SnS, SnS_2, Sn_2S_3, and Sn_3S_4 have been taken from the SGTE (Scientific Group Thermodata Europe) substance (SSUB) database. Thermodynamic description for the liquid phase for SnS was also taken from the SSUB database, and interaction parameters for the liquid phase have been evaluated to reproduce the experimentally observed two miscibility gaps for the liquid phase in this system with an associated model. Currently thermodynamic model parameters for all the phases in the Sn-S system are globally being optimized to reproduce experimentally observed phase boundary data.

05978

Advanced Technology for High-Current Electromagnetic Isotope Separation

B.J. Egle, Ph.D.

Project Description

The 2009 Nuclear Science Advisory Committee (NSAC)–Isotope Subcommittee recommended as a top priority the reestablishment of domestic stable and radioactive isotope enrichment capabilities. Electromagnetic isotope separation (EMIS) was identified as the separation technology that is the most flexible and capable of high enrichment for a majority of the Periodic Table. This project's overarching goal will be to investigate transformational technologies for key systems (i.e., ion source and analyzer magnet) for the electromagnetic separation of stable and radioactive isotopes. The primary aims are as follows: (1) Develop an ion source that is capable of approximately 100 mA of usable ion current with a lifetime greater than 250 hr. The deliverable for this project is a preliminary design for a prototype electromagnetic isotope separator that incorporates novel features compared to current EMIS systems. (2) Investigate the feasibility of alternative magnet technologies used for EMIS systems including superconducting and permanent magnet components.

Mission Relevance

The Department of Energy's Office of Science, Office of Nuclear Physics (DOE-NP) has received the recommendations of the 2009 NSAC isotope report to reestablish a domestic stable isotope enrichment capability. One of the recommendations will require three to six high-current (100 mA) EMIS devices at a cost of $2 million to $3 million per device or an equivalent alternate separation method. The development of innovative ideas to advance the mature technology of EMIS will provide ORNL with a competitive advantage to respond to the anticipated call from DOE for a full-scale stable isotope enrichment facility. In addition to isotope separation, the new ion source technology developed in this project will be directly applicable to ion implantation equipment that is widely used in the semiconductor equipment industry which, in North America, is estimated at $4 billion annually.

Results and Accomplishments

During the initial stages of this Weinberg Fellowship project and during the execution of the DOE-NP-sponsored 10 mA EMIS project, an improved understanding of the requirements and constraints of stable and radioactive/actinide EMIS technology has been developed. The ion source is a primary constraint on the performance of EMIS technology. During a review of existing ion source literature, a new concept for improving ion source performance has been developed. A new concept for the magnet and ion optics system is also being developed as part of this project; Superconducting Spiral Electromagnetic Isotope Separation has the potential of improving isotopic separation while reducing the physical footprint of the device. Additionally, a network of internal and external experts continues to be developed to help consult on both the ion source research and the radioactive isotope EMIS research.

05979

Light-Water-Reactor TRISO Particle-Metal-Matrix Composite Fuel

K. Terrani

Project Description

This project will evaluate the feasibility of an advanced light-water-reactor (LWR) nuclear fuel concept that offers exceptional reliability, high power rating, and ultrahigh burnup levels. The main concept involves incorporating the established benefits of tristructural isotropic (TRISO) coated fuel particles into LWRs in the most effective manner. To achieve this goal, a novel fuel design is proposed where the fuel rod design is fundamentally altered: instead of fissile/fertile pellets clad in zirconium alloy tubing, the fissile/fertile material encapsulated in TRISO particles is directly dispersed in a matrix of zirconium alloy to form an integral rod that contains multiple barriers to fission product release and eliminates the thin-walled cladding. The work performed under this project has identified applicable processing methods and parameters for fuel rod fabrication and is continuing to optimize such. This work is aiming to provide a knowledge foundation specific to this fuel concept with regards to fabrication, in-pile behavior, and reactor physics aspects. This in turn shall provide the basis to move past laboratory-scale experiments to small- and large-scale irradiation testing of this innovative fuel concept for its eventual full-scale deployment.

Mission Relevance

This research is well aligned with the DOE Office of Nuclear Energy goals defined in the Fuel Cycle R&D (FCRD) and LWR Sustainability programs. Specifically, the Advanced Fuels Campaign (AFC) in the FCRD program has begun including this fuel concept in its portfolio of fuel concepts. This fuel concept effectively addresses the needs identified by the AFC for advanced LWR fuels, a revolutionary fuel design that offers exceptional reliability, higher operational margins, and improved accident performance.

Results and Accomplishments

Over the last year significant steps in realization of this fuel concept have been taken. Initially the fuel form was fabricated by hot pressing. The fuel consisted of surrogate TRISO particles (where the uranium-bearing fuel kernel is replaced with zirconia) dispersed in a pure zirconium metal matrix. Some basic processing parameters (temperature, pressure, duration) were established through this early study. After this step, hot isostatic pressing was used to fabricate fuel-rod segments in a more representative cylindrical shape. Various TRISO particles with outermost layer coatings of pyrocarbon, silicon carbide, and zirconium carbide were incorporated into the zirconium metal matrix using this process. The fabrication method readily produced a fully dense matrix that hosts the fuel particles without any damage to them. Extensive characterization of the fuel system has been accomplished and is still ongoing. Scanning and transmission electron microscopy on the matrix and particle-matrix interface has been performed. A successful proposal to Advanced Photon Source at Argonne National Laboratory was submitted, and a micro X-ray diffraction study at the particle-matrix interface was completed to identify the various phases that form during the fabrication stage. Yet the most notable accomplishment is irradiation testing of fuel rods containing surrogate TRISO particles in the ORNL High Flux Isotope Reactor (HFIR). The fuel rods were fabricated to the exact cross-sectional geometry of pressurized water reactor fuel rods with a length of 55 mm. The rods underwent irradiation in the flux trap in HFIR for one cycle (equivalent to ~1.5 years in LWR environments) and were successfully extracted from the core and disassembled in the hot cell; no signs of deformation were observed. Postirradiation examination of these rods will be performed in FY 2012.

Information Shared

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05980

Intelligent Advanced Propulsion Systems

A. Malikopoulos

Project Description

Hybrid electric vehicles (HEVs) have shown great potential for enhancing fuel economy and reducing emissions compared to vehicles powered only by internal combustion engines (conventional vehicles). The main advantage of these powertrain configurations is the existence of two individual subsystems, thermal (internal combustion engine) and electrical (motor, generator, and battery), that can power the vehicle either separately or in combination. The power management control algorithm in HEVs determines how to split the power demanded by the driver between the thermal and electrical subsystem so that maximum fuel economy and minimum pollutant emissions can be achieved. State-of-the-art power management control algorithms cannot guarantee continuous optimum operation of an HEV for all the different driving styles.

The research proposed here intends to develop the theoretical framework and algorithms for making an HEV that continuously realizes its most efficient operating point for any driving style. It is intended to draw from stochastic control theory research in a wide range of areas, including reinforcement learning, game theory, agent modeling, and evolutionary computation, in an attempt to develop the theory and algorithms to address this problem. The long-term potential benefits of this approach are substantial. True fuel economy of HEVs will be increased while meeting emission standard regulations with respect to any driving style. Having the HEV always operate at its most efficient operating point is equivalent to achievement of fuel economy and emissions benefits as fully as possible for that particular HEV configuration; for further improvement, new technologies for individual subsystem (e.g., engine, motor, generator, and battery) should be realized.

Mission Relevance

The research conducted in this project will aim to reduce the discrepancy between posted gas mileage estimates and actual mileage; drivers will be able to evaluate their driving behavior and learn how to improve fuel economy and reduce emissions by modifying it. True fuel economy of vehicles will be increased while meeting emission standard regulations with respect to any driving style; drivers will be able to evaluate their driving behavior and learn how to improve fuel economy and reduce emissions by modifying it. The research conducted in this project will promote scientific and technological innovation to advance the national, economic, and energy security of the United States.

Results and Accomplishments

An extensive literature review was conducted on stochastic optimization and control theory with an emphasis on infinite-time-controlled Markov chains. The theoretical framework along with the mathematical modeling was developed, and the proposed power management control algorithm was implemented on a simple HEV model. The literature review and theoretical development were documented in a paper entitled, "Equilibrium Control Policies for Markov Chains," which will be

incorporated in the proceedings of the 50th IEEE Conference on Decision and Control (CDC) and European Control Conference, held in December 2011.

In an effort towards understanding the impact of a driving cycle on fuel economy, a driving style factor was identified that is highly correlated with fuel consumption. This factor was named the coefficient of power demand, which is described by the product of vehicle velocity and acceleration. At instances of high power demand, the fuel consumption rate of the vehicle is at its greatest. This factor was used to identify the specific parts of the driving cycle that can be altered in order to minimize the overall fuel consumption. To achieve this, mathematical models were constructed that describe driving cycles as well as approximate fuel consumption as a function of the coefficient of power demand. An optimization algorithm was used to find the optimal values of acceleration that will yield the lowest fuel consumption. This information is then utilized to construct a new, more efficient driving cycle.

The research work completed this year established the foundation for future funding opportunities and collaborations with the DOE Vehicle Technologies program. More specifically, the expansion of this work, that is, to ultimately develop autonomous intelligent propulsion systems capable of learning their optimal operation in real time while the driver is driving the vehicle, was proposed to the Vehicle Technologies program. The proposal was granted $200,000 for the FY 2012, with possible extension into FY 2013 for experimental validation using the new Vehicle Systems Integration Laboratory adjacent to the NTRC 2.

Information Shared

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06234

A Current Source Boost Inverter–Based Power Electronic Interface for Grid-Connected Photovoltaic Applications

O.C. Onar

Project Description

This study focuses on utilization of a current source inverter as a single-stage power electronic interface for grid-connected photovoltaic (PV) system applications. Conventionally, PV systems require two or three stages in order to connect them to the grid. All of these conversion stages increase the overall losses and result in lowered conversion efficiency. Moreover, each conversion stage requires a number of power electronic components along with the passive power components, which increase the overall cost. The objective of this study is to reduce the cost, size, and volume of the inverter and increase the efficiency through a new design and control system.

The objective of this study is to utilize a current source inverter with an input inductor instead of an electrolytic dc link capacitor based voltage source inverter. Current source design helps control the input current of the inverter, hence providing maximum power point tracking (MPPT) and is able to boost the

voltage without a need for a boost dc/dc converter or a transformer, as is the case with the voltage source inverter.

Specific goals and research plans consist of computer modeling and analysis, control system design and development through simulations, comparison with conventional configurations, and experimental validation. In computer modeling, models of the PV module, inverter, and control system will be developed using MATLAB/Simulink and SimPowerSystems physical modeling tools. The proposed control system design will include MPPT through input current control and output voltage regulation with grid synchronization through a single-phase phase locked loop (PLL) system. During the comparison with conventional inverters, the operational characteristics of the proposed single-stage inverter will be compared to the other existing grid interconnection schemes. During the experimental validation phase, an experimental setup will be built to validate the applicability and feasibility of the proposed grid interconnection system.

Mission Relevance

The proposed project is highly relevant to the DOE missions on energy resources and environmental quality. Since most of the transportation energy is imported from the foreign countries unstable politically and economically, solar residential applications will enhance the national energy security and independence, as more plug-in electric vehicles will be powered from domestically generated clean energy sources. As America's need for energy grows, the proposed project is capable of meeting the challenge by establishing a cost effective and highly efficient solution for the widespread commercialization of photovoltaic power generation. This would enhance the diversity of the energy sources and greatly reduce the dependence on fossil fuel operated power plants and imported oil. In addition, DOE aims to harness as much renewable power as possible to meet the energy needs. Advances in solar will allow the U.S. to take the advantage of clean, abundant energy for both residential and transportation energy demands. Since the power demand from buildings will increase and plug-in vehicles will introduce a new demand, the grid infrastructure will need a modernization in the near future. However, switching to the locally generated power can reduce the modernization costs of the transmission and distribution infrastructures while also eliminating the possible capacity additions to the current conventional power plants.

Results and Accomplishments

A model of the PV system has been completed. Currently, the verification of the model is in progress by comparing the PV characteristics with other models and manufacturers' data sheets. The electrical equivalent circuit model of the PV has been completed as well. A brief review of most of the available techniques has been completed, and a method that automatically responds to the changes in both irradiance and temperature has been implemented within the current source inverter. Next steps include completing the single-phase PLL implementation of the inverter for grid synchronization. A single-phase space-vector pulse width modulation (SVPWM) has also been created for the inverter's switching sequences and will be implemented within the proposed control system. Building the experimental setup and validating the concept will take place in the following fiscal year.

06235

Real-Time, Portable Neutron Spectroscopy Using a Filtered and Moderated Semiconductor Detector Array

M.J. Harrison

Project Description

The proposed device will use several arrays of high-efficiency thermal neutron semiconductor diode detectors embedded within a moderating medium. These devices are ideal for field use, as they are lightweight, require very little external power to operate, and can achieve high thermal neutron detection efficiency. Each array of detectors will be placed within a moderator and behind various filters to yield optimal specificity for a selected neutron energy range. Unfolding the response of all arrays using standard unfolding algorithms, such as MAXED, will return the incident neutron energy spectrum within seconds. The final optimized instrument is expected to weigh less than 30 lb, complete with batteries and readout display. Computational design verification, benchtop prototype construction, and proof-of-concept testing and evaluation will be performed as part of the project.

Mission Relevance

Detection and identification of special nuclear material (SNM) is a critical mission of DOE. The development of a rugged, handheld instrument capable of not only detecting a neutron source but also identifying the source based on its spectral signature will provide field operations personnel on-site capabilities far exceeding the current technological limit. The work will be most meaningful to the DOE Office of Nonproliferation Research and Development (NA-22). Other agencies likely to benefit from the development of the proposed instrument include the Department of Homeland Security, specifically the Domestic Nuclear Detection Office, and the Department of Defense, specifically the Defense Threat Reduction Agency. Each of these agencies has been tasked with SNM detection goals similar to those of DOE's National Nuclear Security Administration for their respective departmental operations.

Results and Accomplishments

A thorough computational investigation was conducted to determine the effectiveness of using several alternative materials for neutron energy filtration. Given the computational demands of investigating combinations of 39 different materials in the more complex geometry necessary for the instrument, a computationally less burdensome method of eliminating candidates was sought. To this end, a two-stage investigation was performed. During Stage 1, secondary effects such as neutron scattering, thermalization, and reactions were ignored, and the bulk of the investigation was performed from an analytical point of view to simply reduce the design space to a computationally manageable size. Stage 2, however, involved a more realistic approach and was primarily performed using Monte Carlo techniques to better incorporate the aforementioned secondary effects.

First, in Stage 1, each individual candidate material was inserted into a simple Monte Carlo model to determine each element's ability to filter different energies of incident neutron fluxes. A parallel flux uniformly distributed in energy was then directed perpendicularly onto a thin sheet of the candidate material. The flux spectrum then tallied at the opposite face of the sheet was recorded for each of the 39 candidate materials The candidate materials investigated included enriched ^{6}LiF, enriched ^{10}B, and the naturally occurring elements Na, Mg, P, Cl, Co, Cu, Zn, Ga, Ge, As, Se, Br, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Te, I, Ba, Eu, Gd, Er, Hf, W, Au, Hg, Pb, and Bi.

The resulting exit flux spectra were then utilized to estimate an exponential attenuation coefficient at each energy value. This exercise thus provided an array of exponential attenuation coefficients for each candidate material. Next, these exponential attenuation coefficient arrays were utilized to explore the possibilities of using multiple materials to create neutron energy filters with unique and useful characteristics.

Combinations of up to four candidate materials, each at various thicknesses, were then created, and the resulting filtered spectra were computed from an input spectrum using an analytical exponential approximation.

To determine the effectiveness of the filters, a detection spectrum was then approximated by considering the fraction of the flux as a function of energy that was stopped in a 100-µm-thick ^{6}LiF thin film. This ^{6}LiF film was used to approximate the detectors that will eventually be used.

Finally, the detected spectrum for each material and thickness combination was inspected for usefulness using a key metric, called the positive likelihood ratio (LR). First, sensitivity and specificity were computed at intervals over the range of incident energies. From the computed sensitivity and specificity values, a positive LR was determined at each energy bin.

The analytically approximated detection spectrum for each material and thickness combination was thus gauged using the LR calculated at various finite energy bins. Those combinations achieving a high LR as found in Stage 1 were tagged for further investigation. It was found after this lengthy computation that only a few materials of the originally investigated 39 were of any real interest—Cd, enriched ^{10}B, and enriched ^{6}LiF.

During Stage 2, a series of more complex Monte Carlo simulations were developed to better incorporate the effects of scattering and moderation. In this stage, the possibility of adding moderator between filter layers was added. A number of Monte Carlo simulations were prepared to investigate the various combinations of filter materials, their respective thicknesses, and the thickness of an intermediate moderator slab. In total, 9,822 combinations of materials and thicknesses were simulated for the defined geometry.

A detection spectrum was next computed for each combination and analyzed using the LR as performed in Stage 1. This resulted in a number of combinations yielding high neutron filtration performance. Of the originally analyzed 9,822 combinations, those whose performance was rated in the top 10% were kept for further computational refinement, in which the energy step sizes in computing the detected spectra were reduced from 1/4 to 1/10 of an energy decade. Preliminary results from this computational refinement step have shown remarkable promise. Several combinations already yield much better LRs than those computed for the standard Bonner spheres spectrometer (BSS), an outcome predicted to enable this device design to yield significantly better neutron energy resolution than is currently available with BSSs.

Information Shared

An abstract was submitted to the 2011 IEEE Nuclear Science Symposium to be held in Valencia, Spain, in late October 2011. The topic of the abstract covered the computational work discussed above. The abstract was accepted for oral presentation, and an accompanying paper will be submitted to *IEEE Transactions in Nuclear Science* in 2012.

WIGNER FELLOWSHIP

05908

Low-Dimensional Multiferroicity

X. Xu

Project Description

Multiferroic materials exhibit more than one ferroic order simultaneously and thus have many advantages over other materials. For example, multiferroic materials are promising for high density and energy efficient information processing and storage, and possibly solar energy harvesting, because of the multiple ferroic orders and the coupling between them. The big challenge is to find a multiferroic material with a high ordering temperature, large polarization, and strong coupling. One promising way of achieving this overarching goal is to study the existing material and improve its properties by tuning the chemical substitution, structure, and dimensionality. Among many means, tuning dimensionality provides great opportunities: (1) the quantum size effect changes the electronic structure of the nanoparticles drastically compared with the bulk counterparts; (2) the surface and edge states not only give large strain that can tune the materials' properties or even stabilize the phases that are not stable in bulk case, but also introduce completely new states; (3) nanoscale materials allow the possibility of manipulating the individual domains (domain walls), whose dynamics are critical for application. So far, little research has been done on nanoscale physics of multferroics because the former is mostly concentrated on relatively simple system. Our objective is to grow high quality epitaxial multiferroic thin films and tune/study their properties at low dimensionality. This will not only bring more insight into the mechanism of multiferroicity but also help realize the desired material properties.

Mission Relevance

The field of multiferroics is so interesting for fundamental science and commercial application that it was selected by *Science* magazine as one of the top seven "Areas to Watch" in all of science for 2008. Successful fabrication of new types of low-dimensional multiferroics will open up a whole set of new opportunities for fundamental scientific research as well as device making. For example, taking advantage of the unique material tailoring in low dimensions is promising for improving the functional properties of multiferroics. Moreover, multiferroics are promising for a new candidate of solar energy harvesting materials with more efficiency and tunabilities.

Results and Accomplishments

During FY 2011, we are focused on growing $LuFe_2O_4$ films on MgO(111) substrates, based on the conclusion made from the FY 2010 work that this is the best substrate candidate. We studied the growth condition comprehensively. Based on the results we have constructed a growth diagram. The parameter space for growing epitaxial $LuFe_2O_4$ thin films turns out to be a narrow window of temperature and oxygen pressure, which creates significant experimental difficulty. Application of the correct

thermochemistry is the key to preferential formation of the $LuFe_2O_4$ phase. Several conditions must be satisfied simultaneously: (1) high temperature, because $LuFe_2O_4$ is a metastable phase that can only be formed at >900°C; (2) low oxygen pressure, to prevent oxidizing the Fe2+ atoms in the material; and (3) simultaneously, the temperature cannot be too high and the pressure cannot be too low because different desorption coefficients of Fe and Lu atoms cause the Lu:Fe stoichiometry to deviate from 1:2.

Typical $LuFe_2O_4$ films consist of $LuFe_2O_4$ clusters separated by h-$LuFeO_3$ layers and defects. While the observed Neel temperature of the film is very close to the bulk value, the hysteresis is surprisingly weaker, resulting in superparamagnetism in the films. The demonstration of epitaxial growth of $LuFe_2O_4$ thin films and the distinct magnetic properties open up new possibilities for studying multiferroicity of low dimensional $LuFe_2O_4$, tuning of its properties, and eventual functionalization.

Information Shared

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05910

Advanced Algorithms and User Interfaces for Personalized Data Mining of Biomedical Images and Literature

S. Xu

Project Description

With the exploding size of biomedical literature and images published to date, finding biomedical knowledge relevant to one's research interests and professional practice in a timely manner is becoming increasingly challenging. In this project, we will design and implement intelligent query- and behavior-based algorithms and user-friendly interfaces to facilitate biomedical knowledge discovery through accurate and timely access, selection, delivery, and personalized recommendations. Our project goals can be broken down into the following three phases: in Phase I, we will develop advanced image text extraction methods; in Phase II, we will develop user-friendly interfaces for accessing biomedical knowledge, aiming at fostering more natural human-computer communications during an end user's knowledge access process; and in Phase III, we will look for new opportunities to promote biomedical knowledge access through fusing knowledge from multiple sources. Overall, this project aims at developing novel computational tools and methods for facilitating access to and discovering knowledge from biomedical document and image collections.

Mission Relevance

The primary research on this project will focus on developing advanced image and text search models, ultimately merging unique techniques into a powerful software environment for data access and mining. This work is of strategic interest to DOE and in an area of growing science focus at ORNL: Knowledge Discovery. This research area is the science agenda thrust of the Computational Sciences and Engineering Division and has direct relevance to DOE interests in national security, energy assurance, and basic

science. The successful achievement of this research will also result in direct impact across several directorates at ORNL, with important practical applications to NIH and DOD.

Results and Accomplishments

We developed an advanced biomedical image text extraction method that processes biomedical images published in literature for identifying the embedded text. In studying the effectiveness of this new algorithm, we evaluated its performance on a set of manually labeled random biomedical images and compared its performance against other state-of-the-art text detection algorithms.

Generating personalized document summaries that observe the preferences of individual readers was one area of study. We proposed a new personalized document summarization method that observes a user's reading behaviors, including user facial expressions, gaze positions, and reading durations, during his or her past reading activities to infer the user's personal reading preferences. The result of this comparative study shows that the algorithm can produce personalized document summaries superior to those from peer methods.

We proposed a personalized webpage re-ranking algorithm by exploring a user's dwell times in his/her previous readings over individual documents. The algorithm first models concept-word-level user dwell times. To understand a user's personal interest, according to the estimated concept-word-level user dwell times, the algorithm then infers a user's potential dwell time over a new document. Based on the inference results, the algorithm can re-rank webpage search results in a personalized way. Rankings produced by this algorithm were compared with rankings generated by popular commercial search engines and a recently proposed personalized ranking algorithm. The results clearly show the superiority of this method.

Information Shared

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05911

Optical Characterization of Bacterial Dynamics in a Microfluidic Environment

A. Kumar

Project Description

Bacterial motion represents an extremely rich class of dynamical behavior. Bacteria can respond to a variety of external stimulants, and one recently discovered bacterial motility response, termed electrokinesis, is present in proximity to a redox active surface. However, a proper understanding of this motility response and its dependence on concomitant processes is lacking. Such lacunae in our understanding impede progress in the noninvasive control of microbal processes. Hence we propose a research plan that leverages microfluidics and advanced optical characterization to explore this dynamical behavior. A microfluidic system optimized for real-time characterization will be developed. Additionally, two-color velocimetry, total internal reflection microscopy, and optical tweezing will be developed to explore microbial systems. These developments will be used for elucidating electrokinesis and its dependence on various parametric conditions. Such fundamental investigations into bacterial motility are expected to contribute to very relevant issues of alternative energy generation and biological remediation.

Mission Relevance

Fundamental understanding of microbial systems is relevant to the DOE mission of scientific discovery and innovation. Such understanding is expected to benefit prevalent renewable energy systems and environmental remediation projects, and thus the project is also relevant to the DOE mission of energy security. Specifically, the proposed investigation is expected to appeal to the DOE Office of Biological and Environmental Research (DOE-BER).

Results and Accomplishments

During FY 2011, progress was made in the study of bacterial dynamics under the influence of an external electric field. Miniaturized platforms for the investigation of the influence of electrodes and electric fields on microbial dynamics were constructed. Electric-field-induced reduction of biofilm formation and flocculation of microbes like *E. coli* were observed with the use of such a platform. A manuscript summarizing the results was published.

A complementary approach that uses complex microfluidic devices to observe long-term aggregative microbial dynamics is being developed. Some microfluidic devices have been fabricated. Fabrication and design of other microfluidic devices are in progress. These devices are enabling the real-time monitoring of aggregative bacterial dynamics and the influence of external factors on such dynamics.

Information Shared

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05913

Studies of Charge Particle Emitters at the Limits of Bound Nuclei

K.A. Miernik

Project Description

This project aims to better understand nuclear structure evolution. New data will be gained in the decay studies of very exotic radioactive nuclei. The exotic isotopes at and beyond the limits of bound nuclei will be investigated using charge particle spectroscopy methods. Measurement of properties such as emitted particles energies and the correlation between them and the nuclei characteristic half-life allow us to study nuclear structure evolution of very exotic nuclear systems that are not accessible with other techniques. The super heavy nuclei will be investigated at the Joint Institute for Nuclear Research at Dubna (Russia) and at the Heavy-Ion Research Laboratory at Darmstadt (Germany), and new two-proton radioactivities will be studied with the Optical Time Projection Chamber based on Gas-Electron Multiplier technology at the National Superconducting Cyclotron Laboratory at Lansing, Michigan. Novel detection techniques will be developed at ORNL and applied to facilitate the studies of these very rare nuclei.

Mission Relevance

One of the main scientific missions noted in the 2007 U.S. Long Range Plan for Nuclear Science is the identification and understanding of the limits of the Periodic Table of elements as well as understanding of nuclei at extreme proton-to-neutron ratios. The experiments aiming at the nuclei beyond the two-proton drip line and in new super heavy nuclei are particularly well suited to this mission statement. The research on radioactive nuclei, in particular on new chemical elements, is relevant to DOE activities by promoting science about and expanding human knowledge on atomic nuclei.

Results and Accomplishments

The two-proton radioactivity study has been successfully accomplished for the doubly magic nucleus ^{48}Ni. The experiment was performed at the National Superconducting Cyclotron Laboratory at Michigan State University (Lansing, Michigan) in March 2011. It yielded the first unambiguous detection of two-proton emission from ^{48}Ni. The key to this accomplishment was a novel Optical Time Projection Chamber detector as well as a rotating target device developed at ORNL and the University of Tennessee. The rotating target allowed the researchers to use the high primary beam intensity required to produce the extremely rare ^{48}Ni ions. Its application opens possibilities of further experiments on exotic nuclei where withstanding high intensity beam is critical for success. The observation of two-proton emission from ^{48}Ni is important for understanding the structure of open quantum systems such as unbound exotic nuclei [Pomorski 2011, Miernik 2007]. Decay study of ^{43}Cr, a nucleus located in the doubly magic ^{48}Ni region, revealed closely related phenomena of one, two, and three beta delayed proton emission data on ^{43}Cr obtained during the experiment of ^{45}Fe [Miernik 2007, Miernik 2007a], which were analyzed recently and published [Pomorski 2011a].

An experiment searching for the new superheavy element Z=120 was performed in April 2011 at the GSI Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany. This was a first attempt to produce a microsecond activity of the new element Z=120 using ^{54}Cr beam and ^{248}Cm target material originating from ORNL. The dedicated digital data acquisition system developed by the ORNL–UTK collaboration was shipped to GSI and successfully integrated with the analog data acquisition system used at the SHIP recoil separator facility. It was demonstrated that the pile-up signals were detected down to correlation times of around 0.4 microsecond, which facilitates the observation of very short-lived activities. The remaining 100 days of allocated beam time are currently a subject of scheduling GSI accelerator time.

Information Shared

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05914

Control of Ionic Flux by Nanofluidic Diodes

I. Vlassiouk

Project Description

In this project we will construct nanofluidic diodes/transistor devices that can control the ionic flow in nanochannels in a fashion similar to how electron current is controlled by solid state diodes. Such nanofluidic devices coupled with semiconductor elements can be combined into hybrid electrical circuits useful in various biomedical applications where targeted substance delivery is required. Given that nanofluidic diodes can be constructed as small as biochannels, these artificial devices potentially can mimic the biochannels and even perform with the mechanisms/degree of control surpassing their natural counterparts.

Recently we have constructed and theoretically described nanofluidic diodes with large aspect ratios; that is, these devices had a substantial length (>1 μm). Our theory predicts that those devices are operational even with a length smaller than 5 nm. The major goal for this project is fabrication of the nanofluidic devices with sizes of biological channels which allow for precise *external* ion flux control. Such devices have never before been fabricated.

Mission Relevance

Nanofluidics deals with delivery on demand on a femtoliter scale. Given the possibility to integrate the proposed diodes and transistors to the more complex lab-on-chip devices as well as make them compatible to living organisms, such research constitutes the cornerstone for separation/filtration, further miniaturization of the biotechnological devices, and biosensing down to a single molecule.

Several DOE programs will benefit from the project, for example, Biological and Environmental Research, Material Sciences and Engineering, and others.

Results and Accomplishments

We have extended our expertise in thin membranes made from 1-atom-thick carbon material, graphene. Currently, silicon nitride (SiN) membranes can be made no thinner than 20 nm, while graphene membranes are 0.33 nm thick, which gives an opportunity to mimic biological membranes and even surpass them in nanopore dimensions. Given then graphene is electrically conductive, such material allows for external control over the ionic flux through nanopore by several mechanisms.

Such membranes are expected to allow enormously high fluxes with low energy input, which will be highly beneficial for various applications such as water desalination, protein/DNA separation, etc.

In this project we (1) investegated mechanism of graphene growth, (2) developed a process for high quality graphene synthesis, (3) fabricated graphene membranes, (4) measured ionic flux through such atomically thin membranes, and (5) fabricated artificial voltage gated nanopore.

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05915

Unlocking Emergent Phenomena in Complex Materials through Spatial Confinement

T.Z. Ward

Project Description

Two of the most widely studied areas of condensed matter physics are complex materials and nanoscale behaviors. Surprisingly, there has been very little crossover between these two fields, as the majority of the nanophysics research being conducted uses “simple” materials such as metals or semiconductors instead of complex materials such as colossal magnetoresistors or high T_C superconductors. Because of the strong electronic correlation in many complex materials, it is exactly these systems that are the most likely to lead to observations of striking new phenomena under spatial confinement. Indeed, recent studies on several spatially confined manganite systems have led to never before seen behaviors that offer the promise of new device functionalities while broadening our fundamental understanding of emergent phenomena in these materials. This project is the first step in creating a strong ORNL program for understanding and controlling the many electronic correlations that drive complex materials at low dimensions.

Mission Relevance

This project aims to experimentally explore the fundamental mechanisms that drive complex materials and to explore new behaviors under confinement. This is a relatively new concept but is quickly gaining momentum in the scientific community, as recent discoveries show that these techniques may lead to a new class of electronic devices that offer lower cost and energy consumption. As such, this project upholds DOE’s commitment to drive basic scientific discovery in order to drive economic competitiveness. The discoveries made in this LDRD are laying the cornerstones for a paradigm shift in consumer electronics where chaos-driven materials replace existing devices.

Results and Accomplishments

Complex materials can exhibit a wide range of fascinating and, potentially, technologically revolutionary behaviors, such as colossal magnetoresistance, multiferroicity, and high temperature superconductivity; however, in ultrathin or highly strained films, many of these materials have active temperature ranges that are too low for practical applications or lose their exotic properties altogether. This is due to the frustration in the delicate electronic balance present in these systems.

To overcome this hurdle, we used the magnetic properties of iron nanodots to control the electron spin in a frustrated complex manganite compound. The result was a complete recovery of magnetoresistance and active temperature range. It was also discovered that changing the density of the nanodots on the film surface allowed these properties to be highly tunable.

These findings offer a new means to quantitatively investigate the balanced energetics that drive complex materials and promise a simple way to increase and tune critical temperatures in frustrated films for future applications (PRL 2011).

By confining electronically phase separated materials to the same scale as the coexisting electronic regions that reside within, we have found that it is possible to isolate and observe a single or few of these regions as they seed, grow, and transition, which allowed for the effects of electric field, temperature, and current on these processes to be studied. From this, we have made several new discoveries leading to a better understanding of the underlying physics of phase coexistence and the ability to finely tune the dynamics of single electronic domains. These findings are of central importance to several new technologies that rely on phase competition, such as resistive random access memory (faster computing), magnetic cooling (higher energy efficiency), and next-generation bolometry (night vision applications) (PRB 2011).

Invited talks on these findings were given at the American Physical Society March Meeting, the Telluride Workshop on Competing Interactions and Colossal Responses, and the American Vacuum Society 58th International Symposium.

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05981

Algorithmic Challenges in Computational Science on the Path from Petascale to Exascale

M. Berrill

Project Description

I developed a three-dimensional (3D) model for oxide layer formation and growth in the cladding of a nuclear fuel rod. The oxide layer growth has an important effect on both the mechanical and thermal properties of the cladding and has not been modeled in 3D. The growth of the oxide is affected by the

local properties and thermal transport. The different spatial scales for the oxide layer and the fuel rod necessitate the development and use of algorithms that scale and will likely require some form of Adaptive Mesh Refinement (AMR). Additionally, a full coupling to multiphysics models, including stress and thermal transport, is necessary. The project deliverable is a 3D model capable of understanding the oxide layer growth that can be integrated into large models for nuclear fuel.

Mission Relevance

By working on improving the algorithms and underlying scaling limitations, a significant impact on a number of petascale problems can be made. If the efficiency of the model is increased significantly, then it is possible to simulate current problems that would not otherwise be possible. In extended MHD, this can easily lead to discoveries that will help to improve fusion plasmas, such as the conditions in ITER; in climate modeling, it may be possible to better understand weather patterns and climate change that might affect our future. Additionally, many other problems may also be accessible though these improvements as a wide variety of problems have the common need for high spatial accuracy, large simulation times, a variety of timescales, and large-scale modeling.

Results and Accomplishments

Efforts of my R&D targeted two primary areas: NEAMS and plasma modeling. A potential problem for nuclear fuel is oxide growth on the cladding. This oxide growth reduces the heat flux, resulting in higher cladding temperature, and serves as a site for additional corrosion of the nuclear cladding. To date, understanding the oxide growth has relied on experimental measurements and simple 1D models. While these models can predict the oxide growth for a given set of conditions, they cannot account for the growth on the full clad, which experiences a variation across the entire surface. To address this I worked on coupling an oxide growth model with a full 3D nuclear fuel model (AMP). The resulting code will be able to model the variation in the oxide growth across the entire surface by using spatially dependent properties. To date, I have successfully created the basis for the oxide model and validated its accuracy. I created a relatively simple 1D model that could be easily compared with existing measurements and simulations. While this model is only 1D, it does demonstrate the numerical technique used and can be extended to 3D to cover the entire surface of the cladding. An important difficulty to overcome is the large variation in scales between the size of the cladding and the oxide thickness. The model will work on a different spatial grid to allow it to adaptively use the minimum number of calculations necessary to simulate the oxide growth at a particular point. This will be coupled to a nuclear fuel grid using the surface subset of the full simulation. To address the different meshes that are required for the different pieces of the model, I have begun work on a new mesh interface and mapping techniques that will be able to efficiently map the different meshes in parallel across a large-scale computation. This requires a significant amount of research to perform efficient parallel search and mapping in a generalized 3D environment. I currently have a simple search and mapping, but this needs to be extended to an efficient large-scale parallel computation.

Many existing plasma models are able to accurately model complex problems in 3D but are limited in the size/resolution of the problem they can handle because of the computational requirements in solving the magnetohydrodynamic equations. To address this limitation, I am working on extending an existing plasma model (pixie3d) to work on an AMR-based grid. The resulting code will be able to simulate complex problems that would not otherwise be possible. To date, significant progress has been made. A prototype model that adds AMR capabilities to pixie3D has been developed. The model has demonstrated the feasibility of coupling AMR-based grids and has been tested on several problems. Current work focuses on addressing performance issues when scaling to large-scale problems, and improving the numerical accuracy of the solution.

05982

Adaptive Target Tracking in Multipath Scenarios

S. Sen

Project Description

We propose to develop efficient detection and tracking methods for targets moving in a multipath-rich environment using an orthogonal frequency division multiplexing (OFDM) radar. Such environments are critical and challenging to the radar technologies used in both military and civilian applications. To exploit multipath reflections rather than cancel them, we consider a wideband, multi-carrier OFDM signaling scheme. The use of an OFDM signal mitigates possible fading, resolves multipath reflections, and provides additional frequency diversity as different scattering centers of a target resonate at different frequencies. Moreover, we devise adaptive waveform design techniques to select the spectral parameters of the OFDM signal for further improving the detection and tracking performances. The rationale behind the adaptive waveform design (in a closed loop) is to enable better sensing performance by fitting the operational scenario, in contrast to the conventional open-loop systems.

Mission Relevance

The project has direct relevance to DOE's CESAR program. Conventional radar systems, which are designed to operate mainly in open environments, face significant difficulties when targets move in multipath scenarios. Such situations arise in diverse military and civilian applications, such as tracking of ground-moving vehicles or sea-skimmers from an airborne platform. Because of inherent multipath propagation, these systems encounter a number of demanding issues, such as the presence of significant multipath returns over multiple range cells, spreading of Doppler frequency, and sometimes even the absence of any line-of-sight (direct) path between the radar and target. Therefore, this project aims to address these complex problems as realistically as possible to develop an efficient tracking procedure.

Results and Accomplishments

We developed a sparsity-based space-time adaptive processing (STAP) algorithm to detect a slowly moving target with an OFDM radar. We observed that the target and interference spectra are inherently sparse in the spatiotemporal domain, and hence we exploited that sparsity to develop an efficient STAP technique. First, we formulated a realistic sparse-measurement model for an OFDM radar, considering both the clutter and jammer as the interfering sources. Then, we showed that the optimal STAP-filter weight vector is equal to the generalized eigenvector corresponding to the minimum generalized eigenvalue of the interference and target covariance matrices. To estimate the target and interference covariance matrices, we applied a residual sparse-recovery technique that enabled us to incorporate the partially known support of the sparse vector.

Our numerical results demonstrated that the sparsity-based STAP algorithm, with considerably less secondary data, produced an equivalent performance as the other existing STAP techniques. Moreover, we discovered that the OFDM-STAP filter weights were adaptable to the frequency variabilities of the target and interference responses, in addition to the spatio-temporal variabilities. Hence, by better utilizing the frequency variabilities, we proposed an adaptive OFDM-waveform design technique and consequently gained a significant amount of STAP performance improvement.

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05983

Novel Nanotoxicology Studies Using Noninvasive Real-Time Microscopy and Spectroscopy for Physical and Chemical Characterization of Materials and Live Biological Systems

L. Tetard

Project Description

As interest in developing novel engineered materials and the natural extension to associated nanotoxicological effects continue to rise, a parallel development of a metrology toolbox that can contribute to the structural and chemical characterization of such nanosystems is needed. A crucial component in dealing with systems at the sub-micrometer scale is the ability to measure the sought properties and response of a given sample with (1) high spatial and temporal resolution, (2) minimum disturbance, (3) subsurface visualization, and (4) molecular recognition. These abilities can offer a detailed understanding of these complex systems by enabling quantitative study of their structural, physical, and chemical properties. Recently one such characterization tool has been preliminarily demonstrated to offer a unique approach to noninvasive, nanoscale, subsurface visualization of biological materials. Enhanced to operate in an aqueous environment and combined with a novel IR spectroscopy capability, this powerful new tool can be applied to a number of important research issues in nanotechnology, including specifically the environmental and health effects of nanomaterials on living systems.

The proposed research encompasses the following. (1) Begin a research initiative to study nanotoxicity in living systems exposed to nanomaterials at the cellular level using a unique subsurface microscopy technique with integrated spectroscopy. In this objective, plant and animal cells, as well as engineered and naturally occurring nanoparticles, will be targeted. (2) Advance the state of knowledge in nanoscale subsurface imaging and spectroscopy. This objective will be composed of instrument enhancement and investigations of known fabricated nanostructures to provide "standards" for future theoretical analysis of the complicated signals from the proposed technology.

Mission Relevance

While the synthesization and application of nanomaterials are generating great excitement, the safety of nanomaterials to humans, animals, and the environment is also being treated with gravity. For the toxicological, epidemiological, and environmental impacts of nanomaterials to be understood and controlled, it is of paramount importance to have the ability to characterize, quantify, and track the nanomaterial within the biological or environmental system in real time. However, given the small dimension of the nanomaterial, this ability is difficult, if not impossible, using traditional characterization tools. Recognizing the lack of analytical tools with which to assess exposure impact, guide manufacturing specifications, and verify desired end-product functionality, one of the nine grand R&D challenge areas identified by the National Nanotechnology Initiative (NNI) is Nanoscale Instrumentation and Metrology.

The premises of this work have offered great insight to the nanotoxicology community, by demonstrating the ability of our instrument to localize engineered nanoparticles of various sizes and composition inside animal cells. In addition, it holds a great potential for fundamental research or applied material research relevant of the project to the missions of DOE, NIH, DOD, DARPA, or NSF.

Results and Accomplishments

Subsurface imaging. Further developments of the Mode Synthesizing Atomic Force Microscope (MSAFM) and its dynamical aspects were explored, and the results demonstrate the existence of a virtual mode that can potentially be used to improve the subsurface imaging resolution and sensitivity [1]. The results were in good agreement with the theoretical considerations we assumed for the work [1]. MSAFM was also used to investigate the ultrastructure of biological samples, such as plant cell walls and chemically modified plant cell walls [3], and nanotoxicology samples [5].

Molecular recognition. Optical modules were designed to integrate infrared spectroscopy with subsurface imaging and evaluate their potential for chemical information with high spatial resolution. The various modules were tested using two AFM systems. The results are being compared for further optimization. In addition, we demonstrated that optomechanical systems, such as cantilevers, can provide spectrally resolved detection of radiation and thus be an integral part of a spectrometer [2,4]. A series of control samples were investigated to determine the lateral resolution of the technique (nanoparticles, polymers, etc) [4].

Living systems. A series of developments were initiated, including the design of a new liquid cell for imaging, and new probes were considered for the measurements. The results on plant cell walls [3] and macrophages [5] indicate the promises of our techniques. Capitalizing on these new capabilities, a more involved and systematic characterization of the effects of the successive chemical treatments involved in the decomposition process or the maturation of such systems can be envisioned.

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06245

An Accurate and Efficient Computational Methodology for Simulating Disordered Nanoscale Materials

M.G. Reuter

Project Description

Nanomaterials are often suggested as components in numerous next-generation devices, including batteries. Insights from computational studies of nanomaterials can guide the experimental design of these devices; however, nanomaterials are generally too large to simulate with ab initio quantum mechanical methods, especially when chemical defects are present. This limitation has forced the invocation of best-effort, yet often unvalidated, approximations when studying the fundamental effects of disorder on nanomaterials. As such, the principal objective of this proposal is to develop, implement, and apply a computational methodology that will accurately and efficiently simulate both pristine and disordered nanomaterials. A secondary goal is to assess the legitimacy of the aforementioned approximations, which become unnecessary in the proposed formalism. Finally, we aim to apply this framework to (1) determine the persistence of defect-induced effects in nanomaterials; (2) probe the interplay of multiple defects; (3) investigate how, and under what conditions, defects alter the flow of electric current through nanomaterials; and (4) explore interactions, notably charge transfer, between nanomaterials and nearby molecules.

Mission Relevance

Proposed research will be useful in identifying fundamental roles of disorder on the electronic structure and response properties of nanomaterials. The ability to bridge length scales parallels some of the Core Research Activities of the Materials Science and Engineering Division of the Basic Energy Sciences Program in the DOE Office of Science. Also, the computer-aided design of nanomaterials benefits the construction of better batteries and solar cells (for examples), in line with the interests of the DOE Energy Efficiency and Renewable Energy Program.

The development of a general computational algorithm for simulating pristine and disordered nanomaterials of arbitrary size will likely be of interest to several DOD agencies.

Results and Accomplishments

To date, most work has focused on the first objective, the development of a computational framework for simulating disordered and pristine nanomaterials. The main problem is the inversion of an intractably large matrix, and we have succeeded in designing and implementing an algorithm for this task. As will be reported in a forthcoming publication, our algorithm runs roughly one hundred times faster than existing methods and requires no additional assumptions or approximations. The integration of this code with the NWChem package is under way and, when complete, will allow the simulation of both disordered and pristine nanomaterials. We have also begun work on the second objective (understanding current pathways through nanomaterials), by extending existing formalisms for two-terminal devices to the multiterminal devices of interest. This work is incomplete and ongoing.

Publications

Reuter, M. G. and Hill, J. C. 2011. “An Efficient, Block-by-Block Algorithm for Inverting a Block Tridiagonal, Nearly Block Toeplitz Matrix.” Submitted to the Publication Tracking System (ID 33183), Oak Ridge National Laboratory, Oak Ridge, TN.

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