OAK RIDGE
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MANAGED BY UT-BATTELLE
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Laboratory Directed Research and Development Program

FY 2010 Annual Report

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Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2010 ANNUAL REPORT

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
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CONTENTS

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 2010. The associated *FY 2010 ORNL LDRD Self-Assessment* (ORNL/PPA-2011/2) 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 2010 were as follows.

- *Science for Extreme Environment: Advanced Materials and Interfacial Processes for Energy.* Building upon existing strengths in materials science and interfacial molecular processes, the objective of this focus area is to help position ORNL as a world-leader in the discovery and design of revolutionary new materials that will meet future energy needs, with a special emphasis on defining

projects for next-generation technologies for solar energy conversion and energy storage. During the year, the Laboratory invested $5.13 million in 20 LDRD projects. FY 2010 LDRD investments were made in projects to accomplish the following.

- — Develop new method for producing submicron aqueous droplet on demand at the intersection of nanochannels to open new areas of research in the study of catalysis and reaction dynamics of transient chemical and biochemical intermediates in confined environment
- — Make advances in density function theory (DFT) to overcome limitations of approximate exchange correlation functional that failed to describe structural defects and other properties of materials in which strong electron–electron correlation pay an essential role
- — Develop, using a computer-aided design approach, an approach for the design and synthesis of advanced functional materials for energy applications
- — Gain understanding of energy transformation pathways and gain insights in electrochemical energy storage with supercapacitors
- — Synthesize soft materials that have an unprecedented level of architectural control from the molecular to mesoscale
- — Gain a molecular-level understanding of the design principles of the assembly of an artificial photosynthetic unit
- — Develop insights into the stoichiometry of the copper, idium, gallium, and selnium (CIGS) nanoparticles to help reduce defects and poor shelf life of low-cost CIGS with applications in thin film-solar cell
- — Study weld property degradation leveraging advances in computational models and neutron diffraction
- — Develop insights into physics and solid state chemistry of multinary semiconductors to help develop a new class of complex materials with enhanced photovoltaics properties
- — Overcome the effects of recombination and charge carrier losses of polymer-based photovoltaics (PV) cells through better understanding of the science
- — Improve PV efficiency through the creation of new nanostructures
- — Develop insights into oxide interfaces and optical properties to create new approaches for a new generation of PVs
- — Develop understanding of the phenomena of decoupling of various processes from a structural relaxation to help develop new polymeric materials for energy applications

- *Neutron Sciences.* To make ORNL the world's foremost center for neutron sciences, LDRD funds are being used to (1) demonstrate the capabilities of the Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR) and conduct research at the forefront of physics, chemistry, materials science, energy research, and engineering, and structural biology; (2) develop concepts for the next generation of neutron scattering instrumentation at SNS and HFIR; and (3) develop innovative research programs at ORNL and expand the use of neutron scattering to new research applications. In 2010, $2.93 million of LDRD funds supported 17 projects in this area. FY 2010 LDRD investments were made in projects to accomplish the following.
  - — Advance SNS capabilities in protein crystallography
  - — Enable neutron analysis on the structure and function of novel proteins at atomic levels

  - Develop bio-inspired material for solar, hydrogen, bioenergy, and nuclear energy
  - Use neutron scattering techniques in the analysis of the structure, function, and dynamics of biological materials
  - Use neutron solution scattering and reflectometry to model and understand the structural changes associated with virus assembly, assault, and infection at cell membranes
  - Develop a technique of inelastic neutron scattering to study magnetic excitations and relaxation for nano-engineered materials
  - Gain fundamental understanding of the structure in metallic glasses and how the structure features evolve during phase transformation and mechanical deformation
  - Study the fluid-surface interactions and the molecular mobility of CO_2 and methane in coals, shales, and sandstones at temperatures and pressures similar to natural underground conditions
  - Improve data acquisition schemes at SNS to measure transient phenomena at 10 times finer time resolutions than currently possible
  - Demonstrate SNS and HFIR instrument capabilities to study (1) osmotic stress to disordered proteins, (2) material behavior far from equilibrium, (3) inter- and intra-molecular motions in protein crystals and pressure dependence of protein dynamics, (4) magnetic interactions found in organic super conductors, (5) mechanisms behind mixed ion/proton conduction in oxide and ceramic membrane materials used as fuel cell, (6) recrystallization of metallic polycrystals, and (7) dynamical changes on complexation in biological systems; to develop 3D phase structure and 2D fluid flow images using noninvasive, nondestructive, neutron imaging techniques with plants, soils, and rocks; and to support experimental studies of advance materials utilizing broad suite of instruments at SNS

- *Ultrascale Computing and Data Science.* The intent of this focus area is to establish ORNL as a world leader in computing and computational sciences to deliver new insights and to achieve breakthroughs with broad impact for U.S. scientific leadership. Focus area objectives are to provide integrated computational solutions in science and engineering to the major challenges of the Department of Energy, the national security agencies (e.g., National Nuclear Security Administration, the Department of Homeland Security, the Director of National Intelligence), and the nation. Toward this goal, the Laboratory invested $4.21 million during FY 2010 to support 15 projects to accomplish the following.

  - Advance a next-generation, high-performance computing (HPC), nuclear reactor transport solver
  - Develop particle-based predictive thermonuclear plasma modeling capability that is suitable for parallel supercomputer
  - Study the role of cloud computing in scientific discovery by developing tools to make petascale biology and climate data set available through open cloud interfaces and use distributed cloud resources (Goodle, Microscoft, and Amazon) to process these data sets
  - Set up entangled photon quantum communication (QC) test bed with network functionality to explore QC implementation issues
  - Develop tools (runtime infrastructure) for dynamic integration of real-time data into discrete event simulation models executing on peta and larger-scale system
  - Develop scalable algorithm for scalable constrained optimization models with (GB to TB) data that require peta/exascale computational resources
  - Develop solutions to alleviate soft errors in next-generation HPC

  - Develop new model formulation for next-generation multiphysics computational fluid dynamics solver
  - Develop new/revised Message Passing Interface (MPI) standards that will help avoid failures and recover from failures for applications expected to run on new-generation ultrascale computers
  - Develop multiscale computational tools to investigate and optimize key variables of supercapacitors based on nanoporous carbon material
  - Develop tools to infer and predict social dynamics of groups through psycho textual and communications flow analysis
  - Develop high-throughput computational screening approach for rational drug design and drug discovery in areas of systems medicine
  - Develop computational biology toolbox for Cray with improved biological function prediction model that will help translate the exponentially growing genomic data into useful information

- *Systems Biology and the Environment.* Through this focus area, ORNL seeks to build capabilities at the forefront of systems biology, bioengineering, and environmental science and their applications in addressing grand challenges related to energy production and the environment. During FY 2010, LDRD investments totaling $2.03 million were made to support eight projects to accomplish the following .

  - Identify, using neutron scattering capability, metabolic and energetics interdependencies of organisms which have simplest and most efficient symbiotic relationship
  - Develop a next-generation computation system for biological annotation
  - Develop biocatalysts for producing fuels and chemicals from synthesis gas
  - Identify genetic and environmental constraints to primary productivity in model and nonmodel species
  - Develop novel bio-inspired catalytic approaches for transforming lignin to fuel or feedstocks
  - Gain insights to atmospheric CO_2 mitigation through woody mass management
  - Establish microbial consortia for consolidated bioprocessing that will help alter nitrogen and sulfur cycles

- *Advanced Energy Systems.* The intent of this focus area is to stimulate the development of new technologies that have the potential to supply, distribute, and use energy with high efficiency, at low cost, and with low environmental risk. Toward this goal, the Laboratory invested $3.99 million in FY 2010 to support 11 projects in a wide range of energy technologies, including fuel reprocessing separations, advanced fuel cell electrolytes, and radiochemistry application to nuclear forensics. Efforts focused on development of the following.

  - Technology for efficient power transfer to electric vehicles
  - Technology to improve the efficiency of internal combustion engines
  - Methods for removal of americium from spent nuclear fuel
  - Understanding critical pieces of information for advanced high-temperature reactor design
  - Advanced Cermet waste form concepts for the optimal storage of high-level wastes
  - Next-generation radiation transport modeling and simulation
  - Simulation modeling of electric power system at geographic scale

  - — High-efficiency, low-grade waste heat energy convertor
  - — Fusion energy R&D

- *Emerging Science and Technology for Sustainable Bioenergy*. The intent of this focus area is to integrate and strengthen ORNL's comprehensive bioenergy-relevant research capabilities, including geospatial science and technology, to support the nation's creation of a sustainable bioenergy generation and delivery infrastructure. In addition, because bioenergy infrastructure is inescapably and tightly bound to geography, the competencies in geospatial science and technology that this bioenergy focus area is expected to develop will also impact scientific advancement in other disciplinary areas such as climate change science, computational science, national and homeland security, environmental science, and transportation. Toward this goal, the Laboratory invested $0.91 million during FY 2010 to support three projects to model and optimize the biofuel supply chain; develop a bioenergy implementation strategy that addresses environmental, economic, and climate concerns while meeting energy demand; and develop a spatiotemporal datamining framework for remote monitoring of biomass on a regional and global scale.

- *Understanding Climate Change Impact: Energy, Carbon, and Water*. The intent of this focus area is to develop reliable integrated end-to-end climate prediction and assessment capabilities and to develop unique competencies in climate change, climate impacts science, computational science, observational capabilities, national and homeland security, environmental science, energy usage and production, carbon management, and geospatial science and technology. Toward this goal, the Laboratory invested $1.81 million during FY 2010 to support seven projects in the following areas.

  - — New methodologies to assess the predictive skills of climate model outputs and downscaling approaches and reduce the uncertainties
  - — Models to estimate the impacts of climate change on energy infrastructure
  - — Models to estimate/quantify economic losses associated with climate extremes under climate change and socioeconomic changes
  - — Insights into the molecular control of partitioning, transport, and fate of carbon fixed by photosynthesis in plants and its correlation to other measured plant system properties by leveraging SNS capabilities

- *National Security Science and Technology.* The intent of this focus area is to make ORNL a desired provider of innovative technical solutions to compelling national problems that materially improve global, national, and homeland security. In support of this goal, seven LDRD projects were funded for $1.88 million to develop (1) standoff chemical sensors; (2) a navigation system that will perform in GPS-denied environments; (3) active response and countermeasures for cyber-threat; (4) a biological signature identification and threat evaluation system; and (5) rapid radiochemistry for nuclear forensics.

- *Energy Storage.* The objective of this focus area is to enhance ORNL's leadership in electrical-energy storage research and development, with a focus on batteries and electrochemical capacitors, and to deliver new insights with broad impacts for U.S. energy security, national security, and economic competitiveness. In support of this goal, six LDRD projects were funded for $2.36 million to better understand the material behavior underlying the electrochemical performance of advanced batteries and to develop (1) a simulation tool for evaluating safety and performance of batteries; (2) a multiscale, multi-physics model to design safe rechargeable batteries; (3) electrolytes for batteries based on composites inspired by nature; (4) lithium air batteries through metal oxide electrocatalysts; and (5) secondary aluminum ion batteries.

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 2010, $33.8 million was allocated to the ORNL LDRD program to support 163 projects, 96 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	$27,112,000	$4,868,000	$154,365	$106,813
Number of projects	100	58	2	3
Number of new starts	48	45		3
Continuing (2^{nd} & 3^{rd} year of funding)	52	13	2	
Average total project budget (1–3 years)	$619,937	$128,938	$225,549	$59,704
Average project duration	24 months	16 months	24 months	24 months

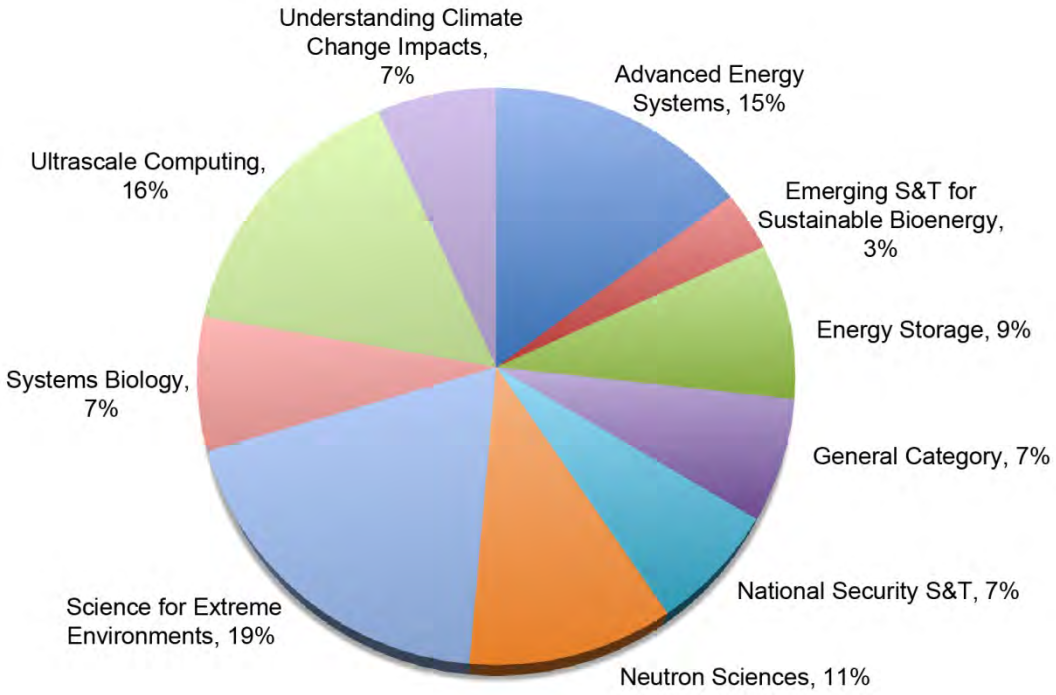

Fig. 1. Level of Director's R&D Fund investment in the Laboratory Focus Area for FY 2010.

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 2010, $4.69 million of the LDRD program was apportioned to the Seed Money Fund to support 58 projects, 45 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

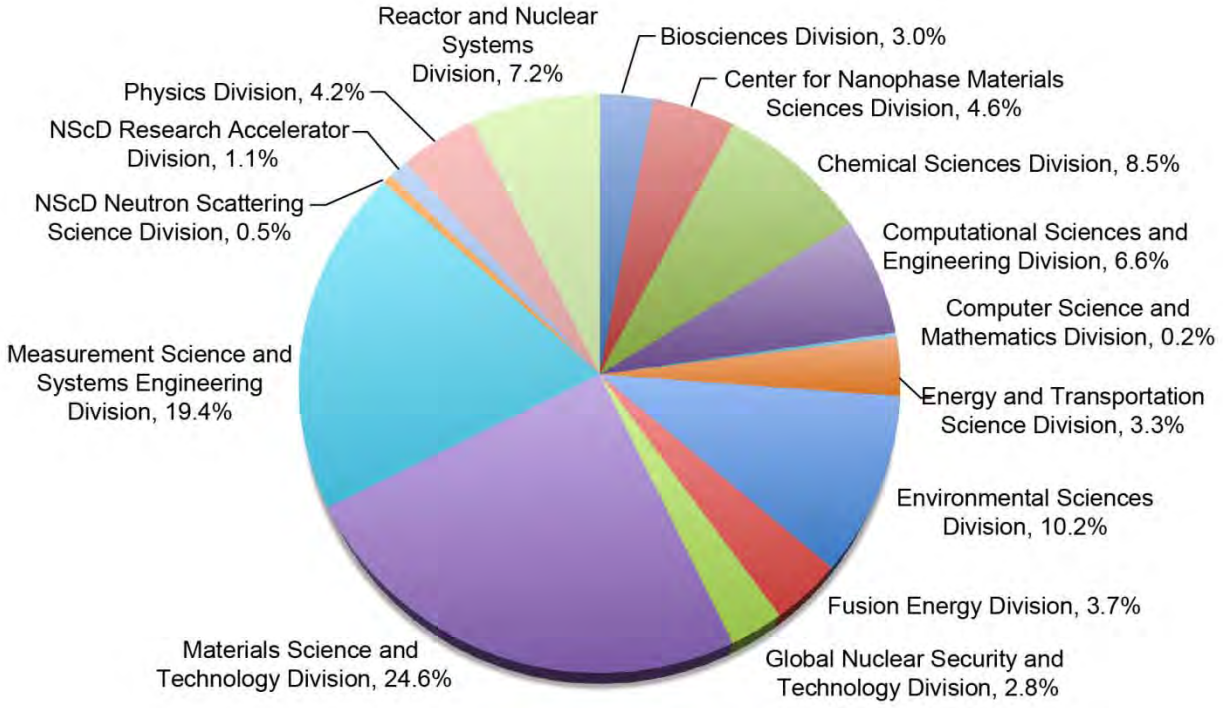

Fig. 2. Distribution of Seed Money Fund by research division for FY 2010.

Fellowship Money Fund

In FY 2010, 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, LDRD-funded, 2-year appointment, and Weinberg Fellowship is a full-time, 2-year appointment funded 25% by LDRD and 75% by program funds.

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.

Report Organization

This report, which provides a summary of all projects that were active during FY 2010, is divided into 13 sections: one for each of the nine Laboratory focus area discussed above, a General 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 2010. Publications resulting from the project are also listed.

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

SCIENCE FOR EXTREME ENVIRONMENT: ADVANCED MATERIALS AND INTERFACIAL PROCESSES FOR ENERGY

05079

Supramacromolecular Assembly of Artificial Photoconversion Units

Hugh O'Neill, Kunlun Hong, and William T. Heller

Project Description

The goal of this project is to gain a molecular-level understanding of the design principles that support and promote the assembly of an artificial photosynthetic unit for the conversion of light into electric or chemical energy. A synthetic system is sought that is capable of self-assembly into a biomimetic membrane structure and is able to incorporate functional catalytic units within a supra-macromolecular structure. Synthetic electroactive block co-polymers can provide a biomimetic environment and self-assemble into nanostructures with tunable phase morphology. Their functionality can be widely varied through choice of monomers and polymerization reactions (e.g., incorporation of binding sites for chromophores and catalysts). We propose to use photosynthetic proteins to understand the fundamental principles of synthetic architectures suitable for solar energy applications. This will lead to an in-depth understanding of the weak intermolecular forces that govern supramolecular assembly and result in a block co-polymer system that can perform in a manner analogous to the natural photosynthetic membrane. This project brings together ORNL's recognized expertise in photosynthesis, polymer synthesis, and neutron science. In addition, our collaboration with the Georgia Tech team (part of the AtlantICC Alliance; http://www.atlanticcalliance.org/index.html), who have expertise in organic photovoltaics, will further strengthen our ability to attract future funding in this area.

Mission Relevance

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

Results and Accomplishments

We report, for the first time, that naturally occurring light harvesting antennae can alter the phase behavior of a poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-PPO-PEO) block copolymer system from micellar to lamellar structures mimicking their role in maintaining the supramolecular architecture of the photosynthetic membrane. Small-angle neutron scattering shows that PEO_{43}-PPO_{16}-PEO_{43} micelles undergo a phase transition from a micellar state to a lamellar structure with a ~60 Å spatial repetition in the presence of plant light harvesting complex II (LHCII). In addition, spectrophotometric analysis indicates that the protein self-assembles in the synthetic membrane structure. The significance of this work is that it provides a novel approach for developing a new class of membrane-based smart material with a well-controlled architecture that is dependent on the assembly of interacting components, and it could also have important implications in self-repair and control of energy transfer in photoconversion devices.

Combined Kumada catalyst-transfer polymerizations were used to synthesize novel amphiphilic electroactive poly(3-hexylthiophene)-*g*-poly(ethylene oxide) (PT-g$(EO)_x)_{30}$ block copolymers. The (PT-g-$(EO)_x)_{30}$ copolymers significantly increase the rate and yield of LHCII-mediated photodependent hydrogen production. The platinum catalyst was formed in situ, allowing direct electronic communication with LHCII. For instance, in the presence of (PT-g-$(EO)_3)_{30}$, hydrogen production was sustained for greater than 100 hours with a maximum rate of 12.1 μmol H_2/h/mg Chl, a 57.6-fold increase compared to LHCII alone. Hydrogen production is more stable under red light compared to white light, suggesting that LCHII is susceptible to photodegradation. Analysis of the fluorescence quenching data indicates that the LHCII molecules are closely associated with the copolymers. LHCII is primarily known for its role in excitation energy transfer. This work provides evidence that, in the absence of a photosynthetic reaction center, it can also perform electron transfer, a role not known to occur in vivo. The ability of LHCII to act as a mediator for photodependent H_2 production shows great promise for the development of a biohybrid solar fuel system. A manuscript is currently being written describing these results.

Information Shared

Iwuchukwu , I., M. Vaughn, N. Myers, H. O'Neill, P. Frymier, and B. D. Bruce. 2010. "Self-assembled photosynthetic nanoparticle for cell free hydrogen production." *Nat. Nanotechnol.* **5,** 73–79.

05090

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

Jimmy Mays, John Ankner, Philip Britt, Mark Dadmun, Kunlun Hong, and S. M. Kilbey II

Project Description

Conjugated polymers hold the key to future fundamental advances in science and technology. A major barrier that hinders the application of conjugated polymers for energy conversions has been a lack of understanding of how conjugation affects structure and properties, which springs directly from a lack of well-defined materials. The objectives of this project are to develop the chemistry necessary for creating tethered, interfacial layers of poly para-phenylene (PPP) and their derivatives on solid substrates and to study how the self-organization and confinement of these polymers impact their nanoscale structure and properties. The surface-tethered layers will be created by functionalized polycyclohexadiene (PCHD) chains with complementary functionality on the substrate. Then they will be converted to PPP brushes by

aromatization. Doping of PPP brushes will yield highly ordered arrays of conducting polymer chains. These materials will be the first well-defined conjugated polymer brushes, and the study of their structure and properties will provide unique insight into the impact of nanoscale confinement on their properties. The work will focus mainly on synthesis of these novel materials, structural characterization via neutron reflectometry/scanning probe microscopy, and conductance measurements. Efforts to study the electrochemical behavior of the systems will also be advanced.

Mission Relevance

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

Results and Accomplishments

PPP brush formation. Ultraviolet and visible (UV-Vis) absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR) have been used to confirm the growth of PCHD brushes and the aromatization reaction. The PCHD precursor polymers have a molecular weight of 4–19k and a narrow polydispersity (PDI < 1.1). X-ray photoelectron spectroscopy (XPS) results further confirmed the formation of PPP brushes as the π- π^* shake-up peak (at ~290 eV) in PPP brushes was almost two times larger than the one from the corresponding PCHD brushes. By varying the spin-coating condition, a wide range of PPP brush thickness (4–108 nm) was achieved with high graft density (0.3–3 chains/nm).

Morphology and crystallinity. A distinctive morphological transformation was identified by atomic force microscopy (AFM) upon aromatization. The surface roughness of PCHD brushes was consistently two to three times lower than that of their PPP counterparts. In addition, the PCHD brushes had an almost featureless surface morphology, while the PPP brushes had a distinguishable grainy structure. PPP brushes exhibited clear grain boundaries in phase imaging, which were not present in PCHD brushes. The typical domain sizes in PPP brushes were between 20 and 80 nm. However, X-ray diffraction did not provide any evidence for PPP crystallinity.

The PPP brushes were also directly grown on Smart Grids™, which have thin SiO_2-based transmission electron microscopy (TEM) viewing windows. The morphology obtained in bright-field TEM imaging was similar to what was found in AFM height micrographs. The grain sizes in TEM and AFM are slightly different, possibly because that the precursor PCHD solution was dropcast onto TEM grids followed by filter paper blotting while the films imaged by AFM were prepared by spincoating. Electron Diffraction of PPP brushes did not demonstrate any sharp crystalline rings, which is consistent with X-ray results.

Optical properties. A blue shift in the absorption peak around 320 nm was found in thicker PPP brushes when compared to thinner brushes with the same molecular weight, possibly due to the fact that there was less surface confinement effect at the top surface which led to reduced effective conjugation length. A Kuhn plot analysis revealed that the effective conjugation length in the PPP brushes was between 5 and 6.

Electrical measurements. Impedance spectroscopy was used to study the brush-based metal–insulator–metal (MIM) structure: heavily doped Si – 2-nm-thick native silicon oxide – ~30-nm-thick PCHD or PPP brushes. By using a Randles model, our equivalent circuit modeling with undoped PPP brushes suggested that the contact resistance in the system was 50 times lower than the measured bulk resistance.

The MIM structure without PCHD and PPP brushes had a measured impedance of 1000 ohm and phase of 90 degree over the entire frequency range that we monitored (20–2 million Hz). For the data sets labeled "air" (i.e., no connection), the low-frequency values are vibrating dramatically, because we are reaching the higher measuring limit of impedance amplitude at this frequency. The MIM structure with polymer brushes showed brush-type-dependent impedance behaviors. At 100 Hz, PCHD brushes had AC impedances that were 20 times higher than those of PPP brushes, while doped PPP brushes showed 10 times lower impedance after 24 h doping in $FeCl_3$ solution. The doping process was expected to be slower in brushes than in powder because the dopant could only diffuse from the brush top surface.

Distinctively different AC phase response was also observed upon the PCHD aromatization and PPP brush formation. The PCHD brush has a phas angle close to 90 degrees, which suggests a nearly pure capacitor behavior. The corresponding undoped PPP brush has two maxima in the phase-frequency plot: one at 20 Hz and another at 100,000 Hz, indicating significant resistor-type contributions from interfacial and orientational polarization mechanisms. The doped PPP brush has an even stronger resistive behavior, corresponding to a significantly increased R2 and smaller C value in the Randles Circuit as compared to PCHD and undoped PPP brushes. In addition, we can extrapolate the frequency-dependent impedance to infinite low frequency in order to estimate DC resistance. The extracted DC conductivity of undoped PPP brushes were in the range of 10^{-10} to 10^{-12} S/cm, which is slightly higher than the reported values for undoped polyacetylene (10^{-9} to 10^{-10} S/cm).

A microscopic four-point probe (M4PP) was purchased and installed in our Hitachi SEM. It is used either inside a scanning electron microscopy (SEM) or under an optical microscope to measure DC conductivity of ultra-thin films. Because we are moving the M4PP into a newly acquired Zeiss SEM, currently we only managed to use it to measure the conductivity of Nafion/Pt-C composites films on flexible substrates (Kapton or Teflon). M4PP measurements on a hard substrate such as a silicon wafer or inside the new Zeiss SEM are still under way.

Patterning. Micropatterning of PPP brushes was successfully achieved with nickel masking and photolithography. The rough edge shown in the AFM cross-section scan was attributed to the thick nickel pattern we used (100 nm), which should be easily optimized later on. Currently we are combining e-beam lithography and nickel masking to make nanopatterns of PPP brushes. A photo-resist pattern generated by e-beam lithography will be used to pattern PPP brushes.

05195

Controlled Hierarchical Self-Assembly of Robust Organic Architectures

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

Project Description

The power to predict and control the assembly of matter at the molecular level is the key to unprecedented control over many intriguing and useful material properties. Although design concepts for the structure-

directed self-assembly of soft materials have emerged from advances in supramolecular chemistry and crystal engineering, general methods for implementing these concepts do not exist. Moreover, materials self-assembled from organic building blocks are often fragile and intolerant to extreme conditions. This project addresses these limitations by utilizing a computer-aided design approach for molecular building blocks that are structurally encoded to create targeted assemblies of predictable architecture and dimensions, and validating the approach by producing robust crystalline materials via dynamic covalent chemistry (DCC). The design strategy entails a novel hierarchical approach (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 involves the reversible coupling carbonyl compounds (aldehydes or ketones) with amines. The strategy is to use carbonyl compounds either as vertices for tetrahedral building blocks or as nodes for frameworks. Both tri- and tetra-carbonyl substituted molecules were identified as synthetic targets.

To date 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 have been 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 frameworks have thus far been unsuccessful, leading instead to amorphous polymers or gels. It is anticipated that some of these highly cross-linked materials may exhibit high surface areas, and characterization using gas adsorption methods is under way.

05285

Mapping Energy Transformations Pathways and Dissipation on the Nanoscale

Sergei V. Kalinin, Stephen Jesse, and Albina Borisevich

Project Description

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

Mission Relevance

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

Results and Accomplishments

To relate the energy transformation pathways on a single-defect level to their atomistic structure, we use ferroic systems as models with nondisruptive and locally reversible transformations. We identified ferroelastic domain walls and bicrystal interfaces as defect structures that (1) are universally present in materials, (2) are well defined on mesoscopic and atomic levels, (3) can be studied both by SPM (switching dynamics) and STEM (atomic and electronic structure), and (4) can be integrated with theory (mesoscopic phase-field models). The *in-line* band excitation SPM and spectroscopic modes of piezoresponse force microscopy have been developed into user-friendly data acquisition and data analysis tools and are now incorporated on five ambient and one ultrahigh SPM platforms in the Center for Nanophase Materials Sciences, as well as on several additional data analysis stations. The switching behavior at grain boundaries and ferroelastic domain walls was probed, and results were found to be in an excellent agreement with mesoscopic phase field modeling. Thus, we have for the first time demonstrated that bias-induced phase transitions can be studied quantitatively on level of a single atomically defined

defect, and corresponding mesoscopic mechanisms can be elucidated. Using this concept, a nanoscale control of switching mechanism using the tip motion has been demonstrated. Furthermore, this approach was extended for probing materials with multiple interacting defects exemplified by disordered and polycrystalline ferroelectrics. In the last year, the prediction that these studies can be extended for energy storage and conversion materials have been experimentally verified, illustrating the feasibility of initial concept.

Follow-on funding has been secured through the Single Investigator and Small Group (SISGR) project "Probing phase transitions, chemical reactions, and energy transfer at the atomic scale: Multifunctional imaging with combined electron and scanning probe microscopy," A. Borisevich, PI.

Information Shared

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05309

Interfacial Reactions of Metal-Fluid Systems at Extreme Conditions

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

Project Description

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

models for metal oxidation in water-rich environments at extreme temperatures, and sets the stage for targeting follow-on proposal calls from the DOE Offices of Basic Energy Sciences (BES), Fossil Energy, and Energy Efficiency and Renewable Energy.

Mission Relevance

The anticipated results of this project and future applications of new methodologies are directly relevant to high-temperature oxidizing environments containing water vapor ubiquitous in energy production. Virtually all combustion environments (gas turbines, reciprocating engines, fossil-fired plants, etc.) contain water vapor. New research capabilities at ORNL provided by this effort will form the basis for targeting future funding opportunities related to the declared DOE BES grand research challenges, especially in the fields of interfaces and extreme environments as identified in the Basic Research Needs (BRN) workshop reports. In particular, the BRN report on Materials Under Extreme Environments specifically identifies that fundamental understanding of the atomic-nanoscale processes resulting in either passivation or degradation of structural metals in contact with high-temperature reactive gas mixtures is critically needed for ultrasupercritical steam electrical power generation facilities, biofuels combustion, and solid oxide fuel cell utilization.

Results and Accomplishments

The feasibility of applying a suite of advanced modeling and characterization techniques adopted from the geochemical community to gain new insight into the detrimental effects of water vapor on the high temperature of stainless steels was successfully established. Molecular dynamics simulations showed that water vapor preferentially displaces oxygen at the metal/fluid interface in air and water vapor mixtures. This finding provides an explanation for how the addition of only 5–10% water vapor to air can so detrimentally affect oxidation resistance when the oxidizing media is still 90–95% air. Secondary ion mass spectrometry D_2O tracer studies succeeded in providing what we believe to be the first successful examples of hydrogen species profiles obtained through the oxidized zone of stainless steels in water vapor. It was found that the D profiles unexpectedly varied markedly among the alloys examined, which indicates mechanistic complexity but also the potential to mitigate detrimental water vapor effects by manipulation of alloy chemistry. Small-angle neutron scattering studies of stainless steel alloy foils oxidized under dry and wet air mixtures showed significant effects of oxidation time on scattering despite the formation of only 1–2 μm of oxide on a 100 μm alloy foil. Initial analysis also suggested that water vapor did not alter the nanostructure of the oxide relative to dry air, which has important ramifications for understanding how H_2O gains access to the oxide and underlying alloy. Inelastic neutron scattering studies were also attempted in order to gain insight into the speciation of hydrogen ingress into oxidizing stainless steels. Although not successful in detecting hydrogen speciation, the attempt did provide a basis for a modified experimental protocol in future work.

05342

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

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

Project Description

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

Mission Relevance

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

Results and Accomplishments

We have already tested and compared computer programs that can perform calculations both at the mean field and at the many-body level in small systems. We have performed the initially proposed calculations in the spherical jellium system and other variations of the model (like the spherical jellium shell with an impurity). In addition we have performed detailed comparisons of DFT approximations and several many-body methods for the Ca+ H_2 system.

We find that current approximations of DFT work well for the spherical jellium plus impurity model in the closed shell configuration. However, current approximations fail in the open shell (magnetic) configuration in the jellium. They fail in the spherical shell model both in the magnetic and paramagnetic states. The spherical shell model resembles the case of a Ca^+ atom surrounded by H_2 molecules. Similar failures are observed in Ca^+ system. Accordingly, we have found cases in which many-body effects play an important role which is difficult to obtain with standard mean field approaches. We find that the introduction of exact exchange in DFT is, in some cases, a key ingredient to improving the performance of current approximations.

We have developed a method to obtain the ground-state wave-function of a many-body electron system to be used as a trial wave-function in QMC calculations. We have validated the method by comparing it with accurate configuration interaction calculations in carbon and oxygen and the state-of-the-art methods used in QMC (energy minimization variational quantum Monte Carlo). We have tested our new method in atomic, molecular systems and clusters. The results were published in *Physical Review Letters*.

Information Shared

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05373

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

S. M. Kilbey II

Project Description

In this project the role of sequence tailoring and reversible physical interactions on the self-assembly of polymer micelles in aqueous solutions is being studied. To enable these studies, a new modular approach for creating centro-symmetric three-armed stars is being developed and used to create star-like polymers. The flexibility enabled through the modular approach is a key feature, allowing diverse sets of materials to be easily created from a library of constituents, thereby simplifying the synthesis. By controlling the composition and sequence of the constituents, the structure, dynamics, and response of the star copolymers can be tailored. In addition to complete and rigorous characterization of the novel materials synthesized, the structure and dynamics of the self-assembled micelles will be examined using dynamic and static light scattering. This project is transformative in that by tailoring sequence and composition, we are able to isolate the role of molecular-level design on self-assembly, nanoscale structure, and dynamics, paving the way for designed materials for a variety of applications.

Mission Relevance

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

Results and Accomplishments

Key accomplishments over the course of the project include (1) characterization of the phase behavior of advanced copolymeric materials incorporating both solvophobic and solvophilic blocks; (2) development of a central, tri-functional core molecule that allows sequential attachment of polymer "arms" by an

orthogonal linking reaction; (3) synthesis of a library of functional polymers suitable for attachment to the central core; (4) characterization of a series of centro-symmetric star copolymers by light scattering; and (5) production of model three-arm stars by sequential orthogonal attachment of different arms. In addition, efforts have been made to test and optimize conditions of attachment using "clickable" base layers grafted to surfaces. In total this project has led to enhanced capabilities in characterization of soft materials using light scattering methods and also fostered new synthetic routes for making complex copolymers. These accomplishments and capabilities have recently attracted new users to the Center for Nanophase Materials Sciences. In addition, the vein of research nucleated through this project will continue through programmatic efforts aimed at investigating how chemical information and interactions integrated into the macromolecules affect their assembly at surfaces and in solution, as well as their nanoscale structure and dynamics.

Information Shared

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05375

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

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

Project Description

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

Mission Relevance

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

detection technology resulting from this research, may be exploited for cross-cutting programs such as national security.

Results and Accomplishments

The first deliverable was design and fabrication of nanochannel crossbar devices. We have successfully fabricated channel crossbar devices in polydimethylsiloxane (PDMS), with channel widths below 1 μm, using combinations of electron beam and optical lithography. For the second deliverable, control of droplet formation and injection into the oil phase, we have developed a method for creating discrete femtoliter-scale (10^{-15} L) water-in-oil droplets, based solely on a geometrically induced reduction in oil/water interfacial area at microfabricated junction orifices. Monodisperse droplets could be created at regular intervals under constant pressure conditions, allowing each droplet to be tracked and manipulated individually in real time, or pressure pulses could be applied to generate one, two, or more droplets per pulse reproducibly, without the need for additional actuation or detection equipment beyond a pressure regulator. For the third deliverable, control of fusion of aqueous droplets in the oil phase, we included a second droplet-generating channel to facilitate on-demand droplet generation and fusion of two or more droplets. With this system, fusion and chemical reaction initiation times on the order of 1 millisecond or less were demonstrated, as well as a reversible chemical toggle switch based on alternating fusion of droplets containing acidic or basic solution, monitored with pH-dependent fluorescence in the product droplet. For the fourth deliverable, we are adapting methods we have previously used successfully for passivating the PDMS channel walls (Jung et al. 2008, *Langmuir* **24,** 4439) to prevent nonspecific adsorption of enzymes in the aqueous channel before capture in water-in-oil droplets.

Information Shared

Jung, S.-Y., Retterer, S. T., and C. P. Collier. 2010. "On-Demand Generation of Monodisperse Femtolitre Droplets by Shape-Induced Shear." *Lab on a Chip* **10,** 2688–2694.

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05388

Multiphase Self-Organized Interfaces for Polymer Photovoltaic Technologies

S. M. Kilbey II, Bobby B. Sumpter, Deanna L. Pickel, William T. Heller, Miguel Fuentes-Cabrera, John Ankner, Robert Shaw, Jihua Chen, Jose Alonzo Calderon, and Mark 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, as well as conjugated polymer/fullerene composites. Understanding how to optimize heterojunction interfaces and to promote long-range order in bulk heterojunction thin films is crucial for the development of 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 is 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 systetms based on conjugated polymers and nanoparticles, including both SQDs and fullerene-based derivatives, have been attained during the first year of activity. For example, new capabilities in the synthesis of well-defined conjugated polymers with appropriate chain-end functionality have been developed, and a new block copolymer-based compatibilizer approach has been used 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 para-phenylenes (OPPs) was investigated using large-scale quantum density functional calculations, and simple models were used to determine what level of theory is needed to understand the photophysics of OPPs. Results from computation were compared to measured optical absorbances of OPPs in thin film form and end-tethered poly(para-phenylenes) that were used to compatibilize electrode-like surfaces. Finally, 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. All of these capabilities are being brought to bear in studies of structure-property relationships of donor-acceptor blend systems.

05423

New Multinary Materials for Solar Energy Utilization

Michael A. McGuire, Gerald E. Jellison, Jr., David J. Singh, and Mao-Hua 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 which 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. Systems that received the most attention in FY 2010 were *Ae*-Cu-*Q* and *Ae*-In-Te, where *Ae* = alkaline earth element and *Q* = chalcogen. These chemical systems are known to contain Zintl-like normal valence semiconductors. Several known compounds were studied, and one new material was discovered.

Results from our investigation of *Ae*-Cu-*Q* systems include the theoretical and experimental characterization of two known materials, $BaCu_2Se_2$ and $BaCu_2Te_2$. Theoretical work shows the $BaCu_2Se_2$ and $BaCu_2Te_2$ to be direct gap semiconductors with calculated band gaps near 1 eV. Calculations also show strong anisotropy. Semiconducting behavior is observed in the selenide, and the measured gap is about 1.8 eV. As prepared this material shows p-type, activated behavior with a carrier concentration of $10^{18}/cm^3$ near room temperature. The telluride, as prepared, has a hole concentration one order of magnitude higher and displays degenerately doped semiconductor behavior. In addition, our study of the Ba-Cu-Te system led to the discovery of a new compound with a complex crystal structure and composition which are still under investigation. This compound appears to be charge balanced and is expected to be semiconducting.

In the $SrIn_2Te_4$-$BaIn_2Te_4$ system, we have demonstrated the influence of the *A* cation on the calculated band gap (~1.3 eV for strontium, ~1.5 for barium), which was also observed indirectly through the subtle color difference between the materials. We have also shown experimentally that a solid solution between these end members can be formed, which should provide a means for tuning the band gap.

05451

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

Ho Nyung Lee, Satoshi Okamoto, Gerald E. Jellison, Jr., Matthew F. Chisholm, and David 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 on 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. We also have found that when atomic layers are substituted by perovskites with a high absorption coefficient, the overall band gap can be lowered by about 50%. This has been confirmed by substituting the Mott insulator $LaCoO_3$ for Bi_2O_2 layers in the layered perovskite $Bi_4Ti_3O_{12}$. Our spectroscopic ellipsometry confirmed the band gap reduction from 3.3 to 1.6 eV. 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.

Information Shared

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05484

Novel Nanostructured Photovoltaic Solar Cells

Jun Xu, Sang Hyun Lee, Bart Smith, Xiaoguang Zhang, Chad E. Duty, Tong Ju, H. N. Lee, and Gerald E. Jellison, Jr.

Project Description

Aiming to increase photovoltaic (PV) efficiency, we will 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 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 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 on 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 the morphological effect of 1D nanostructure on carrier transport in nano-junctions, (2) successful synthesis of n-type ZnO nanocones that are feasible for photovoltaic framework, (3) fabrication of nanocone heterojunctions by depositing p-type ZnTe or CdTe layer on the ZnO nanocone surfaces, and (4) preliminary tests for photovoltaic conversion experiments. In general, we have developed and demonstrated a working nanocone solar cell. Based on these results, our next year's work will be focused on optimization of nanocone junctions, minimization of interfacial defects, and delivery of PV efficiency greater than 5%.

Our modeling shows that for efficient carrier transport a nanocone-based junction is better than a nanorod-based junction. Synthesis of ZnO nanorods and ZnO nanocones was performed using thermal vapor deposition incorporated with a three-temperature-zone furnace. For photovoltaic conversion, ZnO nanocones were synthesized on a transparent substrate that allows solar light transmission. The nanocone-based *p-n* heterojunctions were subsequently formed by depositing ZnTe as shells (matrix) on the nanocone surface using pulsed laser deposition (PLD). A CdTe layer was also deposited on the ZnO

nanocone surface. Preliminary photovoltaic experiments demonstrated that the nanocone-based solar cell is functional under light illumination.

Information Shared

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05512

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

Chad E. Duty, Michael Z. Hu, Ilia N. Ivanov, Gerald E. Jellison, Jr., Lonnie J. Love, Ji-Won Moon, Chad M. Parish, and Tommy J. Phelps

Project Description

Today's highest efficiency thin film solar cell converts solar energy to electricity with an efficiency approaching 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. Nanofermentation uses specialized bacteria to naturally produce nanoparticles at moderate temperatures (~60°C), making it scalable for high-volume manufacturing. Our objective is to demonstrate a process for the large-scale production of low-cost, high-efficiency CIGS thin film solar cells. To achieve this objective, we have divided activities into three main tasks: (1) synthesize stoichiometric relevant CIGS nanoparticles, (2) develop a chemical passivation technique for reducing the number of surface defects and providing nanoparticle stability, and (3) use ORNL's pulse thermal processing to consolidate CIGS nanoparticles into a continuous thin film solar cell on a low-cost flexible substrate material. The primary objectives of the first year were to successfully demonstrate the synthesis of CIGS nanoparticles, explore purification and passivation of the materials, and conduct a preliminary investigation of depositing the materials on a substrate and consolidating the particles into a thin film.

Mission Relevance

Thin film solar cells based on CIGS (Copper Indium Gallium Selenide) benefit from lower fabrication cost and a significantly smaller amount of materials utilization (layer thickness of hundreds of nanometers is 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 conversion efficiency 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, nanofermentation 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 Accomplishments

We have successfully bacterially synthesized multiple batches, from 10 mL to 1 L scale, of 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 our patent application in that the application of

nanofermentation is not limited to only fermentative thermophiles. Product purification was extremely successful with respect to the removal of biomass through filtration and the removal of salts through multiple washings. Surface passivation of cadmium sulfide (CdS) quantum dots (a usual buffer layer of solar cell) was accomplished with the addition of sodium oleate. The oleate-passivated CdS nanoparticles exhibited enhanced emission as shown fluorescence measurements. For deposition, ORNL explored three methods: spin coat, drop cast, and ultrasonic spray. Ultrasonic spray provided the good coverage and uniformity with height ranges varying from 50 to 400 nm. Additional work is focusing on fine control of the layer thickness. Finally, preliminary efforts at consolidation with PTP has been extremely successful. Once the material was deposited and consolidated with PTP, ORNL has a new scanning electron microscope/focused ion beam procedure that removes and examines a cross section of a thin film. Preliminary results are showing grain growth, converting nanoparticles to the desired thin film layers.

Information Shared

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Duty, C. E., M. Z. Hu, I. N. Ivanov, G. E. Jellison, L. J. Love, J.-W. Moon, C. M. Parish, and T. J. Phelps. 2010. "Deposition of CISG Nanofermented Nanoparticles." UT-Battelle Invention Disclosure 201002461. Patent application in preparation.

05571

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

Ramesh R. Bhave

Project Description

The primary focus of this research was the development of novel membrane-based, energy-efficient, integrated separation processes and systems for the production of biofuels using domestic renewable alternatives such as microalgae. In this project we evaluated commercially available membranes and ORNL-fabricated membranes to develop new approaches for selective, efficient, and cost-effective separations. We have investigated biomass dewatering to recover >99% of the water suitable for recycle, which is a critical bottleneck in cost-effective biomass processing. We studied the growth characteristics of a representative microalgal strain (*Nannochloropsis oculata*) cultivated in-house under well-controlled conditions. We evaluated polymeric hollow fiber (polyvinylidene fluoride) and several tubular inorganic membranes composed of alumina, zirconia, and silica with pore diameters in the range of 0.1 to 1 μm with hydrophilic and hydrophobic characteristics to optimize both pore size and surface properties. We have also investigated the effect of several key process parameters to optimize membrane performance such as crossflow velocity, coagulant addition, and backpulsing. We have demonstrated the potential for energy savings with a membrane-based process compared to traditional technologies such as centrifugation.

Mission Relevance

Separations is one of the key focus areas of the DOE Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program (DOE EERE/ITP). New research initiatives in biomass processing using membranes can deliver improved energy savings and reduce water use, which are critically important to

improving the energy efficiency of industrial processes. We anticipate significant benefits to DOE EERE/ITP as a result of this research, focusing on development of novel approaches in separation and purification to improve process and energy efficiency. Membrane-based research in biofuels processing that aims to improve process efficiency and water recovery would be beneficial to the Environmental Protection Agency, as it would reduce waste treatment costs and also improve air quality. The use of renewable resources such as microalgae for producing alternative fuels such as biodiesel using membrane-based separation processes would be of interest to the Department of Agriculture (USDA) and the Department of Defense (DOD). The USDA is actively pursuing research to develop alternatives to fossil fuels, and the DOD supports research in algal biodiesel.

Results and Accomplishments

We showed that a *Nannochloropsis oculata* culture can grow relatively rapidly to produce up to 2 g/L biomass at an illumination intensity between 300 and 1200 lux. This result shows that algae can grow at a desirable rate at low to moderate light intensity, which may be a significant advantage for large-scale continuous production systems. Several enhancements to the cultivation techniques were incorporated, which included porous membrane tubes for more efficient gas diffusion and mixing, pH control, and controlled flow of CO_2/air mixture to harvest up to 100 L biomass. We demonstrated that algal biomass can be efficiently dewatered to remove >99% of initial water content with >75% less energy (1.14 kWh per 1000 gallon) compared to centrifugation (~5 kWh per 1000 gallon).

Results showed that a 0.1 μm membrane gave the best overall performance both in term of flux and permeate quality. Surface-enhanced hydrophobic inorganic membranes (with fluorocarbon and silica) did not show a significant flux increase, indicating surface charge is not rate determining. However, an addition of a small quantity of coagulants (10–50 ppm) with a strong cationic charge such as ferric chloride (with or without polyaluminum chloride) increased flux due to particle agglomeration resulting from charge neutralization of negatively charged algae particles. Backpulsing was found to be critical in maintaining high flux (especially with robust inorganic membranes capable of withstanding high pressures) along with relatively high shear in the feed channel. Although microalgal adsorption reduced flux, backpulsing was effective in minimizing membrane fouling. We also demonstrated that fouled membranes can be effectively regenerated using dilute caustic-based cleaning solutions.

Results also showed flux with inorganic microporous membranes (avg. flux 75–100 L/h-m^2) to be significantly higher compared to polymer membranes (avg. flux 25–35 L/h-m^2) at high biomass loading (>100 volumetric concentration factor). At lower biomass concentration, flux with polymer membranes was comparable to inorganic tubular membranes. Thus, a hybrid membrane system utilizing hollow fiber polymer and inorganic tubular membranes can provide a stable, reliable, efficient, and cost-effective dewatering option for large-scale processing of microalgal biomass for the production of biofuels.

05574

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

Wei Zhang

Project Description

Property degradation of welds in advanced materials severely limits realization of the energy benefits of these materials at extreme service environments. A fundamental understanding of weld residual stresses, microstructure, and properties is critical for enabling the safe, efficient, and reliable operation of welded structures. Progress towards amelioration of weld property degradation has been slow due to the occurrence of complex welding phenomena with different physics, length, and time scales whose synergistic effects on weld failure remain unclear. This project aims to develop a unique capability that will enable a fundamental understanding of weld microstructure-mechanics relationships by utilizing in situ neutron diffraction and advanced high-performance weld modeling. The neutron diffraction will provide time-resolved spatial mapping of microstructure and stress during testing in extreme conditions, emulating those experienced in a harsh service environment. The measured data will be used to validate advanced weld models. In particular, this approach of combining the advanced neutron diffraction experiment and the weld models will be applied to study the high-temperature performance of high-strength steel welds fabricated using friction stir welding (FSW), a newly developed advanced solid-state welding process.

Mission Relevance

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

Results and Accomplishments

This year's effort is mainly focused on two thrust areas. The first one is the development of the next-generation FSW model based on transient, three-dimensional material flow and heat transfer simulation. This advanced model uses the dynamic mesh method, combining the benefits of both Lagrangian and Eulerian formulations, to capture the complex material flow driven by the threaded tool. Parallel high-performance computing is utilized to speed up the analysis. Revealed using massless inert particles, the material is shown to experience very different thermomechanical history depending on the location. Predicted results are consistent with experimentally measured temperature-time profiles and material flow patterns reported in the literature, indicating the model validity. This model is essential to understanding and tailoring weld microstructure and properties based on scientific principles. The second thrust area is the fundamental understanding of weld residual stresses through advanced thermal-stress modeling and neutron diffraction measurement. Weld residual stresses have a crucial effect on the performance and integrity of welded structures such as those in advanced nuclear reactor pressure vessels. In neutron

diffraction, an improved approach is developed to calculate the residual stress field without the use of stress-free lattice spacing. Its applicability is examined and justified in two multipass dissimilar metal welds made of austenitic stainless steel and nickel alloy filler metal using different heat inputs. Finally, for this research and other work, the PI was recognized by American Welding Society and received the Prof. Masubuchi Award for significant scientific and technical contributions to materials joining.

Information Shared

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05836

Femtosecond Electronic Spectroscopy of Complex Nanostructures and Their Functional Assemblies

Yingzhong 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 obtaining 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 enabled us to elucidate exciton diffusive motion in this quasi-one-dimensional material. Currently, our research is focused on time-resolved fluorescence study of the optical properties of selected conjugated polymers, which are chosen in view of their potential for high-efficiency photovoltaic applications.

05837

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

Weijun Yao

Project Description

A neutron electric dipole moment (EDM) can be detected by measuring the difference in the precession frequency of a population of polarized neutrons in a magnetic field when subjected to a strong electric field aligned parallel or anti-parallel to the magnetic field. To minimize systematic effects associated with stray magnetic fields, a simultaneous measurement can be made on a "co-magnetometer," a species that is

known to have negligible EDM (e.g., ^{3}He). Next-generation experiments aim to improve our knowledge of the neutron EDM by two orders of magnitude. One proposed technique utilizes a superthermal process to generate UCNs in superfluid ^{4}He. Polarized ^{3}He is simultaneously introduced into the ^{4}He and serves as a frequency monitor (through the spin-dependent cross section) and as a co-magnetometer. The ^{4}He also serves as a scintillating medium, converting the neutron/^{3}He reaction products into a detectable light signal, and is believed to have a very high dielectric strength. This technique has several challenges directly related to the large-scale low-temperature requirements. We are preparing a series of measurements and calculations designed to address these challenges.

- Measure the dielectric breakdown strength of liquid helium
- Demonstrate injection of polarized ^{3}He into a volume of ^{4}He
- Demonstrate movement of ^{3}He between volumes using heat currents
- Design thermally conductive links to allow a large-scale apparatus to be cooled down with a dilution refrigerator and maintain appropriate temperature gradients

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

In the last fiscal year, the author participated in the operation in combining a dilution refrigerator (DUC) and a high-voltage (HV) test facility in order to measure the dielectric strength in superfuild ^{4}He at temperatures below 1 K at Los Alamos National Laboratory. Several technical issues have been identified on these systems. Meanwhile, the scope of the HV test was expanded substantially to include several experiments such as testing the electrode coating, effect of leakage current, impact of dielectrics, and SQUID effects in high electric field. The expanded HV tests require temperatures between 0.6 K to 1 K. The Experiments 2 and 3 in the list above also require temperatures around 0.35 K to be facilitated by the DUC. In order to move forward with these two experiments, which were originally planned to follow the HV test, the author is constructing a second low-temperature system at the MIT Bates Laboratory, which will be dedicated to HV tests in the near future.

During the last year the author also developed a unique design for a high-power dilution refrigerator that can effectively cool a large volume of liquid helium to 0.3 K for generating 8.9 Å neutrons via superthermal technique in the ultra cold neutron experiments.

05838

Improving the Performance of Lithium Ion Batteries by Tuning the Graphite/Carbon Electrode Surface

Xiao-Guang Sun

Project Description

Rechargeable lithium ion batteries that have been proposed for applications in electric vehicles (EVs) should meet safety requirements and have long calendar lives (>10 years). These, to a larger extent, are determined by the quality of the solid electrolyte interface (SEI) formed on the surface of graphite/carbon electrodes. However, the SEI layer on graphite/carbon electrodes grows with cycling and storage, which deteriorates the battery performance and calendar life. Therefore designing desirable interfaces/ interphases (SEI) are major scientific challenges that must be met to achieve truly innovative breakthroughs in future chemical energy storage devices. The overarching goal of this project is targeted on tuning the surface of graphite/carbon electrodes by pre-deposition of mixtures of different inorganic or organic lithium salts or their combinations with single ion conductors. This approach entails a precision control over formation of SEI layers and opens up a new avenue to solve the critical problems associated with SEI layers.

Mission Relevance

This project involves the synthesis of a series of new lithium borate salts having good SEI formation ability that cannot only be used to form an artificial SEI layer on a graphite/carbon electrode surface (tuned up in this project) but also can be evaluated as promising lithium salts in conventional carbonate solvents to replace lithium hexafluorophosphate ($LiPF_6$), which is not stable at high temperatures. This will benefit DOE's other battery-related programs and offices, such as Energy Efficiency Renewable Energy (EERE), Vehicle Technology, and Batteries for Advanced Transport Technology, etc.

Results and Accomplishments

We have used two different approaches to modify the surface of graphite electrode—direct deposit lithium malonate (LM) on the surface of graphite electrode and use of salt as an additive to carbonate electrolyte mixtures. Both approaches have successfully reduced the initial irreversible capacity loss in the graphite||lithium half cells and improved the corresponding coulombic efficiencies. However, the capacities of the half cells, with and without surface-modified electrodes, continually decrease with cycling, which is due to the poor quality of SEI formed on the bare graphite electrode surface and the lack of mechanical strength of the artificial SEI on the modified graphite electrode surface.

To increase the mechanical strength of the surface coating, we then synthesized single ion conductors based on allyl-group-containing lithium borate salt grafted on allyl-group-containing polymethacrylate polymers via hydrosilylation reaction. It is found that the surface coating with single ion conductors on both carbon and graphite particles could successfully reduce the initial electrolyte decomposition and improve the corresponding coulombic efficiencies; however, they still could not prevent the eventual capacity loss with cycling. This observation primarily resulted from the un-removed platinum catalyst within the crosslinked membrane, which can induce electron tunneling and thus induce more electrolyte decomposition, and therefore capacity loss. Future experiments need to focus on removing the catalyst after the film crosslinking reaction.

We have been successful in securing following-on funding to continue this work under two sponsorships: the DOE Vehicle Technology Program (Hard Carbon Materials for High-Capacity Li-ion Battery Anodes)

and the DOE Materials Science and Engineering Division (Materials and Interfacial Chemistry for Next Generation Electrical Energy Storage).

Information Shared

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05842

Highly Polar Oxides for Photovoltaics Beyond p–n Junctions

Hans M. Christen, Gerald E. Jellison, Jr., Hyun-Sik Kim, and David J. Singh

Project Description

The goal of this project 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 project we seek to (1) understand the fundamental mechanism of the photovoltaic 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 a 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

Initial work during the first months of this late-start project focused on the synthesis of nickel-doped lead zirconate-titanate films and shows a complex, undesired phase separation mechanism under the initially used growth conditions. Approaches to overcome this limitation have been designed with the hope of obtaining band-gap-controlled ferroelectrics in year 2 of the project. Work on highly polar perovskite materials has resulted in a significantly enhanced understanding of the crystal structure of such strain-stabilized ferrite materials. Focus has been on bismuth ferrite, where we find a sequence of strain-induced phase transition that is otherwise only observed in lead-based solid-solution ferroelectrics. Additionally, changes to the growth apparatus are implemented to enable the necessary experiments at higher growth temperatures than currently possible.

05843

Theoretical Studies of Decoupling Phenomena in Dynamics of Soft Materials

Alexei Sokolov and Vladimir Novikov

Project Description

Understanding the 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 (1) decoupling of chain relaxation from segmental relaxation in polymers; (2) decoupling of ionic conductivity from the structural relaxation; and (3) decoupling of protein's biochemical activity from the solvent's viscosity. The major goal of the 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 cells, organic photovoltaic cells, carbon capture), for bio-related technologies (enzymatic activity, bio-inspired catalysis), and processing of lightweight materials (polymers).

Mission Relevance

Soft materials (e.g., polymers, colloids, biomaterials) attract the significant attention of researchers due to their potential application in many fields, from energy and lightweight materials to biotechnologies and biomedical 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 remain a great challenge. The project is focused on development of a fundamental understanding of decoupling phenomena in the 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

We investigated the connection of decoupling phenomenon to the dynamical heterogeneity of polymeric, molecular, and inorganic glass formers. To this end we used the inelastic light scattering to analyze the universal feature of the dynamics in various glass-forming materials—the boson peak. This peak in the THz frequency range is associated with a characteristic length scale of the frozen-in dynamical heterogeneities. We estimated the (heterogeneity) length scale obtained from the boson peak spectra. It has been shown in our previous publications that the decoupling correlates with the steepness of the temperature dependence of structural relaxation (the so-called fragility). So, it has been expected that the decoupling might depend on the length scale of the dynamic heterogeneities. However, our analysis revealed that fragility does not correlate directly to the length scale of the dynamic heterogeneities. Only its density (pressure) dependence shows some correlations with this length scale. The presented results call for a revision of traditional view on the role of heterogeneity in structural relaxation of glass-forming systems and, respectively, in the decoupling phenomenon. In addition, our analysis of coherent neutron scattering data (literature data) suggests that the decoupling phenomena appears in the wave-vector

dependence of the characteristic relaxation time $\tau(Q)$ of the intermediate scattering function. If true, this opens a direct way for analysis of the microscopic mechanism of the decoupling in dynamics.

Information Shared

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NEUTRON SCIENCES

05004

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

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

Project Description

We will study amine-stabilized transition-metal-based nanoparticles for novel, size-dependent magnetic effects and spin dynamics. An integral part of the research is to develop synthetic protocols for magnetic nanoparticles amenable to the requirements of inelastic neutron scattering experiments. The primary means of doing this is to deuterate the ligands of amine-stabilized magnetic nanoparticles. Once sufficient quantities of nanoparticles are synthesized, neutron scattering experiments will be used to elucidate the fundamental magnetic behavior. Metallic nanoparticles are very active fields of research in the basic and applied sciences. These materials are being intensively studied for a wide variety of applications including catalysis and advanced functional materials. The physical constraints resulting from the size of such systems have produced new behaviors, some of which have the potential to be of industrial interest. ORNL is well positioned to take a leadership role in the study of nanoscale magnetism due to the combination of world-class materials synthesis and neutron scattering instrumentation.

Mission Relevance

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

Results and Accomplishments

In the project's first year, we successfully synthesized MnO magnetic nanoparticles with both hydrogenated and deuterated capping ligands. In the second year of the project, the synthetic protocol was developed further to minimize the use of high-cost deuterated 1-octadecanol. The nanoparticles' size and

composition were characterized using scanning transmission electron microscopy, X-ray diffraction measurements, and magnetization measurements. These particles were then used for subsequent neutron scattering measurements as follows: The effects of nanoscale confinement were clearly observed in the neutron scattering experiments; both the structural and magnetic peaks are broadened compared with the bulk. The temperature dependence of the magnetic peak indicates that the antiferromagnetic transition is suppressed to 113 K. To explore the differences in the magnetic behavior of bulk vs. nano MnO in greater detail, we performed polarized neutron diffraction experiments to explicitly separate the magnetic diffuse scattering and compare this with that observed in the bulk. The general conclusion from this work is that the diffuse magnetic scattering is a much more substantial part of the overall magnetic scattering for the nanoparticles than in the bulk. No additional neutron depolarization as a function of temperature (2–300 K) was observed, suggesting that a ferromagnetic component to the magnetism does not develop as a function of temperature, in contrast to claims in the literature based upon bulk measurements. The final 6 months of the project were spent further refining synthetic protocols to grow large quantities of nanoparticle systems suitable for neutron scattering as well as working toward publication of the results of the previous year's efforts in the open literature. Two publications are now nearly ready for submission based on this effort. For the continued development of synthetic protocols, two systems were targeted: Fe_2O_3 and FePt. In both cases, a microwave synthetic technique was employed.

05029

Pushing the Limits: High-Impact Neutron Protein Crystallography

Leighton Coates and Dean Myles

Project Description

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

Mission Relevance

At the time of writing, only nine unique proteins have been studied to high resolution using neutron diffraction that have their atomic coordinates deposited in the protein data bank (PDB). These proteins share a number of similarities; they are all stable proteins which diffract X-rays to well beyond atomic resolution (1.2 Å) and have been studied for many years. Many of the nine proteins studied are available for purchase from all major suppliers of biochemical reagents. Studies on these types of proteins, while providing interesting science, will never yield the high-impact results or publications that are necessary to stimulate wider interest in neutron protein crystallography and recent developments in it. The chances of obtaining peer-reviewed funding to work on proteins of this type is minimal at best. Most peer-reviewed research in the structural biology area is conducted on proteins overexpressed within a host system.

Understanding protein structure and function remains an outstanding grand challenge in biology, and its strategic and fundamental importance in human health, medicine, agriculture, and bioenergy cannot be overstated.

Results and Accomplishments

Bacterial resistance to β-lactam antibiotics is a serious problem limiting current clinical therapy and therefore offers a real opportunity to showcase neutron diffraction as a tool to understand how Toho-1 β-lactamase is able to break down many current antibiotics. Toho-1 β-lactamase is an extended-spectrum β-lactamase that has acquired efficient activity not only to penicillins but also to cephalosporins including the expanded spectrum cephalosporins. During the project we solved and published the first crystal structure of a β-lactamase using neutron protein crystallography. Later on we also successfully perdeuterated the enzyme at the center for structural molecular biology at ORNL and collected a second perdeuterated neutron data set. The two structures that were produced give important information on the catalytic mechanism by which Toho-1 β-lactamase is able to break down many current antibiotics. During the final stages of the project we were able to test one of our crystals on the SNS single crystal diffractometer TOPAZ where we saw diffraction from a protein crystal for the first time at ORNL.

Information Shared

Tomanicek, S. J, M. P. Blakeley, J. B. Cooper, Y. Chen, P. V. Afonine, and L. Coates. 2010. "Neutron diffraction studies of a class A β-lactamase Toho-1 E166A/R274N/R276N triple mutant." *J. Mol. Biol.* **396,** 1070–1080.

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05045

Neutron Structural Virology

Flora Meilleur, William T. Heller, and Dean Myles

Project Description

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

Mission Relvance

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

Results and Accomplishments

The ultimate goal of this project is to investigate the structures of viruses grown from two different sources (baby hamster kidney and insect cells) at pH 7.2 and 6.4 in order to track the virus structural changes in response to pH reduction. Low and neutral pH contrast series data were collected on the BIO-SANS (CG3) beamline at the HFIR in FY 2008 and 2009 for viruses grown from baby hamster kidney and insect cells. The neutral pH data have been analyzed using model-dependent and model-independent methods. In the model-independent method, Guinier approximation is used to determine the radius of gyration, R_g, of the virus particle. The model-dependent analysis using multiple concentric shells of different scattering length density and radius suggests that four shells are needed to fit the data satisfactorily. The analyses showed structural differences between the mammalian- and insect-cell-grown viruses. The results were published in *the Journal of Virology*.

These small-angle neutron scattering experiments show that structural data of functional entities of large size and complexity can be collected and interpreted using the neutron scattering instruments at ORNL. We have applied the methodology developed in this project to another virus. Red Clover Necrotic Mosaic Virus can be used as nano-cargo for drug delivery. We are currently preparing a manuscript to describe its structural analysis by small-angle neutron scattering.

These studies are critical as they illustrate the unique potential of neutron techniques for studying native virus particles, which will help attract the virology community to conduct structural studies using the SNS/HFIR instrument suite.

Information Shared

He, L., A. Piper, F. Meilleur, D. A. Myles, R. Hernandez, D. T. Brown, and W. T. Heller. 2010. "The structure of Sindbis virus produced from vertebrate and invertabrate hosts determined by small angle neutron scattering." *J. Virol.* **84**(10), 5270–5276.

05088

Inelastic Neutron Scattering from Magnetic Heterostructures

Randy Fishman, J. Lee Robertson, Mark D. Lumsden, and Jian Shen

Project Description

Inelastic neutron scattering is the world's most powerful tool to study the magnetic dynamics of solids. But only with the recent development of improved neutron optics and more powerful neutron sources

such as the Spallation Neutron Source (SNS) has it become feasible to study the magnetic dynamics at interfaces and in confined geometries. We will develop the technique of inelastic neutron scattering from magnetic heterostructures consisting of alternating magnetic and nonmagnetic layers. To demonstrate the feasibility of this technique, we shall study Dy/Y and Ho/Y multilayers, which were chosen for the close lattice matches and the large dysprosium and holmium moments. Molecular-beamepitaxy will be used to fabricate heterostructures by repeating bilayers with roughly 45 Å of dysprosiumor holmium and 30 Å of yttrium. Magnetic characterization will be performed using the magnetism reflectometer at the SNS and inelastic measurements will be performed at the High Flux Isotope Reactor (HFIR). Simultaneously, we will develop the theory of inelastic neutron scattering from magnetic heterostructures by using a coupled Green's function technique.

Mission Relevance

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

Results and Accomplishments

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

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

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

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

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

We have also written a paper on the change in spin-wave dynamics from bulk dysprosium to the Dy/Y multilayer geometry. Discrete excitations that appear in an isolated dysprosium layer follow the bulk-like

dispersion when dysprosium layers are coupled by an RKKY interaction through the yttrium spacer. This work was published in *Journal of Physics: Condensed Matter*.

Inelastic neutron-scattering measurements on the Dy/Y multilayer samples prepared by Mankey are expected to begin this fall.

Information Shared

Haraldsen, J. T., and R. S. Fishman. 2010. "Control of Chirality Normal to the Interface of Magnetic and Non-Magnetic Hexagonal Layers." *Phys. Rev. B, Rapid Communications* **81,** 020404.
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05140

Mapping the Protein Structure-Function-Dynamics Landscape

Pratul K. Agarwal

Project Description

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

Mission Relevance

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

Results and Accomplishments

This project has investigated the interconnection between protein structure, dynamics, and function using a multidisciplinary approach on two protein targets. As a first target, the protein rubredoxin from *Pyrococcus furiosus* (RdPf) was radio-labeled and studied under different solvents (H_2O and D_2O), using neutron scattering and computational modeling. In particular, the following neutron studies were performed: (1) specific labeling of Rubredoxin methyl groups with hydrogen remainder deuterated (we measured [on Basis] this sample and a fully deuterated sample) and (2) measured protonated Rubredoxin, hydrated at 0.2 and 0.37 with D_2O (we measured deuterated Rubredoxin hydrated with H_2O at the same hydration levels). The goal of the experiment was to resolve a long-standing debate in the community of the role of solvent in triggering or enabling the local dynamics of a protein. Clearly at low Q, it is apparent that the water dynamics initiates at a lower T then the protein. The combination of MD simulations and neutron scattering techniques has allowed probing the local dynamics on length and time scales of 3 to 20 Å and 10 ps to 2 ns, respectively. These studies were designed to probe the coupling between surface and near-surface hydration water to the local dynamics of the protein over a temperature range from 100 K to 360 K. Computational simulations and experimental data show quantitative agreement over the entire region studied, providing a detailed picture of the thermal evolution of rubredoxin motions. The most important observation of this study has been that the onset of anharmonicity in the protein motions corresponds to the onset of function-promoting properties of the thermophilic rubredoxin. Computational modeling of thermophilic and mesophilic Rubredoxin also allowed interpretation of the neutron data.

Joint computational-experimental strategy was also used to investigate the enzyme DHFR as a second target, particularly for the impact of suppression of dynamics on enzyme mechanism. The role of the solvent in driving the enzyme motions and therefore the enzyme activity has been analyzed by characterizing DHFR catalysis in an aqueous mixture of organic solvents (such as isopropanol). Our studies show that the presence of organic solvents in the medium suppresses the dynamical motions of DHFR (the structure showed little change up until 25% v/v mixture of isopropanol). Follow-on studies are planned to characterize the suppression in motions as an explanation for the decrease in enzyme activity.

Information Shared

Ramanathan, A., P. K. Agarwal, M. Kurnikova, and C. J. Langmead. 2010. "An Online Approach for Mining Collective Behaviors from Molecular Dynamics Simulations." *J. Comput. Biol.* **17**(3), 309–324.

Kamath, G., E. E. Howell, and P. K. Agarwal. 2010. "The Tail Wagging the Dog: Insights into Catalysis in R67 Dihydrofolate Reductase." *Biochemistry* **49**(42), 9078–9088.

05227

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

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

Project Description

Carbon dioxide emissions from anthropogenic sources are frequently directly linked to the rising level of atmospheric CO_2 and to global warming. Carbon capture and sequestration in geological formations is a proposed measure for arresting the rising concentration of atmospheric carbon dioxide. Saline aquifers, depleted oil and gas reservoirs, 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 a barrier to the deployment of this technology. In order to circumvent this barrier, 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 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 2010 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 12 coals from R. Sakurovs' collection at elevated pressure. In the year 2011 we intend to complete SANS/USANS experiments on remaining coals from Sakurovs' collection (August–October 2010). We are going to finalize data reduction and interpretation, perform theoretical evaluation of the obtained results, write and submit papers, and present the results at conferences and meetings.

Mission Relevance

This research is relevant to the Core Research Activities in Geosciences research (Chemical Sciences, Geosciences, and Biosciences Division) and Neutron and X-ray Scattering (Materials Sciences and Engineering Division) within the DOE Office of Basic Energy Sciences. It supports the President's clean coal initiative "to advance technologies that can help meet the nation's growing demand for electricity while simultaneously providing a secure and low-cost energy source and protecting the environment." The practical implications of this work may also be of a 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 practices which may contribute in the reduction of the greenhouse emissions and thus improve environmental quality in the USA and elsewhere.

Results and Accomplishments

A new method of the 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 size. 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 were conducted using 12 samples out of a collection of 20 various coals which were obtained from R. Sakurovs (CSIRO, Australia).

First high-pressure Quasi-Elastic Neutron Scattering (QENS) experiment on the Backscattering Spectrometer (BASIS) at the Spallation Neutron Source (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 complementary SANS data on the phase behavior and adsorption of methane in 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 (May 2010) have shown that replacement of the adsorbed methane by CO_2 starts to occur at an unexpectedly low CO_2 pressure on the order of 25 bar. This result can be understood based on SANS studies of the methane adsorption from CO_2+CH_4 mixtures.

Information Shared

Chathoth, S. M., E. Mamontov, Y. B. Melnichenko, and M. Zamponi. 2010. "Diffusion and adsorption of methane confined in nano-porous carbon aerogel: A combined quasi-elastic and small-angle neutron scattering study." *Micropor. Mesopor. Mat.* **132,** 148.

Sakurovs, R., A. P. Radlinski, and Y. B. Melnichenko. 2009. "Stability of the bituminous coal microstructure upon exposure to high pressures of helium." *Energy & Fuels* **23,** 5022.

05246

Neutron Scattering and Osmotic Stress to Study Intrinsically Disordered Proteins

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

Project Description

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

structure in solution is directly measured. It is expected that this research will provide unique insight into the mechanism of IDP function while simultaneously making advances in the use of neutron scattering for the study of biological systems through the combination with osmotic stress.

Mission Relevance

This research project 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 Biodeuteration 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 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 R01/R21 grant.

Results and Accomplishments

The major scientific accomplishments of the research project for FY 2010 have been (1) the continued development of our combined SANS and osmotic stress approach for studying protein hydration, conformation, and protein-protein interactions; (2) SANS characterization of an IDP pair that undergoes coupled folding and binding; and (3) the preparation, identification, and characterization of our CREB binding protein (CBP) fragments that contain IDP regions.

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. Building upon this work, we began probing the modulation of the HK monomer-to-dimer transition using osmotic stress. With beamtime on BioSANS (Jan. 20–22, 2010 / IPTS-1282), we explored the pH dependence of this transition with SANS and found a transition midpoint of pH 6.8. Using pH 7.4 (68% monomer) and deuterated osmolytes contrast matched in D_2O buffer, we perturbed the HK equilibrium toward the dimer state and found that osmotic pressures up to 70 atm were required to begin to induce changes. These studies are continuing and have been instructive toward applying our SANS and osmotic stress method to understand the hydration properties and structural transitions in IDPs.

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. With the BioSANS (Oct 17–20, 2009 / IPTS-1809) we characterized the NCBD/ACTR complex and the structure of ACTR alone. The SANS structure on NCBD/ACTR complex is in good agreement with the NMR structure, while SANS on ACTR reveals the expanded nature of the unbound, unfolded state. In this way, we gain further insight into the structural flexibility of these IDP regions.

We have characterized a fragment of CBP (F1-CBP) using CD and dynamic light scattering (DLS). CD shows an amount of partial α-helical structure that is consistent with the expected secondary structure. DLS shows F1-CBP to be monodisperse with a hydrodynamic diameter of 14 nm, which closely matches our calculated diameter of 14.4 nm. Similar characterization of a second fragment, F2-CBP, along with further characterization of both proteins by small-angle X-ray scattering (SAXS) and SANS, is planned. We have been awarded BioSANS beamtime (IPTS-4325) for the SANS studies.

Information Shared

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05272

A Study of Real-Space Neutron Scattering Methods

J. Lee Robertson, Wei-Ren Chen, and Chwen-Yang Shew

Project Description

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

Mission Relevance

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

Results and Accomplishments

The results of this project are grouped in terms of the manuscripts prepared during the subcontract period as follows. In Ref. 1 we report a novel Monte Carlo algorithm developed to accurately calculate the spin-echo small-angle neutron scattering (SESANS) spectra. In Ref. 2 we report on a theoretical calculation to investigate the spectral features of SESANS for liquid particles under both repulsive and attractive intermolecular interactions. We found that the SESANS correlation function provides clear spectral features that elucidate the intermolecular correlation among interacting particles. In Ref. 3 we compare spectra between that of a liquid of uniform hard spheres and one of nonuniform hollow hard spheres. This work shows that due to the distinguishable length scales between intramoleuclar and intermolecular spatial correlations, it is possible to recognize the intramoleulcar scattering contribution to the SESANS as the density is varied. In Ref. 4 we explore the sensitivity of SESANS from a theoretical standpoint, and the results suggest there is a physical interpretation of the spatial variable in the SESANS correlation function. In Ref. 5 we investigate the effect of the interparticle potential with broken centrosymmetry on liquid structure and find that centrosymmetry particles and broken centrosymmetry particles exhibit different spectral features in the SESANS data over a wide range of dimension, consistent within their pair correlation functions. In Ref. 6 we find that it is conceptually important to fill in the "gap" in the theoretical calculation of $\gamma(r)$ because these various theoretical approaches provide multiple tools for future research. And finally in Ref. 7 we will report on how our Monte Carlo algorithm can be extended to compute the SESANS correlation function of binary hard sphere particles of different diameters.

Information Shared

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05306

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

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

Project Description

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

Mission Relevance

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

Results and Accomplishments

We worked on two model systems, including zirconium- and calcium-based metallic glasses, to study their mechanical deformation and nanoscale crystallization behaviors. We have carried out in situ small-angle neutron scattering (SANS) experiments at HFIR and, as a demonstration, simultaneous diffraction and small-angle X-ray scattering (SAXS) experiments at the European Synchrotron Radiation Facility (ESRF), for a series of samples under tension and compression and/or also at elevated temperatures. Both SANS and SAXS data for calcium glasses indicated significant changes upon annealing, as indicated by visible interference peaks.

Simultaneous diffraction and SAXS data revealed the structure evolution from atomic to nanometer length scales resulting from the thermomechanical deformation. After initial yielding, the metallic glass sample exhibits a transient softening stage that characterizes the homogeneous flow due to the local atomic structure rearrangement, followed by a strengthening stage that originates from nanoscale crystallization. This finding provides new insights for understanding homogeneous and inhomogeneous flows in metallic glasses from structure changes at multiple length scales.

In addition, a new analysis method has been developed to separate the diffraction pattern of a crystalline phase from the glass matrix in case of partial crystallization, which enabled us to reveal the kinetics of nanocrystallization. In situ, time-resolved neutron diffraction data upon heating zirconium-based glasses have been collected on VULCAN, the engineering materials diffractometer at the SNS. These experimental results, together with the ex situ SANS data (HFIR) and the diffraction data collected on the neutron powder diffractometer (NPDF) at the Los Alamos Neutron Science Center (LANSCE), demonstrated a cascade of crystallization at atomic to nanometer scales controlled by complex chemical interdiffusion. This new mechanism has important implications for understanding the ability of a metallic alloy to form a glass.

In search for evidence of shear-transformation zone, an in situ deformation experiment has been conducted on CG-2 General Purpose SANS at HIFR, with calcium-based metallic glasses. Preliminary data analysis showed little change in the scattering profile under deformation. Meanwhile, in collaboration with Professor T. G. Nieh's group at the University of Tennessee, shear band propagation in a zirconium-based metallic glass during compression was characterized off-line using a high-speed camera. The shear velocity was calculated and further compared with that measured from using strain gages. The experimental results also showed that localized shear occurs in a simultaneous fashion; that is, shear band operates simultaneously across the entire shear plane, rather than in a progressive manner.

Theoretically, we examined the short-range order or cluster structure in zirconium–copper glasses, which provided experimental evidence of a close correlation between the coordination number of unlike bonds and the liquid stability. The initial emphasis has been on implementing molecular simulations that may be compared with experiments. This work will soon be extended to examine the dynamic structure factor. Thermodynamic behavior has been observed through cooling simulations from high temperatures, for three zirconium–copper glasses. Simulations showed three regimes: the conventional "high-temperature" liquid behavior, the low-temperature "frozen-in" glass behavior, and a large transition regime.

Information Shared

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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 Jacob Jones

Project Description

The advent of extremely high neutron flux, unique time event data acquisition, and novel instrumentation at the Spallation Neutron Source (SNS) open 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 "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

This project started on April 1st 2010. We have developed new neutron event data acquisition (DAQ) of proton charges within a one pulse, fast sample environment data rate up to 400 Hz, and new data reduction software to post-synchronize the neutron diffraction and sample environment data. For fast time resolved studies, in order to normalize diffraction pattern to cancel beam fluctuations, proton charges within one pulse need to be precisely collected and cross-linked to the recorded neutron data. A new event data format consisting of proton charge information for each pulse has been developed and implemented at SNS. Compared to the original sample environment DAQ with low sampling rate, a new DAQ system with a reliable high temporal resolution close to a PC time clock resolution was developed. The

timestamps are recorded directly from the time clock on the sample environment computer, which is synchronized with the central timing computer, to ensure the same timestamps from neutron events. With the new developed software VDRIVE, neutron event data with proton charges and sample environment data can be reduced and synchronized to various temporal resolutions from sub-seconds and beyond.

With those newly developed capabilities, we have demonstrated the fundamental concept of asynchronous neutron diffraction measurements by example of continuous heating experiment of phase transition of textured titanium alloy, a charge and discharge phenomenon in a large format prismatic battery, and lattice strain evolutions of a model stainless steel under low-cycle fatigue. Temporal resolutions of these initial experiments are demonstrated from minutes to millisecond.

Information Shared

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05432

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

Andrew D. Christianson, Georg Ehlers, Mark D. Lumsden, Thomas A. Maier, David Mandrus, Stephen E. Nagler, and Cuihuan 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 significant strides in the synthesis of deuterated organic superconductors and organic charge coordination polymers. Samples of deuterated $CuF_2(H_2O)_2$-pyz and κ-$(BEDT\text{-}TTF)_2X$ (X = Cl, Br)

have been synthesized. The first batches of crystals have been delivered, and characterization measurements have been made. Initial neutron scattering experiments on $CuF_2(D_2O)_2$-pyz have enabled the determination of the ordering wave vector characterizing the magnetic order and together with planned experiments should enable the microscopic understanding of the magnetically ordered state. Furthermore, several user proposals for neutron scattering beam time have been successful at the Spallation Neutron Source and the High Flux Isotope Reactor at ORNL. The success of these proposals enables near-term neutron scattering characterization of the targeted samples of organic superconductors and molecular magnets. The theoretical modeling component of this project has made substantial headway on the simulation of the magnetic properties of the organic superconductors and has been able to qualitatively reproduce the phase diagram with a single-band two-dimensional Hubbard model.

05445

In Situ Neutron Scattering Studies of Fuel Cell Materials

Ashfia Huq, M. Parans Paranthaman, Jung-Hyun Kim, and Zhonghe Bi

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 technetium 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; or 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

We envision that this research will become one of the core research activities of the proposed "Center for Materials Chemistry" at the Neutron Scattering Science Division. 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 (CO_2 capture), energy storage, solar energy conversion, phase mapping of correlated electron materials, and synthesis of solid state materials. Thus we believe the outcome of this project will significantly strengthen ORNL's ability to carry out in situ characterization of energy-related materials.

Results and Accomplishments

During FY 2010, the first year of the project, we have made much progress in setting up materials synthesis of various components of fuel cells such as cathodes and electrolytes. We have also made great strides in setting up equipment to synthesize solid materials (Ball-mills and high-temperature furnaces) and to characterize electrochemical properties such as AC impedance spectroscopy, four probe conductance, thermogravimetric analysis, dilatometry, etc., which are crucial for new materials development for SOFC. On the electrolyte materials end, we have concentrated on improving the structural stability of a recently proposed rare earth ortho niobate proton conductor family (1.0% calcium-doped $LaNbO_4$). By substituting tantalum in the niobium site we have been able to increase the phase transition temperature of this material, which is the principal cause of thermal instability of this family of electrolytes. We have also studied the phase diagram of the $Ln(Ba,Sr)Co_2O_{5+\delta}$ layered perovskite system, which is a candidate for cathode material for intermediate-temperature SOFC. We found that the increasing strontium solubility in Ba-site with decreasing size of Ln^{3+} ion from Ln = Pr to Ho. The substitution of strontium for barium in $YBaCo_2O_{5+\delta}$ prevents the phase decomposition at high temperatures, which allows the use of $Y(Ba,Sr)Co_2O_{5+\delta}$ as a cathode in SOFC. Neutron beam time has been allotted this cycle (December 2010) and the next cycle (Feb 2011–June 2011) to carry out in situ neutron diffraction studies for both these systems.

The principal accomplishment in the first year of this project was the construction of an integrated sample environment dedicated for in situ powder diffraction experiment at the Powgen instrument at SNS. An old vanadium furnace, obtained from the Intense Pulsed Neutron Source (IPNS), was modified, and measurements were made in the temperature range of (200–1000°C) using a powder sample of cathode material for SOFC in vanadium can. This furnace was then modified to an atmosphere furnace, which will allow the flow of various different gases using a quartz tube sample insert. The complete ensemble includes a permanent gas manifold system at the instrument equipped with 11 mass flow controllers housed in two separate gas cabinets, one of which is for hazardous and flammable gases. An oxygen sensor is available for measurement of pO_2, and a thermogravimetric analyzer has been added to the furnace for independent measurements of weight gain or loss by the sample, and a residual gas analyzer is connected to monitor the out flowing gas mixture. Each of the separate components has been tested individually. The whole system is expected to be connected and tested at the instrument by the end of the first week of December. The initial commissioning measurements using this multi-probe ensemble are expected to take place in December of 2010. The results from the integrated in situ ensemble will be reported in the future.

In FY 2010 two postdocs, Jung-Hyun Kim and Zhonghe Bi, were identified and hired to work on oxygen conductors (for cathode materials) and proton conductors (for electrolyte materials).

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 thermomechanical 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 (SNS) 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, 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 (DoD) and the National Aeronautics and Space Administration (NASA) because of the unique applications that the proposed approach might generate in defense and aerospace components.

Results and Accomplishments

We have performed the initial, in situ neutron diffraction measurements of recovery and recrystallization in Al-2Mg alloy and a commercial Mg alloy AZ31 using the engineering spectrometer, VULCAN, at SNS in order to understand the kinetics of the processes and the evolution of texture. In Al-2Mg the measurements clearly indicate the strengthening of Cube texture associated with recrystallization. In AZ31, the process that occurred predominantly at the test temperature was recovery associated with reduction in peak width. No significant difference in recovery kinetics was observed in Al-2Mg between different texture components. However, this conclusion must be validated using optimized experiments that will allow more efficient data collection at early times.

We have extended the existing crystal plasticity models to Hexagonal Close Packed systems and also successfully mapped microstructure and texture from experimental samples to three-dimensional simulation domains. The crystal plasticity deformation model captures the texture evolution during deformation plane strain compression as well as the weakening of the basal texture in the presence of shear. An existing nucleation model based on "Excess dislocations" to explain Cube texture formation during recrystallization in Face Centered Cubic polycrystals was used to investigate the weakening of Cube texture during cross-rolling of aluminum.

Since the in situ recrystallization experiments are the first of their kind at SNS, we are learning as we go along to better optimize the experimental conditions to improve the quality of our results. One such area is in rapid specimen heating and the control of sample temperature. We have initiated activities at SNS for exploring various specimen heating techniques which we will exploit in the second round of experiments.

05551

Neutron Imaging of Fluids within Plant-Soil-Groundwater Systems

Hassina Z. Bilheux

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: $I = I_0 \exp(-\mu \cdot \Delta x)$, where I is the transmitted beam intensity, I_0 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

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 μm 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.

Program Development

To disseminate the results of our work and attract new sponsorship, Hassina Bilheux and Ed Perfect organized a special session on "Three-Dimensional Imaging of Earth and Environmental Processes" at the 2010 Goldschmidt Conference, in Knoxville, Tennessee, June 13–18. The session attracted many attendees, including potential sponsors. We have already successfully secured follow-on funding for the application of neutron imaging to geologic CO_2 sequestration (project entitled "Center for Nanoscale Control of Geologic CO_2," funded by the DOE Office of Science) and enhanced geothermal energy development (project entitled "Properties of CO_2-Rich Pore Fluids and Their Effect on Porosity Evolution on EGS Rocks," funded by the DOE Office of Energy Efficiency and Renewable Energy). In the both cases, the sponsors expressed strong interest in the potentials of neutron imaging of water, CO_2, and other fluids in porous geological materials under in situ conditions.

05567

Protein Dynamics: Neutron Scattering Methodological Development

Jeremy C. Smith

Project Description

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

Mission Relevance

Recent DOE press releases, reports, R&D, and budget priorities indicate that this project is well aligned with DOE's neutron scattering research focus for the next 5 years. The present project will begin to address the roadblocks to improving our understanding of the use of computer simulation in the analysis of neutron scattering with computer simulation.

Results and Accomplishments

Inelastic neutron scattering experiments in the protein glass transition were considered. Molecular dynamics (MD) simulation of linear peptides revealed configurational subdiffusion at equilibrium extending from 10^{-ro} to 10^{-o} s. Network approaches and further MD simulations were shown to reproduce time dependence of the subdiffusive mean squared neutron displacement, which was found to arise from the fractal-like geometry of the accessible volume in the configuration space. The role of methyl groups in the onset of low-temperature anharmonic dynamics in a crystalline protein at low temperature was investigated. The methyl groups that exhibit many rotational excitations are located near xenon cavities, suggesting that cavities in proteins act as activation centers of anharmonic dynamics. The dynamic heterogeneity and the environmental sensitivity of motional parameters and low-frequency spectral bands of CH_3 groups found suggest that methyl dynamics may be used as a neutron probe to investigate the relation between low-energy structural fluctuations and packing defects in proteins. Variation of the water model on the temperature dependence of protein and hydration water dynamics was examined at temperatures between 20 and 300 K. The results provide evidence that for some purposes changing the

water model in protein simulations without a loss of accuracy in interpreting neutron experiments may be possible.

Information Shared

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05839

Motional Changes in Biomolecular Complexation

Jeremy 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 ORNL. 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 simulation.

Mission Relevance

Recent DOE press releases, reports, R&D and budget priorities indicate that this project is well aligned with DOE's neutron scattering research focus for the next 5 years. The present project will begin to address the roadblocks to improving our understanding of the use of computer simulation in the analysis of neutron scattering with computer simulation.

Results and Accomplishments

Ligand binding has been is characterized using a simple analytical "ball-and-spring" model and all-atom normal mode analysis of the binding of the cancer drug methotrexate (MTX) to its target, dihydrofolate reductase (DHFR). The analytical model predicts that the coupling between protein vibrations and ligand external motion generates entropy-rich, low-frequency vibrations in the complex, a result in qualitative agreement with the neutron scattering experiment. Also solid foundation has been established for the interpretation of inelastic and spin echo spectroscopy from globular protein complexes.

05901

New Neutron Scattering Experiments at the Spallation Neutron Source

Gregory S. Smith

Project Description

ORNL has the world's highest flux user facility for neutron scattering, the Spallation Neutron Source (SNS). Neutron scattering is a powerful tool to study the structure and dynamics of materials. Several specialized techniques at SNS provide information on materials at a wide range of length (0.1–100's nm) and time (10^{-6}–10^{-15} s) scales. 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, to fully utilize the capabilities of this unique national facility, collaborations need to be established with researchers from many disciplines and institutions. This project will support new experimental studies of advanced materials utilizing a broad suite of instruments at the SNS.

Mission Relevance

A key component of this project is to build new collaborations with external scientists at universities and industry to exploit neutron scattering techniques to understand materials' properties. This will ultimately produce more science at the SNS, a key DOE Basic Energy Sciences user facility. The major portion of the project funds are used to support travel for new users to the SNS and eventually to the High Flux Isotope Reactor (HFIR) facilities. By funding travel costs for new students and post-docs to participate in neutron scattering experiments, we expect to build a stronger future program by introducing new researchers to the capabilities of neutron scattering techniques. In addition, the larger teams of experimenters funded by this project will be better able to take advantage of these facilities provided by the DOE.

Results and Accomplishments

This project was initiated in August 2010. The major accomplishment was to organize the research scientists on the SNS beamlines to help identify experimenters already planning to come to the facility in September. Then, each of the teams was contacted and encouraged to bring extra students or post-docs to increase the scientific effectiveness of their experiments. The funding for those extra scientists was provided though this project. This resulted in 18 new users to the facility working on nine different scientific topics: (1) magnetic reconstructions at a polar antiferromagnetic thin film surface; (2) hydrogen dynamics in lithium borohydride confined to nanoporous carbon aerogels; (3) structure determination of new negative thermal expansion phases $MgHfW_3O_{12}$, $MgZrW_3O_{12}$, $MgHfMo_3O_{12}$, $MgZrMo_3O_{12}$; (4) powder neutron diffraction studies on $Yb_3Ga_xGe_{10-x}$ (x = 6–8) compounds; (5) neutron scattering and reflectivity on P3HT/PCBM bulk heterojunction solar cell devices; (6) magnetic phasing of neutron reflectivity from reconstituted single membranes containing the vectorially oriented voltage sensor; (7) polarized neutron reflectivity on $Fe_{16}N_2$ thin film with giant saturation magnetization; (8) structural studies of semiconductors for solar water splitting: oxygen vacancies and nitrogen doping; and (9) neutron reflectometry studies of the relation between the film structure and the electrical properties of layer-by-layer assembly. The data from all of these experiments are being analyzed.

ULTRASCALE COMPUTING AND DATA SCIENCE

05095

A Knowledge Discovery Framework for America's Transportation System

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

Project Description

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

Mission Relevance

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

develop this capability. Moreover, such a capability will position ORNL as the leader in developing next-generation high-performance computing-driven simulations to address the critical needs of not only the Departments of Transportation and Energy but also other federal agencies with a need to design, test, evaluate, and implement future policies.

Results and Accomplishments

Using Knox County, Tennessee, as a test area, a scenario of new energy technology was described with the market adoption of Plug-in Hybrid Vehicles (PHEV). We developed a modeling approach based on an individual consumer choice model that includes various socioeconomic variables defining sets of static and dynamic input to the model. Particular consideration was given to national data availability and scalability. This modeling and simulation capability allows national simulation of technology penetrations and their impact on climate (CO_2 emission) and electric energy infrastructures. In this spatially explicit model, we developed two novel concepts: a household synthesis model and a simulation of social diffusion of technology adoption using spatial proximity as one of the driving functions. The household synthesis model focused on investigating and developing a dependence-preserving approach in synthesizing household characteristics to support the activity-based traffic demand modeling. For the latter, the simple assumption was made that increasing exposure and awareness of new technology (alternative cars) with and without communication with spatial neighbors (for residents) and colleagues (at work) may provide a positive and a negative impact on potential adaptors. Thus the simulation includes a flexible way to stipulate a distance threshold which increases or decreases the likelihood of an individual adoption choice. The geographic scalability essentially describes the spatial extent of a particular phenomenon, in this case, the activities of a county's population, which in turn defines the volume and complexity of the data included in the simulation. For addressing issues related to daily personal surface transportation (excluding freight) and energy demand and usage, and related emissions, a reasonable argument can be made that routine activities of a county's population are primarily restricted to that county and its surrounding counties. Such activities include commute to work, schools, and other trips for services and recreational needs. The national (tract-to-tract) worker commute data were analyzed to create a database that describes the percentage of worker population of any county whose commute footprint is restricted within that county and the surrounding counties. In the context of scalable simulation, estimating the number of entities (such as worker population) needed to be simulated and the spatial extent for which detailed infrastructure data (roads, points of origin, and destination) needed to be acquired for the simulation provides a very valuable capability. Results from the simulation of Knox County, based on a 10% increase in first-year PHEV adoption, shows that targeted adoption for families with annual income of $60,000 and higher could impact 30% more vehicle miles traveled.

05237

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

Barbara G. Beckerman, Robert M. Patton, Christopher T. Symons, April D. McMillan, Shaun S. Gleason, Ryan A. Kerekes, Vincent Paquit, Carlos Rojas, Laura Pullum, Jillian Gauld, and Robert M. Nishikawa

Project Description

Presently, knowledge discovery and cohesive decision-making capabilities for biomedical applications are hampered by significant gaps in technology for multimodal data analytics. We developed a semi-supervised learning environment that incorporates disparate medical text and images in order to provide a computational framework for data analytics to overcome the gaps. For our framework, "Data Analytics

for Medicine using SEmi-supervised Learning (DAMSEL)," we (1) developed an analytical, automated learning framework and tools for processing multimodality medical data (text and images) for the purpose of data mining and assessment; (2) improved performance, portability, and scalability of this computational framework by leveraging available intelligent software and hardware computing resources and adding functionality to the system; and (3) conducted preliminary validation of the performance on medical data. These aims were accomplished in the context of two biomedical applications: breast cancer (mammography—imaging, pathologies, text reports) and Abdominal Aortic Aneurysm (AAA) (using 3D imaging modalities, such as MRI, in addition to surgical and clinical notes from the patient record). In addition, initial exploration of data for traumatic brain injury (TBI) [using Joint Theater Trauma Registries (JTTR) and related TBI source data] was conducted.

Mission Relevance

DAMSEL has the ability to facilitate the development of more powerful analytical tools by leveraging all of the data in a more effective manner than present approaches permit. These technologies are at the forefront of systems medicine application development and require computationally intensive environments for processing. Potential sponsors for follow-on funding include the National Institutes of Health (NIH) and the Department of Defense (DoD), which have open program announcements and planned initiatives in these areas. For example, NIH's funding opportunity PAR-09-218, Innovations in Biomedical Computational Science and Technology, will support research in tools for data acquisition, archiving, querying, retrieval, visualization, integration, and management; platform-independent translational tools for data exchange and for promoting interoperability; and analytical and statistical tools for interpretation of large data sets. This project is also consistent with such DOE programs as Mathematical, Information, and Computational Sciences, KJ.01.00.00.0; Computer Science, KJ.01.01.02.0; and Computational Partnerships, KJ.01.01.03.0. Other DOE programs that will benefit include national security, intelligence, and biosurveillance applications.

Results and Accomplishments

The project created a multimodal learning framework and tools for the analysis of mammography images and reports and also for abdominal aortic aneurysm (AAA) images and reports. We developed a semi-supervised machine learning framework that integrates the text and image modalities by transforming an image feature vector produced through image processing to a lower dimensional space that is smooth with respect to the problem-specific similarities described in the text reports. The DAMSEL project provides support for combining image and text modalities in previously unavailable ways, but the general framework is also generic enough to support the combination of any number of different modalities that represent different views of the medical problem. The effectiveness of the framework when the secondary modality set is engineered to consist of features representative of the target problem can be dramatic and has been demonstrated via improvement over state-of-the-art results.

The text analysis work for breast imaging produced the following key new capabilities: (1) a genetic-algorithm-based approach to identifying reports of abnormalities; (2) a genetic-algorithm-based approach to identifying key phrase patterns in the language used for the mammography domain; (3) a classifier for mammography documents; and (4) a temporal analysis approach for examining and finding key phrase patterns that behave as precursors to a future event in mammography patients. The key-phrase patterns represent a highly effective set of features for creating cancer-related dichotomies in the data and support the discovery of a valuable image-processing manifold through the framework. Additional work in year 2 included new analyses for the AAA data. This effort resulted in (1) a searchable index of the mammography reports that includes specific information such as labels, date, key-phrase patterns (s-grams), and anonymized patient IDs and can be presented in human- or machine-readable (xml) format; (2) a patient-centered approach that uses all reports per patient and their timestamps to facilitate exploratory temporal data analysis and visualization using information retrieval and classical statistical

techniques; and (3) a searchable index of the AAA reports that includes section-specific fields (i.e., 'Findings,' 'Impression'), dates, and measurements.

The image-processing portion of the project developed techniques for high-performance (1) mammogram analysis, and (2) AAA analysis, providing the ability to extract image features describing biological tissue abnormalities. For mammography, the following techniques were implemented for multicore processing: fractal encoding, fractal encoding segmentation, histogram analysis, region growing/snakes, wavelet-based multiresolution segmentation, watershed, and pattern analysis. The image features support the framework's need for a large set of potentially relevant observables that are combined with the text analysis in the machine-learning environment. The AAA effort focused on the development of automated and semi-automated segmentation tools allowing extraction of (1) the 3D position of the vessels wall (aorta, femoral arteries, renal arteries, and peripheral vasculature); (2) the blood flow position within the vessels wall; and (3) the endovascular stent graft. The image analysis was performed on low- to high-resolution CT scan stacks. Implemented techniques include bilateral filtering, connected component grouping, fast marching, and level-set segmentation. Preliminary work has been done on the quantitative measurement of the vascular structures.

In year 2, we developed a framework for conducting architecture-level dependability analysis of DAMSEL. A system-level fault tree was developed, qualitative analysis was conducted, and a failure modes and effects analysis (FMEA) was conducted. As a result of these analyses, we identified potential failure modes for the system (see Pullum et al).

The project also resulted in a collaboration with the University of Tennessee-Knoxville on a Joint Directed Research and Development (JDRD) project led by Itamar Arel, PhD (PI) on the development of an alternative semi-supervised learning system using Deep Belief Networks. This collaboration between the LDRD and the JDRD allowed us to optimize our algorithms for the learning framework and test the data sets in different environments.

Changes in Research Plan (optional)

Biomedical applications were changed in year 2 to include AAAs and analysis of endoleaks. Work was performed in year 1 on Traumatic Brain Injury, using the Joint Theater Trauma Registry, but lack of access to correlating images prevented the multimodality data analysis and integration. An opportunity arose to work with a data set on AAAs, including CT images and radiology reports and operative notes. This replaced the proposed work on TBI. This data set represented longitudinal patient records ranging from 2–5 years after initial AAA repair**.** Institutional Review Board (IRB) approval was received for all members of the team to have access to the datasets. New team members were also added, including Carlos Rojas and Laura Pullum, Computational Sciences and Engineering Division, and a summer student, Jillian Gauld (Queens University, Kingston, ON). This new application provided a rich source for developing, testing, and validating the methodology and helped provide significant results in year 2. A validation effort to assess the dependability of the DAMSEL architecture was added in year 2.

Grants

Several proposals for funding, based on the results of this project and multimodality data integration concept, are in progress. One involves collaboration with the University of North Carolina, and the other is collaboration with the University of Tennessee Graduate School of Medicine and Emory University (Center for Comprehensive Informatics) on a grant to be submitted to the National Institutes of Health (NIH) in February 2011. In addition, follow-on efforts intended to expand the applicability of the multimodal learning framework to a broad range of medical decision support applications have been proposed as part of a recently awarded NIH center grant in which ORNL has a part.

Information Shared

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05240

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

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

Project Description

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

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

Mission Relevance

The development of a CG/DG method will provide a unique self-consistent approach capable of addressing complex geometries and disparate spatial and temporal scales. Combining the CG/DG method and DOE leadership-class computers will make it possible to perform unprecedented three-dimensional multidomain, multiphysics simulations capable of delivering breakthrough science. Specifically, the simulation of nuclear fuel rod bundles in a nuclear reactor requires the understanding of both conjugate heat transfer as well as fluid-structure interactions. This class of engineering simulation has many physical, mathematical, and algorithmic challenges associated with the complex geometries and disparate spatial and temporal scales that this approach addresses.

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

Results and Accomplishments

Traditional numerical methods for simulating multiphysics and multidomain interactions, ubiquitous among science and engineering applications, rely on either Dirichlet-Neumann Robin-Robin, or mortar methods. These two methods are a weak, often one-way, coupling between the physical domains. As an alternative, we have developed a new general method for multiphysics, multidomain coupling that benefits from the formalism of adjoint-based optimization methods. Two advantages of this approach are that (1) the adjoint-based optimization approach formalizes prior ad hoc attempts to match the scalar or

vector fields at the boundary and (2) this approach admits *different* numerical discretizations, such as finite elements or finite differences, in each physical domain, enabling a wide range of applications to make use of this technique.

This project proposed a new general optimization-based approach where we minimize the difference between scalar and/or vector fields at the domain interfaces subject to the constraining physics in each domain. This year, we demonstrated that this proposed approach is a generalization of the widely accepted mortar methods and will have applicability to a much wider class of problems. Additionally, with an appropriate choice of regularization (either explicit based on generalized cross-validation or implicit based on a premature solver termination dictated by an L-curve), this approach is as efficient and potentially more robust than the existing methods. To demonstrate this, we examined three different classes of problems. First, for a diffusion-reaction problem with an arbitrary number of domains and mismatched discretizations, we showed that the error convergence, as expected, was provably either second (in the H^1 norm) or third (in the L_2 norm) order. Second, we demonstrated the method accurately captured the fluid-structure coupling interactions when the fluid is governed by the nonlinear Navier-Stokes equations and the structure was linearly elastic. Finally, we showed that this method can efficiently represent disparate timescales for a conjugate heat transfer problem with a moderately large Rayleigh number ($O(10^4)$). Lastly, this approach requires little additional implementation effort in existing software efforts, as was demonstrated by using the large-scale LifeV (www.lifev.org) package for these problems.

05243

MPI-3: Programming Model Support for Ultrascale Computer Systems

Richard L. Graham, Thomas Naughton, and Chao Wang

Project Description

Upcoming generations of ultrascale computer systems promise an unprecedented level of computational capabilities and hand in hand provide a challenge to use these systems effectively. Hardware technology challenges are driving these systems to be many-core and multicore systems with immense component counts, and simulation codes, middleware, and system-level software need to be able to run in the face of errors. We will work with the application developer aiming to run on these systems to develop scalable strategies for dealing with such failures at the application and middleware level. We will investigate how to partition the solution between these two levels in the context of the ubiquitous communication standard, the Message Passing Interface (MPI) standard, and present proposed changes to this standard to the MPI Forum for inclusion in the MPI-3.0 standard. We will look at solutions that aim to avoid failures and at scalable mechanisms to recover once such failures have occurred.

Mission Relevance

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

capabilities, and demonstrating the utility of this approach in a small number of scientific simulation codes, we will provide a foundation for developing fault-tolerant simulation codes that will benefit from the enormous potential these emerging platforms provide.

Results and Accomplishments

We proposed extensions and modifications of the MPI standard, for example, the ability for MPI communicators to shrink when processor recovery takes place (users define the recovery policies), the specification of the behavior of several MPI functions, as well as modifications to support recovery from process failure (including functions to set communicator recovery policy, and to aid restarted processes to rejoin existing communicators). Backwards compatibility with the existing MPI standard is maintained. In addition, users have some control over the performance penalties paid for the fault-tolerance support, which primarily affects the use of collective communications, and the communicator recovery mode (local or global).

We also focused on failure detection, separating the monitoring for failure detection from the detection itself, respectively, via detection and consensus mechanisms. These mechanisms are organized using a graph-based topology, each node having the capability of hosting detectors and/or the consensus mechanism. The consensus mechanism implements a methodology for failure determination, interacts with detectors to get monitoring information, and prevents recovery actions during normal termination. Detectors are independent; they can run simultaneously to enable composition; they can perform local or remote monitoring; and they provide monitoring information using an abstract communication mechanism.

Our prototype includes a central threshold-based consensus mechanism based upon suspicion data using a mesh topology. We implemented two remote detectors: a TCP-based keep-alive detector and a probe-acknowledge detector. We used the Open MPI's Modular Component Architecture framework system whereby users can reuse existing capabilities and easily extend the system with new algorithms.

As a result of the work on this project, we have been invited by Professor Yutaka Ishikawa from the University of Tokyo to submit a joint proposal to the Japan Science and Technology Agency to provide the research in support of a fault-tolerant communication library (probably not full MPI) for the Japanese 10 PF system, and the follow-on to that. Professor Ishikawa is the lead for computer system research for those platforms.

Information Shared

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05259

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

Bobby G. Sumpter, Vincent Meunier, Robert J. Harrison, and William A. Shelton

Project Description

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

Mission Relevance

The research and development of this project will have immediate impact into the prime mission of DOE. It fits exceptionally well into the new DOE Energy Frontier Research Centers and additionally should be of considerable interest to the Office of Energy Efficiency and Renewable Energy (EERE). On the computing side of DOE, developing scalable methods that are able to fully utilize petascale systems can enable predictive simulations of entire device structures from first principles, thereby helping to rationally design more efficient materials and functionalities. The fundamental aspects of charge storage, motion, solvation, and de-solvation also have large ramifications to biology because ion channels are quite important in nearly all types of life forms. As such we expect considerable interest from the National Institutes of Health (NIH) and the Environmental Protection Agency (EPA). Efficient energy storage is also of importance to the Global Nuclear Energy Partnership (GNEP). In addition, the potential use of supercapacitors for portable power systems crosscuts the continued and high-priority interest of the Department of Defense.

Results and Accomplishments

Our original project outlined three well-defined objectives. First, we wanted to understand the role of pore size and shape on the processes relevant to adsorption and energy storage. Our work towards that objective has been to provide a quantum mechanical–based model that accurately describes the behavior of capacitive energy stored for the entire range of pore sizes ranging from subnanometer micropores, mesopores, to macropores. Devising such a model was made possible by large-scale quantum calculations performed on the NCCS computational resources (Jaguar and Eugene). Remarkably, our model has already been accepted as the state-of-the-art description of carbon-based supercapacitors [see

Nature Materials **7**, 845 (2008) and *Chemical Society Reviews* **38**, 2520 (2009)]. A particularly appealing feature of our approach is that it can be easily and effectively applied to any pore size and any type of electrolyte. Its predictive power has now been used to devise a new type of supercapacitor (an exohedral capacitor), as is detailed by Huang et al. (2010a). Impressively, this novel predicted behavior for exohedral capacitance was subsequently validated by experimental studies [see *Nature Nanotech* **5**, 651 (2010)]. Our related work was also featured on the cover of the *Journal of Materials Research* (Huang et al. 2010b).

Second, we proposed modeling the explicit dynamics of the solvation/desolvation processes. This work is still under way, but considerable progress was made. We have identified realistic atomistic models for porous materials to be used as templates for studying dynamics and have carried out large size and timescale molecular dynamics (MD) runs for a number of these. Additionally, we have also established collaboration with Professor Rui Qiao from Clemson University through the HERE program in order to supplement our portfolio in this area. Through this collaboration, we have studied the distribution of K ions in electrified slit-shaped micropores with pore widths (W) ranging from 9.36 to 14.7 Å using MD simulations (Feng et al. 2010a). We have examined in detail the main factors that govern the distribution of K ions in electrified micropores: (1) the long-range electrostatic ion-ion repulsion, which always drives ions toward the two slit walls, (2) the nonelectrostatic ion-slit wall attractions, (3) the hydration of ions, which drives ions toward positions where they maximize interactions with their hydration water molecules, (4) the interactions between an ion's hydration water molecules and their surrounding water molecules, and (5) entropic effects that drive the ion and water inside the slit toward an uniform distribution. The highlight of our results is that K ions form a well-hydrated single layer in the center of negatively charged slit pores with pore width between 10 and 14.7 Å. Such an ion distribution differs qualitatively from the prediction by the classical EDL theories and is caused primarily by the ion hydration effects. In slits with a width of 9.36 Å, the K ions form separate layers near each slit wall. We found that the electrostatic ion-ion repulsion plays only a minor role in such a transition. Instead, the enthalpic effects associated with the interactions between the hydration water molecules of the K ion with their surrounding water molecules were found to lead to this interesting behavior. Based on the K ion distribution observed in electrified slits with 10 Å < W < 14.7 Å, we proposed a sandwich model to predict the scaling of the slit pore capacitance as a function of its pore width. This model is shown to be capable of predicting the anomalous enhancement of capacitance that has been experimentally observed in micropores with similar widths. However, curvature effects are indispensable for a quantitative description of the experimental capacitance values, further implying that the microporous carbons have a local pore geometry that are closer to a cylinder shape rather than that of a slit.

Additionally, we have examined organic electrolytes (Feng et al. 2010b) and ionic liquids (Feng et al. 2010c). Details of the energy barrier for entering sub-nanometer pores to in aqueous electrolytes are given by Feng et al. (2010d) Briefly, there is an energy penalty to enter sub-nanometer pores because ions have to shed part of their solvation shell. The magnitude of such an energy penalty plays a key role in determining the accessibility and charging/ discharging of these subnanometer pores. Atomistic simulation of Na^+ and Cl^- ions entering a polarizable slit pore with a center-to-center width of 0.82 nm showed that the free energy penalty for these ions to enter the pore is less than 14 kJ/mol for both Na^+ and Cl^- ions. The surprisingly small energy penalty is caused by the van der Waals attractions between ions and pore walls, the image charge effects, the moderate (19–26%) dehydration of the ions inside the pore, and the strengthened interactions between ions and their hydration water molecules in the subnanometer pore. The results provide strong impetus for further developing nanoporous electrodes featuring subnanometer pores.

Third, we proposed to explore the role of pore chemistry beyond carbon nanopores, including effects of chemical functionalization and other types of elements for the porous materials, including oxides. This topic is relevant to the effect of pseudo-capacitance, where fast and reversible redox reactions

occur at the interface. This is a very interesting topic that has only been studied experimentally in the past few years but to which very little theoretical work has been devoted. We have made significant progress in this area, hinging on our team's expertise in chemistry in nano-confined systems. We have provided the first systematic study of carbon nanostructure functionalization through single atom doping for all the relevant atomic species such as B, N, O, F, Si, P, S, Se. We also collaborated with various international groups to corroborate our findings with their experimental results, leading to a number of high-impact publications in international journals (see full listing of publications). In addition, we have continued to work on the materials aspects of the supercapacitor science, focusing on the promising graphitic nanoribbons materials, for which we collaborated with the group of Millie Dressehaus at MIT in a publication in *Science* (Jia et al. 2009) and another in *Phys. Rev. Lett*. (Cruz-Silva 2010a), on the intriguing metal-oxide nanotubes, solid electrolytic-carbon interactions, and finally, semiconducting polymers with carbon nanotubes and graphene.

This has been a timely project in the area of energy storage materials and has already begun to show tremendous international recognition (see journal references and invited talks listed as follows). Energy storage is clearly an important topic that is strategically aligned with the DOE mission for a secure and sustainable energy future. In the past 2 years, we have witnessed a large effort put forth to develop the Energy Frontier Research Centers, the Energy Innovation Hubs, and the focus from the Office of Advanced Scientific Computing Research (OASCR) to push the computational capabilities for energy science forward towards exascale. The subject LDRD effort has contributed towards providing an ORNL foundation along these lines.

Notable from this work are the strong collaborations formed with Georgia Tech (G. Yushin), Drexell University (Y. Gogotsi), and Rice University (P. Ajayan) and its synergistic, but complementary, connections to the ORNL Fluid Interface Reactions, Structures, and Transport (FIRST) Energy Frontier Research Center. In the teams' work, the focus was on structural details of realistic pores (e.g., well beyond slit-pore or cylindrical pore models) and to begin to examine a hybrid energy storage process known as pseudo-capacitance. The objective is notably distinct from the FIRST center's scope, where effort is on understanding, predicting, and controlling interfacial transport and reaction at idealized planar and nano-textured surfaces. Finally, it should be highly noted that this was a vibrant and creative team partnership that exemplifies the power of an excellent team effort.

Program Development

The research and development of this project will have immediate impact into the prime mission of DOE. It fits exceptionally well with the anticipated calls by DOE Office of Basic Energy Sciences for Energy Innovation Hubs (one of which will be solely devoted to electrochemical storage) and from DOE Energy Efficiency and Renewable Energy (EERE). Because of the achievements made in this project, we have been invited to take part in ORNL workshops set up to delineate the path to prepare proposals for these calls. We have also participated in the DOE Workshop on Computational Materials Science and Chemistry for Innovation that has led to the publication of a report (http://www.ornl.gov/sci/cmsinn/index.shtml). In addition, the fundamental aspects of charge storage, motion, solvation, and desolvation have large ramifications to biology because ion channels are quite important in nearly all types of life forms. As such we expect considerable interest from the National Institute of Health (NIH) and the Environmental Protection Agency (EPA). Efficient energy storage is also of importance to the Global Nuclear Energy Partnership (GNEP). In addition, the potential use of supercapacitors for portable power systems cross-cuts the continued and high-priority interest of the Department of Defense.

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Invited Talks/Presentations

"On Exploring Structure-function Relations at the Nanoscale: Energy Storage Applications," Ecuador, First International Nanotechnology Congress, Quito, Ecuador (2010).

"Theoretical and Computational Modeling of Carbon-based Supercapacitors," 6th International Symposium on Computational Challenges and Tools for Nanotubes, Montreal, Canada (2010).

"Discussion Leader for sp2 Carbon Materials,"Gordon Research Conference on Defects in Semiconductors, NH (2010).

"Computational Modeling of Carbon Nanostructures for Energy Storage Applications," IEEE Nano 2010, Seoul, South Korea (2010).

"Theoretical and Computational Modeling of Carbon-Based Supercapacitors," ASME 2010 International Mechanical Engineering Congress, Vancouver, Canada (2010).

"Theoretical and Computational Modeling of Carbon-Based Supercapacitors," Symposium on Research Opportunities in Electrochemical Energy Storage, Argonne, IL (2010).

"Exploring Structure-Property Relationships of Nanaoscale Graphitic Systems," International workshop on organic electronics and spintronics, Nagoya, Japan, 2010.

"Self-Assembly and Nanoscale Confinement for Manipulating Structure and Properties of Materials," University of Tennessee, Chemistry/Materials/Physics seminar (August 2010).

"Energy Storage and Conversion: How can Theory, Modeling, and Simulation Help," ORNL Symposium on Solar Energy and Energy Storage (September 2010).

"Theoretical and Computational Studies of Energy Conversion and Storage," University of Tennessee, Chemical and Biological Engineering Seminar (September 2010).

"Computational and Theoretical Nanoscience," invited lecture for CNMS educational outreach program (April 2010).

"Exploring Structure-Property Relationships in Nanoscale Graphitic Systems," MRS International Meeting, Cancun Mexico (August 2010).

"Modeling Capacitive Energy Storage in Carbon Nanosystems for Supercapacitors," Theory and Simulation of Nano-scale Materials Workshop, CINT, Sandia National Laboratories, Albuquerque, NM (2010).

"Exploring Structure-function Relations at the Nanoscale Using Large-scale Calculations," colloquium at San Luis Potosi, Mexico (2009).

"On Exploring Structure-function Relationship at the Nanoscale Using First Principles Modeling," special seminar at Rensselaer Polytechnic Institute, Troy, NY (2009).

"Theoretical and Computational Modeling of Carbon-based Supercapacitors," MRS Fall Meeting Boston (2009).

"Theoretical Nanoscience and Computational Modeling at Length-scales Relevant to Experiment," 11th International Conference on Advanced Materials, Cancun, Mexico (2009).

"Theoretical Modeling of Carbon Nanostructures for Energy Storage and Nanoelectronics Applications," International Conference on Advanced Materials (ICAM09), Rio de Janeiro, Brazil (2009).

"Guiding Electrons in Carbon Nanostructures Using Topological Defects," 76th annual meeting of the SEAPS, Atlanta, GA (2009).

"Computational Studies of Nanomaterials for Energy Storage Applications," YESS, Saclay, France (2009).

"Why Do We Need Large-scale Simulations in Nanoscience Anyway?" colloquium at LSU, Baton Rouge LA (2009).

"Carbon nanostructures for energy storage and nanoelectronics applications," colloquium at NCSU, Raleigh, NC (2009).

"Capacitor Models for Various Regimes, Carbons, and Electrolytes," the 2009 Advanced Automotive Battery and Capacitor Conference (AABC-09), Long Beach, CA (2009).

"Theoretical Model of Nanoporous Carbon Supercapacitors," the 64th American Chemical Society Southwest Regional Meeting (SWRM), Little Rock, AR (2008).

"A Universal Model of Nanoporous Carbon Supercapacitors," the International Conference on the Theory and Applications of Computational Chemistry, Shanghai, China (2008).

05274

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

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

Project Description

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

Mission Relevance

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

Results and Accomplishments

Several technical advances resulted from this research; however, the overall accomplishment was the introduction of a new fine-grained computer-based method for attributing affective meaning to single documents. Our algorithm extends affective meaning from the basic extraction of affect terms to include identification of affective relationships between entities found in texts. This objective is achieved in three sequential steps. First, we developed a technique for building a large affect lexicon from initial seed word lists and common sense knowledge embedded in open source resources like WordNet and ConceptNet. The well-known PageRank algorithm was adapted to regulate the flow of affective meaning from seed lists to other terms in the English lexicon. Second, affect terms from the affect lexicon are identified in the context of a document. Third, affective relationships among entities are discovered in the text by regulating the spreading activation of affective meaning from affect terms to entities. For example, "John loves Mary" describes a "liking" relationship between John and Mary. Finally, we incorporated these algorithms into a software prototype called TEAMSTER. The Java prototype has a graphical user interface that illustrates in different panels the results of the various steps of the extraction of affective meaning in a document. The prototype also includes an automated search interface for multiple document retrieval. When a single document is loaded, it highlights affect terms in a scrolling window; affect intensities are plotted as a word series. A pruned graph of the document is displayed, which users can further prune by selecting affects and entities. Finally, the extracted affect-entity relationship diagram is presented. TEAMSTER integrates open source code to perform entity extraction, tokenization, word stemming, part-of-speech tagging, and other natural language programming tasks. The affect propagation algorithm was validated using a high-affect 50-document subset of the MPQA corpus. These documents were manually annotated for affects, entities and affective relationships. Eleven free parameters in the affect propagation algorithm were optimized using simulated annealing. The optimized affect propagation algorithm was found to perform 74% better than comparable random guess models. The results demonstrate that the affect propagation algorithm is a good start toward computer-mediated extraction of affective/connotative meaning from text, but further progress is still needed before it can approach the accuracy of human judgment. Additional studies were performed to identify influential social actors in a social network graph using sentiment analysis techniques. The PageRank algorithm was used to propagate social actor influence through the social network with limited success. Accomplishments in program development are ongoing. We have held discussions with DHS Human Factors Division, Heather McCallum-Bayliss, Incisive Analysis Program Manager at IARPA; Rebecca Goolsby, Office of Naval Research; and Alenka Brown-VanHoozer, DOD-CIO/ASD-NII. We have also provided two briefings to representatives of the intelligence community. As these discussions continue, our objective is to identify relevant BAAs scheduled for release in FY 2011, or prepare unsolicited proposals for submission. We are working with local program managers who have contacts in the intelligence community toward this objective.

Information Shared

Schryver, J. C., E. Begoli, A. C. Jose, and C. Griffin. 2010. *Inferring Group Processes from Computer-Mediated Affective Text Analysis.* ORNL/TM-2010/277, Oak Ridge National Laboratory, Oak Ridge, TN.

05282

High-Throughput Computational Screening Approach for Systems Medicine

Pratul 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 and medicinal and computational drug design chemists 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 Genomic Science (formerly GTL:Genomics) initiative. The project will allow development of high-performance computing tools and software for characterization of biomolecular-biomolecular interactions, which is an important components of Genomic Science Program goals. The fundamental understanding of the biological processes occurring at the molecular level in the living cell, as enabled by the project, has fundamental implications in energy and environmental research. The project is relevant to the DOE Office of Biological and Environmental Research (DOE BER) as well as the Office of Advanced Scientific Computing Research (DOE ASCR). The proposed research for development of tools and software for systems medicine is relevant to human health. Therefore, it is relevant to the mission of the National Institutes of Health (NIH), in particular to the National Institute of General Medical Sciences (NIGMS). The outcome of the research would lower time and cost for discovery of new medicine and, therefore, promote human health.

Results and Accomplishments

Our underlying approach for identification of the allosteric sites is based on the characterization of protein dynamics (or slow conformational fluctuations) in relation to the rate-limiting steps in the catalytic cycle of enzymes. We have developed and used theoretical modeling and computational simulations that allow refining of the factors that enable the identification of allosteric sites. Specifically, we have focused on mapping the protein residues from the active-site to surface regions that are the prospective allosteric sites.

Using the developed approach, we have successfully identified allosteric sites for two 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, in addition to identification of the allosteric sites, our computational studies also enabled us to obtained detailed insights into the mechanism of catalysis for the target enzymes.

The high-throughput docking infrastructure has been developed for determining the best binding pose of the ligands with the enzyme targets given the receptor binding (allosteric) sites. The infrastructure has been deployed on ORNL's Jaguar supercomputer. 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. The computational screening was then deployed to handle large chemical libraries.

In the second phase of this project, a full compound library (with about 625,000 drug-like compounds) has been screened against the two medical targets. For FabG, a list of 400 compounds has been prepared (100 compounds each for 4 allosteric sites) based on the use of the high-throughput screening methodology. This list is currently being refined using semi-empirical electronic structure methods. For this phase, we are interacting with the structural biologist and computational chemists at St. Jude's Medical Research Center. Further, the results are being validated against an experimental screening (performed by our collaborators). The correlation between the experimental (wet-lab) screening and the computationally predicted results is being used to further refine the high-throughput screening methodology. Once the optimization of the computational screening methodology is achieved, for the top results based our screening, we will proceed to perform crystallographic studies of the enzyme in presence of the ligands.

Information Shared

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Kamath, G., E. E. Howell, and P. K. Agarwal. 2010. "The Tail Wagging the Dog: Insights into Catalysis in R67 Dihydrofolate Reductase." *Biochemistry* **49**(42), 9078–9088.

Ramanathan, A., and P. K. Agarwal. 2010. "Evolutionarily conserved linkage between enzyme fold, flexibility, and catalysis." *PLoS Biology*, under review.

Ramanathan, A., A. Savol, C. J. Langmead, P. K. Agarwal, and C. S. Chennubhotla. 2010. "Organizing conformational diversity relevant to protein function."*PLoS One*, under review.

05294

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

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

Project Description

Nuclear technology now permeates virtually all aspects of the American economy and is a necessary part of any U.S. energy security strategy. Predictive nuclear energy simulations will involve the modeling of the many physical phenomena that are inherently coupled, including Boltzmann radiation transport, and will require tremendous computational resources. Experiences in many fields have demonstrated that in coupled-physics calculations, a three-dimensional Boltzmann transport solver requires most of the computational resources because of its seven-dimensional phase space. We will extend an existing production-quality parallel transport solver to develop a first-of-a-kind capability that creates a mathematically consistent two-level approach to addressing the significant multiscale (in phase space) challenges associated with predictive simulation of novel reactor concepts. Through hierarchical domain decomposition in full phase space, we will amortize the inherent spatial sweep scaling limitation of traditional transport solvers to fully utilize the multicore architectures in present and future leadership-class computing platforms. We will advance the next-generation high-performance computing (HPC) nuclear reactor transport solver to establish ORNL as the sole source for massively parallel multiscale neutronics codes by incorporating a scalable algorithm that provides a consistent multilevel approach to the multiscale problem in a coupled-physics environment.

Mission Relevance

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

Results and Accomplishments

This project has exceeded several exceptional technical achievements and was a major component in the winning Consortium for Advanced LWR Simulation (CASL) DOE Energy Innovation Hub proposal, which will revolutionize advanced modeling and simulation for nuclear reactor analysis. Through the LDRD funding, the Denovo transport code has been enhanced to include an efficient massively parallel space-energy decomposed eigenvalue solver, which is required for nuclear reactor physics, and has efficiently utilized up to 200,000 cores of Jaguar for solving several large-scale nuclear reactor analysis benchmark problems. The primary technical achievements include (1) porting Denovo to the Jaguar hardware and demonstrating scalability to 200,000 cores; (2) developing of an eigenvalue transport solver

for reactor simulation applications; (3) demonstrating fidelity for several target nuclear energy benchmark simulations; (4) developing a novel space-energy domain decomposition algorithm for eigenvalue transport problems; and (5) demonstrating the use of Denovo in multiscale nuclear energy applications, including both fuels and reactors, with resolved materials. The CASL project has provided follow-on funding that will enable the tight-coupling of Denovo with many other physics packages, and the distribution of Denovo to a broad spectrum of expert reactor analysts in the commercial nuclear industry to provide a far-reaching impact for the nuclear energy community. In terms of quantifiable milestone accomplishments, Denovo has

- met the 2010 DOE Joule program milestone for demonstrated scalability on Jaguar;
- met the OLCF-3 requirements as a Tier 1 application for the next-generation HPC hardware bid; and
- been part of a winning the INCITE proposal, *Uncertainty Quantification for Three-Dimensional Reactor Assembly Simulations,* with a successful renewal spanning 2010–2011 for over 26 million CPU-hours.

Additionally, Denovo-related work has contributed to two PhD dissertations, currently in candidacy, by Rachel Slaybaugh, University of Wisconsin, and Steven Hamilton, Emory University.

Information Shared

Evans, T. M., K. T. Clarno, and J. E. Morel. 2010. "A transport acceleration scheme for multigroup discrete ordinates with upscattering." *Nucl. Sci. Eng.* **165,** 292–301.

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05384

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

Luis Chacón , Diego del-Castillo-Negrete, Raúl Sánchez , and Daniel 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 time scales 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 U.S. magnetic fusion program and may contribute to ensure a good scientific/technological return on U.S. 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 U.S. scientific prominence in the world.

Results and Accomplishments

Several key milestones have been met in this project to date. These include (1) mathematical proof of elimination of finite-grid instability and exact energy conservation with implicit PIC; (2) generalization of the delta-f energy-conserving approach to full-f; and (3) the assessment of particle subcycling and orbit averaging in implicit PIC. The first accomplishment is a key development, as it demonstrates our premise that fully implicit, energy-conserving PIC can be free of deleterious numerical instabilities, both spatial and temporal. This paves the road to truly efficient kinetic modeling of plasmas, which is the main goal of this project. The second accomplishment enables the treatment of completely general temperature profiles, which was a major limitation of earlier work. This is another important aspect of this project, necessary for the development of a first-principles predictive capability. The third and final accomplishment proves our premise that the accurate integration of orbits in phase space is of the essence for a reliable long-term simulation using implicit time-stepping techniques. In particular, we have proved that a careful numerical treatment of particle orbits is directly related to good momentum conservation properties, and that lack of care in this regard results in late-time solution degradation. Put together, these accomplishments place this effort on a very solid scientific foundation and set the stage for strong future impact.

05387

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

Christian Engelmann and Sudharshan 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

The accomplishments of this project are on track with the original milestone schedule in both areas, checkpoint storage virtualization and software redundancy. While the checkpoint storage virtualization aspect targets checkpoint/restart time improvements for low-overhead resilience against detected soft errors, the software redundancy work aims at a new and entirely different resilience approach in HPC that detects and corrects SDC as well. This year's accomplishments in checkpoint storage virtualization are (1) an aggregated checkpoint storage prototype using either memory or solid-state disk storage for faster checkpoint/restart times and (2) a file system in user space client for a transparent file system mount point of the checkpoint storage system. This year's accomplishments in software redundancy are (1) a prototype that supports n-modular redundancy for Message Passing Interface (MPI) applications that dramatically improves resilience and (2) a significant amount of insight into redundancy approaches for MPI runtime environments and applications. Efforts in disseminating results and attracting new sponsorship include (1) proposing follow-on research to DOE's Office of Science, (2) outlining the need for follow-on research in a white paper submitted to the NSF, (3) publishing accomplishments at a major conference (SC 2010), and (4) presenting the research and development challenges and accomplishments at appropriate forums.

Information Shared

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05410

Massively Parallel Algorithms for Scalable Exascale Data Analysis

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

Project Description

We will develop scalable algorithms for the analysis of moderate size (gigabytes ~ terabytes) measurement/observational data that require petascale/exascale computational resources. Specifically, we will propose 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

During the first year of the project, we made successful progresses in both application domains. We implemented two well-known NMF algorithms using the CUDA programming model: the alternating least squares (ALS) and the alternating nonnegative least squares (ANLS). By carefully optimizing the memory storage and access patterns on GPUs for tall-and-skinny matrices commonly seen in NMF, our implementation is able to achieve the speed of 120 GFLOP/s and outperform the hyper-threaded CPU implementation, as well as the program directly using the CUBLAS library, in most cases. Our work enables us to perform NMF and therefore large-scale dimension reduction in tractable time and makes it a feasible solution to real-time applications. Contrary to the common belief that GPU can accelerate computation if it can be parallelized, our experiments show that when the target dimension, k, is small (<32), the same parallelized algorithm could be twice as fast on a CPU as compared to a GPU. In other words, if the matrices fit in the L1/L2 cache of the CPU, the CPU instead of the GPU should be chosen to handle the task. However, as k increases, the benefit of using GPU cards becomes prominent.

We devoted a significant amount of our first-year resources in developing software for analysis of large-scale neutron scattering data. To date, we have achieved the following: (1) we created a simulation that can generate a test data set for the evaluation of the fitting algorithms; (2) we implemented four distinct optimization algorithm classes for fitting parameters; (3) we were able to execute the fitting algorithms with a parallel neutron scattering simulation on OIC; (4) we identified that the real bottleneck in the fitting process was scattering function evaluation, and we proposed and implemented two parallel algorithms that utilized both openMP and MPI; and (5) keeping the next-generation HPC architecture in mind, we also implemented the neutron function evaluation algorithms on GPU. A common challenge in a non-convex optimization problem is limiting the number of expensive function evaluations required by the optimization routine. Therefore, the key to success is fast function evaluation. Our initial results show that on the GPU card (Nvidia GTX 8600) of a Mac laptop, we can achieve more than 50 times speedup than a hyper-threaded CPU-based function evaluation.

Information Shared

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05413

Wavelength-Division Multiplexed Quantum Communication Network

Ryan S. Bennink, D. Duncan Earl, Phillip G. Evans, Warren P. Grice, Travis S. Humble, and Raphael 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 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 U.S. 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) is a multidisciplinary endeavor that fits well within DOE's missions of cross-cutting science integration and discovery, particularly advanced computing technologies for progress in clean energy, nuclear security, complex materials, etc. This was recently brought to light in the American Competitiveness Initiative (ACI), in which QIS was highlighted as a national priority and DOE was given the task of "overcoming technological barriers to the practical use of quantum information processing…." The development of a QC network for transporting quantum information between distant locations directly addresses the ACI challenge.

In addition to benefiting DOE, the project is directly relevant to a number of federal programs. Agencies under the Department of Homeland Security, Intelligence Advanced Research Projects (IARPA), National Security Agency (NSA), Central Intelligence Agency (CIA), and the Department of Defense Army Reseach Office (ARO) are currently funding projects in quantum computing and quantum communication. The development of quantum communication network will directly benefit these programs.

Results and Accomplishments

Nearly all aspects of the project progressed as anticipated in FY 2010.

Entangled photon source. The source of broadband entangled photons that forms the heart of the QC network was designed, constructed, and characterized. The source is one of the brightest in the world (inferred quantum efficiency of 10^{-8}), covers a substantial portion of the telecom C and L bands (1550–1600 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), which ranks it among the fastest QKD sources in existence. The bit rate of the complete QKD network is expected to be ~1% of the bit rate at the source, due to fiber network loss and low detector efficiency (limitations that affect nearly all QKD systems).

Dedicated WDM fiber network. For the first version of the QC network, proof-of-principle WDM functionality was demonstrated using commercially available tunable spectral filters. The transmission spectra of these filters were measured at a number of different channel wavelengths. Fiber interferometers for detecting time-bin entanglement at two network terminals were constructed and characterized in terms of interference visibility and stability.

QKD stations. A field-programmable gate array (FPGA) was obtained and programmed to register, time stamp, and correlate photon detection signals for subsequent data processing. Additionally, this project spurred collaboration with the National Institute of Standards and Technology (NIST) to develop self-differencing avalanche photodiode detectors that will be cheaper and faster than commercially available detectors. Prototype detectors were fabricated and characterized, and show promising results.

Information Shared

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05429

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

Kalyan S. Perumalla, Sudip K. Seal, Vinod Tipparaju, and Srikanth 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 (e.g., models with multimillion social behavioral agents and multimillion Internet hosts). Moreover, the domain solution approaches call for dynamic, runtime integration of newly arriving data about ground truth into the running ("live") simulations. 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 (at least one scenario from each of) 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 have now 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).

Optimizations are being incorporated in the runtime (such as using lower-level messaging interfaces and realizing new buffer management mechanisms) to improve efficiency. New social behavior/network models are close to completion; are being prepared for porting, testing, and scaling to Jaguar; and are expected to represent a major advance in that area via novel infusion of PDES (Perumalla and Seal 2010). Systematic analysis of PDES runtime dynamics on massively parallel platforms is under way, with current results documented in a publication (Carothers and Perumalla 2010). Opportunities are being uncovered for exploiting the new PDES execution capabilities with new projects from sponsors in industry.

Information Shared

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Perumalla, K. S., and S. K. Seal (2010). Reversible Parallel Discrete Event Execution of Large-scale Epidemic Outbreak Models. IEEE/ACM/SCS International Workshop on Principles of Advanced and Distributed Simulation. Atlanta, GA, USA, IEEE Computer Society (Best Paper Finalist).

05550

Computational Biology Toolbox for Ultrascale Computing

Igor B. Jouline, Bhanu Rekepalli, Andrey A. Gorin, and Christian 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 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

Nearly all deliverables planned for the Year 1 have been met or exceeded.

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. 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 scales until 48,000 cores.

05561

Evaluating the Role of Cloud Computing for Scientific Discovery

Rob Gillen and Sudharshan 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 FoundationNSF 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 U.S. 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.

SYSTEMS BIOLOGY AND THE ENVIRONMENT

05133

Carbon Drivers of the Microbe–Switchgrass Rhizosphere Interface

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

Project Description

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

Mission Relevance

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

Accomplishments

We successfully (1) designed microcosms enabling us to semi-hydroponically grow plants under anexic conditions to collect, and accurately identify root exudates; (2) identified some of the major root exudates

derived from the switchgrass cultivar "Alamo" using high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GCMS) methods; (3) set up microcosms to identify exudates from three different switchgrass cultivars exhibiting distinct root architectures to look at genotypic variation; (4) designed a method and apparatus for labeling of plant material using an airtight, closed circulation CO_2 chamber for producing ^{13}C labeled plant biomass and exudates for soil incubations; (5) conducted soil incubations using synthetic exudate analogs; and (6) developed the initial simple compartment model of microbial community dynamics. During FY 2010, we will finish publications from data collected in previous years and complete follow-on experiments under the new BER Scientific Focus Area funded last year.

Information Shared

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05199

Next-Generation Computational System for Biological Annotation

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

Project Description

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

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

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

Mission Relevance

The capabilities developed by this research will be relevant to the DOE/BER Systems Biology Knowledgebase program and areas of data management and analysis in support of annotation for key DOE Office of Biological and Environmental Research (BER) programs such as Genomic Sciences

Systems Biology, the Joint Genome Institute (JGI) partnership, Bioremediation, Microbial Sequencing, and Genome Annotation that will be critically dependent on appropriate computational capabilities for data management, annotation, and support of experimental direction. The prototype developed in this project will demonstrate a new approach that could be expanded for these programs and the larger research community.

Results and Accomplishments

A number of whole genome transcriptome data sets for *C. thermocellum* were collected under normal and ethanol stress conditions using older standard gene expression array technology, newer high-density tiling array technology, and high-throughput sequencing. Analysis methods were developed or integrated and improved to determine differential expression and quantify genes and other features such as operons. Tools were also developed for visualization of both tiling array data and gene expression as determined by sequencing (RNAseq) data in conjunction with genome annotation. Analysis using these tools shows that transcription in the bacterial cell is much more complicated than previously known. We were able to detect the presence of several previously unknown features such as 5' regulatory RNAs, small regulatory RNAs, and alternative transcription start sites including ones in the middle of annotated genes.

Inference of genetic regulatory circuits depends on many things including accurate genome annotation, correct quantification of the genes in the cell, precise structure of operons including transcription start sites, quantification of the transcription factors in the cell, and accurate models for the association of transcription factors to binding sites. Conventional data models (e.g., Genbank files) are inadequate for assembling data of different types into a computational model of the genetic regulatory network because they do not adequately describe concepts associated with regulatory networks and the underlying assumptions of the data used to generate these models. Over the course of this project, we investigated multiple data representation alternatives including SMBL, XML, Chado, and RDF/XML. The goal was to find a model that was appropriate for representing a genetic regulatory network. We were able to determine that BioPAX (built on RDF/XML) is a community adopted data standard that is capable of representing Genetic Regulatory networks. We developed two alternative methods for linking traditional genome annotations to the BioPAX standard. First, we implemented a proof-of-concept annotation representation based on the Semantic Web (RDF/XML). This approach allows one to merge the BioPAX annotation directly with annotation data using the SPARQL query language. Second, we explored the approach of directly importing all of the concepts stored in raw ontologies and the raw data from expression experiments into a Chado relational database schema. The relational database approach is currently better suited to production use, whereas the Semantic Web-based representation is better suited for sharing of scientific data and transparency. Future advancements in Semantic Web technologies may also make it suitable for production.

Program Development

Since this project began it has become clear that transcriptomics will be the "next big wave" in systems biology research based on rapid advancements in sequencing technology and RNAseq. With the new Illumina technology using 100× sample multiplexing, RNAseq data will be more cheaply generated than alternative technologies so it was fortuitous that we focused on this area. We have discussed incorporating RNAseq transcriptomics as part of the JGI sequencing and annotation pipeline with the JGI management. As a preliminary test they have agreed to sequence 12 samples from some of the *Caldicellulosiruptor* genomes being studied by ORNL's BioEnergy Science Center using their Illumina sequencing machines. We will process this data using the RNAseq analysis pipeline created as part of this project. Successful results in this project could include additional *Caldicellulosiruptor* transcriptome RNAseq samples sequenced by both JGI and ORNL and eventually could include an expanded ORNL annotation pipeline which would include transcriptome analysis as a new product for all researchers. Newmodifications to the

ORNL annotation pipeline are being made using some of the methods developed in this project that will help transition toward this eventual future.

The $3.2 million American Resource and Recovery Act (ARRA)–funded Knowledgebase R&D project (Dr. Susan Gregurick, Program Manager for Computational Biology, DOE Office of Biological and Environmental Research) developed the Implementation plan for the new DOE Systems Biology Knowledgebase. There are six high-priority scientific objectives including one on *Microbial Gene Expression Regulatory Networks*. Robert Cottinghamis is PI of this project and also an author of this scientific objective, which is very likely to be part of the next phase expected to be funded in FY 2010.

We have ongoing discussions with Battelle Corporation, the Defense Department, the Department of Homeland Security, and the University of Tennessee faculty about using RNAseq transcriptomics for biodefense forensics, as well as an approach for studying host pathogen interactions.

Information Shared

Quest, D. J., M. L. Land , T. S. Brettin, and R. W. Cottingham. 2010. "Next Generation Models for Storage and Representation of MicrobialBiological Annotation." *BMC Bioinformatics* **11**(Suppl. 6), S15.

05201

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

James G. Elkins, Rishi Jain, Abhijeet P. Borole, Jonathan Mielenz, Zamin Koo Yang, Yunfeng Yang (David),
and Brian H. Davison

Project Description

Biosynthesis 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 will 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 project 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 interest in gasification

routes and has funded one demonstration plant for syngas conversion to ethanol. 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 (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–mass spectrometry (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 threefold 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. 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. Mutants have been generated and await further phenotypic characterization. A series of fermentation studies examining CO as the sole carbon and energy source with and without light were also completed.

05221

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

Mircea Podar, Robert Hettich, Martin Keller, Dean Myles, and Jeremy 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 have obtained draft sequences for both genomes using a combination of 454 Titanium 8kb paired-insert library and Illumina paired end library sequencing. Analysis is ongoing for genome closure.

Detection and isolation of novel nanoarchaea. (1) Detection of nanoarchaea in environmental samples, using universal and specific primers. A large number of samples (>60) were analyzed using 454 sequencing and specific full length sequencing of nanoarchaea 16S rDNA, including deep sea hydrothermal samples from the Mid Atlantic Ridge, Guaymas, Lao, Juan de Fuca, Indian Ocean, numerous samples from terrestrial sites around the world. A manuscript detailing the results of these studies is in preparation. (2) Enrichments for cultivation. We have set up batch cultures and continuous fermentation systems to maintain, enrich and isolate novel nanoarchea from both marine and terrestrial sites. (3) We have developed an affinity isolation method to be used for isolation of novel nanoarchaea. The system uses antibody against *N. equitans* that is coupled to paramagnetic beads. This system has been tested on *I. hospitalis-N. equitans* and is being applied to isolate novel nanoarchea species from environmental samples or from enrichments. The same approach could be used for the isolation of other organisms as well.

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 data is being analyzed and two publications are planned, one is in advanced manuscript stage. We are in the process of developing an RNA sequencing approach to analyze general transcripts as well as small regulatory RNAs.

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.

Program Development

"From genomes to metabolomes: Understanding mechanisms of symbiosis and cell-cell signaling using the archaeal system *Ignicoccus–Nanoarchaeum*." Grant proposal submitted to DOE, September 2010.

Information Shared

Campbell, J., G. Flores, A. L. Reysenbach, and M. Podar. 2010. "A global biodiversity study of marine and terrestrial hyperthermophilic nanoarchaea." Poster at ISME 13 Meeting, Seattle, August.

Giannnone, R., M. Podar, and R. Hettich. 2010. "Elucidating the parasitic/symbiotic association between the archaea *Ignicoccus hospitalis* and *Nanoarchaeum equitans* via differential proteomics." Poster at American Society of Mass Spectrometry Meeting, Salt Lake City, June.

Podar, M. 2010. "Functional genomics and diversity of hyperthermophilic Nanoarchaea." Thermal Biology Institute 2nd Annual Research Associates Meeting, Bozeman, MT, June 9.

Podar, M. 2010. "Functional genomic and evolutionary insights into the *Nanoarchaeum–Ignicoccus* relationship." ISME 13 Meeting, Seattle, August.

Podar, M. 2010. "Integrated proteomic and transcriptomic analysis of the *Ignicoccus hospitalis–Nanoarchaeum equitans* relationship." Extremophiles Meeting, Azores, September.

05256

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

David J. Weston, Yunfeng Yang (David), Rich Norby, Stan Wullschleger, and Christopher 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 plant model species (*Arabidopsis*, soybean, and poplar), we will use a comparative network approach to identify groups of genes that are conserved among species and that are associated with net CO_2 assimilation and energy absorbance. These conserved genes or gene networks (i.e., modules) will provide a scaffold by which orthologous genes from non-model species can be further evaluated for associations with net CO_2 and energy gain. We will test this approach using switchgrass, an important non-model species that is adapted to a wide range of environments. Cultivars from contrasting habitats will be collected and used to evaluate within-module gene sequences and expression variation to net CO_2 and energy gain under heat stress and recovery conditions. Completion of the proposed work will provide a systematic framework for identifying genetic and environmental constraints on plant productivity in non-model organisms.

Mission Relevance

Our research is relevant to several areas of interest to DOE: bioenergy, carbon cycle science, global climate change, and ecology. This is especially true as it relates to the development of novel approaches that would allow us to conduct functional genomics on non-model organisms. Our challenge is to have a well-developed and tested capability in the next 12 months. If successful, we believe that our efforts will contribute to the strategic goals of the DOE Office of Biological and Environmental Research (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

Our results from physiological, biochemical, and expression profile analyses indicate that soybean has greater rates of photosynthesis under warming than do *Arabidopsis* and poplar due to genome wide reprogramming of the antioxidant system and both expression and expansion of HSP17 gene family members.

To gain further insight into the underlying mechanisms of photosynthetic tolerance to warming, we investigated within-species variation in the antioxidant system, and HSP17 and HSP70 gene expression among geographically diverse ecotypes of *Arabidopsis* and the moss *Physcomitrella patens* to warming. By measuring reactive oxygen species (ROS) production, total antioxidant capacity, photosynthesis, respiration, and network analysis of expression profiles, our initial results indicate that the same mechanisms driving among-species thermotolerance are also driving within-species thermotolerance. These results are currently being corroborated with non-model species of ecological relevance through a collaborative Joint Directed Research and Development (JDRD) project with Aimee Classen at the University of Tennessee. If our initial results are confirmed, this will imply that there is a homogeneous evolutionary strategy (canalization) for adaptation of plants to warm habitats and future climatic conditions. These findings will be useful as we begin to model species susceptibility to climatic change in 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) a JDRD project (PI Aimee Classen, University of Tennessee, Knoxville); (2) a successful Feedstocks Genomics proposal (PI Victyor Buscov, Michigan Technological University); and (3) the Plant-Microbe Interaction Scientific Focus Area. Invited talks and presentations include (1) the UCLA medical genomics group, (2) University of Missouri Integrative Biology Program, (3) iPlant Consortium, (4) the American Society of Plant Biologists, and (5) the 2010 Gordon Research Conference.

05481

Novel Zeolitic Carbon Support for Catalytic Bioethanol Production

De-en Jiang, Michelle Kidder, Zili Wu, Jane Y. Howe, Steven H. Overbury, and Sheng 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 rhodium. Recently, it has been shown that confinement of the rhodium 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 the DOE Office of Energy Efficiency and Renewable Energy (EERE) Biomass Program and the joint DOE–U.S. Department of Agriculture (USDA) program on biofuels.

Mission Relevance

Catalysis is core to DOE's missions. The proof-of-principle study of this 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 the formation of longer chain alcohols. Therefore, this project will position us to attract new funding from DOE such as EERE's Biomass Program. For example, President Barack Obama announced on May 5 that DOE plans to invest $786.5 million in American Resource and 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

The deliverable for the first year was a reliable protocol to load rhodium nanoparticles into the carbon support. We met this goal by testing various conditions to load rhodium nanoparticles into nanopores of mesoporous carbons, which we have in great quantity. The final sample was characterized by a combination of secondary electron (SE), bright field transmission electron, and high-angle annular dark field images (z-contrast). The results showed that we achieved the goal of loading rhodium nanoparticles inside the channels. On average, rhodium particle size is 2 ~ 4 nm. With this gained experience, we started making zeolitic carbons by depositing carbon-forming precursors (cations of special ionic liquids) into the cages and channels of a crystalline inorganic zeolite, NaX. We used two salts for the ion exchange process. Followed by filtration, washing, drying, and carbonization at 800°C, the zeolitc carbon was obtained. We then analyzed the carbon content in the two zeolitic carbons by performing thermogravimetric analysis (TGA) in air to oxidize the carbon. We found that carbon was successfully formed in both samples. The deliverable for the first year for our computational effort was a basic understanding of the reaction mechanisms of syngas-to-alcohol catalyzed by rhodium. We met this goal in the sense that we focused on the key reaction steps, since the complete reaction network is rather complicated. By using supercomputers, we first determined the reaction path of the CO dissociation step on a model rhodium nanoparticle surface. We found a quite large barrier (53 kcal/mol), indicating the difficulty for pure rhodium to activate CO and the necessity of adding promoter elements. We applied a monolayer of manganese atoms on the rhodium surface and found that the barrier for CO dissociation is dramatically reduced to 25 kcal/mol. This implies to our experimental effort that coating a layer of manganese atoms on the rhodium particles may greatly help CO conversion and oxygenate selectivity.

05548

Catalytic Conversion of Lignin Feedstocks for Bioenergy Applications

Wei Wang, Tommy J. Phelps, Abhijeet P Borole, Timothy J. Tschaplinski, Ji-Won Moon, and Baohua 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 may benefit from metal-based nanoparticle catalytic depolymerization. We will investigate novel photocatalytic approaches by transforming lignin to value-added fuel or feedstocks. Our hypothesis is that lignin may provide value-added chemicals through photochemically catalyzed depolymerization reaction using structurally modified TiO_2 nanocatalysts under visible light. While current methodology uses TiO_2 and UV light for complete oxidation of organics, we investigate novel transition metal–doped nanocatalysts, which lowered the bandgap energy with effective sunlight absorption and increased lignin conversion efficiency. To further advance catalysis of lignin for value-added components, we also investigate 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 thus 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 first year of the project, we made progress in the following areas.

Screen conventional TiO_2 catalysts on lignin depolymerization. We studied photodegradation of lignin with commercially available TiO_2 catalysts from different sources including Degussa P-25 TiO_2, Nanotek TiO_2, and Sigma-Aldrich products and also studied synthesized TiO_2 by conventional methods with different structures (rutile, anatase, and amorphous) and with different morphologies (nanoparticles, nanorods, nanotubes, and nanowires). These pure TiO_2 catalysts could degrade organic dyes and lignin under UV light, but none of them showed observable efficiency under visible light. We also observed that catalytic efficiency of phase-mixed TiO_2 (e.g., anatase-rutile mixed phase) is higher than single-phase TiO_2 catalysts under UV light.

Development of new structurally modified TiO_2 nanocatalysts. We have developed new wet-chemical methods to synthesize band-gap-narrowed TiO_2 catalysts in the forms of nanoparticles, nanotubes, or thin films on electrodes by introducing metal and nonmetal elements (Cr, V, N, C) into the lattice of TiO_2. Light absorption of these doped TiO_2 has been characterized, and enhanced visible light adsorption and remarkable photocurrents under visible light have been confirmed. Our studies revealed that the band gap energy of pure TiO_2 (~3.2 eV) could be remarkably reduced to ~2eV. Compared with pure TiO_2, which

only absorbs light in UV region with wavelengths <380nm, the doped TiO_2 catalysts expanded their light absorption in visible region up to ~600 nm, leading to enhanced utilization of solar light. We also synthesized and evaluated catalysts made by bio-inspired methods.

Photocatalytic depolymerization of lignin under visible light. We examined photodegradation of organic dyes, methylene blue, and methyl orange under visible light and found that the dyes could be degraded with Cr-doped or N/V-codoped TiO_2 nanoparticles, whereas pure TiO_2 had no such capability. We examined the photodegradation of lignin (molecular weight ~ 60,000) in water. It was observed that the lignin concentration slowly decreased in the presence of Cr-doped or N/V-doped catalysts under visible light. Our preliminary results also showed that the lignin photodegradation could be accelerated under applied voltage. Fourier transform infrared spectroscopy (FTIR) and gas chromatograhy–mass spectrometry (GC-MS) analyses revealed the presence of breakdown by-products or some unidentified components with low molecular weights in the catalytic photochemical process. These products are likely fragments of degraded lignin polymers.

05572

Mitigation of Atmospheric CO_2 through Management of Woody Biomass

Anthony W. King, Tristam O. West, and Neng Zing

Project Description

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

Mission Relevance

This assessment of CO_2 emissions mitigation potential in management and best use of woody biomass is relevant to DOE missions in energy resource analysis and management, environmental quality, and science, particularly those of the Office of Biological and Environmental Research (BER). The results of this project will allow for the proper inclusion of woody biosequestration in analyses of fossil-fuel-emissions mitigation portfolios to avoid dangerous climate change. It will also strengthen DOE's portfolio of carbon cycle science. Results of this project will benefit the U.S. Department of Agriculture Forest Service or any other federal agency involved in evaluation and eventual implementation of strategies to mitigate fossil fuel emissions. It will directly benefit those looking at biosequestration and indirectly those looking at other alternatives by establishing a robust scientific base for woody biosequestration and its role in any mix of strategies.

Results and Accomplishments

We have identified current wood harvest and storage as a proxy for woody sequestration potential constrained, to first approximation, by land availability, forest productivity, cost of extraction, etc. Estimates of current global wood harvest are on order 1–1.5 Gt carbon per year. Approximately 30% of that estimate is waste burned or left to decay at harvest. Additional carbon is lost during conversion to wood products, with only 20–25% of delivered wood harvest sequestered in long-lived products or landfills. We estimate accordingly that current global wood product sequestration is on order 0.1–0.2 Gt carbon per year. Allowing for realistic intensification of production, efficiency, and management, potentials for woody biosequestration on order 0.1–1.0 Gt carbon per year are perhaps likely. In a complementary top-down analysis we find that an unconstrained theoretical global potential of 10.0 Gt carbon per year is reduced to 6 Gt carbon per year after accounting for agriculture and other land-use constraints. This potential is further reduced to 3.5 Gt carbon per year when conservation of forestland for biodiversity and other ecosystem services is considered. The allowance for other uses of wood produced on forested land reduces the potential for carbon sequestration and emissions mitigation further to an upper estimate of perhaps 2.5 Gt carbon per year. The bottom-up and top-down analyses together suggest a realizable potential for woody biomass sequestration in the range of 0.1 to 3.0 Gt carbon per year.

05833

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

David Graham

Project Description

Anaerobic digesters use microorganisms to convert complex polymers into smaller organic compounds, including biofuels. While most studies focus on carbon flux in these digesters, understanding nitrogen and sulfur fluxes will be essential for maintaining 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 sequester and deplete their precursors from waste. This project will characterize nitrogen and sulfur flux in cellulolytic systems and develop biochemical tools for monitoring enzymatic activity in complex mixtures. Microbial co-cultures of cellulose-degrading bacteria and nitrate- or sulfur-reducing microorganisms will alter the nitrogen and sulfur cycles and create evolutionarily stable, mutualistic consortia. When one member of these consortia can be genetically altered, we can modify the system to increase cellulose degradation rates, reduce nitrogen and sulfur residues, and produce novel, high-value bioproducts.

Mission Relevance

This project will demonstrate engineered systems of microbial co-cultures for consolidated cellulose bioprocessing. The results, reagents, and tools developed here will serve as preliminary data for future grant proposals in biofuel, carbon cycling, waste management, and bioprocessing areas. This project anticipates future funding initiatives from the DOE Office of Biological and Environmental Research (BER), as it addresses two primary goals: develop biofuels as energy resources and determine the relationships between climate change and terrestrial processes. These activities could also provide the basis for Environmental Protection Agency (EPA) or U.S. Department of Agriculture (USDA) funding to reduce greenhouse gas (GHG) emissions from bioprocesses and alter the nutritional content of fermentation residue for animal feed products. Microbiological and biochemical expertise developed in

this project will be deployed in a BioEnergy Science Center (BESC)–funded enzymological task during FY 2011. Follow-on funding is also being pursued through a University of Tennessee–led collaborative proposal to the National Science Foundation (NSF).

Results and Accomplishments

Since its inception during December 2009, this project has progressed quickly towards meeting the first-year goals. Defined, minimal growth media have been developed for the cellulose and hemicellulose-degrading bacteria *Caldicellulosiruptor bescii, Caldicellulosiruptor obsidiansis,* and *Clostridium thermocellum*. Expensive and complex nutrient supplements were replaced with individual vitamins, based on genome-enabled metabolic predictions. Specific nitrogen and sulfur source requirements have been identified for these organisms, substantially reducing levels of those nutrients added to the growth media. We are currently using these minimal, defined media to develop co-cultures of compatible thermophilic microorganisms with enhanced substrate range and metabolic versatility. These platforms will be used to expedite metabolic engineering for biomass deconstruction and waste product reduction.

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 mixed microbial communities. β-Glucosidase, endoglucanase, and xylosidase activities can now be measured rapidly with high sensitivity. Additional high-throughput assays permit the rapid analysis of biomass in complex matrices (as total protein) and total alcohol production during fermentation. These methods are now being used to evaluate the effects of nitrogen and sulfur concentrations on pre-treated poplar fermentation. New studies of co-cultures are applying these analytical methods to rapidly assess changes in biomass deconstruction and ethanol production.

Information Shared

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

ADVANCED ENERGY SYSTEMS

05214

Development of Cermet High-Level-Waste Forms

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

Project Description

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

Mission Relevance

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

Results and Accomplishments

During the second year of this project, we continued to make outstanding progress on the two major thrusts. The first is the development of the cermet waste form, which is composed of a ceramic phase and a metal phase. In the first year of the project, we demonstrated that a cermet material could be formed from only the simulated liquid HLW and simulated undissolved solids. A critical demonstration during the second year has been the successful use of only the intrinsic components of the waste from the aqueous separations of the used nuclear fuel (UNF), as well as the waste from the hardware components and proposed recovery and recycling of the zircaloy fuel cladding materials, to form a high-metal-content cermet. Significantly, this cermet is ~100% waste (i.e., with the exception of oxygen)—no nonwaste constituents have been added. The second major effort was directed toward modeling the resulting cermet materials. We have developed and refined methods and tools needed to guide the preparation and tailoring of the cermet waste forms and to model the resulting materials so that we can project their performance in terms of thermodynamics and heat transfer. To date, we have accomplished the following:

- Assembled and begun testing experimental equipment for denitration of simulant waste solutions to produce oxide powders, conversion of reducible components to metals, and hot pressing of the mixtures to cermet forms

- Produced the first cermet pellet from the simulated liquid waste from aqueous UNF reprocessing without the use of additives to tailor the ceramic or metal phases

- Identified problematic constituents arising from the recycling of the zircaloy fuel cladding materials and developed and tested alternate cermet formulations and production pathways

- Produced a cermet pellet from the simulated liquid waste from aqueous UNF reprocessing plus the residual simulated waste resulting from the proposed recycle of the UNF zircaloy cladding materials and fuel assembly hardware—again, without the use of additives to tailor the ceramic or metal phases

- Characterized the resulting cermets by different methods including scanning electron microscopy, laser flash thermal analysis, and X-ray diffraction

- Created a thermal transport model to predict the heat transfer and temperature profiles within the heterogeneous cermet waste form

- Identified anisotropy in the samples analyzed (cermet material appears to be orthotropic with higher radial conductivity)

Information Shared

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05224

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

Graydon L. Yoder, David E. Holcomb, Roger A. Kisner, Fred Peretz, Glenn Romanoski, John B. Wilgen, David Williams, Dane Wilson, Dennis Heatherly, and Adam Aaron

Project Description

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

Mission Relevance

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

Results and Accomplishments

Three months of testing the corrosion behavior of SiC (used for the test section), Inconel 600 (used for loop construction), and Flexitallic gasket material (used as a seal between the SiC test section and the remainder of the loop) at 700°C using FLiNaK salt was completed. Results of these tests showed little or no corrosion of the SiC and gasket and approximately 250 μm of corrosion in the Inconel 600, which was determined to be acceptable for loop operation. A detailed design of the SiC test section and seals between the loop piping and pump sump tank was completed, and purchase orders were placed for these

components. The air cooler design was completed, and the air cooler was fabricated. The pump design was also completed, and a purchase order for the pump was placed. The remainder of the loop design is approximately 95% complete. The inductive heating power supply that will be used to supply power to the test section was installed.

Although construction of the loop was not completed in FY 2010, follow-on funding was secured that will (1) allow it to be completed in FY 2011, (2) add additional capability to the loop by providing a salt cleanup system, and (3) initiate additional testing in FY 2012 designed to examine the behavior of fluidic diodes in FLiNaK salt. Additional proposals have been written to perform high-temperature instrumentation testing and development in the loop, and to begin testing of high-temperature liquid salt heat exchangers.

Information Shared

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05266

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

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

Project Description

Our goal is to demonstrate the potential of immobilized liquid membranes (ILMs) with inorganic supports for extracting americium while operating in a crossflow configuration. Known fuel reprocessing protocols can remove uranium and plutonium but do not remove americium, preventing the close-packing of waste due to heat load issues. Considering that the current used nuclear fuel quantities nearly match the legal capacity for a U.S. geological repository site in terms of heat load generated by americium-241, it is essential that the americium is removed from used fuel. Our work builds upon the information on organic substrate–based ILMs that could not be deployed due to their instability in the harsh environment of nuclear fuel waste. Our ILMs will have inorganic supports, designed from ORNL legacy technology, that are robust. Thus, the ILM technology developed in this project will facilitate the long-term storage of the ~59,000 tonnes of waste that grows at a rate of 2300 tonnes/year by accomplishing americium removal and alleviating the heat load issues.

Mission Relevance

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

Results and Accomplishments

In the past year, operating conditions and configurations for our system were established for the successful separation of an americium surrogate (U^{VI}). The results from condition variation testing directed us to develop membrane modifications that allow the system to operate under a wider range of operating pressures. A single pristine membrane showed uranium separation of 72% after 4.25 days. Maximum transfer efficiency was seen in the first 24 h period. The higher efficiency seen in the first day in comparison to the efficiency seen in consecutive days suggests our final system configuration piece (not yet implemented) would offer enhanced separation efficiency. Shorter tests (28 h each) were conducted to validate the cycling effect on the membrane durability. During testing, the membrane was cleaned between each cycle so that the system could be run under identical conditions to ascertain the effect of only the uranium radiation and abrasive solvent environment on the modified membrane. Three separate 28 h cycles showed reproducible U^{VI} transfer of 20 ± 3% in 28 h.

05349

Variable Valve Actuation to Enable Highly Efficient Engines

James P. Szybist, James C. Conklin, James E. Parks, Charles E. A. Finney, K. Dean Edwards, Essam A. Ibrahim, and Norman Love

Project Description

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

Mission Relevance

The purpose of this project is to improve the efficiency of internal combustion engines, thereby reducing fuel consumption. Reducing fuel consumption is a high priority for the DOE Vehicle Technology Program, which is actively funding research efforts in this area. The project aided program development in several ways. First, the work with the six-stroke engine cycle has been integrated into a DOE project currently funded by the Vehicle Technology Program. The existing DOE project is aimed at increasing the efficiency of engines in unconventional ways, such as alternate thermodynamic cycles and through thermochemical recuperation. The six-stroke engine cycle research strengthens this project by enabling on-engine demonstrations of these technologies, including an application where the six-stroke cycle will be used in conjunction with thermochemical recuperation. Second, the new VVA engine capability put in place by this project was a critical to bringing in a new CRADA project with an industry partner aimed at

investigating techniques to make Homogeneous Charge Compression Ignition (HCCI) combustion more robust and, therefore, commercially applicable to gasoline engines.

Results and Accomplishments

This project added a new VVA engine capability at ORNL. This highly flexible research tool has already resulted in new program development as well as an upgraded research platform on which to perform ongoing research. Using this engine, ORNL has demonstrated engine efficiency improvements relative to conventional spark ignition combustion with overexpanded engine cycles and HCCI combustion.

The thermodynamics of the water injection event for the six-stroke engine cycle were modeled. Results show that injecting hot water into recompressed exhaust gases yields additional extractable power. The six-stroke cycle was implemented on the VVA engine, demonstrating the full range of control authority that can be achieved with the engine valves and actuators. No additional power was recovered with the water injection due to long water evaporation timescales, but efforts will continue under a DOE-funded project. Continuing research in this area will implement different injection technology to decrease the water droplet size and evaporation timescales. The modeling effort resulted in a publication in *Energy* and a patent application. Six-stroke cycle results will be published in FY 2011.

A new experimental platform was commissioned that is capable of measuring the performance of thermoelectric devices. The experiment is highly instrumented and generates temperature and space velocity conditions relevant to engine exhaust conditions. The thermoelectric research is aimed at enhancing heat transfer through the thermoelectric devices. Thermoelectric results were published in the *Journal of Automobile Engineering* and presented at the Directions in Engine-Efficiency and Emissions Research (DEER) conference. A second journal publication is currently in draft form.

Information Shared

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05369

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

Matthew Scudiere and John McKeever

Project Description

As hybrid electric vehicles become more prevalent, there is a need to transfer the power source from gasoline on the vehicle to electricity from the grid in order to mitigate requirements for onboard storage as well as reduce dependency on oil by increasing dependence on the grid (our coal, gas, and renewable instead of their oil). Traditional systems for trains and buses rely on physical contact to transfer electrical

energy to vehicles in motion. This is not practical for vehicles of the future. Evanescent waves in loosely coupled transformer systems can theoretically provide the mechanism for this power transfer over a significant fraction of a meter without physical contact over a significant fraction of a meter, eliminating the need for precision alignment between vehicle and power source.

Initial results from an earlier seed money project demonstrated efficiencies around 30% in the laboratory, but simulations indicated that efficiency percentages in the high nineties were possible with proper tuning. This has now been verified in the lab for power levels up to 4 kW. To efficiently transfer tens of kilowatts, large currents and voltages in the 15–20 kHz frequency range are required, and components that meet these requirements are readily available with today's technology.

As with most development efforts, there are trade-offs that needed to be more fully explored. Initial simulations indicate that while the efficiency is rather flat as a function of frequency near the region of interest, the resonance and power transfer are not. The power transferred is regulated by the operating frequency and load impedance, which can span a rather large range. The problem is that the efficiency also varies with load and is reduced as load increases for higher power levels. In most cases the peak load power did not occur at the same conditions as the peak efficiency. Furthermore, skin effects, eddy current losses, and proximity effects, which can increase significantly with frequency, curtail the upper limit of the operating frequency. Also, efficiency decreases with increasing distance between the two antennas as the flux coupling becomes weaker. Our task will balance the physics and economics to optimize power transfer.

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

Mission Relevance

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

Results and Accomplishments

The first year focused on defining operating parameters achievable with present-day technology and incorporating the results into a full-scale laboratory demonstration unit that was used in the second year to measure and verify these parameters.

During the second year, a full-scale laboratory apparatus was completed that allowed for measurements of efficiency, power, component stress, currents, voltages, and magnetic fields at various operating conditions.

This demonstration unit was designed using analysis and simulations to operate between 15 and 30 kHz with a resonant frequency of 25 kHz. Efficiencies ranged from the low to high nineties for power levels of

1–4 kW load power at a 10 in. gap between antennas. This distance is more than sufficient for most vehicles in use today.

This work generated a patent for a frequency operating point below the resonance value, whose efficiency is much higher than the efficiency at the resonant operating frequency. While the total power level is reduced at this new operating point, it is still more than sufficient to provide the desired power levels.

05424

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

John C. Wagner, Thomas M. Evans, Scott W. Mosher, Douglas E. Peplow, and John 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 radiation from an improvised nuclear device in an urban environment; and NNSA, related to M&S to support nuclear nonproliferation and safeguards.

Results and Accomplishments

The project team has met or exceeded all first-year milestones. During the first year of effort, the team developed ideas and methods for overcoming the two foremost technical challenges to constructing a powerful and uniquely capable Monte Carlo–based radiation transport package for high-performance reactor core simulations. A new hybrid deterministic/Monte Carlo k-eigenvalue transport method was developed that overcomes a major limitation of the conventional Monte Carlo approach by distributing computational effort, and hence statistical precision, uniformly across the region of interest. Additionally, a Monte Carlo domain-decomposition algorithm was developed that will enable us to exploit the computational power that high-performance computing platforms (like Jaguar) provide. Though the first-year deliverables did not require any preliminary results, a detailed initial test of the hybrid method was conducted, and the results clearly demonstrate the more uniform statistical convergence that can be obtained with this new approach. For the problem considered, the hybrid method provides a speedup factor of 6 to 10 (depending on computational parameters) over a conventional Monte Carlo simulation; larger speedups are expected for problems that are computationally more challenging, such as more realistic three-dimensional reactor models, which are the ultimate target application for this work. Although additional testing is currently in progress, the initial results indicate that this research project will have a significant impact on reactor modeling and simulation.

Information Shared

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05469

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

James Nutaro, Teja Kuruganti, Kalyan S. Perumalla, Arjun Shankar, and John Stovall

Project Description

Our goal is to develop and demonstrate a capability to simulate electric power systems at a geographic scale and with a sufficient scope of electrical, mechanical, control, and communication components to explore monitoring, control, and cybersecurity issues in the Smart Grid. Specific applications include (1) the production of synthetic frequency measurement network (F-Net) and 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 that are critical to the operation of a future electric grid.

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 a load 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.

05470

Microelectromechanical Systems–Based Pyroelectric Thermal Energy Scavengers and Coolers

Scott R. Hunter, Panos Datskos, Slobodan Rajic, and Nickolay V. Lavrik

Project Description

The project focuses on developing of 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 electrical power. The project objectives are 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 aim of the project is to demonstrate that overall electrical energy conversion efficiencies in the range of 20–30% and efficiencies up to 80% of the Carnot efficiency limit are achievable with scaled arrays (up to 106 converter elements). These energy conversion efficiencies are greater than those previously demonstrated, or proposed, for any other type of waste-heat energy recovery technology. This 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 first year (FY 2010) 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. We expect the first

patent application be submitted to the United States Patent and Trademark Office within the next 3 months.

The DOE Office of Energy Efficiency and Renewable Energy offers significant funding opportunities in the Industrial Technologies Program for new energy efficiency approaches, and during the next year of the project 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 2011.

Results and Accomplishments

Our efforts during FY 2010 focused on (1) designing and modeling the operation of a resonating bimorph pyroelectric capacitor structure, (2) fabricating test cantilever and pyroelectric capacitor structures, and (3) setting up the temperature-controlled test station for characterization and temperature cycling of the fully integrated pyroelectric capacitive devices. We made significant progress in accomplishing all these tasks as summarized below.

We modeled the operation of a thermally controlled and electrically assisted bimorph capacitive structure to understand the device performance requirements and to assist in the design and fabrication of the pyroelectric energy conversion structures to be fabricated in the second year of the project. These modeling studies show that tip deflections of several tens of microns, with temperature differentials of 200°C, are possible with multilayer pyroelectric capacitive cantilever structures that are 1–3 mm in length and of optimized thickness. Based on these simulations, we designed our first set of bimorph and pyroelectric capacitor test structures. We fabricated pyroelectric capacitors from two types of pyroelectric material to explore the issues involved in the fabrication and operation of these temperature-cycled capacitive structures, and their integration into resonating cantilevers to form pyroelectric current generating devices. The first is a polyvinylidene fluoride–trifluoroethylene copolymer (PVDF-TrFE or copolymer)–based capacitor. We have also explored aluminum nitride (AlN) as a pyroelectric material in the capacitive microcantilever structures. A series of simple cantilevered bimorph structures have been fabricated to understand the thermal resonating properties of millimeter-sized structures. Bilayer and trilayer thermally responsive structures have been fabricated from low thermal expansion SiO_2, higher thermal expansion aluminum, and much higher thermal expansion SU-8 in a first attempt to understand the thermal and mechanical responsivity of these structures. A test setup has been assembled to temperature cycle the bimorph test cantilever structures and to characterize the pyroelectric and electrical current generating properties of the AlN capacitive structures. This test setup consists of a Labview-controlled temperature controller and TE cooler module, a firewire video camera used to obtain images of the moving cantilever structures, and an accurate three-dimensional translation stage that will enable us to accurately position the cantilever structures between the hot and cold source and sink.

Information Shared

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05531

Plasma Heating to Enable Fusion Energy Plasma Material Interface Research

John B. Caughman, Tim Bigelow, Steffi Diem, Richard H. Goulding, Donald L. Hillis, Martin Peng, Dave Rasmussen, and John B. Wilgen

Project Description

A recent report to the Fusion Energy Sciences Advisory Committee (FESAC) 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 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 heat and control 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 or whistler waves. Such an approach needs to be demonstrated with high magnetic fields (~1 tesla) in a cylindrical magnetic mirror geometry. We propose to create and heat a high-density plasma to identify critical issues. We will use diagnostics and modeling to measure and verify plasma performance to determine electron temperature/density power scaling, wave-coupling mechanisms, needed magnetic field shape, and optimized launcher configurations.

Mission Relevance

The DOE Office of Fusion Energy Sciences recently conducted a series of Research Needs Workshops to determine the key research opportunities, called the research thrusts, 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. The 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 is $50 million to $100 million each.

Results and Accomplishments

The primary objectives of the first year were to complete the experimental device, start the theoretical work of modeling wave-plasma interactions, develop a launcher for whistler wave production, develop diagnostics for plasma characterization, and begin plasma production. Substantial progress has been made in each of these areas.

The experimental device consists of a central vacuum chamber surrounded by two magnet pairs on either side. The vacuum chamber has a number of flanges for diagnostic and wave-launching access. The chamber was pumped down and leak checked, the magnets were tested to 1000 amps, and initial plasma operation was demonstrated in August.

The geometrical ray-tracing code RAYS is being used to model electron cyclotron and Bernstein wave propagation and absorption. The code was modernized 10 years ago and is currently being rebuilt and benchmarked. Initial benchmarking of the code against a slab model with a sheared magnetic field showed good agreement. Our current effort is focused on developing a simple slab model of the cylindrical geometry in this project.

The initial work with launcher development has concentrated on the whistler wave launcher. The whistler wave is circularly polarized, so the linearly polarized wave coming out of the rectangular waveguide needs to be converted. The launcher that will interface with the chamber has been made, and a squeeze polarizer has been made that is circularly polarized to within ±3%.

The initial plasma diagnostics for the experiment will focus on measuring the plasma density and electron temperature to determine and understand the efficiency of electron heating. An existing 70 GHz interferometer will measure the plasma density, a Langmuir probe will make a radial scan of the plasma density and electron temperature, and the temporal evolution of the electron temperature via ECE will be made with a heterodyne radiometer. All of the parts and interfaces for these diagnostics have either been received or installed. The Langmuir probe assembly has been installed on the main chamber, and the interferometer horn interfaces are ready for installation.

05556

Highly Efficient Refrigeration Systems Based on Advanced Magnetocaloric Materials

Boyd M. Evans III, Don M. Nicholson, Orlando Rios, David L. West, Gerard M. Ludtka, Omar Abdelaziz, and Edward A. Vineyard

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 which 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 U.S. commercial buildings and 15% of total worldwide energy consumption. Magnetic refrigeration, which exploits the MCE, 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. The project directly supports the Building Technologies Program's *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 MCE 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 MC alloys using combinatorial sputtering. The combinatorial equipment has been designed, fabricated, and is in the process of being installed. While the combinatorial equipment was being built, bulk alloys of material 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 iron and/or copper 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 iron and copper and that it is possible to manipulate the Curie temperature using these materials.

Information Shared

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05840

Closing Technology Gaps with the Development of Advanced Fusion Experimental Facilities

Arnold 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 despite limited success in delivering on past promises 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

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. A preliminary study on irradiation effects on a copper alloy has been performed to analyze the suitability for the Fusion Nuclear Science Facility (FNSF) centerpost. In addition, a two-dimensional design optimization study has been completed on the cooling channel design for the FNSF centerpost.

EMERGING SCIENCE AND TECHNOLOGY FOR SUSTAINABLE BIOENERGY

05200

Evolution and Optimization of the Biofuel Supply Chain

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

Project Description

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

Mission Relevance

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

Results and Accomplishments

We developed a national database and geographic representation of the major components of the biofuel supply chain: a highway, rail and waterway transportation network, county-level biomass supply curves (tons by price level), potential refinery locations, and distribution centers. Clustering and central feature identification techniques created the potential preprocessing, refineries, and distribution centers. Each potential link in the supply chain (field to preprocessing, preprocessing to refinery, refinery to distribution, distribution to demand) was associated with a distance by mode. Ethanol demand scenarios modeled the replacement of 10%, 20%, or 30% of gasoline assuming growth in travel and improved

mileage. The Biofuel Infrastructure Logistics and Transportation model (BILT) minimizes the total annualized cost of supplying the demanded ethanol from the available biomass. The model selects the source and quantity for all of the biomass, preprocessing, and refinery locations and sizes, volumes sent along each link, and the county-level distribution. A web-based interface displays national biomass data and model results including transportation demand by route. Initial testing focused on four states (Pennsylvania, Maryland, Virginia, and West Virginia). A serial implementation solved the problem close to optimality within a few minutes but required 24 hours to reach proven optimality. A parallel solver implementation on the Jaguar supercomputer using only 128 nodes solved to optimality in about 3 min. Tests have also been performed on a quad processor version of the Gurobi MIP solver. The model is now being integrated into a national long-range economic model.

05238

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

Ranga Raju Vatsavai, Auroop R. Ganguly, Forrest M. Hoffman, Thomas Paul Karnowski, Christopher T. Symons, and Varun Chandola

Project Description

This project is addressing two key research challenges that are essential to realizing U.S. energy security, a task that has figured prominently in the recent Office of Biomass Program report. These two challenges are (1) a cost-effective solution to continuously monitor biomass and (2) scalable solutions for species-level information extraction from high-resolution images. Conventional techniques are not adequate for continuous biomass monitoring over large geographic regions. Change-detection techniques, such as differencing, significance testing, and probabilistic approaches, are not sufficient for identifying changes in croplands. We are addressing this problem by developing new spatiotemporal data mining (STDM) approaches with specific focus on (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 using modern computing infrastructure, especially distributed and cloud computing.

Mission Relevance

With recent government emphasis on biofuel development for reducing dependency on foreign oil and reducing carbon emissions from energy production and consumption (e.g., DOE Office of Energy Efficiency and Renewable Energy's Office of Biomass Programs, Biomass Multi-Year Program Plan), the landscape of the United States and many other countries is going to change dramatically in coming years. However, biomass monitoring (changes over time) over large geographic regions using remote sensing images poses several challenges. The 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

We developed a basic biomass monitoring framework on MODIS 16 day time series data. We automated several tasks to facilitate continuous monitoring of biomass. We developed a novel change detection technique based on Gaussian Process (GP) learning. We did thorough experimentation and compared GP-based change detection against three major techniques. Our experimental results showed that GP-based technique is not only more accurate than others but is also capable of detection crop changing patterns, which other techniques 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, and this work was rated as one of the top papers and was invited for publication in a leading journal. We have developed a data mining–based time series segmentation method to derive phenology indices from NDVI data and compare 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 demonstrated that that data-driven methods could be effectively employed to provide realistic estimates of vegetation phenology indices using remote sensing data. These results were widely disseminated through publications in leading conferences, journals, and presentations.

Information Shared

Chandola, V., and R. Vatsavai. 2010. "Scalable Hyper-parameter Estimation for Gaussian Process Based Time Series Analysis." 2nd ACM KDD Workshop on Large-Scale Data Mining.

Chandola, V., and R. Vatsavai. 2010. "Multi-temporal Remote Sensing Image Classification—A Multi-view Approach." NASA Conference on Intelligent Data Understanding (CIDU).

Chandola, V., and R. Vatsavai. 2010. "Scalable Time Series Change Detection For Biomass Monitoring Using Gaussian." NASA Conference on Intelligent Data Understanding (CIDU) (chosen as one of the best papers and invited to a journal).

Chandola, V., and R. Vatsavai. 2010. "An In Depth Scalability Analysis of a Gaussian Process Training Algorithm." SC Workshop on Latest Advances in Scalable Algorithms for Large-Scale Systems (ScalA).

Chandola, V., D. Hui, L. Gu, R. R. Vatsavai, and B. Bhaduri, 2010. "Using Time Series Segmentation for Deriving Vegetation Phenology Indices from MODIS NDVI Data." 2nd IEEE ICDM Workshop on Knowledge Discovery from Climate Data: Prediction, Extremes, and Impacts.

Tetrault, Robert, Brad Doorn, Alison Goss Eng, Alex Philp, Budhendra L. Bhaduri, and Ranga Raju Vatsavai. 2010. "Emerging geospatial science and technology for sustainable bioenergy."*1st International Conference and Exhibition on Computing for Geospatial Research & Application (COM.Geo),* ACM Press, Washington, DC (panel).

Vatsavai, R. 2010. "Large Scale Remote Sensing Data Mining: Recent Progress in Biomass Monitoring and Change Detection." Invited talk at NASA/ESIP federation meeting.

Vatsavai, R. 2010. Invited panel presentation at the 1st International Conference and Exhibition on Computing for Geospatial Research & Application (COM.Geo).

Vatsavai, R., and B. Bhaduri. 2010. "A Hybrid Classification Scheme for Mining Multisource Geospatial Data." *GeoInformatica: An International Journal on Advances of Computer Science for Geographic Information Systems,* Springer.

Vatsavai, R., and V. Chandola. 2010. "High-performance Spatiotemporal Data Mining." Invited poster at Fall Creek Fall meeting.

05557

Decision Support for Secure and Sustainable Bioenergy System

Paul Leiby, Rocio Uria Martinez, Gbadebo Oladosu, Cheng Liu, and Erin Webb

Project Description

Biofuels are hoped to advance environmental goals, improve energy security, and provide economic and social benefits in a sustainable manner. But 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 U.S. 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 U.S. 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

Project activities and progress toward goals were consistent with the milestones laid out for FY 2010, under the 2-year project plan.

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, 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 seven stages in the feedstock's path from farm to biorefinery enabling a detailed analysis of logistics related to feedstock transportation, preprocessing, and storage and includes three U.S. regions.

Coding/implementation is done with GAMS/Symphony 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. IBSAL 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 will be adapted for fuel infrastructure and vehicle 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.

Key Findings and Possible Applications. 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. Applications will allow the testing of alternative biofuels technologies and pathways and alternative configurations of the biofuels system and thus provide measures of energy, economic, and environmental sustainability.

UNDERSTANDING CLIMATE CHANGE IMPACT: ENERGY, CARBON, AND WATER

05212

Uncertainty Assessment and Reduction for Climate Extremes and Climate Change Impacts

Auroop R. Ganguly, Marcia L. Branstetter, David J. Erickson III, Shih-Chieh Kao, Evan A Kodra, Esther S. Parish and Karsten J.K. Steinhaeuser, with Nitesh Chawla, Subimal Ghosh, Vipin Kumar, Michael Steinbach (all no-cost academic collaborators), and Pierre Ngnepieba (partner through HBCU Program)

Project Description

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

Mission Relevance

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

Results and Accomplishments

New capabilities have been developed to produce predictive insights on climate extremes along with their uncertainties based on climate model simulations and observations. A set of tools in extreme value theory, time series analysis, nonlinear dynamics, and data mining have been carefully leveraged or improved for this purpose. Novel insights have been developed for temperature extremes, defined as regional warming and heat waves, as well as extreme precipitation events and droughts. Nonlinear data mining algorithms and sophisticated mathematical approaches have been developed which suggest the possibility of extracting data-guided insights from observations to complement climate model observations. The ability to leverage information content in oceanic indices has been suggested, along with the possibility of developing new insights about the science of climate teleconnections. The possibility of developing predictive insights on tropical cyclones based on a combination of data mining and physics-based modeling is being explored. While the bulk of the work has not been published yet, the line of research has already attracted attention in the scientific community and sponsoring agencies, resulting in invited presentations at conferences or workshops organized or sponsored by the American Geophysical Union and the Environmental and Water Resources Institute of the American Society of Civil Engineers, the National Science Foundation (one workshop in next-generation data mining and another in uncertainty quantification), NOAA, EPA, Centers for Disease Control, 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 is chairing two sessions at the 2010 Fall Meeting of the American Geophysical Union in December, one on climate-related extremes and another on uncertainty quantification for climate. The science contributions from the project have been peer-reviewed papers which are at various stages of the publication, acceptance, revision/review cycles. The project has added value through the use of the tools for impacts assessment, for example, a climate change assessment support for DOD's 2010 Quadrennial Defense Review report.

Information Shared

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Ganguly, A. R., K. Steinhaeuser, S.-C. Kao, E. S. Parish, M. L. Branstetter, A. Sorokine, A., and D. J. Erickson. 2010. "Trends and geographical variability in hydro-meteorological extremes for the 21st century from a climate model." 3rd International Perspective on Current and Future State of Water Resources and the Environment, Environmental ad Water Resources Institute of the American Society of Civil Engineers.

Ganguly, A. R., K. Steinhaeuser, E. A. Kodra, and S.-C. Kao. 2010. "Evaluating projected changes in mean processes, extreme events, and their spatiotemporal dependence structures." 2010 Fall Meeting of the American Geophysical Union, GC41B: Use of Observations for Evaluating CMIP5/IPCC Simulations.

Kodra, E., S. Chatterjee, and A. R. Ganguly. 2010. "Exploring Granger causality between global average observed time series of carbon dioxide and temperature." *Theoretical and Applied Climatology*, DOI: 10.1007/s00704-010-0342-3 (published online before print).

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Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2010. "An exploration of climate data using complex networks." *ACM SIGKDD Explorations* **12**(1), 25–32.
Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2010. "Complex Networks in Climate Science: Progress, Challenges and Opportunities." NASA Conference on Intelligent Data Understanding, San Francisco, Oct. 5–7.
Steinhaeuser, K., N. V. Chawla, and A. R. Ganguly. 2010. "Complex networks reveal persistent global / regional structure and predictive information content in climate data." 2010 Fall Meeting of the American Geophysical Union, San Francisco, December.
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05232

Decadal Prediction of the Earth System after Major Volcanic Eruptions

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

Project Description

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

Mission Relevance

In FY 2009, the DOE Office of Biological and Environmental Research (BER) funded a multilab proposal led by ORNL, titled "Ultra High-Resolution Global Climate Simulation to Explore and Quantify Predictive Skill for Climate Means, Variability, and Extremes," for 5 years totaling $8.595 million for ORNL. It included much of the work stemming from this project as a base for future work. In addition, a BER project titled "Development of Frameworks for Robust Regional Climate Modeling" has been funded for 3 years starting in 2010 for $1.65 million, and the project goals use the base global high-resolution climate model work developed from this project. Additional climate science efforts at ORNL and nationally are citing increased spatial resolution as a necessary component to follow-on research, so this work will have a very broad benefit to global simulation capabilities. Because of the early funding successes associated with this project, the project was ended early to allow a reallocation of funds to other efforts of interest to the LDRD climate change initiative program.

Results and Accomplishments

Technical accomplishments include completed production runs of a cyclical 1850, or "preindustrial," baseline configuration using the spectral atmospheric model with the Community Climate System Model v4 (CCSM) for nominally one degree and third degree high resolution model configurations and datasets.

This model output is a resource available to the general climate community from which to perform experiments such as a comparison of high resolution model runs in the industrial period, or to identify model sensitivities from a background state. The model development work has been incorporated into the Community Earth System (CESM) Respository. This model is also the base from which ensemble 1960–2000 simulations are being completed through follow-on projects. Performance improvements of appoximately 80% have been achieved through compile time adjustments and loop reorderings and have been implemented into the CESM trunk as well. Early high-resolution simulations of the spectral model uncovered an unphysical "ringing" of the cloud physics parameters. Research within this project identified the time-stepping algorithm as the cause of an unsmooth generation of wavelike convection features that, with collaborator Mark Taylor at Sandia National Laboratories, has been remedied with a subcycling of cloud physics parameters.

As a result of early project efforts, the input datasets and parameters settings to produce a global energy balanced one and one-third degree resolution has been established. The one degree resolution produces similar energy balance compared to other atmospheric dynamical cores within the CESM and shows improved midlatitude cloud and radiation budgets. The one-third degree resolution model exhibits overall energy balance; however, this project has identified issues with the subgrid-scale water cycle that require long-term investigations of the effects of resolution on cloud and precipitation formation. A manuscript outlining these results in detail is being prepared for the *Journal of Climate.*

A 10 year preindustrial and 1960–2000 atmospheric simulation has been performed to generate higher resolution (1 degree) aerosol datasets from state-of-the-art emissions data. These improved aerosol datasets will become the inputs for an improved version of the one-third resolution simulation. These datasets contain monthly varying amounts, as compared to the previous decadally averaged values for each month, and will provide the basis for predictability studies ongoing at several institutions.

05241

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

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

Project Description

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

represent climate–biogeochemistry–land use feedbacks. The integration delivered here bridges that gap, making it possible to now evaluate critical assumptions and hypotheses in climate change assessments that require full consideration of climate change feedbacks.

Mission Relevance

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

Results and Accomplishments

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

We have exercised the full CLM-IMAGE interface in fully coupled mode and have accomplished the two-way exchange of information with the Global Land Model (GLM) code of George Hurtt, having maintained contacts with his group as he transitioned this year from University of New Hampshire to University of Maryland. As an operational demonstration of the generality of our coupling approach, we have now made the modifications necessary to perform two-way coupling with a second integrated assessment model, the GCAM model developed at Pacific Northwest National Laboratory. Two additional manuscripts describing the results of this coupling framework are being prepared for submission.

05482

Climate Change Impacts on Energy Infrastructure

David J. Erickson III, Marcia L. Branstetter, Steven J. Fernandez, Auroop R. Ganguly, Karsten J. K. Steinhaeuser, and Thomas J. Wilbanks

Project Description

We applied a detailed climate analysis of the Community Climate System Model 3 (CCSM3) simulations, including temporal trends and extreme event frequency estimates to assess hydropower, power plant cooling, and energy infrastructure in vulnerable regions. A consequence of this work is an initial assessment of the sources of uncertainty in these estimates, which can be used to guide research on the underlying climate models and decision support frameworks. The results of this work will be useful, both to those involved in the planning and development of sources of electricity, as well as the broader climate change science community. The project will focus on one source of renewable energy in two U.S. regions, as determined from a science assessment. This assessment will evaluate the uncertainties in the predicted impacts, both in terms of mean effects and potential for extreme events, and the critical knowledge gaps in connecting climate models with energy resources. The result of this analysis could, in and of itself, be useful in guiding related research efforts. The objective of this project is to develop and demonstrate methods and tools to estimate the potential impacts of climate change on methods of hydro and wind energy production.

Mission Relevance

The project will simulate the energy needs, usage, and demand for DOE and will allow the creation of a fully coupled model of climate and feedbacks with the energy generation system. The project has placed, in a consistent way, the 26,000 substations and 6,000 energy production plants on a climate modeling grid (120 × 120 km). The project provides a unique modeling framework that is directly germane to DOE's investment in climate simulation and energy demand/generation projections. A tentative partial award to the Transmission Planning (FOA 68) including four of the co-PIs was selected for funding on June 23, 2010, at reduced budget. The ORNL anticipated value is about $500,000; however, additional guidance from the DOE National Energy Technology Laboratory is forthcoming. Briefings have been prepared and presented to the Defense Threat Reduction Agency (DTRA) and European Command. We have been invited to propose against a BAA for DTRA projects expected in September. Work will be presented to the DTRA S&T conference in preparation for the call.

Results and Accomplishments

The project built the Foundation Level Data Set (on CCSM4 grid, T85), created a Landscan data set (population) (on CCSM4 grid, T85), computed the electric customers (on CCSM4 grid, T85), and overlaid the 26,500 substations (on CCSM4 grid, T85). We also sampled the climate model (CCSM3, T85) output for temperature increases and heat wave days. We have initiated the swapping of CO_2 flux from energy model (VERDE) netcdf files and temperature increments corresponding to new atmospheric CO_2 concentrations (CCSM/CAM4.1) netcdf files, created a matrix of scenarios, and continued to make this project and calculations a "Jaguar-scale climate problem." We are at the point where the CO_2 emissions impact atmospheric CO_2 and have a coupled two-way feedback between the climate model and the energy grid. Essentially, the detailed information characterizing the 26,500 substations have been recollated and placed on a T85 CCSM grid. The total electric customers have been computed with Bailey-Young techniques. The carbon emissions per customer (watts per customer) have been placed on the T85 climate model grid. The CCSM temperatures for the present and future have been extracted from the climate model output and placed on the same grid as the VERDE substations. This capability is

distinctly ORNL's by virtue of the requirements for exascale computing and domain knowledge of energy security issues. This capability will benefit the Virtual National Grid Simulation Center at ORNL.

05501

Enabling Plant Systems Biology Investigations for Carbon Cycling and Biosequestration Research

Udaya Kalluri, Hassina Z. Bilheux, Shaun S. Gleason, and George 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 will (1) develop, adapt, and apply 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. Progress made in this project is expected to place ORNL in an advantageous position to compete for funding from an anticipated DOE Office of Biological and Environmental Research (BER) solicitation for a center for carbon cycling and biosequestration and also in complementing renewal efforts at the BioEnergy Science Center.

Mission Relevance

The present project attempts to address significant technological and knowledge gaps in systems biology studies of plants by (1) developing plant in vivo system profiling technologies; (2) simultaneously employing -omics and high-resolution phenotyping tools to study system dynamics; and (3) developing an initial framework for systems level analysis, modeling, and identification of key network nodes relating to carbon fate and transport. 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." Successful completion of the project will position us to pursue future funding opportunities related to the declared grand research challenges within DOE BER programs in the areas of climate change forcing, response, and mitigation; feedstock genomics; and plant-microbe science.

Results and Accomplishments

Salient progress towards developing a CT-imaging technique to study live plants included (1) optimization of sample generation with a specified container, (2) achieving resolution of ~100 μm without system calibration (indicating ~50 μm is achievable), (3) successful live whole-plant scanning at $512 \times 512 \times 512$ voxels in under 30 min and whole plant reconstruction, and (4) refining the image output using suitable algorithms to filter noise. Salient progress in developing the neutron imaging technique included (1) optimization of plant growth using aluminum containers and sand, (2) successful demonstration of neutron imaging capabilities at CG1D although CG1 is not an imaging beamline, (3) achievement of ~70 μm resolution, (4) increased understanding of conducting dynamic studies, (5) acquisition of data from water phantom samples that could quantitatively inform water uptake in plants, and (6) performance of neutron CT. Salient progress in developing suitable modeling approaches included (1) an extensive literature search; (2) development of a protocol, equations, and strategies for simulation of example chemical species, hormone, and enzyme transport; and (3) image processing using

test samples with ongoing efforts to refine boundary geometry extraction from test images. These first-year accomplishments are central to undertaking systematic systems biology experiments in year 2 of the project. Successful demonstration of the ability to gain new insights with the integrated experimental and modeling approach of this project is expected to significantly advance plant biology research.

05528

Enhancing Climate Impact Integrated Assessment for Water through Climate Informatics

W. Christopher Lenhardt, Marcia L. Branstetter, Anthony W. King, Line Pouchard, Kao Shih-Chieh, and Dali 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

We focused our area of inquiry on the Rio Grande basin, developing a specific set of use cases to drive the development of the project. In support of our first task, we are developing a comprehensive inventory of climate projections, hydrological observations, historical climatologies, and geographical attributes for the purpose of cross-disciplinary climate assessment. We have currently accumulated about 331.3 GB of

water-related data relevant to the project. These data include Community Climate System Model Version 3 (CCSM3) post-processed model data and some preliminary CCSM4 data, MODIS remote sensing data, International Boundary Water Commission data, and representative U.S. Geological Service data. We developed a proof-of-concept tagging system for the metadata intended to facilitate the cross-disciplinary identification of variables and annotations contained in datasets of interest to hydrology and related science. This proof-of-concept tool provides the foundation to develop additional enhancements as outlined in the proposal. The Earth System Grid (ESG), a DOE-funded effort, is the main venue for the dissemination of CCSM and related climate model results. We are working to link our efforts with ongoing efforts at ESG. Activity in this area includes (1) several meetings with the ESG ORNL PI and team; (2) a plan to publish our analytical results through ESG; and (3) acquired deeper understanding of the ESG infrastructure, which, in turn, is guiding the focus of our tool development effort. During the summer we hired two undergraduates to assist in our work, one from East Tennessee State University and one from the University of Tennessee. One student helped with our data gathering effort, and the other did the coding for the tagging tool. In preparation for building the proof-of-concept system, we acquired a 9 terabyte data storage device that will be brought online early in FY 2011.

Information Shared

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05893

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

Benjamin L. Preston

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 geographic information system (GIS) environment to address this knowledge gap. The Hazards U.S. Multi-Hazard Model (HAZUS-MH) will be parameterized for a cross section of U.S. 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. Reanalysis products from the National Centers for Environmental Prediction (NCEP) 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 U.S. 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 project also seeks to contribute to the development of more integrated assessment tools for estimating future impacts. This work is most relevant to the DOE 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

The project was approved on August 26, 2010, providing limited opportunity during FY 2010 to make significant progress on research objectives. Nevertheless, the following activities have been undertaken:

Task 1. Cross-sectional hazard simulation experiments under current climate. A postdoctoral fellow with expertise in regional climate modeling has been hired. Preliminary work in utilizing the Weather Research and Forecasting (WRF) regional climate model for the simulation of historical climate extremes has begun, and a list of relevant historical extremes has been compiled which will be used to select events for WRF simulations and characterization. An additional research staff member from the ORNL Environmental Sciences Division has been retained on a part-time basis to undertake preliminary work on GIS hazard simulations.

Task 2. Cross-sectional hazard simulation experiments under future climate. Work on this task has yet to be undertaken as it is dependent upon completion of a number of upstream research tasks.

Task 3. Analysis of socioeconomic influence on the impacts of historical extreme events. A historical population database has been developed for the United States at the county level, with annual population estimates from 1900 to 2009. This database has been incorporated into a GIS environment for visualization.

Preliminary indices of climate extremes for the United States have been developed at 0.25 decimal degree resolution based upon a range of National Oceanic and Atmospheric Administration (NOAA) observational data sets and NOAA/NCEP reanalysis products for the period 1960–2008. These indices have been incorporated into a GIS environment for visualization, and work has begun in using these hazard indices to rank different U.S. regions based upon exposure to extremes. This will subsequently enable estimation of historical changes in population exposure to different climate hazards.

Historical data for hazard losses have been acquired for the period 1960–2008 for a number of hazard types, and work has commenced on incorporating these data into a GIS environment.

Multiple metrics of social vulnerability have been identified, including the Social Vulnerability Index as well as time series for poverty rates. Another vulnerability index (the Human Security Index) has been developed by researchers at the National Climatic Data Center, and discussions have commenced regarding the potential use of this index in the current project.

A statistical software package has been purchased to facilitate data management and analysis across the range of modeling platforms currently in use.

Task 4. Analysis of socioeconomic influence on the impacts of future extreme events. A population scenario generator has been developed that undertakes stochastic sampling of historical county population birth, death, and migration rates and applies these values to the baseline population (year 2009) to estimate future population changes. This approach is considered an improvement upon the methods

outlined in the original proposal, as it captures key underlying processes (such as migration) and is more explicit in its treatment of uncertainty. The approach results in scenarios of low, medium, and high population at the county level in annual time steps from 2010 to 2030. These data are currently being compared with county population projections produced by various state agencies to test their plausibility. Robust empirical relationships have been identified at the county level between population size and housing and the number of commercial enterprises. Work is under way to integrate these relationships with the population scenario generator to enable future scenarios of housing and commercial enterprises.

NATIONAL SECURITY SCIENCE AND TECHNOLOGY

05216

Multiphoton Entangled States for Quantum Information Science

Warren P. Grice, Ryan S. Bennink, Philip G. Evans, and Travis S. Humble

Project Description

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

Mission Relevance

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

Results and Accomplishments

Accomplishments from 2009 include the design of the first ever down-conversion source that emits photons that are free of both spectral and spatial entanglement. The source is based on collinear type-II down-conversion, a geometry that eliminates walk-off effects and maximizes the overlap of the interacting fields. Using this design, we were able to achieve a single-mode emission rate of 123,000 pairs s^{-1} mW^{-1}, making it the brightest such source in the world. Photons from that source were entangled in their polarization degree of freedom using a novel arrangement of waveplates and calcite beam displacers. In 2010, the spectral properties of the source were characterized using a specially

constructed dual monochomator that makes it possible to measure the wavelengths of the two photons both independently and in coincidence. Using this device, it was shown that the degree of spectral entanglement can be controlled by adjusting the bandwidth of the pump laser and, moreover, that the right bandwidth eliminates the spectral entanglement entirely. The high brightness and exceptional spectral and spatial purity make our down-conversion source ideal for entanglement of multiple pairs of photons. This was to be demonstrated by extending the beam displacer technique from two photons to four. This approach is more efficient than techniques used by other groups, since it facilitates the generation of four-photon entanglement without requiring two-photon entanglement. At the close of the 2-year project, the four-photon scheme was completely aligned. The four-photon state is ready to be verified, pending the acquisition of additional single-photon detectors.

Information Shared

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05228

Integrated Navigation System for GPS-Denied Environments

Stephen F. Smith, Miljko Bobrek, Charles L. Britton, Milton Nance Ericson, Michael S. Summers, and James Anthony Moore

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 (U.S. 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 assets by DOE, the National Nuclear Security Administration (NNSA), and the DOD is the heavy dependence on GPS for accurate position information in the field. However, the use of GPS is at times unreliable (typically only ~85% coverage) and even subject to "spoofing" by an adversary. The obvious consequences of inaccurate (or no) position information can be severe, up to and including injury or death of personnel or loss of key assets (i.e., special nuclear materials). Although autonomous INS units have been proposed as short-term backups to GPS reception during outages, these units are too costly (>$5K), heavy, bulky, inaccurate, and power hungry to be deployed except in a few specialized applications. For most venues, a much more robust, inexpensive technique is needed, especially where GPS outages occur due to jamming or foliated terrain and in buildings and underground scenarios. This project directly addresses this need. Specific U.S. Government agencies that could benefit from applications of this technology include DOE (research facilities, electrical distribution, and environmental monitoring), NNSA (production-plant assets and materials transportation), DOD/DHS (personnel/vehicle tracking, combat and emergency operations, plus logistics), and the Department of Transportation/Federal Aviation Administration (reliable navigation and timing).

Results and Accomplishments

We have thus far continued the 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 radionavigation band. A new variant of this system developed this year replaces the existing LORAN format (discontinued by the U.S. 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 largely completed, and detailed performance simulations are under way; a patent disclosure is also in preparation. In addition, a U.S. patent was issued on TPS (December 1, 2009) and two more patents allowed (October–November 2010). 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 vastly outperform current INS units [based on optical and microelectromechanical (MEMS) systems technologies] in accuracy, stability, size, weight, power, and cost. A key electronic advancement we have achieved is the use of tightly balanced, fully differential oscillator circuitry to convert DC bias drifts to common-mode effects, thus drastically reducing the long-term phase noise in the differential output signals. Coupled with advanced auto-zeroing techniques, we have demonstrated nearly a factor-of-100 improvement 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 drifts; a U.S. Patent application is being currently prepared. 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.

05281

Distributed Computational Intelligence for Active Response to Cyber-Threat

Louis Wilder, Erik Ferragut, Craig A. Shue, Brent Lagesse, and Chris Rathgeb

Project Description

Computer and network attacks continue to grow exponentially, and the insider threat has become widespread. Currently, the intrusion detection system is the mitigation technique used to thwart these attacks. Misuse detection is the most common type of method used by the system. Yet, these systems are limited in their ability to detect zero-day attacks and suffer from high false positives. Additionally, they have poor scalability and have little or no situational awareness.

Our project goal is to develop a unique capability in anomaly detection and active response to intrusions in Internet Protocol networks using both statistical host-level learning of normal user behavior and distributed computational intelligence for near-real-time reaction. This extends traditional intrusion detection tools by employing advanced probabilistic modeling to advance the statistical analyses. Quantified normal behaviors are shared ontologically within a hierarchical learning framework that will allow distributed monitoring, comparison, and storage of normal usage profiles. The framework also reacts to perceived threats (e.g., isolating network elements, or actively reconfiguring system components to prevent intrusion spread). This kind of analysis and defense capability is an indispensable aid for system administrators. It also provides users the ability to monitor system behaviors with previously unavailable detail.

Mission Relevance

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

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

Results and Accomplishments

The resulting research has produced a prototype software framework that employs temporal ontologically based information in our anomaly detector for distributed intrusion detection with an active response. The framework provides algorithms that combine elements of learning, adaptation, and evolution to address the analysis and correlation of intrusion data.

While researching the ontology-based approach, we discovered that using Latent Dirichlet Allocation as a method for classifying anomalous behavior over port events was viable for network monitoring. In addition, distinguishing whether anomalous behavior is malicious or benign has been a grand challenge; we have initiated an investigation of using Petri Nets to model this behavior and to provide a solution.

Looking forward, we have extended Petri nets to account for multiplayer control, utility functions, and concurrent behavior in preparation for active response.

This research will benefit the Space and Missile Defense cyber operations center in Huntsville, Alabama, and will also provide a cyber defensive solution to the Automated Metering Infrastructure for Smart Grid applications programs at DHS and DOE.

This year the tasking was focused considerably on the development of probabilistic algorithms for the hierarchical framework, especially in file integrity data and network traffic packet header captures across the ORNL perimeter, as well as system log data on user hosts.

Bayesian Statistical Learning. We developed an advanced probability model using Bayesian online learning to determine parameters of a semi-Markov model of inter-arrival times. Although semi-Markov models are generally difficult to train, we took advantage of the highly stereotypical nature of computer-generated log events to extract dominant patterns using a lightweight, real-time algorithm. Furthermore, as the model is probabilistic, it can be used to automatically generate thresholds having a preselected false positive rate.

Obtaining System Data for Ontology Development. We created sensors that capture live data for profiling where situational awareness, anomaly detection, and automated response are all based on profiling. These sensors capture events from system logs on Microsoft Windows, Linux, and the Macintosh operating systems, network-packet header data, and file modification events from our file integrity checkers. We have created automated data reduction algorithms for the log data. We have aligned the sensor output with domain-relevant ontologies, and further refinements are ongoing.

Information Shared

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05437

Standoff Detection and Imaging of Chemicals

Ali Passian, Arpad Vass, Larry Senesac, and Thomas Thundat

Project Description

Development of novel standoff detection and imaging methods that can overcome the drawbacks of present techniques is essential in defeating the terrorist threat posed by the use of explosives and chemical and biological (CB) agents. 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 and imaging 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

Currently, there is a strong interest expressed by defense and national security agencies for developing standoff detection and standoff chemical imaging techniques with high sensitivity and selectivity. Standoff detection of chemical signatures is critical, and its applications range from obtaining precise chemical composition of CB warfare agents to determining the signatures associated with improvised nuclear devices (INDs). Another application will be for the verification of decontamination of weapons, buildings, vehicles, airplanes, and equipment after exposure from an attack. Obtaining chemical signatures of CB agents with extremely high selectivity and sensitivity using a man portable device is critical in many areas such as homeland security, military, national defense, and monitoring the clandestine production of weapons of mass destruction. Proposals on selective and sensitive detection of explosives, chemicals, and agents are entertained by many agencies such as the Department of Homeland Security (DHS), the Air Force Research Laboratory (AFRL), the Defense Threat Reduction Agency (DTRA), the Defense Advanced Research Projects Agency (DARPA), and the Office of Naval Research (ONR). Many private companies are also interested in licensing the device once proof-of-concept is demonstrated. The RePAS technique can find applications that range from water and food quality monitoring to environmental remediation and medical diagnostics. The present project aims to develop a device with a broad IR range for increasing selectivity. A wider wavelength range for RePAS will help to apply this method in early cancer diagnosis. For example, the probing end of the RePAS can be incorporated into tools for colonoscopy and biopsy. The National Cancer Institute (NCI) of the National Institutes of Health (NIH) is very interested in imaging applications for cancer detection, detection of margins in surgical removal cancer tumors, and imaging flat lesions related to colon cancer.

Results and Accomplishments

After procuring necessary materials, planning experiments, and designing apparatus, the proposed investigations, based on experiments, began to produce preliminary results. A number of interesting observations have been made that have provided optimism in the RePAS technology. We have observed IR absorption-induced changes in temperature on target surfaces in a standoff fashion; however, this fascinating effect needs further investigation. Furthermore, some strong evidence of QCL light-induced changes in explosive residues using an IR camera warrant more study. We have investigated the effects of illumination angle on IR-absorption and the effects of laser power, both important parameters that must be taken into account in the field. Another important undertaking was the initial characterization of the background spectra of different surfaces and materials in order to gain a better understanding of the challenges involved with the in situ environments of the target analytes. In addition we looked into bioanalyte targets and the use of cantilever sensors as a replacement for conventional light detectors. In our software efforts, we made initial progress towards providing absolute detection (without reference signal) and algorithms for identification of chemicals using multiple peaks. Hardware improvements included the design and construction of four QCLs in a signal assembly.

Program Development

Many program managers visited ORNL for live demonstration. We are confident that success of this project will result in follow on funding from many agencies including the Joint Improvised Explosive Device Defeat Organization (JIEDDO), the U.S. Air Force, Army, Navy, and the Department of Homeland Security (DHS). In addition, we are receiving solid interest from industry on the IP involved in this technology. We have also received interest from U.K. Ministry of Defense. Our JIEDDO program manager, Dr. Mike Rafailov, is extremely interested in standoff imaging. However, he needs preliminary

data to share with General Oats and Dr. Jose Colon for securing funding. Dr. Rafailov also asked us to put the program in the $8–10 million range rather than present it as a small project for obtaining preliminary data. Mr. David Lagandere and Maj. C. J. Maldonado have expressed very high interest in using the standoff imaging for health applications. Mr. Lanagndere is already funding a microcantilever biosensor (health) application for the U.S. Air Force. He would like us to team up with a commercial company for developing a standoff (small area) imaging technique. Captain Mark Stoffel of ONR has been an enthusiastic supporter of our standoff technology. Captain Stoffel made a special trip to National Academy building just to listen to a talk the PI gave on this technology. He is very much interested in funding phenomenological studies on this idea. The MARS company is very interested in the standoff chemical detection and chemical imaging. They are considering funding detection of food pathogens at this time. They have also expressed interest in large area imaging with chemical recognition. Dr. K. K. Law of China Lake visited us to form a teaming arrangement with Boeing Inc. for a standoff imaging technique for the U.S. Navy. Dr. Law is currently calling for Small Business Innovation Research/Small Business Technology Transfer (SBIR/STTR) quantum cascade laser development in support of our project. Other interested program managers who visited us include Dr. Mike Shepard of DHS and Dr. Richard Lareau of the DHS Transportation Security Laboratory (TSL). We have received licensing enquiries from companies such as Raytheon. They have been in contact with Mrs. Renae Speck of OTT. We are currently working with Pranalytica, Inc. (Los Angeles, California) to develop a standoff prototype. They have also expressed an interest in licensing. We have also received interest from Daylight Solutions, Inc. (our QCL vendor), about commercial collaboration/licensing.

Information Shared

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05477

Cyber Defensive Countermeasures

Justin M. Beaver, Robert M. Patton, Xiaohui Cui, Christopher T. Symons, Brian A. Klump, Gregory C. Hinkel, Mark A. Floyd, and Brian 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 and/or a location beacon, 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 U.S. Cyber Command.

Results and Accomplishments

During this first year of the project, we focused on the data exfiltration detection and response capabilities. The paragraphs below summarize the accomplishments in each of these areas.

Unauthorized data exfiltration detection. With the wealth of data that is available on a computer host, we investigated three different approaches to characterizing anomalous behaviors in users and processes.

The first approach dealt with the analysis of host log files and extracting relevant data from the volumes of log messages produced during a computer's operation. We developed and implemented an algorithm that leverages s-grams and temporal clustering to identify those significant events in host log files. On average, the algorithm discarded 99.2% of the log file data while still identifying the relevant log messages. An invention disclosure for this algorithm is in development.

Our second approach to exfiltration detection was to extract and analyze data at the kernel level of computer operation in order to characterize user and process behaviors. We developed and implemented a model for identifying anomalous user behaviors by analyzing sequences of system calls. The model characterizes normal behaviors by maintaining a library of normal sequences and alerts on sequences that are not captured in the library. This approach was tested and found to be a viable discriminator of anomalous user and process behaviors. A conference paper has been submitted detailing the results.

Our third approach was focused on a method to fuse data from multiple sensors into a reliable detector of unauthorized data exfiltration behaviors. The challenge in this piece is to discriminate data exfiltration behaviors from normal behaviors. Progress made with this fusion approach includes the development and implementation of a large-scale complex temporal pattern discovery algorithm that is driven by an evaluation of discrimination power. Evaluation of this algorithm's performance is expected in the coming year of work.

Active response through dynamic honeypots. The focus for the active response element of this work was to develop the software infrastructure for performing real-time response actions. Our approach to active response for data exfiltration events is to secure the sensitive data by quarantining malicious user

sessions, and employ deceptions to keep an intruder engaged, allowing for both the capture of forensic data and the extrusion of nonsensitive or misleading data in lieu of the real data. Our progress in the active response area of this effort includes development of several components of this approach, described as follows.

To support the quarantine of malicious remote sessions, we developed a prototype implementation of process migration. Actively running user processes are relocated to a virtual machine where they are insulated from the files they are attempting to steal. 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 but the mirrored files are 0/null padded. Therefore, once the unauthorized exfiltration is detected, the offending process is re-mapped to the mirrored file system to prevent the extrusion of the sensitive data.

To support the forensic analysis of malicious behaviors, we developed a means for host-based forensic data acquisition that leverages the DTrace UNIX real-time probing capability to capture system call data. This provides insight into the system-level operation of malicious users/processes and allows for the identification of exemplar exfiltration behaviors.

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

An ontology for biothreat scenarios has been developed that will allow us to identify and organize concepts relevant to the BioSITES knowledgebase. A BioSITES Scenario describes a series of events before, during, and after a biothreat attack. Currently, scenarios are synthesized based on our understanding of the biology of an organism; however, in the future we expect that scenarios would be based on real intelligence collected in the field. Scenarios also describe both the support information that needs to be assembled and the algorithms that are used in the system to identify components of a threat.

The architectural attributes of BioSITES were evaluated, and the resulting analysis concluded that scalability and data interoperability were likely to have the greatest impact on system performance. Tactics to address these attributes were reviewed, and for the initial prototype system we choose to use semantic web approaches to facilitate data interoperability and message-oriented middleware and decoupled data analysis (sometimes referred to data parallel analyses) to address scalability. Technology selection was made based on these tactics. Once a prototype is in place, scalability data will be collected and analyzed.

Catalog development in the first year focused on the developed of scenarios. For example, in one scenario we identified genome resequencing projects in the National Center for Biotechnology Information (NCBI) short read archive for *Clostridium botulinum* and *Clostridium difficile* that will be used in one of our prototype demonstrations.

The development of the BioSITES core subsystem is ongoing. Sensors—the computational agents that monitor high volumes of data for signs of biological threats—have been designed and implemented. The sensor interface is complete and has been designed based on the "Common CBRN Sensor Interface" published by the DoD and technology used in real-time digital communication systems. Research is under way to develop the decision logic needed to transform the output from multiple sensors into actionable BioSITES advisories. Our first attempts at this are in progress. Implementation of the components that categorize and route data to the appropriate computational agents (sensors) is complete. The current categories are based on published standards by the NCBI sequence read archive and include those common to today's systems biology research.

This project is the first ORNL effort toward a novel bioinformatics component of a biodefense strategy. In conjunction with a new Lawrence Livermore National Laboratory (LLNL) biodefense bioinformatics collaboration, this effort and elements of the DOE Knowledgebase R&D project, we are beginning to develop a core strategy that completely redefines biodefense bioinformatics from 20th century concepts of threat organisms to what could be the bioengineered and synthetic biology threats of the 21st century. While revolutionary, this is needed to defend against those future threats. The strategy for developing this project into a program involves three aspects: (1) interactions with federal agencies, (2) partnering with key institutions, and (3) promoting general awareness of the project. This past year that has included interactions with agencies including the Defense Threat Reduction Agency, the Department of Homeland Security, and the Federal Bureau of Investigation.

05573

Rapid Radiochemistry Applications in Nuclear Forensics

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

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 postdetonation 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 (NA-22 and NA-45); the Department of Homeland Security (Domestic Nuclear Detection Office); and the Department of Defense (Defense Threat Reduction Agency). Agencies such as the Department of State and the FBI are users of nuclear forensics data as well.

Results and Accomplishments

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. We have completed a thorough review of the relevant scientific literature for existing work on the applications of thermochromatography to radiochemical separations (roughly 500 publications). This review has evaluated the existing work—most of which has previously been applied only to the separation and detection of short-lived nuclides in accelerator-based new element/new isotope production experiments—to the challenges of nuclear forensics. Our work has identified that there are significant gaps in the thermodynamic data available, and that the existing literature provides relatively few cases in which the adsorption enthalpy is known for a suite of relevant species. We are now planning to examine the possibility of modeling the species-wall interactions for the cases where the thermodynamic data are known to see if we can reproduce experimental data so as to expand the predictability of separations. We are also exploring the operational parameter space with our model so as to determine the optional configuration(s) for separations. Two graduate students at the University of Tennessee began working on this project in FY 2010, and the work forms the core of their graduate research.

Information Shared

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ENERGY STORAGE

05374

Materials Behavior Underlying the Electrochemical Performance of Advanced Batteries

Sheng Dai, Nancy J. Dudney, Karren L. More, Ed Hagaman, Bob Shaw, De-en Jiang, Shannon M. Mahurin, Andrew Payzant, Claus Daniel, and Edgar Lara-Curzio

Project Description

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

Mission Relevance

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

electrical energy storage devices by focusing on a few key processes that underlie the electrochemical performance of advanced lithium batteries.

Results and Accomplishments

A number of facilities and instruments have been developed and put in to operation that advance our technical capabilities in the area of electrical energy storage research, particularly in the area of lithium batteries. A liquid flow cell was developed for the Hitachi HF3300 TEM/STEM instrument by Hummingbird Scientific, and initial tests were conducted using a platinum-based catalyst in conductive saline solution. From the initial assessments, the liquid cell provided a resolution of less than 3 nm. A battery test facility is currently operational and is equipped with instruments for assembling and characterizing energy storage devices such as batteries, specifically lithium ion batteries, and capacitors. A suite of instrumentation has been installed including a fully functional glove box that permits assembly of energy storage devices under inert atmospheres, an automatic crimper reproducibly assemble coin cells, and a coin cell disassembling tool to characterize samples after cycling. In addition, two instruments are presently in use to characterize coin cells—a Maccor battery test system and Solartron analytical system—that are both fully automated systems with multiple channels for battery testing and electrochemical measurements.

Our computational modeling focused on understanding the properties of novel electrochemical window electrolytes. The operation of lithium-ion batteries depends on the high electrochemical window of the nonaqueous electrolyte such as ethylene carbonate and propylene carbonate, which have a voltage window of less than 5 V. To achieve higher voltages and hence high energy density, new electrolytes must be developed. Sulfones represent a type of electrolyte with a voltage window higher than 5 V. To further improve upon the sulfones, which showed wide electrochemical stability windows in excess of 5.0 V vs. Li/Li+, we used quantum mechanical calculations to explore how substitution by fluorine affects the HOMO-LUMO gap, which is related to the reduction-oxidation properties of the electrolyte. We found that substituting the three hydrogen atoms on one methyl group of methoxyethylmethyl sulfone (MEMS) with fluorine increases the HOMO-LUMO gap from 6.4 eV to 7.0 eV, which indicates better resistance to redox chemistry. However, we found that replacing all the hydrogen atoms in the molecule with fluorine actually decreases the HOMO-LUMO gap to 5.8 eV. These computational results indicate a delicate control of the electrolyte property by substitution and offer a useful guide for directing our synthesis effort towards the right target.

Finally, a Bruker ElexSYS E580 electron paramagnetic resonance (EPR) system has been installed that couples pulsed and continuous-mode operation capabilities with a wide temperature range from 4 K to 450 K to probe materials with unpaired electrons such as free radicals as well as many transition metal ions. Free radicals play an important role in the formation of solid electrolyte interphase (SEI) layers, which makes EPR a valuable technique in battery research. Initial experiments using the EPR, which were essentially a response to the significant interest from ORNL users, focused on paramagnetic catalyst samples. As an example of effectiveness of this technique, EPR spectra were obtained at three different temperatures for an MFI-zeolite sample with iron and copper substituted into the matrix to modify the catalytic properties of the material. Using the low-temperature capabilities of the instrument, we resolved the hyperfine features of the copper species and measured the presence of the iron.

05428

Tough Electrolytes for Batteries—Composites Inspired by Nature

Nancy J. Dudney, Wyatt Tenhaeff, Adrian Sabau, Sergiy Kalnaus, Kelly Perry, Karren L.More, Kunlun Hong, Xiang Yu, John Anker, Jimmy Mays, Suxiang Deng, Erik Herbert, George Pharr, and Stephen Paddison and Brad Habenicht

Project Description

All solid state batteries will be far safer than current lithium-ion technology containing flammable electrolytes. However dry polymer, glass, and ceramic electrolytes are all at least tenfold 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 lithium 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 the 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 lithium-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 U.S. energy portfolio and as such is highly relevant to the DOE mission (Office of Basic Energy Sciences and Office of Energy Efficiency and Renewable Energy) and other federal agencies including the Department of Defense and the Department of Homeland Security. 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

Good progress has been made on the first three of five milestones. Bilayers of thin films of Lipon and two different PEO+$LiClO_4$-based electrolytes (<~1 μm each) have been 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 synthesis 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.

Information Shared

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05483

Development and Verification of Multiscale, Multiphysics Models to Enable the Design of Safe Rechargeable Batteries

Hsin Wang, Edgar Lara-Curzio, Wei Cai, Wei Zhang, Zhili Feng, Balasubramaniam Radhakrishnan, and Gorti Sarma

Project Description

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 lithium-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 lithium-ion batteries in transportation applications. Our goals in this project are to develop multiphysics, multiscale models to assess the propensity of cells and batteries to thermal runaway events; establish experimental verification of those models; and ultimately have a suite of tools to enable the design of robust, safe batteries.

Mission Relevance

The project is closely related to DOE current missions on energy independence and energy storage. Electric vehicle and battery development depends on the safety and reliability of the cells. The availability of the tools to be developed in this project will enable ORNL to respond to solicitations from the Vehicle Technologies and energy storage programs of the DOE Office of Energy Efficiency and Renewable Energy. The widespread deployment of lithium-ion batteries for transportation will not happen unless these batteries can withstand internal shorts without undergoing thermal runaway. Similarly, ORNL will be well positioned to respond to funding opportunities in the mobile applications market to address current and future Department of Transportation rules regarding the transportation of lithium-ion batteries in aircraft. The availability of the tools to be developed in this project will place ORNL in a unique position to lead national programs to address these challenges.

Results and Accomplishments

FEA modeling. The simulation of the pinch test is based on the numerical solution of governing conversation equations of mechanical energy by the finite element method. First, a simple analysis was

performed to simulate the pinch test on a solid aluminum brick. Second, deformation during the pinch test on a prismatic lithium-ion battery cell was simulated using the validated procedure.

Mechanical and thermophysical properties. The cells were opened and the thermal diffusivity of the "jelly-rolls" was tested in the through-thickness and in-plane directions. Mechanical properties of the cell materials were also tested. Components such as the separator, copper, and aluminum current collectors were taken from the jelly-roll, and the stress-strain curves of the materials were generated. Other characterizations carried out include optical microscopy and scanning electron microscopy for imaging and analyzing the damaged layers.

Test rig design and setup. The test setup consists of a servo-hydraulic mechanical testing machine equipped with digital controllers for load and displacement and full feedback control; an environmental chamber with IR-transparent windows to contain gases and by-products from lithium-ion battery thermal runaway events; sets of spheres of different diameter and materials; and attachment rods to transfer compressive loads into prismatic batteries.

Internal short circuit testing. A series of ISC tests were performed to create internal shorts with controlled size and volume: 800 mAh prismatic cell phone cells were subjected to the pinch test using balls with diameter ranging from 0.25 to 3 in. in diameter. In order to achieve control of the initial short size, the loading speed, the short detection threshold, and stop mode were studied. Five 1.5 Ahr lithium-polymer cells were tested. The pinch tests were clearly able to distinguish regular cells and cells with special separators.

Mesoscale simulation of internal short circuit. A phase field simulation tool was developed for a model electrode-electrolyte system that couples the evolution of the potential field and the concentration fields. The model is capable of tracking the spatial variation of the electrode potential and the concentration within the electrode as a function of discharge time. The simulations are also able to capture the overall discharge kinetics as a function of the current. The mesoscale simulations will be used to predict the electrochemical heat source that contributes to thermal runaway.

Information Shared

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05506

Achieving Rechargeable Lithium-Air Batteries through Metal Oxide Electrocatalysts

Ye Xu, William A. Shelton, Gabriel M. Veith, Nancy J. Dudney, Jane Y. Howe, and Jason P. Hodges

Project Description

Lithium–oxygen has one of the largest theoretical energy densities of any practical electrochemical couple at nearly 12 kWh/kg. Prototype lithium-oxygen cells based on carbon cathodes suffer substantial overpotentials in both discharging and charging and rapid capacity loss with cycling. Several recent studies have reported improved overpotentials and capacity by including organometallic compounds, metals, and metal oxides to carbon cathodes. The improvements nonetheless remain quite insufficient, and these studies are very limited in the mechanistic understanding that they provide of the cathode ORR

(oxygen reduction reaction)/OER (oxygen evolution reaction), which has already proved to be a significant flaw in light of very recent discoveries made by us and other groups that solvent decomposition is accountable for much of the observed electrochemical activities. By using a combination of state-of-the-art density functional theory (DFT)–based modeling techniques and synthesis, characterization, and electrochemical testing methods, we will study Li-ORR/OER on representative model catalytic materials. Our study will generate understanding of 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 single 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

In Year 1 we developed a theoretical framework for using extensive DFT results to represent lithium–oxygen surface electrochemistry and successfully constructed functional lithium-air test cells based on stationary graphite foam cathodes and lithium metal anodes. Measurements of discharge and charge *I-V* curves are now routinely carried out. Nanoparticles of platinum, gold, and MnO_2 catalysts have been synthesized in carbon matrices and tested.

We made significant progress in revealing and understanding the fundamental reaction electrochemistry. We evaluated the activity of gold and platinum toward lithium-ORR theoretically. The reduction of molecular O_2 occurs at 1.51 V (vs. Li/Li^+) on gold and 2.04 V on platinum. Lithiation of O_2 significantly weakens the O-O bond, so Li_xO species are expected to be the main discharge products instead of Li_xO_2, which means that the surfaces would be left with chemisorbed oxygen upon charging (OER). In subsequent ORR, the stability of the oxygen species is therefore a key factor that determines the overpotential, which is predicted to be *smaller* on gold than on platinum, in contrast to O_2. These results were published and represent the first attempt in the literature at theoretical analysis of the lithium-ORR mechanism on metals.

Another important discovery that we made is that nickel current collectors, which were employed in many previous studies, can decompose carbonate-based electrolytes, leading to the formation of insoluble lithium-carbon moieties on the cathode. This strongly suggests that the electrochemical activities previously reported for systems using metal current collectors and similar electrolytes were due largely to electrolyte decomposition. These important findings have been described in a manuscript recently accepted by the *Journal of the Electrochemistry Society*. We have switched to an ORNL proprietary porous conductive graphite foam (made by J. Klett of the Materials Science and Technology Division) as combined cathode and current collector.

To better understand the role of carbon itself, we have already begun exploring model carbon materials experimentally and investigating possible lithium–oxygen surface species on several carbon motifs

theoretically. Preliminary results suggest that the (0001) basal plane of graphite is very inert and offers low ORR activity, whereas edges and defects are substantially more active. A manuscript describing the new findings on carbon is in preparation.

Information Shared

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05547

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

Gilbert M. Brown, Sheng Dai, Nancy J. Dudney, Hansan Liu, Timothy J. McIntyre,
M. Parans Paranthaman, and Xiao-Guang Sun

Project Description

The objective of this project is 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 will take advantage of new developments in electrolytes and we will develop an advanced electrolyte/electrode composition utilizing 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, and a cathode electrode material will be selected to so that the mobile $AlCl_4^-$ species will be directly intercalated or intercalated as an Al(III) ion. In the first year, materials issues will be addressed, and we will characterize the fundamental cell performance (voltage) and optimize electrolyte composition, anode composition, and cell kinetics. In the second year a prototype battery system will be constructed and optimized to maximize the specific energy output.

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 to include batteries made from novel materials that would increase the level of energy storage per unit volume and decrease dead weight while maintaining stable electrode–electrolyte interfaces. In this project we propose to develop a battery with these characteristics that has the possibility to be transformational. We propose to develop an aluminum ion battery based on an ionic liquid electrolyte.

Results and Accomplishments

Progress has been made toward the development of a high-specific-energy density, rechargeable aluminum or aluminum-ion battery. A new rechargeable battery concept, the Al/λ-Mn_2O_4 cell,

Anode:	$Al + 7\ [AlCl_4]^- \leftrightarrow 4\ [Al_2Cl_7]^- + 3\ e^-$
Cathode:	$Mn_2O_4 + 4\ [Al_2Cl_7]^- + 3\ e^- \leftrightarrow AlMn_2O_4 + 7\ [AlCl_4]^-$
Net reactor:	$Al + Mn_2O_4 \leftrightarrow AlMn_2O_4$

where a room-temperature ionic liquid ethylmethylimidazolium chloride-aluminumtrichloride (EMIC-$AlCl_3$) is used as an electrolyte, is being investigated. This system will have several advantages over current lithium-ion battery designs and previous attempts to develop aluminum batteries: higher energy density due to the tri-electron reaction of aluminum, lower cost because of abundant aluminum resources, safer operation owing to nonflammable ionic liquids, and elimination of the issues of oxide film and hydrogen evolution on aluminum battery anodes which plagued aluminum in aqueous electrolytes. The electrochemical windows of 1-ethyl-3-methyl imidazolium chloride (EMIC)-$AlCl_3$ melts as a function of the ratio of excess $AlCl_3$ to Cl^- has been determined, and 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-$AlCl_3$. The aluminum anode is prepared by mechanically removing the surface oxide film with a polishing treatment. The electrochemical behavior of aluminum metal in an acidic melt (rich in $AlCl_3$) was studied by cyclic voltammetry (CV). A sequence of 100 CV cycles at a low scan rate was used to study aluminum dissolution and deposition on an aluminum anode. The results validate the good cycleability of this reaction. Two cathode material candidates, spinel λ-MnO_2 and $AlMn_2O_4$, are being investigated in terms of structure, redox reactions, and reversibility. The redox behavior of a λ-MnO_2 electrode was determined in acid melt. The cell open circuit voltage (OCV) measured when no current is flowing, is 2.0 V. The redox peaks show λ-MnO_2 is active in an acid melt, but the mechanism needs further investigation. The redox behavior of the $AlMn_2O_4$ electrode was also investigated in acid melt. The OCV is 0.7V, and the redox peaks show the possibility of Al^{3+} intercalation in $AlMn_2O_4$ spinel structure.

In summary, an acidic EMIC-$AlCl_3$ melt is suitable as electrolyte of this new battery but limited by a narrow electrochemical window. Aluminum anode shows good reversibility in acid melt, while dendrite formation is still a problem for long-term operation. λ-MnO_2 and $AlMn_2O_4$ are potential cathode candidates, but the redox mechanism and reversibility need further investigation. In addition to continuing the investigations in progress, we will investigate improved ionic liquid-based electrolytes that do not utilize the $AlCl_4^-$ anion and optimize their rate capability in an effort to improve the cathode performance.

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05566

Predictive System Simulation Capability for Evaluating Safety and Performance of Batteries

Sreekanth Pannala, Jagjit Nanda, Adrian Sabau, Hassina Z. Bilheux, Partha Mukherjee, Srikanth Allu, Christian Shaffer, John A. Turner, William A. Shelton, and Nancy J. Dudney

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 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 this year, parallel but well-coordinated and integrated activities have been pursued to not only develop multidimensional simulation tools for batteries but also pursue novel experimental techniques 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) 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.

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GENERAL

05315

Active Control of Surface Plasmonics with Ferroelectricity

Jian Shen, Gyula Eres, Ilia N. Ivanov, Katya Seal, and Zhenyu Zhang

Project Description

The discovery that light can be squeezed into subwavelength structures has revolutionized conventional optics. These interactions, known as surface plasmons, occur when the conduction electrons at a metal/dielectric interface resonantly interact with external electromagnetic fields. In this regime highly conductive metallic layers become transparent, capable of field concentration, tunable spectral response, and enhanced absorption, and promising dramatic innovations in renewable energy, single molecule spectroscopy, and signal transmission. Discovery and exploration of plasmonic phenomena have been limited to static (passive) structures. However, the most exciting applications of plasmonic phenomena occur in the visible spectral range with active control of the plasmonic response. In this project, we are studying the fundamental mechanisms leading to active control of the plasmonic response in the visible range using ferroelectric materials to create extreme field gradients resulting in a highly nonlinear response at the metal/dielectric interface. The wide bandgap and the highly nonlinear behavior of ferroelectric materials coupled with periodic metal structures offer unique access to surface plasmonic phenomena in the visible range. This project represents the first step toward developing a strong ORNL program for plasmonics research based on integrating advanced materials synthesis capabilities with fundamental understanding of materials requirements for active control of plasmonics.

Mission Relevance

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

Results and Accomplishments

In this project, our goal was to achieve active control over the plasmonic response of metallic nanostructures in the visible range using ferroelectric materials as a tunable substrate. The tuning was to be achieved by creating extreme field gradients across the substrate, resulting in large changes in the dielectric response at the metal/dielectric interface. For this goal, we prepared diffusion-aggregated gold nanoparticle clusters on $LuFe_2O_4$ ferroelectric substrates. An external electric field was applied to control the plasmonic response at the metal/ferroelectric. It was found that the reflectance and surface-enhanced Raman response of the composite could be altered by the application of an electric field, demonstrating direct and active control of the plasmonic response, as proposed in the project.

$LuFe_2O_4$ was selected as the ferroelectric substrate because it exhibits high dielectric tunability at fairly low electric fields over a broad temperature range close to room temperature. Gold nanoparticle clusters with individual nanoparticle diameters of 20 nm were prepared by a solvent method. Reflectance measurements over a wavelength range from 200 to 3000 nm were obtained with a Cary 5000 spectrophotometer. Surface-enhanced Raman scattering (SERS) spectra at an excitation wavelength of 785 nm were obtained with a laser microscopic confocal Raman spectrometer, equipped with a thermoelectrically cooled charge-coupled device detector with a spectral resolution of 1~2 cm^{-1}.

For applied electric fields as low as 50 V/cm, a clear change in the SERS intensity as well as reflectance was observed. Below this value, the optical response showed little change with increase in applied field. This threshold behavior, which originates from the unique charge ordering behavior of $LuFe_2O_4$, provides the rare advantage of enabling extremely large changes in the dielectric constant for applied fields above the 45 V/cm threshold. The maximum change in reflectivity observed at a wavelength of 1500 was ~10% at an applied field of 75 V/cm, despite averaging effects due to the large beam size. The maximum change in the SERS response at the same applied field was as large as 65%. These changes were repeatable over multiple cycles, demonstrating the controllability and robustness of the response.

In order to simulate the experiment, numerical calculations based on the Finite Different Time domain (FDTD) method were performed. The cross section of the Raman intensity estimated at a fixed wavelength of 785 nm showed increases with the applied voltage bias. Good agreement was found between experiment and theory for the Raman intensity increase with the application of a bias voltage (within a factor of ~2). The simulations results also replicate the threshold behavior observed in experiment. The qualitative and quantitative agreement between the experimental results and the numerical estimates from FDTD suggest that the increase in the SERS signal at higher voltages is represented accurately by the simulations. This implies that the application of an applied field results in a local refractive index change in the multiferroic (LFO) substrate, and this index change, then, is the primary mechanism for enabling the tuning or control of the optical response of the gold clusters, as verified through the Raman and reflectance data.

We have demonstrated active tuning of the plasmonic response of gold nanostuctures by the use of modest electrical fields on an LFO substrate for applications as tunable SERS templates. The estimated refractive index change is of the order of magnitude of related work (~0.03) even at dramatically lower applied electric fields. The SERS enhancement is significant at ~65%. Numerical calculations suggest that the local refractive index change of the substrate accounts for the dominant portions of the optical response of the plasmonic structure. This demonstration of repeatable and reversible changes in the optical response of the nanostructures paves the way for real-time active control and tuning of SERS templates for label-free chemical sensing. One can then conceive of sensing a wide variety of molecules with the same template, an important advancement in the field of chemical sensing. The electronic polarization characteristics of LFO indicate that one may also achieve high switching speeds for device applications pertaining to the computing and communications industry. Enabling refractive index changes

at low voltages also allows for the possibility of plasmonic circuitry at voltages that are within the realm of practical use.

This work is currently being prepared for publication.

The successful culmination of this project is marked by experimental results that demonstrate important scientific advances in the field of plasmonics. We anticipate that this work will serve as a platform for further development of plasmonics research, both outside and within the laboratory, thus establishing ORNL as a strong force in this increasingly prominent research area. Based on the current scientific results, further program development will be sought through DOE as well as external funding.

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05565

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

Michael Z. Hu, Kui Yu, David W. DePaoli, Gerald E. Jellison, Jr., and Michael T. Harris

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 recently discovered thermodynamic equilibrium–driven mechanism, via a noninjection process approach, has received initial success in producing a new class of nanocrystals—that is, magic-size molecular-species quantum dots (MSQDs). For the first time, it appears that nanocrystals can be made in significant quantities with essentially identical size. During the first year of this project, we have met project goals and have made significant new discoveries. Highlights of first-year progress follow. (1) Demonstrated success in intermediate scale-up (40×) of CdSe MSQD synthesis. The results, which indicate products with superior properties compared to those from smaller-scale synthesis, justify further engineering development as planned in the second year. (2) Investigated thermodynamic properties of QDs, uncovering new scientific understanding supporting our thermodynamic equilibrium mechanism–based approach. We have obtained evidence of postsynthesis cooling rate effect on nanocrystal crystallinity and photoluminescence emission and discovered the possibility for reversible transformations of MSQDs. (3) We collected data for chemical reaction kinetics and QD characteristics and identified synthesis windows. Characterization of QD products with ORNL's aberration-corrected electron microscope (ACEM) uncovered important new information, including clarification of the controversial issue on fundamental structure of MSQDs and verification of the co-existence of nanocrystals and amorphous species/phases. (4) We initiated process engineering analysis and modeling of nanocrystal formation. MSQD formation represents a novel, but general, scientific phenomenon that could lead to an innovative process technology for creating various new material systems (such as CdSe, CdS, CdTe, or CdSeTe) with high impacts on energy and many other applications.

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05569

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

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

Project Description

The project aimed and succeeded in the identification of a new super-heavy chemical element of the periodic table with atomic number Z=117. The short-lived radioactive ^{249}Bk target produced from the curium and americium seed material irradiated during two years at the ORNL High Flux Isotope Reactor (HFIR) was used in this experiment. Over 22 mg of ^{249}Bk, the radioactive isotope having Z=97 protons and N=152 neutrons, were chemically separated at the ORNL Radiochemical Engineering Development Center (REDC) in the first half of 2009. At the end of June 2009, the ^{249}Bk was transferred to the Institute of Atomic Reactors at Dimitrovgrad (Russia) for target fabrication. The rotating target wheel containing six ^{249}Bk target sectors was transferred to the Joint Institute for Nuclear Research (JINR) at Dubna (Russia) in July 2009. The irradiation of ^{249}Bk with a ^{48}Ca beam of 252 MeV and 245 MeV energy, started at the Flerov Laboratory of Nuclear Reactions (FLNR) of JINR at the end of July 2009 and lasted 150 days. Two isotopes of new chemical element Z=117 were identified among fusion-evaporation reaction products. Five decay chains of 293(117) isotope and one long decay chain starting at 294(117) isotope were observed, leading to the identification of 11 new super heavy nuclei.

The results were published by the Dubna–ORNL–Las Vegas–Livermore–Vanderbilt–Dimitrovgrad collaboration in *Physical Review Letters* **104,** 142502 in April 2010. An increased stability with larger neutron number observed for newly identified super heavy nuclei represents an experimental verification for the existence of the predicted Island of (Enhanced) Stability for Super Heavy Elements. The original publication triggered over 200 articles in popular and scientific media, including *New York Times, Science, Physics Today,* and others.

Mission Relevance

The discovery of a new chemical element is an increasingly difficult high-profile scientific achievement, as could be seen from the media reaction to the announcement of the Z=117 discovery. The studies aiming for super heavy elements help to establish and understand the limits of the periodic table of elements and of atomic nuclei. The decay properties and production cross section of new isotopes identified in this study helped us to understand the structure of the heaviest nuclei and the underlying nuclear forces binding nucleons together. The decreasing alpha-decay energies and correspondingly increasing half-lives with the increasing neutron number of odd-Z isotopes created suggestive evidence for approaching the predicted magic neutron number N=184.

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

supported by the DOE Office of Science for the studies of new super heavy nuclei, also helps the nuclear security and nuclear forensic fields, where the efficient detection of different kinds of radiation is important. These electronics may be operated in various modes adapting to changing experimental conditions thanks to their digital and programmable circuitry.

While at present there are two laboratories capable and authorized to run intense ^{48}Ca and ^{50}Ti beams (above 1 particle-microampere) on radioactive trans-actinides targets (JINR Dubna, Russia, and GSI Darmstadt, Germany), two other laboratories are coming on-line and intending to pursue the super heavy elements studies, Spiral 2 part of GANIL at Caen, France, and RIKEN near Tokyo, Japan. Success of the current experiment on element Z=117 (with ORNL-produced target material) created a high demand for the continuation of trans-plutonium elements production and chemistry at HFIR/REDC. We expect it will lead to the creation of a new program at DOE targeting super-heavy element research. Already now, in addition to the ongoing joint project at Dubna, GSI Darmstadt and GANIL Caen are proposing collaboration with ORNL, to jointly continue research on super heavy elements.

Within this project, 30 mg of ^{243}Am oxide were provided in September 2010 for a new joint experiment on Z=115 isotopes aiming for a direct Z-identification of SHE decay products, to be performed at the TASISpec facility (GSI, Darmstadt, Germany) in 2011. A new digital data acquisition system (concept developed through this project) is foreseen to be used in 2012 in the experiment searching a new element Z=120 at the SHIP facility (GSI Darmstadt).

Results and Accomplishments

Over 22 mg of ^{249}Bk activity (having a half-life of 320 days) were separated at the ORNL REDC, from over 50 g of curium and americium seed material irradiated with neutrons at the ORNL HFIR for about two years. The project co-author, J. Ezold (ORNL NSTD), was the trans-plutonium "campaign 74" manager at REDC. Following the Material Transfer and Scientific Collaboration Agreement, established in 2009 between ORNL and JINR Dubna, this material was transferred to Russia within three weeks after final purification. Six ^{249}Bk arc-shaped targets, suitable for irradiation with intense heavy-ions beams, were made at IAR Dimitrovgrad. The irradiations at the DGFRS started in July at the FLNR Dubna and lasted till the end of February 2010, with a total of about 150 days with beam on target and a total beam dose of 4.4×10^{19} projectiles. K. Rykaczewski and J. Roberto participated in the experiment in August 2009 and September 2009. Two isotopes of new chemical element Z=117 were identified among fusion-evaporation reaction products. Five decay chains of 293(117) isotope and one long decay chain starting at 294(117) isotope were observed, leading to the identification of 11 new super heavy nuclei. These results were published in *Physical Review Letters* **104,** 142502 in April 2010. Measured alpha-decay properties for newly identified super heavy nuclei indicated an increased stability with larger neutron number. It represents an experimental verification for the existence of the predicted Island of (Enhanced) Stability for Super Heavy Elements.

This publication triggered a lot of popular and scientific media attention—the news on the discovery of element 117 appeared in *New York Times*, *Science*, and *Physics Today*, and garnered over two hundred other articles.

The new digital data acquisition system foreseen to be used during the search for Z>117 chemical elements has been designed by two project participants, R. Grzywacz and K. Rykaczewski. The first items related to this novel digital data acquisition system, the equipment and software, were delivered in September 2009. Further hardware purchases will follow the funding ($435,000) recently received from DOE for continuation of the studies on super heavy nuclei.

Information Shared

Over two hundred articles in popular and scientific media, including *New York Times* (Apr. 7, 2010), *Science* (Apr. 15, 2010), and *Physics Today*.

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Ezold, J. 2010. Presentation at American Nuclear Society meeting, Knoxville, September.

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Oganessian, Yu. Ts., F. Sh. Abdullin, P. D. Bailey, D. E. Benker, M. E. Bennett, S. N. Dmitriev, J. G. Ezold, J. H. Hamilton, R. A. Henderson, M. G. Itkis, Yu. V. Lobanov, A. N. Mezentsev, K. J. Moody, S. L. Nelson, A. N. Polyakov, C. E. Porter, A.V. Ramayya, F. D. Riley, J. B. Roberto, M. A. Ryabinin, K.P. Rykaczewski, R. N. Sagaidak, D. A. Shaughnessy, I. V. Shirokovsky, M. A. Stoyer, V. G. Subbotin, R. Sudowe, A. M. Sukhov, Yu. S. Tsyganov, V. K. Utyonkov, A. A. Voinov, G. K. Vostokin, and P. A. Wilk. 2010. "Synthesis of a New Element with Atomic Number Z = 117." Phys. Rev. Lett. **104,** 142502 (published Apr. 9).

Roberto, J., 2010. Presentation at James Madison University, Harrisonburg, VA, Mar. 27.

Roberto, J., 2010. Presentation at ORNL Lecture Series, Oak Ridge National Laboratory, Oak Ridge, TN, Apr. 30.

Roberto, J., 2010. Plenary lecture at 21st International Conference on Applications of Accelerators in Research and Industry, Fort Worth, TX, Aug. 8–13.

Roberto, J., 2010. Keynote lecture at National Organization of Test, Research, & Training Reactors (TRTR) and International Group on Research Reactors (IGORR) Conference, Knoxville, TN, Sept. 20.

Roberto, J., 2010. Public lecture at the "Friends of ORNL" meeting.

Roberto, J., 2010. Public lecture at ETEC meeting.

Rykaczewski, K. 2010. "Decay studies at and beyond the limits of known nuclei." *Bulletin of the American Physical Society* (BABS), October (contains abstracts of the APS Division of Nuclear Physics Meeting, Santa Fe, NM, November 2010).

Rykaczewski, K. 2009. Presentation to Faculty of Physics, Warsaw University, Poland, May.

Rykaczewski, K. 2009. Presentation to ORNL REDC, July.

Rykaczewski, K. 2009. Presentation at Third Joint Meeting of the Nuclear Physics Divisions of the American Physical Society and The Physical Society of Japan (Hilton Waikoloa Village, Big Island, Hawaii, Oct. 16.

Rykaczewski, K. 2010. Presentation at University of Tennessee, Knoxville, Apr. 26.

Rykaczewski, K. 2010. Presentation at HRIBF DOE review, Oak Ridge National Laboratory, May 17.

Rykaczewski, K. 2010. Invited talk at International Conference Nuclear Structure 2010, Berkeley, CA, Aug. 10.

Rykaczewski, K. 2010. Presentation at DOE review of Isotope Program, Oak Ridge National Laboratory, Aug. 17.

Rykaczewski, K. 2010. Presentation at Fall Meeting of American Physics Society Division of Nuclear Physics, Santa Fe, NM, November.

05570

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

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

Project Description

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

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

Construction of the High Magnetic Field Helicon Plasma Source has been completed, and the device itself has been commissioned (goal 2). Experiments are under way, but device power has been limited due to the fact that our 100 kW rf amplifier is not yet operational. However, experiments utilizing a low-power (3 kW) rf amplifier have achieved helium plasma densities up to 10^{19} m^{-3} for pulse lengths up to 2 s, as confirmed both through Langmuir probe and microwave interferometer measurements, at a forward power level of only 1.6 kW. This is a higher-than-expected density for this power level. The magnetic field strength in the helicon region for optimum plasma production was observed to be 0.14 T and is approximately the expected value for this plasma density and species. Hydrogen operation has also begun. Based on initial operating experience, it should be possible to quickly optimize high power, long pulse performance (goal 3) with hydrogen once the 100 kW amplifier becomes available.

Information Shared

Goulding, R. H., et al. 2010. "Progress on the ORNL high power, high particle flux helicon hydrogen plasma source." *Bull. Am. Phys. Soc.* **55**(Nov.), 255.

05844

Scale Dependency in Dynamic Downscaling of Extreme Climate Events over Complex Topography

Anthony W. King, David J. Erickson III, Auroop R. Ganguly, and W. Christopher Lenhardt

Project Description

Our objective is to test the hypothesis that an increase in spatial resolution in dynamical downscaling to 4 km improves accuracy and reduces uncertainties in local to regional simulation of climate and weather extremes in regions of complex topography. Climate simulations from the Community Climate System Model (CCSM) Version 3 at T85 resolution (approximately 1.4°, 156 km at the equator) were downscaled to 64, 16, and 4 km horizontal spatial resolution using the Weather Research and Forecasting Model (WRF) in a downscaling centered over Phoenix, Arizona. We investigate how differences in spatial resolution of the regional climate model used in the downscaling affect differences in the accuracy and uncertainty of simulated extremes, evaluating whether the differences are statistically significant. These simulations require high resolution data for model input and testing. The determination of statistically significant changes must be done in the context of intrinsic variability and uncertainty arising from many different sources. Accordingly, while we focus on scale-dependent uncertainties in climate extremes, we do so within a comprehensive characterization of other uncertainties in dynamical downscaling. As part of this characterization, we develop a knowledge framework, a system of concepts and vocabulary, for communicating uncertainty in downscaled climate change projections.

Mission Relevance

The project complements DOE missions in the science of climate change and energy security. In particular, the project is relevant to growing programmatic Integrated Assessment opportunities in the DOE Office of Biological and Environmental Research. The area of climate impacts and adaptation is a growth area for DOE, the National Science Foundation, and the National Oceanic and Atmospheric Administration (NOAA) as evidenced by recent solicitations and the planned National Climate Services of NOAA, and will benefit from the improved understanding of climate downscaling proposed by this project. Similarly this project will benefit developing programs within the Department of Defense and the Department of Homeland Security. Results and capabilities developed during this project are being utilized in development of a proposal to the Strategic Environmental Research and Development Program (SERDP) RCSON-12−02 Statement of Need on climate change impacts in pursuit of follow-on funding.

Results and Accomplishments

Our results support the hypothesis that increases in spatial resolution in dynamical downscaling improve accuracy and reduce uncertainties in local to regional simulation of climate extremes at least in regions of complex topography. CCSM3 output under the SRES A2 scenario were provided as boundary conditions to WRF for the periods 2000–2009 (CCSM_control) and 2030–2039 (CCSM_future). Global Forecast System reanalysis data (0.5° resolution) from the National Weather Service's National Centers for Environmental Prediction were provided to WRF as boundary conditions for the period 1991–2009 (NCEP_WRF). Observations for the downscaling region of daily and monthly climate normals (1971–

2000), the U.S. Daily time-series station data contributing to those normals, and daily precipitation and temperature extremes were obtained from the National Climatic Data Center. From analysis of CCSM_control simulation results for the period 2000–2005, and using the NCEP_WRF simulations at 4 km resolution as the reference baseline, we find that bias, standard error, and spatial variance decline as spatial resolution of the WRF downscaling increases from 64 to 16 to 4 km for both heating degree days (HDD) and the intensity of heat waves. Bias and spatial variance in cooling degree days (CDD) also decline as spatial resolution increases, but standard error in CDD shows no such scale dependency. At least part of the bias reduction for CDD is associated with better resolution of the mountains northeast of Phoenix. Results for precipitation particularly with regards to extremes are less clear, perhaps because of the relatively short simulations available for the analyses, but average daily precipitation does appear to be better simulated with increased downscaling resolution.

Information Shared

Das, D., E. Kodra, K. Steinhaeuser, S.-C. Kao, A. R. Ganguly, M. L. Branstetter, D. J. Erickson, R. Flanery, M. Martinez Gonzalez, C. Hays, A. W. King, W. Chris Lenhardt, R. Oglesby, R. M. Patton, C. M. Rowe, A. Sorokine, and C. Steed. 2010. "Uncertainty and Extremes Analysis to Evaluate Dynamical Downscaling of Climate Models." Abstract and presentation, 2010 American Geophysical Union (AGU) Fall Meeting, San Francisco.

SUMMARIES OF PROJECTS SUPPORTED THROUGH THE SEED MONEY FUND

BIOSCIENCES DIVISION

00525

Nonlinear Plasmonic Nanocircuit for Data Communications

Ali Passian

Project Description

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

Mission Relevance

The project entails developing the next-generation integrated circuit that will have much higher performance, smaller size, and lower power requirements. This is relevant to high technology applications that depend on high performance electronics, such as nuclear security, space research, high performance computing, and other DOE national security missions. The preliminary results, if successful, are expected to attract funds from DOE, Defense Advanced Research Projects Agency, National Aeronautics and Space Administration, Air Force, and other defense-related agencies. These agencies have calls directly related to the technology involved in this project. 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 proposed investigations based on experiments and theoretical modeling of a single-nanoparticle optically excited plasmonic device (nanosystem) began to produce preliminary results. 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. 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 this effect cannot be neglected even if the ultimate desired project outcome envisioned—that is, high

frequency modulation based on the direct plasmonic effect—can be achieved. Post-experimental calculations have been started to interpret the experimental results and optimize the performance of the nanosystem. The theoretical modeling is currently ongoing to support the acquired experimental data.

Information Shared

Passian, A., S. Koucheckian, S. B. Yakubovich, and T. Thundat. 2010. "Properties of index transforms in modeling of nanostructures and plasmonic systems." *J. Math. Phys.* **51,** 023518.

Passian, A., L. Tetard, R. Farahi, B. Davison, A. Lereu, T. Thundat, S. Gleason, and K. Tobin. Accepted. "Trends in high spatial high spectral resolution material characterization." IEEE proceedings, *Future of Instrumentation*.

05855

A Resonant-Based Grave Detector

Arpad Vass, Charles Van Neste, Thomas Thundat, Marc Wise, and Lee Hively

Project Description

This concept involves transmission of electrical energy through the earth-ground plane. Movement of ground charges produces electromagnetic (EM) waves that propagate along the surface radially from a transmitter. This form of wave is conventionally known as a surface or Zenneck wave. A nonradiating system will be designed and assembled to generate electrical standing waves through the earth surface, linking the transmitter and the receiver. The receiver then collects the surface waves and passively integrates them (through resonance) over a period of time. The second step will be to determine if this surface wave can excite bone, allowing for its detection using either an electrical rod attached to an oscilloscope or by acoustic transducers placed along the ground. In previous experiments conducted by the investigators, bone was observed to have a resonance at approximately 2 kHz.

Mission Relevance

Locating shallow, clandestine graves containing human remains continues to remain one of the greatest challenges for law enforcement, military, and human rights organizations worldwide. The primary goal of the project is the development and testing of a system that uses the transmission of electrical energy through the ground to create a unique resonance in association with human bone, taking advantage of the piezoelectric properties of bone, thereby allowing for its detection.

The project has ties to national security, the environment, and science. Locating clandestine graves assists military operations and law enforcement endeavors worldwide. Modulation of the transmitter to frequencies other than 2 kHz can help identify and locate subsurface anomalies important in detecting oil and natural gas deposits and other natural resources.

Results and Accomplishments

The first phase of the project was dedicated to completing preliminary engineering designs and determining manufacturing specifications, as well as evaluating potential hazards associated with high voltage research. Three months into the project, parts were ordered corresponding to the established designs and specifications. Acquired components (which were much more expensive than originally priced) included 10 gauge enameled magnetic wire, power amplifiers, transformers, high voltage capacitors and resistors, toroid, and the exoskeletal framework. Assembly of the unit and fabrication of

critical components was initiated. In addition, progress was made in (1) preliminary design construction for fabricating this device modularly to allow for increased mobility in the field and (2) evaluating other applications for this technology extending past clandestine grave detection.

05862

Developing mRNA-Based Multiplex PCR Assays to Detect Viable *Salmonella* in Food

Yunfeng Yang (David), Yongchao Li, PhiAnh L Waldon, Thomas Thundat, and Anthony V. Palumbo

Project Description

Salmonellosis is one of the most frequent food-borne diseases, imposing a serious public health issue in both developed and developing countries. Accordingly, diagnosis of *Salmonella* food-borne pathogens is a major concern. An ideal diagnostic technology should be rapid, sensitive, accurate, robust to interference, and capable of discriminating viable from nonviable cells. However, none of the current technologies used in the industry meet these requirements. Recently, we have been approached by the industry for novel ideas of diagnostic technologies. A survey of the field has revealed that reverse transcription polymerase chain reaction (RT-PCR) holds great promise for a breakthrough, but there exist valid concerns of interference from the food matrix and associated sensitivity and accuracy. In this project, we tackle these concerns by developing multiplex RT-PCR assays using a combination of a set of primers that specifically PCR-amplify *Salmonella* spp. The performance of multiplex RT-PCR will be evaluated in pure cultures of *Salmonella* spp. or in the presence of a food matrix of meat or egg, in addition to the efficiency of discriminating viable from dead cells. The successful accomplishment of this proejct will generate necessary preliminary results for a novel technological platform of *Salmonella* diagnosis in food that could attract follow-on funds.

Mission Relevance

This research builds off ORNL's expertise in detection of bacteria in the environment. Although this project is focused on food-borne pathogens, methods developed here have potential applications that are relevant to DOE and national security missions. The methods can be applied to threat organisms that could be used by states or terrorist organizations.

Results and Accomplishments

A set of primers targeting the *Salmonella*-specific regions or gene loci has been examined: (1) ttrA gene encoding a tetrathionate reductase; (2) ttrR gene encoding a response regulator component; (3) a specific region of housekeeping gene rpoD encoding a sigma factor; (4) iagA, an invasion associated gene; (5) iroB gene encoding a glucosyl-transferase-like protein; (6) invA, the invasion A gene; and (7) ompC gene encoding a major outer membrane protein. Multiple PCR primers were designed and ordered for each gene to improve the odds of generating specific DNA bands from PCR reactions.

Almost all of the ordered primers were capable of generating PCR bands from DNA template (data not shown). However, only some could detect PCR bands from cDNA template, making them useful for differentiating viable cells from nonviable ones.

Multiplex RT-PCR assays were then conducted by combinations of these primers, aiming to identify a single RT-PCR condition that was applicable for the selected primers. One-milliliter cultures of

Salmonella cells were grown overnight to stationary phase. The bacteria were killed by exposure to 70% ethanol for 20 min. After 12 or 24 hours, both viable and nonviable cells were subject to Trizol treatment, followed by the use of the RNeasy Mini Kit (Qiagen) to extract RNA. Remnants of DNA present in the extracted RNA will be digested by DNase I. Subsequently, 0.3 μg RNA will be reversely transcribed into cDNA and used as template for PCR amplification. Multiplex PCR using a 0.8 μ*M* primer mixture composed of all the selected primers was carried out. In control experiments, the presence of traces of DNA was examined by using the RNA sample as template in PCR.

A combination of a set of primers (ttrA forward, GTGGGCGGTACAATATTTCTTTT; reverse, TCACGAATAATAATCAGTAGCGC; iroB forward, TGCGTATTCTGTTTGTCGGTCC; reverse, TACGTTCCCACCATTCTTCCC; ttr forward, ACTGCCGATAAATGCACGTT; reverse, CTTTTTTCCGCCAGTGAAGA; invA forward, CGCTCTTTCGTCTGGCATTATC; reverse, CCGCCAATAAAGTTCACAAAG; invA forward, GTGAAATTATCGCCACGTTCG; reverse, CATCGCACCGTCAAAGGAA; rpoD forward, CCGATGAAGATGCGGAAGAAGC; reverse, CAAACGAGCCTCTTCAGCCT) was able to generate bands of expected sizes. The PCR condition was 94 degree 2 min (94 degree 30 sec, 55 degree 30 sec, 72 degree 1 min) for 35 cycles, 72 degree 10 min. Clear RT-PCR bands were detected for viable cells but not for cells prepared at 12 or 24 hours after ethanol treatment, suggesting that these primers were effective for differentiating viable from nonviable cells under the given condition.

Multiplex PCR was tested for detecting *Salmonella* in the presence of food matrices—minced meat or egg. However, to date no bands were successfully generated. Nanodrop reading indicated that the extracted RNA was of poor quality, so it is necessary to modify the existing DNA extraction protocol to remove possible inhibitory components in the food matrices that prevent the success of reverse transcription or PCR.

05879

White Light Produced by a Scalable Biosynthesized Zinc Gallate Mixture

Ji-Won Moon, Tommy J. Phelps, Chad E. Duty, Gerald E. Jellison, Jr., and Lonnie 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.

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. This research is framed during FY 2010–2011, starting in July 2010, and

have requested 9.3% of total budget for FY 2010. In the second and final year of the project, all the tasks proposed in the original proposal will be completed.

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 solid state lighting. Our goal is “white light” via mixtures of zinc gallates, which emit red, green and blue, to facilitate the R&D program of 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 at low power use, 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 to green energy related to resource saving but also to nanomaterials application to devices. Project results will affect white light research itself as well as support basic information to produce a spinel-type precipitate in which there are no reducible metals in the biologically mediated incubation 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 are being incubated with all ingredients from the outset or incubated with only the electron donor and microbes to obtain enough biomass prior to precursor addition. After checking optical density, ionic metal precursors such as zinc and gallium in an exact molar ratio and doping elements such as manganese and chromium are beng dosed according to the molar ratio at a given time during the incubation. Currently, we use 10 mL medium scale; in the second year the medium will be scaled up to 1 L. Subsamples are processed through centrifugation, washing, and stored by mixing with methanol for phase identification and emission measurement and blending for white light.

In the first year, we alleviated chance exposure and toxicity of raw materials for safety considerations. One of main raw chemicals previously used was anhydrous gallium chloride, which is highly moisture sensitive and produces hydrochloric gas during the preparation of the precursor metal solution. We have tested gallium nitrate ($Ga(NO_3)_3)\cdot xH_2O$ based on previous results; $x = 8$ (Berbenni et al. 2005) and $x = 12$ (Loeffler and Lange 2004). Our studies have shown that pure zinc gallate can be produced when using the metal precursor based on $x = 12$ without the interference of nitrate (e.g., nitrate reduction); however, only an amorphous phase resulted when $x = 8$.

Based on the emission of blue light from biologically produced zinc gallate and X-ray diffraction (XRD) data that confirmed the phase, the production of green and red light sources were pursued using manganese- and chromium-doped zinc gallate, respectively. For green light $ZnGa_2O_4:Mn_{(0.004,\ 0.008,\ and\ 0.04)}$ and for red light $ZnGa_2O_4:Cr_{(0.004,\ 0.008,\ and\ 0.02)}$ were synthesized. To confirm the preferred site of manganese incorporation into manganese-doped zinc gallate subsequent to different emission properties, we replaced or added metal precursors such as $Zn_{0.96}Mn_{0.04}Ga_2O_4$, $ZnGa_{1.92}Mn_{0.08}O_4$, and $ZnGa_2O_4:Mn_{0.04}$. The crystal chemistry of all synthesized samples will be confirmed by XRD and emission using a fluorometer.

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. A white paper was submitted to that agency.

Information Shared

Moon, J.-W., T. J. Phelps, L. J. Lonnie, C. E. Duty, G. E. Jellison, Jr., and R. J. Lauf. 2010. *Nanofermentation Induced Nanomaterials under Nonreducible Elemental Systems.* UT-Battelle Invention Disclosure IDN 201002436, DOE SN S-115,488.

05890

Bioelectrochemical Petri Plates for Isolation of Novel Electrogenic Microorganisms

Abhijeet P. Borole

Project Description

The project consists of development of a novel bioelectrochemical device for isolation of microorganisms capable of electricity production. The device includes an anode, a cathode, and a separating membrane. The two electrodes are connected electrically via an external circuit and a variable resistor. The goal of the project is to develop a device that allows growth of colonies of electrogens to enable their isolation as pure cultures. This ability will enable purification of electrogenic organisms, which cannot be isolated via traditional microbial culture techniques. The device can be used to understand microbial diversity related to extracellular electron transfer and is directly related to electricity and biohydrogen production. Potential sponsors for future work include the DOE Office of Biological and Environmental Research, the Department of Defense, and companies interested in commercialization of this technology.

Mission Relevance

The project is relevant to development of new energy resources and needed technology for production of bioenergy and biofuels such as hydrogen and electricity. As such, it is related to renewable energy and national security related to energy self-sufficiency. Specific programs that may have an interest in this technology include the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE), DOE Office of the Biomass Program, the Defense Advanced Research Projects Agency, the Office of Naval Research, and the DOE Office of Biological and Environmental Research. The device developed in this study will be used in a project in 2011 funded by DOE EERE to investigate development of microbial fuel cell technology for treatment of process water from biorefineries. Specifically, the bioelectrochemical plate will be used to isolate microorganisms from biorefinery microbial fuel cells (MFCs), which are capable of conversion of fermentation inhibitors such as furfural, HMF, and phenolics molecules to electricity. Study of such organisms may help in development of strategies to overcome inhibitory effects to biofuel-producing organisms. This work will be conducted in collaboration with the National Renewable Energy Laboratory.

Results and Accomplishments

Two different types of bioelectrochemical (BEC) plates were constructed. The first one consisted a ferricyanide cathode and was made up of two disposable Petri plates joined together and separated by a

Nafion membrane. A carbon cloth was used as the anode material. This device was used in the anaerobic chamber and inoculated with a electrogenic consortium from acetate-fed MFCs. A load of 250 ohms was used between the anode and the cathode. A small current was observed after incubation for 3 days at room temperature, indicating growth of electrogenic organisms. Sufficient growth of cells was not observed to enable visual observation, so a second plate with controlled voltage, air diffusion, and nondisposable material was made. This plate was operated using an air cathode and resulted in significant growth of microorganisms on the anode electrode surface. The microbial biofilms were examined under microscope and appeared to be made up of homogeneous colonies of organisms. Further purification can be done by repeated streaking on the BEC plates. Thus, the utility of the plate in growing and isolating electrogens from anode consortia was demonstrated. The plate has potential to be used in understanding microbial and protein diversity of extracellular electron transfer-capable microorganisms in projects such as the Permafrost project and others via omics and imaging technologies resident at ORNL.

CENTER FOR NANOPHASE MATERIALS SCIENCES

05876

Probing Photovoltaic Processes at the Single Interface Level

An-Ping Li, Kirk Bevan, Gyula Eres, TaeHwan Kim, and Ho Nyung 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 for 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 will demonstrate that new experimental tools and materials expertise unique to ORNL can address this critical scientific challenge. Specifically, the ORNL four-probe scanning tunneling microscope will be used 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 reveal the correlation between the photovoltaic process and the local interfacial properties at the single interface level. The success of this research will 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. The success of this project will provide a key component to future initiatives 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

We have characterized the cleaved cross-sectional surfaces of $SrTiO_3$ crystals using a scanning tunneling microscopy method. The structural and electronic properties have been examined, which revealed heterojunction interfaces with some peculiar periodic patterns on the cross-sectional surfaces. On the materials growth front, we have advanced the pulsed laser deposition technique to allow for doping of TiO_2 films. The doping effect and electrical properties have been examined. On the theory side, a major has effort has been given to the simulations of phase separations associated with mechanic strain field.

We have devised a Monte Carlo method to simulate the segregation of the phase domains by considering several factors. The first is the thermodynamic energy of the coexisting phases, which depends on the temperature and the applied stress and is also a function of the local chemical composition. The second factor is the energy of the phase boundaries, which is expressed as the square of the gradient of the phase field variable. The strain energy is nonlocal whose range is the size of the phase domains; therefore, it is difficult to include in an efficient simulation. We approximate the strain energy by the surface-to-volume ratio of the phase domains. Because the presence of the domain boundaries releases the strain, the higher the surface-to-volume ratio, the lower the strain energy is. Adding these terms together, our Monte Carlo simulations show segregations of several different types of phase domains, which will be compared with experimental observations.

05889

Rapid Functional Recognition Imaging in Scanning Probe Microscopy

Sergei V. Kalinin and Stephen Jesse

Project Description

We propose a scanning probe microscopy (SPM) data acquisition, processing, and control method for rapid quantitative mapping of local properties and functionality in inorganic, molecular, polymer, and biological systems. The method, further referred to as functional recognition imaging, is based on the rapid acquisition and automatic de-noising, classification, and interpretation of spectral, multimodal, or multispectral data sets (multidimensional data) at each spatial pixel. This recognition step substitutes for classical homodyne-based data processing or simple postprocessing of multidimensional data. Recognition data can be stored as an image, used as a feedback signal, or used as a trigger to control more complex microscope operations such as manipulation or communication. When successful, the project will open a direct pathway for rapid recognition imaging in all areas of nanoscience by providing a bridge between advanced computational and modeling capabilities and SPM data.

Mission Relevance

The proposed paradigm for functional imaging potentially allows revolutionizing the landscape of scanning probe microscopy by providing a reliable bridge between advanced modeling capabilities and experimental data that can be incorporated during in-line microscope operation. The recent DOE Grand Challenges and DOE workshop documents list the capability to probe and manipulate matter and information on the nanoscale as one of the key targets for DOE research, suggesting high relevance for energy-related fundamental research. The specific topic in this work—energy losses during mechanical tip-surface contact—are highly relevant to fundamental aspects of mechanical behavior and friction in spatially confined systems. Furthermore, methods for biological imaging and recognition are remaining a traditional priority for the National Institutes of Health. Recognition imaging microscopy offers an ideal pathway for this funding by providing a method to differentiate cells based on their phenotype. Hence, cancer and molecular imaging programs are a natural source of funding. Notably, the proposed algorithm can be potentially used in conjunction with other detected signals, including optical, mass-spectral, or microwave.

Results and Accomplishments

We have demonstrated the recognition spectroscopic imaging for rapid identification of biological, molecular, and atomic species in the SPM experiments. In this, the spectroscopic response (e.g., force-distance curve or broadband excitation response) is acquired on a spatially resolved grid on the sample

surface, yielding three-dimensional (or higher) spectral images and simplified using principal component analysis. The objects are identified using characteristic shape, for example, yielding appropriate identifiers. The neural net is trained for recognition of the single-pixel response with the principal component analysis (PCA) components as input and the identifier as output. Thus trained neural net is subsequently used for identification of the (unknown) objects in the subsequent imaging, for which shapes or other trivial identifiers are no longer available. This approach has been demonstrated for separation of *M. lisodeicticus* and *P. fluorescense* bacteria based on electromechanical response in a liquid environment. The studies have been extended for the rapidly acquired force-distance curves in SPM obtained from dynamic data. Furthermore, its viability has been demonstrated for other spectroscopic imaging modes, including energy loss spectroscopy in scanning transmission electron microscopy.

Information Shared

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CHEMICAL SCIENCES DIVISION

00508

Whole Community Proteomic Characterization of Synthetic Human Gut Microbiomes in Gnotobiotic Mice

Robert Hettich, Alison Russell, Patricia Carey, and Nathan VerkBerkmoes

Project Description

This exploratory research program focuses on the development and demonstration of advanced mass spectrometry (MS) techniques for the characterization of synthetic microbiomes in gnotobiotic mice. The work is being conducted in collaboration with Prof. Jeffrey Gordon (Washington University) as a key demonstration of a technological approach to characterize the complex microbiomes that influence both health and disease in mammalian systems. The first aim is focused on the experimental demonstration of MS technology to acquire comprehensive proteome data from a variety of synthetic microbiomes from gnotobiotic mouse samples; the second task focuses on bioinformatic analyses conducted with newly emerging microbial genome data; and the third aim seeks to use an isotope labeling approach to examine temporal metabolic activity in the various microbiomes. Our work will provide key scientific information to the gut microbiome research community.

Mission Relevance

This work is directly tied to DOE research objectives, particularly within the Office of Biological and Environmental Research (BER), that are focused on the development and demonstration of advanced technological approaches for characterizing microbes at a systems biology level, in particular for research ranging from bioenergy, carbon-cycling, and bioremediation. In particular, research directives within DOE BER are highly focused on technologies that can reveal protein information for natural microbial communities. As part of its exploratory roadmap initiative, the National Institutes of Health (NIH) has formulated a research program entitled “The Human Microbiome Project.” We have been able to leverage some of the research results from this project to secure a newly funded NIH HMP project, which involves our metaproteomic capabilities at ORNL to study the human gut microbiome.

Results and Accomplishments

We have completed development and demonstration of an integrated experimental/computational approach for obtaining comprehensive proteome data from a variety of synthetic microbiomes from gnotobiotic mouse samples. In particular, we have developed and optimized a new cellular processing method based on detergent lysis/protein solubilization that was found to be vastly superior for obtaining deep proteome coverage from microbiota in mouse cecal samples. When combined with measurements from a new high performance LTQ-Orbitrap-Velos instrument, we were able to identify greater than 2,000 nonredundant proteins from a seven-member microbial consortia in five separate mouse cecal samples. This work revealed the need for better bioinformatics tools to differentiate unique from

nonunique peptides in genome-related microbial species. Computational work was conducted to compare the predicted vs. experimental "peptidome" to ascertain the level of uniqueness expected, and measured, in these samples. We have extended this approach to evaluate a more complex 12-member microbial consortia system from gnotobiotic mice cecal samples, in order to study how these microbial communities impact, or respond to, diet-induced changes in the mouse. In particular, the microbiota from gnotobiotic mice fed either high-fat or low-fat (chow) diets were examined in detail with this new experimental approach. We were able to measure between 3,000 and 5,000 nonredundant proteins in each sample, and found that the high-fat diet not only yielded more total microbial protein identifications but also revealed a much higher level of metabolic activity in amino acid metabolism, carbohydrate metabolism, and protein translation.

Information Shared

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00514

An Ionic Liquids–Based Ion Detector

Peter T. A. Reilly

Project Description

Ionic liquids have been used to create an ion detector whose response is essentially independent of mass. This ion detector comprises an electron multiplier integrated with an ionic liquid reservoir. Ions of any size impact the surface of the ionic liquid in vacuum, whereupon ions from the liquid of the same net charge and polarity are ejected. The interaction of particulate ions with ionic liquids is being explored as a function of particle kinetic energy, mass and charge. The ability to detect ions without mass dependence is the last major hurdle for the direct analysis of mass-specific species such as whole ribosomes, RNA, DNA, or even viruses.

Mission Relevance

A DOE strategy within the arena of biological and environmental research, including genomic and related biological sciences, is to create fundamentally new bioenergy sources and conversion processes. The development of a mass-independent detector will permit the rapid analysis of high-molecular-weight biological components that are relevant to our energy future. This improvement in analysis rate will facilitate the discovery and evaluation of new energy source materials as well as efficient conversion processes.

The mission of the National Institutes of Health will be greatly enhanced by the capabilities this detector will provide. The high mass capability of the detector will enable the direct measurement, characterization, and identification of complex mixtures of proteins, protein complexes, RNA, DNA, and even viruses. The ability to analyze complex biological systems rapidly will accelerate advances in proteomics. The Department of Homeland Security and the Department of Defense are greatly interested in the rapid analysis of bacteria and viruses to analyze bioterrorist attack locations and battlefield settings. This innovation enhances these analyses.

Results and Accomplishments

A new type of detector for large ions was tested. A small amount of low-vapor-pressure ionic liquid was applied to the surface of a metal conversion electrode to enhance the detector response for large ions, for which commercial detectors do not work well. Several observations were made in these preliminary experiments. The ionic liquid tested permitted a high vacuum of up to the 10^{-7} torr range to be achieved, a sufficient condition for operation of most mass spectrometers. However, the ionic liquid self-ionized rapidly once the electrode applied electric field was larger than a certain threshold. To prevent such ionization, a small metal mesh electrode was inserted at the opening where the large analyte ions enter the detector. The voltage applied to this metal mesh electrode was typically 100 V. Sharp corners near the liquid were all rounded to give a fairly uniform electric field. Most of the effort was spent in optimization of the detector geometry design and testing. Ions were generated by electrospray ionization at ambient conditions. The ions were introduced from an aerodynamic lens and guided through the quadrupole ion guide. The detector was placed just below the guide exit lens. The distance to the electrode was also optimized during this study to avoid self-ionization of the ionic liquid. This was necessary because the applied voltage on the quadrupole rods was different for different molecule sizes. The detector response was monitored during operation of the quadrupole ion guide, with a limiting orifice at the entrance of the aerodynamic lens open and closed. On several occasions, our setup showed significant response to the large ions. At optimized conditions, no background signals were detected. Once the analyte ions were introduced into the aerodynamic lens, the detector responded. Overall, the heavy-ion detector worked for large ion detection. However, a more clever design will be required to prevent self-ionization of the liquid.

Our work with low energy ions (<100 eV) suggested that ionic liquids do not eject small ions from a low energy impaction process. The particular ionic liquid selected does not seem to alter that result. The data indicate that large ions reflect from the ionic liquid surface without penetration and subsequent ejection of small ions. However, results from higher energy experiments suggest that the ionic liquid medium does produce secondary ions at a much lower energy threshold than a standard metal surface. We have been successful at detecting large single-charged ions in the 200 kDa range with only 2 keV of kinetic energy. There does not seem to be a lower mass limit for this effect. It has been theorized that there is a kinetic energy threshold for penetration of the large ion into the ionic liquid bulk. We have strived to determine the upper size/mass ion detection limit as a function of kinetic energy.

05860

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

Peter V. Bonnesen, Kunlun Hong, Jun Yang, and S. M. Kilbey II

Project Description

Biocompatible poly(amidoamine) PAMAM dendrimers of generation 4 (G4) or greater are receiving 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 (1) 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 endgroups in a well-defined manner; (2) from this dendrimer prepare a series of multivalent ligand–dendrimer conjugates in which two different bioactive molecules have been attached to the alternating endgroups; and (3) 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).

Mission Relevance

The project aims to increase the 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 National Institutes of Health (NIH) or the National Cancer Institute (NCI). There could be significant benefits in the areas of drug delivery for (e.g., cancer) therapy and imaging, 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” (from NCI website).

Results and Accomplishments

We have evaluated and refined the underlying chemistry for attaching a precursor arm to a PAMAM dendrimer surface, from which we can then attach a second branch. Each branch will later be functionalized with a different bioactive molecule using orthogonal chemistries. We have established a useful protocol for attaching the precursor branch and have refined the analytical techniques used to evaluate the structural changes to the dendrimer. In collaboration with our NIH colleagues, we have revised the target dendrimer core size, selected appropriate modifying groups to impart better biocompatibility, and selected the candidate bioactive molecules. The revised dendrimer-bioactive molecule-conjugate targets were designed to enable a clearer assessment of the effect of the alternating arrangement of the bioactive molecules on the final multivalent ligand–dendrimer conjugates on biological activity, as compared with, for example, a random arrangement of the bioactive molecules on the dendrimer surface.

We plan to complete the synthesis and characterization of the target G4 PAMAM dendrimer functionalized with two different bioactive molecules (available from NIH), in which the bioactive molecules are connected to the dendrimer surface in a generally alternating arrangement, by way of alternating branches. These two bioactive molecules will also be attached to the surface of a G4 PAMAM dendrimer in an uncontrolled, random spatial arrangement. After characterization, the biological activity of the dendrimer conjugates will be evaluated in suitable bioassays through collaborators at the NIH.

05875

Electrolytic Hydrogen Production: A New Materials and Structural Approach

Elias Greenbaum, Philip D. Rack, Ivan I. Kravchenko, Barbara R. Evans, and Charlene A. Sanders

Project Description

The focus of this project 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 is defined as production of a >90% H_2 stream with <10% O_2 content. Another measure of success is demonstration of >80% steady-state electrical energy to hydrogen conversion efficiency for newly reported hydrogen and oxygen evolving electrode materials. Turner et al. report conversion efficiencies of 56–73% for typical commercial electrolyzer system efficiencies. These values will serve as a point of reference for our work. We show that our approach makes sparing use of readily available materials and naturally integrates with modern methods of manufacturing and telemetry.

Mission Relevance

The scientific and technical problem that this project addresses is the economical production of carbon-neutral hydrogen and oxygen via the electrolysis of water. Our solution is the use of readily available materials, very-large-scale integration (VLSI) device technology, inductively coupled power transmission, 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 a DOE core mission: “Promoting America’s energy security through reliable, clean, and affordable energy.” This project supports that mission with new ideas that can lead to economical domestic production of carbon-neutral hydrogen and oxygen.

Results and Accomplishments

Progress has been made in Task 1, Laminar Streaming, Proton-Conducting Pores and the Cross-Migration of H_2 and O_2. Nickel cathode and anode electrodes were deposited on opposite sides of a 100 mm diameter × 500 μm thick silicon wafer. A rectangular grid of 500 μm diameter pores was etched in the spaces between the electrodes. The patterned wafer was held vertically in a “sandwich” test chamber with separate anode and cathode compartments. Ion conduction between the compartments was achieved via the pores. At the start of the test, both compartments of the test apparatus were sparged with a nitrogen gas steam to remove dissolved atmospheric oxygen from the electrolyte. An electrolysis current of 250 μA DC was applied to a cathode/anode pair in a static electrolyte. After an hour of electrolysis, analysis of the contents of the gas in the headspace of the hydrogen compartment indicated ~99% H_2 and ~1% O_2. Not every experiment produced this result. Room vibrations and pressure differences observed as oscillating liquid levels between the anode and cathode compartments increased the oxygen component to 5–10%. This problem was anticipated. We have several backup plans to solve the problem: filling the pores with proton-conducting polymers, increasing the concentration of electrolyte from 10 m*M* KOH to higher values (>1 *M*), and the use of an electronic pressure-regulating device. We have learned a good deal about the use of this newly constructed apparatus during the course of this reporting period.

Information Shared

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05880

Nuclear Materials FTIR

Linda A. Lewis, Rick Moyers, and Denise 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, 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 has 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

Because the project was initiated late in FY 2009, the effort was extended into FY 2010. To date, the FTIR (reflectance mode) has been leased, radiological work requirements completed, samples identified, and a required blackbody calibration source ordered and received. Data collection was completed the first week of November 2010, and the data is now being processed. The materials tested were UO_3, UO_2F_2, U_3O_8, UO_2, UO_3, UF_4, and NH_4NO_3.

The FTIR spectrometer used for the measurements was a modified Bomem MR254 with a ZnSe beamsplitter. It was anticipated that the reflectance measurements would push the limits of the system sensitivity, with reflected signal levels less than 1% of the total energy hitting the samples. To eliminate scattered light due to the optics and maximize the signal to the detectors, the input collimator was removed. The detector field of view was 45 milliradians, with a 1 in. beam diameter at the beam splitter.

A folding mirror was used to enable horizontal operation of the instrument, with the samples and calibration source located on the floor just in front of and below the instrument. The folding mirror was an 8-in.-square, 3.2-mm-thick aluminum mirror (ThorLabs Item Number ME8S-G01). The calibration source was a custom Bodkin Engineering extended source blackbody with 3-in.-diameter circular surface area. Blackbody calibration data was taken both before and after each sample measurement. A two-point calibration (at 25°C and 50°C) was used.

The folding mirror and instrument were fixed in place for all data collection. A careful alignment was made so that the center of the instrument's field of view was over the center of the blackbody, and the blackbody position was marked on the floor of the test chamber so that it could be removed and replaced with the test sample in the same position. Spectral resolution was set to 8 cm^{-1} and sweep speed was set to 32 kHz. The detector preamps were set to auto-ranging mode to achieve maximum signal for each data point.

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

05870

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

James 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 will be 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 will be 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. Work is proceeding to apply our inductive modeling tool to data taken from live tumors. A major aspect of this work is to make the inductive modeling engine capable of exploiting ORNL's supercomputing resources.

05881

Thwarting Online Deception and Phishing with Honeypots and DNS Analysis

Craig A. Shue, Gregory C. Hinkel, and Frederick T. Sheldon

Project Description

Criminals impersonate legitimate institutions and defraud users through the Internet. In phishing attacks, criminals send deceptive e-mails 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 $3 billion.

Phishers must obtain e-mail 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 domain name service (DNS) access patterns. With extensive real-time data from trap e-mail addresses (or honeypots) at external sites and ORNL, combined with ORNL server logs, we will examine phishing Web crawler access patterns. This will enable us to (1) prevent crawlers from harvesting our users' e-mail addresses, (2) block spam from the crawlers' networks, and (3) determine whether a campaign is Internet-wide or targeting 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 DOE.

Our approach has broad implications for other federal agencies, including the Department of Defense, the Department of Homeland Security, and the Federal Bureau of Investigation. 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 honeypot systems for distributing trap e-mail 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 the Information Technology Services Division. 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 Internet service provider 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 e-mail messages or adjusting the information we release to these visitors. Future efforts will refine these measurements.

05884

Drag Reduction with Superhydrophobic Surfaces

Charlotte Barbier and Brian 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 will expand 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 Naval of Research for their vessels, and the Department of Agriculture for irrigation applications.

Results and Accomplishments

The slip boundary condition was implemented in OpenFOAM and validated with theory. A series of calculations was run for two different slip lengths (25 and 50 μm) for a cone-and-plate geometry. 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. For the experimental part, a rheometer was identified at CNMS and the experimental setup was designed. The work done during FY 2010 is on the right track to achieve the goals planned for FY 2011.

05888

Development of Real-Time Optimization Methods for Neutron Scattering Experiments—Where to Measure and When to Stop

Y. Jiao, K. An, P. F. Peterson, X.-L. Wang, and S. D. Miller

Project Description

In advanced neutron scattering, there are strong interests in the research community to study in situ dynamic or kinematic behaviors of materials under varying temperature, magnetism, pressure, and electric fields. The major challenge is that materials often react to changing conditions in heterogeneous and unpredictable ways: parts of the material may exhibit interesting behavior, while the rest does not; characteristics of a material may change dramatically within a very small range of temperatures, but do not vary much outside that range; as the pressure increases, molecular structural changes of a material may appear and then disappear; and the list goes on. We developed a new iterative, dynamic sampling approach that adjusts an experiment's plan on the fly, based on the actual observations, to dynamically decide the area of interest (where to measure) and the minimum measurement time required to obtain sufficient data (when to stop). The novelty of our approach is threefold: (1) processing of streaming event data in real time, (2) developing robust algorithms that can handle various material samples and experimental settings, and (3) interfacing and controlling the instrument in real time. While experiment optimization on neutron instruments faces the same fundamental challenges, specific solutions are highly dependent on the instrument. For the proof of principle, we choose an engineering diffraction beam line, VULCAN at the Spallation Neutron Source, as our test bed with a real neutron diffraction experiment.

Mission Relevance

Neutrons are used by scientists to explore a wide spectrum of problems in the fields of physics, biology, chemistry, materials science, etc. Ideally, scientists want to be able to capture the intriguing moments when transformation occurs inside the material and to obtain sufficient amounts of data so that statistically significant conclusions can be drawn. Due to the exploratory nature of scientific experiments, scientists usually do not possess the precise knowledge of where or when these moments occur, nor do they know exactly the minimum measurement time required to obtain sufficient data prior to the experiment. As a result, precious beam time may be wasted and scientific discoveries may be delayed. One of the long-term goals of the neutron scattering sciences community is to be able to conduct experiments the way radiologists do magnetic resonance imaging oday: data are visualized and analyzed as the procedure is progressing, and decision support software, in real time, helps doctors to decide where they should investigate further. This project aims to take a step toward that goal. The success of this project can help accelerate scientific discoveries and can potentially save the research community millions of dollars.

Results and Accomplishments

We have successfully designed, implemented, and deployed software modules that provide real-time uncertainty analysis and optimization support to scientists. A Restful web service interface seamlessly connects the optimization components to the existing data acquisition system (DAS). The design of the software architecture follows three main principles: simple, modular, and extensible. First, we choose the RESTful web service paradigm instead of a SOAP-based web interface for its simplicity and stateless nature. This feature significantly reduces the amount of bookkeeping on the server side and allows for faster processing. Second, our fitting, visualization, and optimization tools are implemented as separate modules that can be mixed and matched to solve specific problems. Finally, we decoupled data analysis from data acquisition to allow both systems to expand independently. This work combines experiment

optimization and remote instrument control. Unlike the traditional push-based control, we adopt a pull-based control mechanism: When DAS is ready, it will pull information from the web server. In other words, DAS has full control over whether or not to use the optimization service at all. This feature is critical to ensuring the safety of experiments as any control instructions issued to the instrument, bypassing DAS, could pose potential safety risks.

Information Shared

Jiao, Y., K. An, P. F. Peterson, X.-L. Wang, and S. D. Miller. 2010. "Development of Real-Time Optimization Methods for Neutron Scattering Experiments —Where to Measure and When to Stop." American Conference on Neutron Scattering, Ottawa, Canada, June 26–30.

Jiao, Y., K. An, P. A. Zolnierczuk, P. F. Peterson, X.-L. Wang, R. A. Riedel, and S. D. Miller. 2010. "RESTful Web Services for Neutron Scattering Experiment Optimization." Poster presented at New Opportunities for Better User Group Software, Gatlinburg, TN, Oct. 10–13.

COMPUTER SCIENCE AND MATHEMATICS DIVISION

00522

DNA Separation Using Electrophoretic Traps

Fedor Rudakov

Project Description

The ability to separate biomolecules according to sizes is required for a wide variety of applications including DNA sequencing, genotyping, mutation analysis, and diagnosis of diseases. Usually, separation by size is achieved by electrophoretical transport of charged biomolecules through a sieving media using uniform electric field. We present an alternative design that allows separating biomolecules of a particular size from a mixture without performing complete separation of the sample by size. Our design allows independent manipulation of biomolecules of different sizes along any pathway in two dimensions while keeping them highly concentrated. By manipulating the speed of the photoelectrophoretic trap, biomolecules of a particular size can be selectively separated from the mixture.

Mission Relevance

This is a basic research program that will benefit ongoing fundamental computational research for the DOE Office of Basic Energy Sciences program being conducted by scientists at the Center for Engineering Science Advanced Research and at the Computer Science and Mathematics Division. It will also benefit other DOE research programs in biology and life sciences.

Results and Accomplishments

We have demonstrated (both computationally and experimentally) selective separation of DNA fragments using optically directed transport. Separation is achieved by manipulation of the speed of the photoelectrophoretic trap and is based on the capability of the biomolecules to “keep up” with the trap, which is size dependent. Biomolecules inside the trap remain highly concentrated, which prevents band broadening due to diffusion. In addition, biomolecules can be translocated along any pathway in two dimensions independently from each other. Our methodology enables tight control over the separation process and can potentially provide very high resolution. The results are summarized in our article in *Applied Physics Letters* and were presented at 3rd International Multi-conference on Engineering and Technological Innovation. Our publication received “Session’s Best Paper Award.”

We studied dynamics of DNA fragments in a periodic potential and demonstrated their separation. The results are summarized in our article in *Applied Physics Letters.*

Information Shared

A. Braiman, F. Rudakov, and T. Thundat. 2010. "Highly Selective Separation of DNA Fragments Using Optically Directed Transport." *Appl. Phys. Lett.* **96**(5), 053701; paper also selected for the Feb. 15, 2010, issue of *Virtual Journal of Biological Physics Research.*

A. Braiman, T. Thundat, and F. Rudakov. 2010. "DNA Separation on Surfaces." Appl. Phys. Lett. **97**(3), 033703; paper also selected for the Aug. 1, 2010, issue of *Virtual Journal of Biological Physics Research.*

Project team. 2010. Presentation at 3rd International Multi-conference on Engineering and Technological Innovation, July 2; received the Session's Best Paper Award.

05877

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

Fedor Rudakov

Project Description

We propose a novel approach to sensing of chemicals that, unlike any other existing technique for standoff detection, is capable of distinguishing between molecules with very close structures. The basis for our technique is Rydberg-state spectroscopy followed by microwave-based detection. The target molecules are first excited to the 3s Rydberg state and then pass through the 4p, 5p 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."

Mission Relevance

The proposed technique for standoff detection is scientifically novel and may find multiple applications. For example, due to 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 vibrations. 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 detection of complex organic molecules and clusters. The proposed design may also find applications in nuclear cycle monitoring and non-proliferation control.

Results and Accomplishments

We started work on the project in October 2010 (FY 2011). To perform a proof-of-feasibility experiment we acquired the Rydberg spectrum of diazobicyclooctane (DABCO). The molecule is excited to the 3s Rydberg state by 266 nm laser pulses and then probed out of that state by two-photon ionization using a dye laser. The spectrum is read out by probing the remotely generated plasma with microwave radiation.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

05867

Identification and Rapid Screening of New and Unique Plant Sources for Biofuels

Bruce G. Bunting, Sam L. Lewis, Mike Bunce, and Blake L. Joyce

Project Description

In this project we evaluated a number of nontraditional plants for their ability to produce compounds that could be used as partial substitution for petroleum-derived fuels, in order to expand biofuels beyond commonly used ethanol and fatty acid methyl esters. This evaluation included plant selection, acquisition and characterization of the plant extracts, evaluation of fuel properties and specifications of the extracts, evaluation of emissions and combustion characteristics of the fuel blends, and generalization of our evaluation procedures into a recommended practice. This ORNL project has a parallel University of Tennessee–Knoxville (UTK) funded project in the Plant Sciences Department related to selection of the plants and obtaining samples of the extracts.

Mission Relevance

The plants discovered and techniques developed could potentially expand the range of biofuel source material available and could also serve as genetic roadmaps for improving plants to product more fuel-useful extracts. DOE programs that could benefit would be the Office of Biomass (increased and more diverse supply combined with rapid screening techniques) and the Vehicle Technology Program (improved understanding of fuel chemistry and property effects). The experimental procedures used for evaluating the fuels can serve as standard procedures for evaluating new and emerging biofuels.

We have not, as yet, procured follow-on funding. However, the techniques of this research have been used to support three research proposals: (1) partnering with the University of Georgia and others in the area of fuels from pyrolysis (did not win), (2) partnering with Johns Hopkins and others in the area of fuels from pyrolysis (awards not announced yet), and (3) an ORNL proposal to the U.S. Marine Corps to evaluate the local generation of biofuels in areas of military deployment (pending for 2011). Discussions were also held with ORNL program management related to matching this research into our DOE Office of Biomass research portfolio or our Department of Agriculture research portfolio, but no match was found. UTK is also exploring several funding avenues for continuing this research.

Results and Accomplishments

UTK identified six plants as having potential as biofuel sources and obtained samples. Two of the extracts were obtained in both a raw and partially refined form, resulting in a total of eight plant extracts. The plants were (1, 2) *Copaifera,* “diesel tree,” raw and steam distilled; (3) *Aleurites moluccana,* “kukui” or “candlenut”; (4, 5) *Pittosporum resiniferum,* “petroleum nut,” raw and cold stabilized; (6) *Cymbopogon*

martii, palmarosa; (7) *cymbopogon flexuosus*, "lemongrass" or "citral"; and (8) *Dictamnus alba*, anethole, "burning bush." Detailed chemistry was run on each of the extracts using gas chromatography (GC-MS).

The plant extracts were then blended at 20% levels (B20) in 2007 certification #2 ultralow-sulfur petroleum diesel fuel and sent to an outside laboratory for property and chemistry determination per ASTM D7467 (Standard Specification for Diesel Fuel Biodiesel Blend). None of the B20 blends passed all of the ASTM requirements, failing one or more of the following: cetane (ignition behavior), flash point (vapor safety), filter plugging, oxidation stability, and ash and residues.

Finally, the B20 blends were run in a single cylinder research engine at the National Transportation Research Center to determine ignition, combustion, and emissions properties. Some of the B20 blends provided worse performance than the #2 diesel fuel in the areas of fuel consumption and/or emission levels of carbon monoxide, hydrocarbons, or smoke. However, three of the blends produced equivalent or better performance than the base diesel fuel.

We attempted statistical correlation of these results, but the number of fuels was too small and the fuels too diverse to uncover direct linkages between plant characteristic and fuels performance. Analysis is continuing and will be used as a basis for future publications, proposals, and as part of a UTK PhD thesis.

Overall, the procedures developed proved to be useful for evaluating potential new fuels; we identified and studied several new plant sources for biofuels; we now have a database of chemistry, properties, and engine performance for these new fuels; and we established collaboration with UTK Plant Sciences for future research and proposals.

Information Shared

Joyce, B. L., B. G. Bunting, S. L. Lewis, J. S. Choi, J. S. Storey, F. Chen, and C. N. Stewart. 2010. "Fuel Properties of a Novel Plant-Based Biofuel from *Copaifera* Reticulate." Poster presentation at American Oil Chemists Society Annual Meeting, May.

05873

Computational Simulation of Catalytic Biomass Pyrolysis

C. Stuart Daw, Charles E. A. Finney, and Sreekanth Pannala

Project Description:

We are 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 data and evaluate potential barriers to commercial scale-up. Addition of catalytic materials to biomass pyrolizers has been recognized as a promising step to reducing problematic tar products, but to date there has been no development of comprehensive reactor models to interpret experiments or to aid in scale-up of reactor designs. This project will utilize two computational codes to simulate catalytic biomass pyrolysis reactors: MFIX (Multiphase Flow with Interphase eXchanges), a DOE-sponsored code for general multiphase flow simulation, and a modified version of an ORNL-developed steady-state code for fluidized bed combustion of coal. Both codes will need to be adapted for biomass chemistry, physical properties and pyrolysis operating conditions and then compared with appropriate experimental data for validation

Mission Relevance

In joint discussions among the national labs and DOE, thermochemical catalytic pyrolysis has been identified as one of the most promising areas for near-term research and development towards production of renewable transportation fuels from biomass. Currently, there are no comprehensive simulation tools that can model the existing pilot-scale pyrolysis reactors being used by national labs to develop a basic understanding of the chemistry and kinetics of biomass pyrolysis and which can also be used to evaluate how those results can be scaled up to commercial process conditions. Such tools are needed to interpret results from and guide experiments and assessment commercial process options. DOE's Integrated Biorefinery platform views computational scale-up tools as a major technical challenge and objective. Along with DOE, both the Department of Agriculture and the Department of Defense have identified biomass pyrolysis as a major potential source of renewable transportation fuels with tie-ins to sustainable land use, carbon sequestration, and energy security.

Results and Accomplishments

During FY 2010 we were able to recruit Sudharshan Renganathan, a post-Masters researcher from Georgia Institute of Technology, to assist in the modification and validation of the MFIX code for simulating pyrolysis of wood. Sudharshan came to ORNL last June. Under the direction of Sreekanth Pannala and Charles Finney, he has spent most of his effort in defining values of several key hydrodynamic and heat transfer parameters in MFIX needed to simulate the conditions typical for bubbling bed wood pyrolysis studies currently being run at the National Renewable Energy Laboratory (NREL) and the Pacific Northwest National Laboratory (PNNL). In addition, Sudharshan has also expanded his MFIX parameter evaluations to include pyrolysis reactors at the Korean Institute of Science and Technology (KIST), with which we have recently begun a collaboration.

For the steady-state reactor model, Stuart Daw has reviewed and modified key submodels in the original FORTRAN code used to account for bubble dynamics and bed expansion, and he has added new submodels that account for wood particle segregation (relative to the primary bed particles), particle heat-up and devolatilization rates, and volatile yield and composition (including tars). It is expected that in the next few weeks all of the steady-state submodels will be implemented in MatLab and available to begin studies of parametric sensitivity and trend comparisons with MFIX and experimental pyrolysis data from the literature and our collaborators.

A $10,000 subcontract was also implemented with Prof. J. S. Halow at Waynesburg University in Pennsylvania to provide data from experimental ambient temperature measurements of wood particle mixing in a full-scale bubbling bed reactor built to simulate the experimental laboratory bubbling bed reactor at NREL used for measuring pyrolysis kinetics. Prof. Halow utilizes a unique magnetic tracking system (developed previously in collaboration with ORNL) to directly monitor the motion of simulated biomass particles as they mix with and segregate from the primary bed particles. The mixing and segregation processes are critical to the ultimate yields of liquid hydrocarbons from pyrolysis because they directly affect the degree of contacting between the biomass particles and the other gases and solids in the reactor. This is especially important in catalytic pyrolysis, because the catalyst is typically present on the surface of the primary bed particles.

05885

Rapid Bidirectional Cantilever-Based Anemometer for Engine Intake and Exhaust Gas Recirculation Flow and Mixing Characterization

James E. Parks, Sam Kim, and Thomas Thundat

Project Description

Cantilever sensors were studied in simulated gas flows to evaluate the approach as a means to measure exhaust flow in engine applications at high rates of speed. The emphasis is to develop a sensing technique that will allow characterization of advanced exhaust gas recirculation systems to optimize, via feedback controls, engine emissions and fuel efficiency performance.

The overarching goal is to provide a technique for measuring the complex gaseous flows in internal combustion engines so that models of these processes can be validated and engine designs can be improved. Modern diesel engines are attaining significant improvements in fuel efficiency while simultaneously greatly reducing criteria pollutant emissions by operating in advanced combustion modes that are fundamentally different from traditional stratified charge combustion. To achieve the advanced combustion, high rates of exhaust gas recirculation are require; thus, understanding the air and exhaust gas handling of engines becomes more critical. Industry has detailed models of the processes, but techniques to validate the models do not exist. The cantilever sensor would be used as a validation tool if successful.

Mission Relevance

The project is relative to engine research that directly impacts both energy security and environmental quality. Research tasks are directly designed to support ongoing efforts in the DOE Office of Vehicle Technologies. Other federal agencies that may benefit from the research include the National Aeronautics and Space Administration (NASA) and the Defense Advanced Research Projects Agency (DARPA). Propulsion research in both of these agencies may benefit from a sensor capable of rapid flow measurement in hostile environments.

Specific to the internal combustion engine application that the project targets, these engines will continue to be a primary transportation powertrain for decades to come. To reduce petroleum consumption and improve national energy security, reductions in petroleum use are necessary, and the improvements in engine technology by advanced diagnostics techniques can enable the practical implementation of those reductions.

Results and Accomplishments

A piezoresistive microcantilever manufactured by Cantimer was studied with simulated exhaust gas flow. The cantilever sensor was inserted into gas flow controlled by a mass flow controller in flow ranges with linear velocities typical of those experienced in engine manifold systems. The flow was sensed by the cantilever in both forward and reverse directions relative to the cantilever physical position. The ability to measure both forward and reverse directional flow is important as pressure pulses in engine manifolds can create reverse flow conditions from the valve operation of multiple cylinders. The flow of gas induced bending of the cantilever, which was detected and quantified by changes in the resistance of the cantilever due to the piezoresistive effect.

Forward and reverse flow was accurately detected by the cantilever. A forward flow rate of 1000 sccm produced an increase in resistance of 0.4 ohms, and similarly, a reverse flow rate of 1000 sccm produced

a decrease in resistance of 0.4 ohms. However, the nominal resistance of the sensor was 2419.9 ohms; thus, the differences obtained in the signal were not very large in comparison to the overall resistance. An increase in the induced resistance change is likely necessary and could be made by moving to a larger cantilever device. A search has begun for vendors that could supply a larger cantilever sensor. Another limitation is in the method for measuring the resistance change; the existing wheatstone bridge technique had a significant time constant that needs to be reduced for fast response. Future work will focus on these limitations and implementing the technique in an actual engine.

ENVIRONMENTAL SCIENCES DIVISION

00524

Nanoparticle-Hydrogel Sensors for Trace Detection of Explosives in Groundwater

Wei Wang, Qingzhou Cui, and Liyuan Liang

Project Description

This project was to develop and synthesize a simple, inexpensive, intelligent sensing material with high sensitivity and selectivity to rapidly detect explosives in contaminated groundwater in situ. We fabricated the sensing materials by simultaneously introducing colloidal photonic crystal nanoparticles and molecular recognition functions into a network of polymer hydrogel. The wavelength of diffraction by the synthesized hydrogel was designed to vary in the range of visible light. Either change in volume or lattice spacing of the embedded photonic crystal structure would induce the color change upon interaction between specific molecules such as TNT explosives and designed functional groups in the polymer hydrogel. Thus, the new hydrogel allows the identification and determination of explosive molecules in water. The new technique potentially reduces the labor and analytical costs associated with sampling and laboratory analysis.

Mission Relevance

One of the key needs of DOE Subsurface Biogeochemical Research is developing new methodologies for detection and identification of organic and inorganic contaminants in groundwater at DOE sites. Techniques for rapid screening and detection of explosives are a specific need by federal agencies, such as the Department of Defense and the Department of Homeland Security.

Results and Accomplishments

Synthesis of colloidal nanoparticles and fabrication of polymer hydrogels. We synthesized highly surface-charge-enhanced, monodisperse polystyrene and silica nanoparticles, and assembled them into colloidal photonic crystal structure in water. Additionally, we developed protocols to embed the colloidal photonic crystal structure in a polymer network in the hydrogel form. We fabricated polyacrylamide hydrogels through chemical crosslink by ultraviolet-induced reaction, as well as developed a new method to produce polyvinyl hydrogels through physical crosslink by a thermal treatment.

Functionalization of nanoparticle-polymer hydrogels. The key component of this research was to make the hydrogel film with molecular recognition functions so as to selectively identify and analyze aqueous chemicals of interest. We introduced the molecular recognition function into the polymer network in the nanoparticle-hydrogel material through combined chemical modification and molecule imprinting processes. In a polymerization reaction of the hydrogel, we imprinted 1,3,5-trinitrobenzene (TNB) or 2,4-dinitrotoluene (DNB) molecules, the analogues of explosive TNT, as the target molecules in the hydrogel. Meanwhile, we chemically grafted functional groups of vinylbenzene into the polymer network

to enhance interaction between polymer hydrogel and the analytes through enhanced van der Waals force, hydrophobic force, and specific π-π structural interaction, so as to make the hydrogel materials highly selectivity. We also optimized conditions for the hydrogel fabrication to maximize the hydrogel volume change for increased sensitivity by adjusting cross-linker concentration, monomer-to-crosslinker ratio, imprinted molecule concentration, and hydrogel film thickness.

Evaluation of polymer hydrogel sensors for detecting explosives in water. We tested the TNB and DNT detection in water, and achieved a detection limit at ~0.1 mmol/L level with a portable Ocean Optics spectrometer system. Interferences from solution pH and background electrolytes Na^+, Cl^-, and NO_3^- ions were studied and subtracted from the measurements.

05854

Hydrogel-Encapsulated Solids for In Vivo Contaminant Availability Testing During Ingestion by Large Vertebrates

Mark S. Greeley and Scott 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, will be 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 new 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 the test subjects. 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 and thereby demonstrate the in vivo solubilization of this model metal contaminant in the fish test systems. In support of the in vivo studies, the kinetics of in vitro lead diffusion and leaching from hydrogels were also characterized for both water and simulated gastric solutions. Furthermore, using a range of known lead concentrations added to the hydrogels, 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.

To complete the proof of principle of this new contaminant bioavailability testing approach, we still need to show that solubilized contaminants are actually absorbed by the intestinal tract during hydrogel passage. Thus future efforts will focus on conclusively demonstrating that the lead fraction solubilized during passage through the fish gut is proportional to actual lead uptake from the gastrointestinal tract. In addition, some failures of hydrogels encapsulating certain soil types to pass intact through the gut in preliminary testing suggest that further work is needed to understand the effects of sample characteristics on hydrogel polymerization if this method is to be capable of assessing contaminant bioavailability across a diverse range of ingested solids.

05871

Plasmonic Effects for Improved Photocarrier Generation in Thin Film Solar Energy Materials

Katyayani Seal, Xiaoying Xu, Claudia Troparevsky, Yuan Li, Zhenyu Zhang, and Baohua 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 will use 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

The project incorporates fundamental research in the fields of photovoltaics, energy conversion, and plasmonics research and is thus directly relevant to the DOE renewable energy program, specifically the Solar Energy Technologies Program (SETP). 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

In FY 2010 we 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-infrared range.

We 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.

For our next step, the modified films will be coated with a spacer layer of SiO_2 (to prevent fluorescence quenching). A layer of fluorescent dye in a polymer matrix will then be spin coated on the sample. The fluorescence from the sample will be measured to verify whether an enhancement in the fluorescence quantum yield has been achieved. The sample will also be investigated for directional emission. Both phenomena in conjunction should lead to a large increase in fluorescent downshifting efficiencies, demonstrating the advantages of using plasmonic nanostructures towards augmenting downshifting yields.

Theoretical modeling will also be performed to determine the optimum structures for maximizing the quantum efficiency of the structure. The work will provide the proof of principle for the use of plasmonic effects towards improved photocarrier generation in thin-film solar energy materials.

05892

Testing Nonthermal Plasma as a CWA Decontamination Method

Meng-Dawn Cheng

Project Description

The project was designed to test the feasibility of using cold plasma as an alternative to solution-based methods for decontamination of chemical warfare agents (CWA) that deposited on the sensitive weapon platforms and systems. The nonthermal or cold plasma was generated by an electrical or radiofrequency powering method and contains a high level of reactive species such as free radicals. The reactive species react with CWA and chemically "degrade" or "destroy" the agents in a short time (typically minutes); the end-products of the decontamination are benign gas species such as carbon dioxide. Nonthermal plasma decontamination leaves no residue trace on the material treated. We demonstrated the effectiveness of the nonthermal plasma decontamination on the surface of C-17 polymer airframe composite material.

Mission Relevance

Use of a wet chemical-based method for decontamination of chemical and biological warfare agents (CWA and BWA) has been known to cause significant material degradation and loss of tensile strength of a stainless steel structure in previous tests. The solvent-based decontamination also leaves a significant quantity of polluted water, potentially causing secondary pollution that could increase human exposure and health risks. We tested an alternative method that is dry, potentially clean, and leaves no trace residues—the Atmospheric Pressure Non-Thermal Plasma (APNTP) jet. The APNTP is scalable so it is conceivable to scale up the technique for large areas to be decontaminated.

Results and Accomplishments

A bench-top commercial APNTP was used to produce the jet for this quick turn-around test. The jet has a nozzle that produces a line-shaped jet. The initially proposed use of a pulsed high-power laser plasma as one of two NTP power sources did not yield stable APNTP as expected. The laser approach created breakdown successfully; however, the reactive species rapidly recombined, virtually eliminating the

decontamination power. The repetition rate of laser firing (10–20 Hz) was too slow to generate stable seed for NTP production based on emissions spectroscopy and the current measured on charged particles. Also, we had no laser that could fire faster than 20 Hz to confirm our initial hypothesis.

CWA simulant–contaminated samples of the composite C-17 material, 12 × 4 in. in size, were prepared by adding a known amount of CWA simulant to the surface of the C-17 material. The surface strip of the sample, which has both clean and contaminated sections, was entirely exposed to the plasma. Plasma-treated surfaces were visually inspected for crack and color changes, because there is some concern that exposure to nonthermal plasma will degrade the polymer matrix of the fiber-reinforced composite over time. This could have led to cracking, color alteration, or changes in the mechanical properties of the composite material. Thus, extended exposure to NTP (~10 min) served as an upper bound of damage that could reasonably be expected from repetitive short duration (30 s) decontamination treatments. A digital image of the samples was taken for detailed computerized image analysis.

A breakdown potential on the C-17 samples was evaluated using a commercial 200 W APNTP instrument and found to occur at a scanning height of 1.5 cm from the material surface. Since the plasma did not have a cooling apparatus, the temperature at this distance was 100°C as a result of radio frequency (RF) heating on the head that also heated the plasma. Field operation should include a cooling component. Subsequent reduction of the RF power to 150 W mitigated the thermal damage issue, and the temperature at 1.5 cm was about the room temperature. Decontamination results indicate that the RF-discharge APNTP was able to remove the simulant completely in 3 min at a rate of ~3.7 mg/min. The removal was 99.997% complete based on follow-on gas chromatography–mass spectroscopy analysis of grab samples, and three-dimensional topographic imaging showed no sign of damage on the surface.

The aerosol electrometer readings on-line during the decontamination did not indicate an alarming level of charged particle generation. The readings were comparable or slightly higher than those commonly found in indoor air. However, the total mass of the particles (assuming the unit density of particles) generated was calculated to be on the order of femtograms based on the measurement using the Scanning Mobility Particle Sizer (SMPS®), which also showed that the nanoparticles peaked at about 10 nm during the operation.

The RF-discharge nonthermal plasma is an effective alternative to surface decontamination. The engineering scale requires additional studies. We were able to accomplish the proposed activities. The project (funded at $27,000 in FY 2010) has yielded a return of 5.5 fold by wining a SERDP award of $150,000, which would enable continued research and development of the RF-discharge and other types of discharge technology to be used for a new APNTP technology for surface cleanup.

FUSION ENERGY DIVISION

05852

Parallelization in Time of Numerical Simulations of Plasma Turbulence: A New Avenue Towards Enabling Future First-Principle Modelling of Fusion Plasmas

Raul Sánchez , Luis Chacón , Debasmita Samaddar, and David Newman

Project Description

The merits of controlled thermonuclear fusion in magnetically confined plasmas as a clean and efficient future energy source will be put to the test in the $20 billion International Thermonuclear Experimental Reactor (ITER) under construction in France, which has been identified as one of the highest priority items on the DOE research agenda. DOE and the fusion community are also convinced that, in order to exploit ITER optimally, first-principle numerical simulations of ITER burning plasmas with predictive capabilities will be required. The Fusion Simulation Project (FSP) is a $20 million per year, 15 year effort through which DOE intends to fund research aimed at delivering such a capability. But important difficulties still lay ahead. The most important one is the large disparity that exists between the scales of the microturbulence (1 μs, 1 mm) governing transport processes and the scales over which plasmas are confined (100 s, 1 m). The disparity gets even larger if a truly first-principle approach is taken, since gyro-motion times and gyro-radii (and maybe even Debye lengths) would have to be resolved. The combination of the small time steps required to capture the relevant physics and ensure numerical stability together with the long intervals over which calculations must be carried out makes direct numerical simulation of ITER-like plasmas currently unfeasible, even with the most powerful parallel supercomputers available. Indeed, current parallel technology can in principle deal successfully with any disparity in the spatial dimension, but these techniques do not carry over to the temporal dimension the intrinsic serial nature of the temporal coordinate, which prevents from splitting the temporal domain in pieces handled by separate processors and still preserve causality. Recently, however, techniques have been proposed that achieve somewhat of a temporal parallelization by paying the price of iterating the solution several times and correcting it properly to preserve causality. The theoretical benefit is not to reduce the computing time by the number of processors used but is somewhat more modest when one takes into account the number of iterations the cycle must be repeated. One such scheme is the so-called *parareal framework*, recently proposed. In this project, we have explored whether the parareal scheme, previously only tested in simple and nonturbulent problems, may be applied successfully to a fusion-relevant, turbulent plasma in the presence of a strong magnetic field and provide an additional route that might make ITER-like simulations achievable in the near future.

Mission Relevance

The benefit of being able to do efficient time parallelization of numerical simulations is enormous, not only for the fusion community but to many other fields as well. This new capability will have a large

impact in any field in which numerical simulation of turbulence is required, such as fusion plasmas but also combustion, aerodynamics, fluids, astrophysics, and many others. In addition, not only will longer simulations be doable, an efficient parallelization of time will also allow better use of the computational resources that are becoming available with the new series of supercomputers. Indeed, these offer hundreds of thousands of processors, but many of the state-of-the-art codes for turbulence simulations do not scale well beyond a few tens of thousands. Regarding DOE programs, a successful time parallelization scheme of fusion codes will have an impact on the direction and priorities of the aforementioned Fusion Simulation Project as well as on currently state-of-the-art fusion codes funded under the DOE Scientific Discovery through Advanced Computing program and other DOE initiatives. Additional programs that may benefit from this work are those dealing with climate and astrophysical turbulent plasmas (i.e., the Sun, accretion disks, supernovae, etc.), mostly funded either by the National Science Foundation or DOE.

Results and Accomplishments

The main accomplishment of this project has been to prove that the parareal technique converges in turbulent conditions allowing an effective parallelization in time of a fusion-relevant, turbulent code. This is indeed a nontrivial outcome, since there were a priori arguments by which it should have been expected that the parareal scheme should fail in turbulent environments, mostly due to the expected high variability of the solutions with minimum changes in the initial conditions. The code that has been used is the BETA code that simulates plasma turbulence driven by the dissipative-trapped electron mode in slab geometry. It is also important to remark that the application of the parareal scheme is not straightforward in any problem, since it requires the identification of an approximation to the problem that is fast to evaluate but still close enough to the actual solution of interest to be useful for preserving causality. Many lessons learned during this project regarding how such approximation must be made will be useful in the future. Regarding quantitative results, we were able to parallelize in time a BETA simulation using 88 processors that yielded a ninefold speed-up in a simulation that would have taken almost two days if run serially. Finally, we have also developed strategies to better utilize computational resources during the moments within the parareal cycle in which many of the processors stay idle.

Information Shared

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MATERIALS SCIENCE AND TECHNOLOGY DIVISION

00505

Nanoporous Inorganic Membranes for High-Efficiency Organic Separations

Ramesh R. Bhave

Project Description

The goal of this project was to demonstrate the potential of nanoporous inorganic membranes to perform organic separations with high throughput and acceptable selectivity. We investigated the transport and separation mechanisms using nanoporous inorganic membranes with precisely controlled characteristics and robust morphology. Dense polymer membranes have been used for organic separations but lack the long-term reliability and operating characteristics required for large-scale industrial applications. In this project we studied several nanoporous membranes, both commercially available and those fabricated at ORNL, with pore sizes in the range of 2 to 5 nm. We studied the retention of several organic materials such as polyethylene glycols (PEG), lube oil, and oligosaccharides (OLS). We used the pore flow model to analyze the results and to determine separation characteristics in the viscous flow regime.

Mission Relevance

Membrane separations are energy efficient as compared with distillation and for several years have been a part of call for proposals from the Industrial Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE). The goals of this project are aligned with the DOE EERE mission to improve the efficiency of separation and energy-intensive processes. We anticipate that successful completion of the project could result in novel cost-effective technology to reduce energy consumption and increase efficiency of many energy-intensive industrial processes such as chemical/petrochemical and biomass conversion to fuels, a key DOE mission. Research in inorganic nanoporous membranes for the purpose of developing energy-efficient alternatives to traditional separation processes such as distillation, evaporation, and extraction would have broad applications. The Environmental Protection Agency would benefit as membrane processes reduce waste volumes and have the potential to significantly improve air quality and minimize environmental impact.

Results and Accomplishments

We have evaluated the ability of synthesized and commercially available membranes to retain polyethylene glycols with molecular weights (MW) ranging from 200 to 6000 and lube oil with molecular weight around 300. We also evaluated several OLSs such as raffinose (MW 504), maltopentaose (MW 829), and maltoheptaose (MW 1153). The separative layer was titania due to its ability to provide high flux and solute retention compared to other materials such as alumina and silica. The membranes were fully characterized using gas and liquid permeance supported by dynamic pore size (DPS) distribution. Separation characteristics for samples containing PEG were analyzed using gel permeation

chromatography (Phenomenex Polysep column). Lube oil solvent mixture were analyzed gravimetrically and samples containing OLS were analyzed using high pressure liquid chromatography (Phenomenex Rezex column). DPS analysis revealed microstructure consisting largely of uniform pores with narrow pore size distribution.

We demonstrated solute retention of 80–90% for PEG and OLS with molecular weight around 1000 with 2 nm membrane. Lube oil retention with 2 nm membrane was low (~20%), which suggests membranes with pore diameter <1 nm may be required for separations involving solutes with MW <500. Permeation measurements showed relatively high permeability with nanoporous inorganic membranes up to 25 L/h-m^2-bar depending on feed properties and degree of solute retention. For solutes with MW >500, concentration polarization and solute pore wall interactions reduced flux due to viscous flow and increased retention. Results also showed that feed mixture with large difference in physical property such as viscosity is responsible for separation in the viscous flow regime as predicted by the pore flow model. In the case of OLS solute retention increased with feed mixture compared to pure component retention, indicating that concentration polarization and solute pore wall interactions are more dominant, resulting in substantially higher retention. This result suggests that nanoporous membranes would show acceptable selectivity in industrial applications that involve separation of complex feed mixtures.

05848

Reversible Electrostatic Carrier Doping by Ferroelectrics for High On/Off Ratio Field Effect Switches

Ho Nyung Lee, Matthew F. Chisholm, and Takeshi Egami

Project Description

Electrostatic modulation of charge carriers lies at the heart of semiconductor technology. With this project, we aim to apply the same basic concept to obtain much larger and more fundamental changes in correlated electron oxides than those that can be achieved in conventional semiconductors. In particular, we aim to demonstrate the feasibility of a high on/off ratio switch based a combination of epitaxial ferroelectrics and hole-doped correlated electron oxides (CEOs). In these materials, injected charges are expected to be concentrated within 1 or 2 nm of the interface, in contrast to the much larger length scales found in semiconductor transistors. Since this will dramatically influence the channel's carrier density, we expect that the electronic behavior can be artificially controlled by the ferroelectric polarization. Thus the novel approach proposed here will allow us to play a crucial role in the development of advanced oxide electronics through manipulation of materials' functionalities at the atomic scale.

Mission Relevance

The central goal of this project is to gain fundamental understanding of electrostatic carrier doping with ferroelectric-CEO field effect heterostructures. Therefore, the materials to be investigated are highly relevant to DOE missions because of their potential usefulness for materials in various applications, including information storage, sensors, actuators, and solar energy generation. Thus, the work proposed here is an ORNL opportunity for world leadership in understanding yet unveiled physical properties arising from interactions at well-defined interfaces. The quest for functional oxide heterostructures will also contribute to a broad range of basic and applied research programs. Our innovative approach to manipulating electronic ground states by high-speed switching of ferroelectric polarization may potentially benefit industry and federal agencies such as the Department of Defense and the Defense

Advanced Research Projects Agency, since the oxide-based field effect transistors are very promising for many technical applications such as sensors, energy and information storage, and piezoelectric devices.

Results and Accomplishments

High-quality ferroelectric thin films in field-effect transistor (FET) structures play a key role. Thus, epitaxial synthesis of CEO/ferroelectric bilayers on conducting substrates has been conducted. By using such samples, this research has enabled the successful demonstration of high on/off switching ratio for the first time. A clear metal-insulator transition is observed with a drastic change in resistivity by changing the polarization direction. A dramatically high switching ratio ($\Delta R/R = 100{,}000\%$) has been obtained in $(La_{1-x}Sr_x)MnO_3$ ($x = 0.2$ and 0.5) films. This is a drastic improvement over the previously reported best record value of 20%. Comparing it with electronic transport we speculate that the charge carrier mobility is modified by the creation of a very clean, highly conductive LSMO/PZT interface due to the ferroelectric field effect. In case of magnetism, while we have observed only a small change in total magnetization between two polarization-switching states, the systematic change in Tc has been found, confirming the change in Tc found from the DC transport measurement. We envision that the successful completion of this project will have a big impact on the study of nonvolatile information storage devices and on attracting future funding. Currently, testing our prototype transistors is under discussion with a semiconductor memory company.

05856

Spin Excitations and Multiferroic State of Doped $CuFeO_2$

Randy Fishman, Feng Ye, and Jaime Fernandez-Baca

Project Description

Due to the strong coupling between the electric polarization and the 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 project 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 gallium-doped $CuFeO_2$ compound (3.5% gallium 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 recently submitted to *Physical Review B*. 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 an invited talk about this work during the June 2010 meeting of the American Neutron Scattering Society in Ottawa.

Information Shared

Haraldsen, J. T., F. Ye, R. S. Fishman, J. A. Fernandez-Baca, Y. Yamaguchi, K. Kimura, and T. Kimura. 2010. "The Multiferroic Phase of Doped $CuFeO_2$ Identified Using Inelastic Neutron Scattering." *Phys. Rev. B Rapid Commun.* **82,** 020404.

05861

High Throughput Synthesis and Chemical Modification of Graphene Materials for High Capacity Supercapacitors

Nidia C. Gallego, Vinay V. Bhat, and Cristian 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 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 in order 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 400 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 still 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 specific capacitance varies between 56 F/g (initial RGO) and 82 F/g (RGO treated at 600°C). These values are lower than those of a high-surface-area carbon used as reference (280 F/g for Maxsorb™ with 2200 m^2/g); however, the area-normalized specific capacitance of graphene materials (14 $\mu F/cm^2$ for unmodified RGO) is higher than that of Maxsorb (12.7 $\mu F/cm^2$), approaching the theoretical limit allowed by the size of electrolyte ions.

Future work will focus on improving the dispersion of graphenes for enhanced electrolyte access and higher gravimetric specific capacitance. We will also explore chemical modifications that are expected to induce additional pseudocapacitance contributions and increase the total charge stored.

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

Jun Qu, Huimin Luo, Nancy J. Dudney, Dong Ma

Project Description

Current lithium-ion battery capacity is mainly limited by the low charge capacity (372 mAh/g) of the graphite anode. Silicon has the highest 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 due to 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. The silicon shell accommodates lithium ions, while the copper core functions as the built-in current collector and provides strong mechanical support. 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

In FY 2010 we successfully fabricated copper-silicon core-shell nanowire arrays. The nanowires are several micrometers long with shell diameters of 300–350 nm and core diameters of 150–200 nm. Raman spectroscopy examination indicated that the silicon shells are primarily in the amorphous phase, which is preferred for the anode application. First, a couple of two-electrode coin-type half-cells have been assembled for the copper-silicon nanowire arrays. Galvanostatic cycling was carried out in a potential range of 2.0–0.005 V using a constant current charge–discharge protocol at rates from C/30 to 10C. The initial testing results are very encouraging: (1) great potential for high capacity—the capacity for the first two cells reached ~1000 mAh/g, already 3× the theoretical capacity of a conventional graphite anode, and the capacity can be further increased by increasing the Si/Cu ratio with the potential up to 3000 mAh/g; (2) excellent capacity retention with 95% after 39 cycles at various charge–discharge rates; (3) insignificant capacity drop for a higher charge–discharge rate up to 1C due to the highly conductive copper core; and (4) near 100% coulombic efficiency after the first cycle. No silicon pulverization or core-shell delamination was detected under scanning electron microscopy after 50+ charge–discharge cycles.

The planned work for FY 2011 includes (1) improvement on the nanowire distribution and morphology, (2) reduction of SiO_x on the nanowire surface to decrease the irreversible capacity, (3) characterizations of the nonstructural and compositional evolutions induced by lithium-ion insertion–extraction, and (4) further electrochemical evaluation using half-cell and/or full-cell configurations.

05866

Synthesis of High-Performance Lignin-Derived Biothermoplastics

Rebecca H. Brown, Tomonori Saito, Deanna L. Pickel, Joseph M. Pickel, Frederick S. Baker, and Amit K. Naskar

Project Description

Lignin is the second most abundant natural polymer, accounting for up to 30% by weight of wood. Lignin is a valuable by-product of the paper and pulp industry that is currently utilized in a variety of low-value applications and as fuel for the paper mills. The overarching intent of this project is to establish chemical synthetic routes for producing lignin-based thermoplastics, which will increase the value of lignin by-products. Today's available lignin-based bioplastics are primarily thermosets, and therefore nonrecyclable. This project aims to move well beyond current state-of-the-art lignin products

and demonstrate the capability to synthesize inexpensive and high toughness biothermoplastics from biomass lignin feedstocks. The specific objectives are (1) characterization of lignin residues from multiple commercial biomass sources; (2) prepolymerization of lignin to produce higher molecular weight polymer precursors; (3) synthesis of thermoplastics and thermoplastic elastomers from selected lignins; and (4) determination of structure-property relationships of lignin-derived bioplastics. The development of new value-added lignin products may lead to significant enhancement to the economics of ethanol production in future biorefineries.

Mission Relevance

Significant potential for development of lignin biomass feedstocks as value-added products exists, and such development relies on the identification of new markets for this valuable natural biopolymer. Although research is being conducted at ORNL to produce materials from lignin, including carbon fibers and nanoporous carbons for energy storage sponsored by the DOE Office of Energy Efficiency and Renewable Energy, none is focused on the development of high performance thermoplastics from lignin. The successful development of lignin-based thermoplastics will allow for the manufacture of fully bio-based composite materials to complement efforts in lignin-based carbon fibers. Additionally, the development of new value-added lignin products will impact the economics of ethanol production in biorefineries, a major focus area of the BioEnergy Science Center at ORNL. Additionally, sustainable biopolymers are an area of interest for the National Science Foundation and the Department of Agriculture. The U.S. chemical, automotive, and aircraft industries will benefit through improved competitiveness, sustainability, and energy efficiency in processes and products.

Results and Accomplishments

During FY 2010 chemical synthesis routes to the formation of lignin-based thermoplastics were demonstrated. Through careful tuning of reaction conditions, higher molecular weight lignin fractions were achieved through a chemical reaction while maintaining solubility in tetrahydrofuran and alkaline solution. A significant increase in glass transition temperature (T_g) from 107°C to greater than 160°C occurred due to changes in lignin structure.

These fractions of higher molecular weight lignin were then used in a series of grafting reactions to form links to other pre-polymers that have soft segments. The synthesized block copolymer product is a thick, sticky brown solid, a hybrid of the dark brown powder lignin and clear viscous liquid rubber. The viscosity and shear modulus of the lignin-rubber copolymer increased by two orders of magnitude over the neat polymer soft segment or a blend of both components, proving that chemical bonding did occur. At the highest lignin content obtained, shear thinning behavior was observed in the synthesized copolymer. The invention was elected to be pursued by the ORNL Technology Transfer Group, and the patent filing process is under way. While much progress has been made, continued studies are necessary to achieve sufficient mechanical properties for use of lignin-based copolymers as industrial thermoplastics.

Information Shared

Mielenz, J. R., F. S. Baker, A. K. Naskar, C. C. Eberle, R. E. Norris, Jr., and J. M. Pickel. 2009. "Genetically Modified Lignin-Derived Bio-Thermoplastics for Polymer Matrix Composites." UT-Battelle Invention Disclosure 200902293. Patent application in preparation.

05872

Can Neutrons Do It: Probing Performance of Lithium-Ion Batteries In Situ

Zhili Feng, Xun-Li Wang, Ke An, Stephen E. Nagler, Wei Zhang, Claus Daniel, Hsin Wang, Camden R. Hubbard, and Nancy J. Dudney

Project Description

High power lithium-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 its capacity fades due to internal degradation. Factors contributing to the performance of lithium-ion batteries are very complex and vary significantly with the electrode materials, battery manufacturing processes, as well as charge–discharge 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 delithiation, lithium transport, and the buildup of internal stress and temperature that contribute to the performance of battery. Addressing this need, the project aims to develop an innovative in situ neutron diffraction experiment approach to probe lithium-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 the electric vehicles—the capability of comprehensive nondestructive diagnostics of "real" battery and battery package performance under realistic operation 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 the major DOE initiatives on high-power batteries for automotive applications and electric storage infrastructure. Specifically, it offers the unique capability to nondestructively "see" inside a large-format prismatic battery cell to understand and quantify the chemical, thermal, and mechanical processes and determine how these might affect the overall cell durability and performance of degradation-resistant electrode materials and manufacturing and 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 successfully completed the first set of experiments in FY 2010 at the Spallation Neutron Source with two different battery types. The experiments yielded rich information that made it possible to determine the local SOC inside the battery by means of a novel neutron diffraction approach developed in this research. This 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 charge–discharge cycles. Our effort in FY 2010 clearly demonstrated the feasibility of using neutron diffraction techniques to study the local SOC changes inside a large-format battery. The results are being prepared for publication. The project received strong interest and support from a major automotive original equipment manufacturer and a battery manufacturer, which provided to the project large-format lithium-ion batteries representative of those used in hybrid electric vehicles.

05874

High-Efficiency and Low-Cost Photovoltaic Cell Wafers via Plasma Arc Lamp Processing of High-Purity Silicon Powder

Andrew A. Wereszczak, Chad E. Duty, H.-T. Lin, and Gerald E. Jellison, Jr.

Project Description

The project 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 substantially decrease. Furthermore, with appropriate solar cell processing, 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, creating opportunities to pursue and 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 Solar Technology Program of the DOE Office of Energy Efficiency and Renewable Energy (DOE EERE). 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 the DOE EERE Solar Technology Program, other agencies involved with solar R&D (e.g., Tennessee Valley Authority) would eventually benefit from the project.

Results and Accomplishments

The progress in the first 6 months of the project was better than expected. Approximately two dozen silicon-melting trials were completed with the 700 kW plasma arc lamp. Numerous independent processing parameters were examined, including the choice and surface preparation of the mold material, mold geometry, source and purity of the silicon powder, sources of contamination, quantity of powder to place in the mold, lamp intensity and duration, flow and wetting characteristics of the melted silicon, and remelting response. A first breakthrough occurred in early September when a large and dense silicon billet was fabricated. It was sufficiently large and mechanically robust to enable machining into a test piece for metallography and electrical and optical property measurements. 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), the complex dielectric constant, absorption coefficient, and carrier concentration. This was very encouraging because it shows that the sought-after proof of principle (i.e., making a net shape silicon wafer) for this project was almost within reach.

05882

Using Small Angle Neutron Scattering (SANS) to Determine Gas Hydrate Pore-Scale Distribution

Claudia J. Rawn, Gernot Rother, Kenneth C. Littrell, Tommy J. Phelps, and William 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 due to 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 account funding this project was opened on June 24, 2010. The focus of the project to date has been to build a system to use with the existing SANS pressure/temperature cell. The system was designed to deliver methane through one port, H_2O/D_2O mixtures through a second port, have a vacuum connected to a third port, and pressure transducer to the fourth. Most of the components to build a stand-alone system that could be portable to various SANS beamlines (e.g., CG2 in the cold guide hall of the High Flux Isotope Reactor at ORNL or one of SANS instruments at the National Institute of Standards and Technology) were ordered and received by September 30, 2010. In addition to the new components, an existing syringe pump was refurbished and software was written to control the pump and to track the water flow needed to keep the system at a constant pressure. A proposal for general user beamtime on the CG2 SANS at ORNL was written and submitted for consideration.

05883

Synthesis of Ultrastrong Three-Dimensional Networks from sp^2 Carbon Using Low-Energy Molecular Transformation

Gyula Eres

Project Description

This project will 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 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, the project has potential to remove current obstacles and create totally new applications for sp^2 carbon materials.

Mission Relevance

Stronger and lighter materials made from carbon are of great interest to DOE initiatives such as advanced energy technologies involving 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.

Results and Accomplishments

The project was started with only a small effort this year. The notable accomplishment was the growth of high-quality, single-layer graphene on copper foils. Lifting off and transfer on substrates such as SiO_2 on silicon was also developed. The graphene was characterized using scanning electron microscopy, optical microscopy, and Raman spectroscopy.

05887

Controlling the Catalytic Properties of Metal Films in the Quantum Regime

Paul Snijders, Xiangshi Yin, Ao Teng, Kirk Bevan, John Wendelken, and Hanno Weitering

Project Description

Metal nanostructures have enormous economic importance in industrial applications such as catalysis, photovoltaics, and information storage. We have investigated the effect of the quantum mechanical confinement of electrons in continuous and granulated ultrathin metal films on their electronic and magnetic properties. Using quantum confinement we can control the two most important factors

determining catalytic properties: the energy of the electrons and the electron density at the surface of the films. Moreover, confinement can induce magnetism in otherwise nonmagnetic metals. We have grown ruthenium quantum films of different thicknesses. Two different growth modes resulted in interesting properties for catalysis and nanoengineered magnetism. Accordingly, electronic and magnetic properties of these films were studied both in situ and ex situ using scanning tunneling microscopy, X-ray photoemission spectroscopy, and superconducting quantum interference device measurements.

Mission Relevance

The project is directly relevant for the science mission of DOE: we will utilize quantum mechanical effects to directly control catalytic action, pushing the field forward from catalyst discovery to true catalyst design—a goal stated in the DOE report *Basic Energy Needs—Catalysis for Energy.* The project is also relevant for the Defense Advanced Research Projects Agency (DARPA) since it promises the design of a nanoscale catalyst for decentralized and on-demand hydrogen production for clean energy. The DARPA program Surface Catalysis for Energy (DARPA-BAA-08-48) has expressed interest in work that would follow the proof of principle in this project. We have been successful in obtaining follow-on funding for continued research in this direction through the DOE Office of Basic Energy Sciences (ERKCS87).

Results and Accomplishments

Despite initial difficulties to grow quantum stabilized films, two surprising discoveries were made. Due to an unexpected growth mode of ruthenium on silicon, the project has split into two directions and the stage of water splitting has not yet been reached. Nevertheless, both directions have progressed well. First, ruthenium deposition on silicon unexpectedly resulted in the growth of ruthenium nanocrystals with a very narrow size distribution. While ruthenium in bulk form is paramagnetic, we have surprising evidence that these ruthenium nanocrystals are (weakly) ferromagnetic, potentially opening new avenues towards nanoengineered magnetic materials. The second direction was started in order to obtain atomically flat films of ruthenium (instead of the nanocrystals that were obtained on silicon substrates) for controlled catalytic water splitting experiments. We are using a nearly lattice matched palladium substrate in this direction of research. Our results suggest that quantum stabilized ruthenium thin film growth can be obtained. These are the first transition metal quantum films ever realized. Against expectations, this growth mode only appeared after a high temperature annealing step. This contrasts with all other known quantum stabilized film growth that only survives (far) below room temperature. High temperature access to quantum mechanically tunable nanoscale metal films bears great promise not only for academic model systems but, more importantly, for real industrial applications. Currently, we are performing further experiments to conclusively establish ferromagnetism in the nanocrystals to reach publication stage, and we are optimizing the flat quantum film growth to study water splitting in well-defined samples.

MEASUREMENT SCIENCE AND SYSTEMS ENGINEERING DIVISION

00510

Development of Computational Methods for Neurobiological Imaging Research

Shaun S. Gleason, Ryan A. Kerekes, Richard Ward, Barbara G. Beckerman, Michael Dyer, David Solecki, and Stanislav Zakharenko

Project Description

Neurobiologists are interested in understanding how neurons form complex synaptic circuits during development and how these processes are perturbed in diseases. Neuronal migration and maturation during development play a critical role in how neurons ultimately function. Development of computational methods to extract pertinent information from the large three- and four-dimensional image data sets has not kept pace with available imaging technologies. This project will develop a set of analysis methods that allows researchers to discover relationships between the anatomical and migratory characteristics of neurons and their ability to function in a network of cells. These methods will provide a foundation upon which a comprehensive suite of tools can be developed. The biological questions that these tools will address strike at the foundation of many neurological disorders including Alzheimer's, Parkinson's, and schizophrenia.

Mission Relevance

Although the initial application of this research is for analysis of cellular morphology and migration within animal models, the results may be applicable to cellular analysis of morphology and migration for plant materials targeted for bioenergy. In addition, the techniques learned during development of motion tracking methods for neuron cells may be useful for motion detection in security applications where people must be monitored in a facility. The same concept may be applied to intelligent energy delivery (e.g., of light, and heating, ventilating, and air conditioning) by monitoring and tracking the location of people within a facility and delivering energy based on location and activity, or task. This work will benefit the National Institutes of Health (NIH). The project addresses the needs of a program entitled "NIH Blueprint for Neuroscience Research," which looks for new methods, tools, instrumentation, etc., that will have benefit to multiple National Institutes, such as Neurological Disorders and Stroke, and Biomedical Imaging and Bioengineering. Also, the project can benefit the Department of Defense, particularly in the areas of neuronal interfacing for prosthetics and traumatic brain injury.

Results and Accomplishments

Our collaborators at St. Jude Children's Research Hospital provided us with a large data set of retinal horizontal neuron imagery. The dataset consists of 95 confocal image stacks of developing mouse retinas, each covering an area of 200 × 200 μm and a depth of roughly 150 μm and containing on the order of 10-20 neurons. The images were acquired from both wild-type and knockout genotypes at various stages

of development, ranging from postnatal day 1 to postnatal day 13. Three individual cells were manually cropped from each volume, resulting in a total of 285 single-cell volumes in addition to the original whole-field volumes. We developed new algorithms to automatically detect and segment the soma (cell body) and dendrites of each neuron in the single-cell volumes. For the somas, we detected the center of the soma using morphological grayscale erosion, and we segmented the soma using a level-set segmentation technique. For the dendrites, we developed a technique for finding an appropriate threshold that separates the fluorescent cell material from the background to create a binary volume. We developed an intensity-based three-dimensional skeletonization technique to thin the resulting binary volume and localize the centerlines of the dendrites while preserving their structure and topology. We compared a small subset of our detected dendritic centerlines to those generated manually on the same cells by our collaborators at St. Jude, and we observed 80% similarity of dendrite position on average between our results and the manual results. In most instances, the differences were due to missed branches or false branch detections in one of the algorithms. Using the segmented soma and dendrite skeleton, we developed an algorithm to compute the graph structure of the dendrites in terms of nodes and edges. From this structure, we were able to compute several features of the cells, including dendrite positions, angles, lengths, and branching order, that may be discriminatory with respect to genotype. We are currently working to develop this feature set and quantitatively characterize all the neurons in our dataset with respect to these features. In addition, we have developed neuron migration analysis tools that can track the motion of multiple neurons in culture in a completely automated fashion. Tracking is performed on the soma, the leading and trailing processes, and the centrosomes within the cell. Time lapse movies of moving cerebellar neurons in culture were captured on a fluorescent microscope by our collaborators at St. Jude.

The focus of the research in FY 2010 has been on the continued development of tools to perform automated morphological analysis of fields of retinal neurons, extending the 2009 work on individual neuron analysis. The morphology of a neuron consists of the cell body, or soma, and the dendrites that extend from the soma that allow the cells to transfer signals between one another. Algorithms have been written and tested to automatically identify all of the somas within a field of retinal neurons and then trace the individual neurites of these cells. Once this is done, the morphological features are extracted from the dendritic trees such as number of dendrites, length of dendrites, branching patterns, angle of branches, etc. These features can then be used to compare one neuron to a database of neurons so that a researcher can locate similar morphological features within a historical database. Three new publications were written in 2010 as part of this project.

Finally, a grant proposal was submitted to the NIH focused on the development of computational tools to quantify neuronal migration in cell cultures and histological slices. This grant was submitted in February 2010. It was reviewed and was not funded. We are in the process of preparing a resubmission of this grant for March 2011.

Information Shared

Kerekes, R. A., S. S. Gleason, R. A. P. Martins, and M. Dyer. 2010. “Fully automated segmentation and characterization of the dendritic trees of retinal horizontal neurons.” BSEC 2010: Annual ORNL Biomedical Science and Engineering Conference.

Kerekes, R. A., S. S. Gleason, N. Trivedi, and D. J. Solecki. 2010. “Automated method for tracing leading and trailing processes of migrating neurons in confocal image sequences.” *Medical Imaging 2010: Image Processing*, Edited by Benoit M. Dawant and David R. Haynor (Eds.), *Proceedings of the SPIE* **7623,** 76233T–76233T-10.

00515

Remote Microfluidic Platform Using Smart Materials and Structures: A Diagnostic and Interventional Tool for Critical Structural Anomalies during Fetal Development

Boyd M. Evans III, Timothy E. McKnight, M. Nance Ericson, John B. Wilgen, Justin S. Baba, Anthony Johnson, Ken J. Moise, Jr., Allen J. Tower, and Douglas J. Villnave

Project Description

This multidisciplinary project involves the development of highly miniaturized, remotely activated, microfluidic valving systems. The project involves investigating thermally responsive polymer materials based on poly(*N*-isopropylacrylamide) or p(NIPAAm) and the development of radio frequency (RF) methodologies for remote activation of these materials. P(NIPAAm)-based polymers exhibit a dramatic reduction in size as temperature increases through a lower critical solution temperature (LCST), which can be influenced by copolymer formulations of the material. This property will be used to create a "normally closed" valve that can be thermally opened via wireless RF excitation. The scalability of this responsive-polymer approach will enable the production of wireless valving systems suitable for a wide range of flows. Such valves will provide value for both industrial and research applications and will be particularly useful as wireless, implantable biomedical devices. Towards this end, we focus development on the fabrication and testing of a remotely actuated valve designed for therapeutic intervention of congenital diaphragmatic hernia.

Mission Relevance

The DOE mission statement includes the overarching theme to promote scientific discovery and innovation to strengthen U.S. economic competitiveness and to improve quality of life through innovations in science and technology. Scalable wireless valving systems can dramatically impact all sectors of industry and technology by providing means of controlling fluidic transport using wireless signaling, with specific advantages in distributed control and actuation networks, harsh environment systems, and control elements where interconnectivity limitations impact system design. Our chosen proof-of-principle target, fluidic intervention in congenital diaphragmatic hernia, will demonstrate the technological advances of the project in a sector that will realize the most immediate benefit—implantable valving systems for therapeutic applications.

Results and Accomplishments

This effort is a collaboration between a medical team (Baylor College of Medicine), a commercial biomedical device manufacturer (NuMed Inc.), and ORNL. Baylor and NuMed have both made significant in-kind contributions to the effort. NuMed has designed and fabricated a number of custom balloon valves, compatible with our valve design. Our surgical collaborators at Baylor have procured animals and conducted preliminary animal tests of the tracheal occlusion approach using the NuMed balloon implant modified with our polymer valve system. The polymeric valving system has been fabricated and optimized for operation at physiological temperatures using remote and direct thermal powering. The valve system comprises a thermally reactive copolymer annulus surrounding an internal heating element and an external solid valve body. The current embodiment of this configuration has been designed to insert into the 0.060 in. inner diameter valve lumen of a dual-lumen balloon implant, supplied by our commercial collaborator, NuMed Inc. A flow stand has been assembled enabling the simultaneous evaluation of multiple independent valves. In flow tests simulating the operating pressure of the fetal trachea (80 mm water column pressure), the current embodiment of this normally closed valve has demonstrated stopped flow in the closed condition (room temperature) and up to 6 mL/min in the fully

opened position (45°C). This embodiment uses a reactive polymer valve body of a copolymer of *n*-isopropylacrylamide and dimethylacrylamide, with a transition temperature (LCST) between the closed and open state of ~42°C. An RF heating circuit has been designed and demonstrated to remotely actuate the polymer valve. The system is comprised of external driving electronics and a miniaturized coil pickup integrated as the power source for the heating element of the implantable valve system. The current embodiment of this system uses a commercially available, off-the-shelf ferrite core (1.5 mm diameter, Fair-rite Type 78) and has been demonstrated to inductively couple >30 mW of power wirelessly from an external coil antenna to the implanted series resonant circuit, consisting of the coupling inductor, a series capacitor, and an impedance-matched resistive heating element. Fetal tracheal balloons, manufactured by our industrial collaborator, have been modified to feature "always-open" polymeric valves using copolymer formulations with LCST below physiological temperature. These valves have been implanted in fetal lambs under the approval of ORNL-ACUC tracking Protocol 0390, October 28, 2009. Preliminary studies have been conducted which evaluated the deployability of the miniature valve system and the impact of these valves on fetal lung volume.

Program Development

The project has successfully submitted a proposal to the National Heart Lung Blood Institute of the National Institutes of Health under the support of NIH program manager Dr. Carol Blaisdell; 1R21HL108250-01 entitled "Wireless Valve for Dynamic Tracheal Occlusion Therapy."

Information Shared

McKnight, T. E., A. Johnson, K. J. Moise, Jr., M. N. Ericson, J. S. Baba, J. B. Wilgen, and B. M. Evans III. 2010. *Remote Actuated Valve Implant.* U.S. Patent Application 20100241241, file March 23.

00519

Dual Waveband Passive Longwave Infrared (LWIR) Uncooled Imager

Scott R. Hunter and Nickolay V. Lavrik

Project Description

The project is to develop an entirely new and innovative technique for obtaining infrared imagery that can be overlaid with visible images in the same device. In our technique, photon tunneling is utilized with thermally actuated bimorph structures to passively convert midwave or longwave infrared to visible radiation that is then overlaid on the visible light image. This can be accomplished by fabricating the infrared imaging structures using optically transparent materials (400–750 nm range). Visible light from the scene will pass through the structures and can be used to image the scene in the visible, while the infrared detector structure simultaneously converts the incoming infrared radiation to a visible signal that is overlaid on the visible image. This technique allows very high sensitivity imaging with near background limited performance (no electronic readout noise sources) using small pixel pitches and scalable to large pixel array sizes (1000 × 1000 pixels or larger—there are no inherent constraints on the upper array size limits) in an extremely low power, low cost imager. The goal of the project is to explore the unique advantages of this dual wavelength imaging approach with the modeling and fabrication of a well-developed proof-of-principle device.

Mission Relevance

The value of dual waveband infrared cameras is particularly apparent under low ambient lighting conditions, or when a target or individual is camouflaged or hidden in the surrounding environment, such as in perimeter security situations. Under these conditions, potential targets and individuals are not easily recognizable using either visible of infrared imaging techniques separately, but the combined images give a clearer image of the potential target and surrounding threats. Since this device images thermal signatures, there are many energy conservation applications, such as building heat loss and manufacturing process controls, where heat loss can be monitored and controlled. Research and development of dual wavelength infrared imagers is an active research area with funding from the Department of Defense. These dual wavelength imagers can be used for rifle sights, vehicle navigation, perimeter security, ground and aerial reconnaissance, and other night vision applications. The Defense Advanced Research Projects Agency and the Army's Night Vision Labs are actively funding R&D on innovative dual wavelength imaging techniques to achieve their missions. Present imagers use two separate cameras that are bulky, power and computer processing hungry, and expensive.

Results and Accomplishments

The following research tasks were performed on this project during FY 2010 to demonstrate the unique advantages of the present dual wavelength imaging technique and to show the feasibility of the approach. The FY 2010 tasks focused primarily on fabrication and testing of small bimorph pixel arrays and optimization of their optical and structural parameters using finite element analysis (FEA). Our optical modeling using the finite difference time domain method allowed us to identify geometries and optical thicknesses of pixel elements that enhance conversion of thermally induced pixel deformations into modulation of the optical intensity in the visible. Results of our thermal and mechanical FEA modeling indicated in favor of cantilever versus bridge bimorph structures. Arrays of thermally sensitive bimorphs that are transparent in the visible and absorbing in the infrared were demonstrated. The photon tunneling test rig constructed in the initial (FY 2009) stage of the project was used to evaluate overall functionality and to quantify performance of the fabricated pixel arrays. Two array formats, 1×10 and 20×30, were used in these tests. Achieved figures of merit include temperature responsivity of 1.2 μm/K and estimated noise equivalent temperature difference of approximately 100 mK. The latter figure of merit indicates a level of performance comparable to that of conventional, single waveband, uncooled infrared imagers. Therefore, we have demonstrated a viable technology of a dual waveband imager particularly suitable for applications in rifle sights, nighttime vehicle navigation, surveillance, and aerial reconnaissance.

05853

Nanomechanical Oscillators for Ultrasensitive Electric and Electromagnetic Field Detection

Panos Datskos, Slobodan Rajic, Nickolay V. Lavrik, and Thomas Thundat

Project Description

Our proposed effort seeks to demonstrate the feasibility of using micro/nanomechanical oscillators to detect electric and electromagnetic fields. Time varying electric field sensing is usually achieved using an antenna and receiver. However, these antenna-based approaches do not exhibit high sensitivity over a broad frequency (or wavelength) range. An important aspect of the project is that, in contrast to traditional antennas, the dimensions of these nanomechanical oscillators are much smaller than the wavelength of the electromagnetic wave. In our approach the detection of static electric fields and/or time varying electric

fields (electromagnetic waves) is based on the detection of the force on electrically charged nanomechanical oscillators. Nanoscale mechanical structures have already proven potentially useful for the detection of small (attonewton) forces, which will enable the measurement of small electric and electromagnetic fields. To achieve both high dynamic range and wide spectral response, we need to design a system where the cantilever operating frequency is tunable. During the project, we will design and fabricate a nanomechanical oscillator for E-field detection. In addition, we will characterize the fabricated nanomechanical oscillators by measuring their responses to time varying electric and electromagnetic fields.

Mission Relevance

Highly sensitive nanomechacical E-field detectors will have a tremendous impact in many applications, such as the detection of small strength fields from global positioning system signals inside buildings. Specific Department of Defense needs for electric field sensing are described in the recent Defense Advanced Research Projects Agency (DARPA) BAA 09-34. DARPA program manager Dr. Devanand Shenoy has expressed great interest in utilizing micro/nanomechanical systems for electric field sensing. The great promise of these devices in detecting both static and time varying electric fields stems from this initial feasibility study. Other implications of this technology can be envisioned in environmental science, homeland security, and DOE applications. A more efficient electric grid may be a result of the accurate and inexpensive detectors of low frequency E-fields surrounding power lines. In addition, technologies capable of identifying centrifuge locations as well as other counterproliferation technologies are likely to result from this study.

Results and Accomplishments

The following research tasks were completed during FY 2010 to demonstrate the unique advantages of the present dual wavelength imaging technique and to show the feasibility of the approach. The FY 2010 tasks focused primarily on fabrication and testing of nanomechanical oscillators and their adaptation for detection for constant and time varying electric fields. We evaluated several designs of microfabricated oscillators, including pillar-shaped and cantilever-shaped resonator structures. Gold-coated cantilever structures fabricated using silicon nitride as a structural material were found to be most promising for creating one-dimensional arrays of E-field detectors. Implemented devices relied on a straightforward technological sequence suitable for scaled-up fabrication. We assembled a test rig based on optical readout and tested a series of cantilever resonators in the frequency range 1 kHz to 30 MHz. An electrical charge on the cantilever tips was created by applying a DC bias between the metal layer on the cantilever and a metal counter electrode at 1–5 mm away from the cantilever. The value of the charge located on the tip was evaluated using finite-element analysis modeling. Consistent with our analytical predictions, less stiff cantilevers showed higher sensitivity and were selected for subsequent, more detailed studies. In summary, we demonstrated the feasibility of the innovative concept of a cantilever-based E-field detector that integrates an antenna, a high Q resonator, and a frequency mixer on a very compact platform. Using heterodyning, we achieved detectability of E-fields in the sub-millivolt per meter range in the kilohertz to megahertz frequency range. Further improved sensitivity can be obtained by integrating a high charge density electrete into the resonating element.

Information Shared

Datskos, P., S. Rajic, N. Lavrik, and T. Thundat. 2010. “Nanomechanical Electric and Electromagnetic Field Sensors.” UT-Battelle Invention Disclosure 201002376, DOE S-115,422. Patent application in preparation.

05858

Fabrication of Ultrathin Graphite/Graphene Films

Ivan Vlassiouk, Nickolay V. Lavrik, Sheng Dai, and Panos Datskos

Project Description

Since its first introduction in 2004, graphene quickly has become a wonder nanomaterial of unexhausting interest to many researchers due to its unique properties. Despite graphene`s high potential for unlimited applications, a reliable source of graphene is still a bottleneck for further development. Recent advances in chemical vapor deposition (CVD) growth and in chemical techniques based on reduction of graphene oxide appear promising in providing the routes for the desired high throughput supply of graphene. In this project we intended to investigate a new, low temperature technique for consistent ultrathin graphite/graphene membranes fabrication with a large surface area. We relied on graphene synthesis through a CVD technique. Several approaches were used (different carbon sources/temperature ranges) with the purpose of understanding whether technologically attractive low temperature CVD graphene growth could provide graphene that possesses high electronic and thermal conductivities suitable for the majority of applications.

Mission Relevance

The project outcome will constitute a cornerstone for a successful development of various applications based on a single layer of graphite. Graphene shows a gigantic potential virtually in every DOE mission area, such as membranes technologies, energy, computing, and waste treatment. Graphene possesses unique electronic properties with membranes of this material showing high potential for separation and filtration. Graphene can be used as a substitute for indium tin oxide in various solar applications, construction of diverse nanoelectromechanical systems, etc.

Currently we are working on follow up funding from the Defense Advanced Research Projects Agency.

Results and Accomplishments

We have shown that CVD growth of continuous monolayer graphene on copper foils or thin films can be performed at temperatures as low as 800°C, similar to those for CVD growth on nickel. Despite some structural defects, such monolayer graphene possesses high electrical and thermal conductivities that justify its utilization in numerous applications where its thermal management, transparency, and conductance are desired. Structural disorder, as evaluated from the Raman G-band and D-band ratio (I_G/I_D), gradually increases with lowering the deposition temperature and can be related to a decreasing size of monocrystalline graphene domains, L_a. The corresponding decline in the electrical conductivity is close to a linear function of L_a, while the thermal conductivity (as evaluated from the relative anti-Stokes intensity) is a much weaker function of L_a, with an apparent power dependence $K \sim L_a^{1/3}$. The thermal conductivities measured from the temperature dependence of the G-band position result in almost order-of-magnitude greater values.

Depending on the disorder degree, CVD graphene shows high thermal ($K \sim 1200$ $WK^{-1}m^{-1}$, measured using temperature-induced G band position shift) and electrical (5×10^{-4} $ohms^{-1}$, for doping levels of 10^{12} cm^{-2}) conductivities suitable for various applications. Optical absorbance has a nondetectable dependence on the disorder and equal to 0.023 (pi times fine structure constant) for a single graphene layer.

05859

Multimodal Biometric Recognition of Noncooperative Subjects at a Distance

Chris B. Boehnen and Ryan 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, Department of Justice, and others. While still incomplete, the project has been successful in helping to attract follow-on funding. A proposal developed as a follow-on to this project has made the second round of a Biometrics Identity Management Agency BAA to survive 60+ initial proposals into 11 final round proposals. We will not know whether we have been selected for funding out of the final round for several months.

Results and Accomplishments

The system design has been finalized. Initial hardware has been purchased and is undergoing final assembly. We are anticipating a mid-October completion date once we receive the final necessary hardware, which is on order from two vendors. The project is approximately at the end of Task 2. We have started work on Task 4, which is development of algorithms for performing biometric recognition.

Some small additional hardware purchases will be necessary as we found some hardware components were more expensive than initially anticipated for the versions we required. We also determined that use of laser illumination for iris sources creates safety concerns that can be avoided through the use of light-emitting diodes (LEDs) and have altered our design accordingly. However, LEDs are significantly more complicated in terms of collimating at a distance and have hence created a larger technical challenge.

Several technical challenges are highlighted for follow-on work that are not apparent from the literature. We expect follow-on funding in the biometrics as a result of this work.

05863

A Next-Generation Three-Dimensional Imaging and Analysis System for Ballistics Forensics Identification

Christopher J. Mann, Philip R. Bingham, Thomas P. Karnowski, and Shaun S. Gleason

Project Description

Firearms are the most commonly used weapons in violent crimes, and the bullets and shell casings ejected from a given firearm have a unique signature or pattern stamped into them as a result of the firing process. This signature can potentially be used to tie a bullet or shell casing back to a specific firearm, and hence to a specific individual that may have committed the crime. Current ballistics identification technology employed by the federal and local law enforcement communities has several problems that reduce the utility and accuracy of existing systems. These problems include outdated two-dimensional ballistic imaging technology and inaccuracies in the automatic signature matching algorithms. Our project seeks to develop the next-generation ballistics identification (NexBID) technology by employing three-dimensional (3-D) phase-shifting microscopy methods for ballistics imaging and state-of-the-art pattern 3-D matching algorithms with an eye towards both laboratory-based and field-portable systems.

Mission Relevance

The development of a prototype system will enable ORNL to be the technology driver for state-of-the-art ballistics identification technology for the next decade. Successful development of the technology will be of tremendous interest to national security organizations such as the Department of Defense, the intelligence community, and the Department of Justice (more specifically, Bureau of Alcohol, Tobacco, Firearms and Explosives [ATF]; Federal Bureau of Investigation; and state law enforcement offices).

Results and Accomplishments

The 3-D phase-shift instrument produced as a result of this project shows great potential for fast and accurate imaging of a number of microscopic and macroscopic samples. Improvements in the sample handling system, as well as utilizing light sources with increased power, will lead to a more robust system capable of imaging a wider variety of samples. Thus far, we have shown nanometer resolution imaging of ballistics samples with high speed image capture and output. The pattern matching algorithms we have developed have demonstrated a 95% success rate in matching a casing to a specific firearm make. Another exciting feature of this work is the use of Wavelet transforms for phase reconstruction, an area of interest for future work. The potential use of three or more wavelengths holds promise for imaging accurately with large dynamic ranges. We are currently in discussions with the ATF and other organizations who are interested in developing this work further.

05878

Neutron Imaging for the Determination of Tumor Margins

Trent L. Nichols , Hassina Z. Bilheux. Philip R. Bingham, ; Jack S. Brenizer, Jr.; George W. Kabalka.; Amy K. LeBlanc.; Alfred M. Legendre; Robert L. Donnell.; Maria Cekanova; Anton S. Tremsin; Kenneth L. Watkin.; and Laurentia M. Nodit

Project Description

The project will produce 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 not seen in standard optical approaches. This research explores the application of neutron imaging to enhance medical pathological specimen analysis using the cold guide (CG-1) beamline at the High Flux Isotope Reactor (HFIR). Neutron images will be obtained with a resolution of 10–15 μm by collimating the beam with a pinhole or micropore neutron collimator. Specimens of melanoma, sarcoma, and breast cancer will be 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 at 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 the proposed effort is the attempt to use boron and deuterated water to improve contrast between healthy and tumor tissue. Specially prepared histochemical stains will be 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, there are expected to be contrast differences 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 in June with discussions with colleagues on how best to perform the experiments at the CG-1 beamline at HFIR. There are many technical issues to address in order to improve the resolution to 10–15 μm or perhaps down to 1–2 μm. These are being actively pursued with calculations and simulations. At this point, the best resolution can be obtained by mounting high resolution film next to the specimens with a thin gadolinium film in between. This would provide a resolution of approximately 2 μm, which should be adequate for the current experiment. This assembly will be held in place between two thin aluminum plates held together with a vacuum supplied by a roughing pump.

The specimen preparation has been going forward with the acquisition of requisite supplies. Since the tissue cannot be placed in paraffin, as is customary, a meat cutter such as used in a deli will be obtained to cut the thin tissue specimens. Several specimens have been made using ethanol, deuterated alcohol, and formalin. The requisite approvals for bringing and handling these biological materials have been obtained. Protocols for fresh (not fixed) tissues specimens are being addressed and should be completed soon. Tissues will be mounted on quartz and aluminum slides. These specimens will be imaged during the next HFIR cycle that begins in early October.

The boronation of the standard tissue stains, hematoxylin and eosin (H&E), is progressing well. Eosin has been boronated with a carboranyl group, which will significantly increase the contrast. The chemical characterization should be completed in a few days, at which time it will be used as a stain to investigate the visual appearance. When this is completed, the efforts will be focused on boronating hematoxylin, which is a greater challenge since the molecule will have to be built rather than using substitution reactions as was done in the case of eosin.

There will be time to perform some of the early experiments at GG-1 at HFIR in October and November. Time has been requested for January, and it is anticipated that some or all of the time requested will be rewarded. At this time, the project is on time to get results to present to potential funding sources late next spring or early next summer.

GLOBAL NUCLEAR SECURITY AND TECHNOLOGY DIVISION

05850

Liquid Medium Position-Sensitive Thermal-Neutron Ionization Chamber

Thorwald L. Van Vuure, Gomez W. Wright, Zane W. Bell, Jason P. Hayward, and Ronald G. Cooper

Project Description

All instruments at the Spallation Neutron Source (SNS) are limited to some extent by the flux that their detectors are able to handle. A new detection principle is required to make a quantum leap in event rate capability. Brookhaven National Laboratory and ORNL have accomplished this by running a detector in ionization mode, where all previous position-sensitive detectors used proportional mode. This opens up a possible next step in development that does not use scarce, low density ^{3}He gas. We propose to search for a suitable liquid medium containing ^{10}B. If a suitable molecule can be found that exhibits characteristics required of a detector medium, 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. Unfortunately, the effort expended on the facilities for generating more neutrons has not been matched by a development effort in detection. As a result, all instruments currently operational, under construction, or being designed at the SNS are limited in some measure by the available detectors. This project is focused on the basic science underlying a new detector type capable of meeting the requirements of these instruments.

Results and Accomplishments

Dr. Van Vuure compared the potential liquids and concluded that borazene was the best candidate due to 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 placed with Boroscience International for 25 g of borazene.

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 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.

Unfortunately the borazene vendor, Boroscience International, 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 is under way for another supplier.

Mr. Wright is now leading the effort to procure borazene, arrange for transfer of the liquid into the detector prototype, and perform tests with neutrons. He has developed a contact in the Center for Nanophase Materials Sciences who has agreed to transfer the liquid.

NEUTRON SCATTERING SCIENCE DIVISION

00480

Hydration-Driven Processes in Bioenergy: Testing a Novel Neutron Scattering Approach

Hugh O'Neill, David C. Baker, and Sylvia E. McLain

Project Description

Water plays a vital role in the development of biofuels. Currently, the production of cellulosic ethanol is limited by the low solubility of cellulose in water and because natural cellulose contains appreciable amounts of lignin, which is also largely water insoluble. The structural barrier provided by lignocellulose to water hydration in potential biofuel feedstocks is an important factor determining the recalcitrance of biomass to undergo hydrolysis. In fact, studies concerning the economic potential of cellulosic ethanol as a potential biofuel cite lignocellulose pretreatment efficiency as a primary factor leading to increased profit and production capability. A microscopic understanding of hydration structure on the atomic length scale (0–10 Å) of lignocellulose and its constituents is critical to understanding fundamental processes of bioenergy production. Using neutron scattering techniques, we aim to (1) synthesize deuterium-labeled cello-oligosaccharides and (2) determine the structural and the hydration properties of these cellulosic materials.

Mission Relevance

One of the DOE missions and indeed initiatives for the future is to increase the use of alternative fuel sources to help curb our dependence on a gasoline economy. The work for this project will lead to the greater physical understanding of hydration in cellulose-based materials, where the recalcitrance of cellulose to water is currently a limiting factor to cellulosic ethanol production. This investigation is a step towards more efficient use of biofuel as a potential fuel source. DOE will benefit most from this research, as it directly falls under one of the DOE directives of enhancing research in biofuels as an alternative fuel source.

Results and Accomplishments

Aqueous solutions of cellobiose (4-*O*-β-D-glucopyranosyl-D-glucose) with molar ratio of 1:63 cellobiose:water (~0.88 *M*) were measured using neutron diffraction enhanced by isotopic substitution. These measurements were performed using the SANDALS diffractometer, which is specifically designed for measuring liquid diffraction, at the ISIS facility in the United Kingdom. The neutron data analysis from this experiment has been completed, and the modeling of this data is largely complete. A series of simulations have been performed using a program—Empirical Potential Structural Refinement (EPSR)—specifically designed to model amorphous systems using neutron diffraction data as a necessary constraint to this model. Our EPSR measurements upon refinement give $-CH_2OH$ rotamer populations (designated as ω and ω′) that are very close to the values reported from nuclear magnetic resonance (NMR) data, as

well as from NMR data acquired by us at 0.88 *M*. Further EPSR refinements on the φ–ψ angles (the torsional angles that make up the glycosidic linkage of the two sugar residues) are under way. A manuscript is in preparation.

Synthetic studies in the preparation of deuterated methyl cellobioside and methyl cellooligosaccharides have been carried out. We have refined the procedures for selective hydrolysis of cellulose to produce cellooligosaccharides of DP 2–6, with a preference for producing the DP 4 (tetrasaccharide) compound. A Raney nickel exchange process is then used on their methyl glycosides to exchange D or H at most C–H sites on the molecules that are attached to –O– groups. To date we have deuterated samples of the methyl (and deuteriomethyl) di-, tri- and tetrasaccharides with precise levels of deuteration that are available for neutron studies. The overall synthetic process to the cello-oligosaccharides includes isolation and purification as their peracetates. The peracetates are then converted to their respective methyl glycosides and deuterium exchanged by the Raney nickel process in D_2O.

00500

Neutron Scattering Characterization of Sol-Gel Drug Delivery Systems

Hugh O'Neill, Gary A. Baker, Eugene Mamontov, and Volker S. Urban

Project Description

The aim of this project is to investigate the diffusive properties of model drugs within sol-gel drug delivery systems of relevance in bone repair and joint replacement, using a combination of quasi-elastic neutron scattering (QENS) and small-angle neutron scattering (SANS). This project addresses a major scientific bottleneck in drug delivery research, namely, the ability to characterize the distribution and diffusion of guest molecules in host carriers. We anticipate that the combination of QENS and SANS can provide unheralded benefits in the characterization of both the structural and dynamic properties of realistic drug delivery materials, by providing information where other characterization techniques used to date have provided only indirect or qualitative evidence, or in cases where other approaches have failed entirely. This will be the first demonstration of using QENS to measure the dynamics and diffusion of pharmaceuticals within confined environments relevant to drug-delivery platforms.

Mission Relevance

The DOE Office of Basic Energy Sciences, particularly the Chemical Sciences, Geosciences and Biosciences Division, has active programs that focus on the investigation of interactions at interfaces and also the influence of weak interactions on transport in complex, real-world materials. Demonstration of the unique capabilities of neutron science for biomedical research would attract future funding and also generate a new user community at the neutron facilities in ORNL. The National Institute of Biomedical Imaging and Bioengineering (NIBIB) recently had several calls for proposals in areas such as "Biomaterials and Biointerfaces," "Enabling Technologies for Tissue Engineering and Regenerative Medicine," and "Bioengineering Grants." The work proposed here would be well suited to these calls.

Results and Accomplishments

The structure and dynamic properties of a sodium benzoate–silica composite material, a model drug delivery system, were analyzed by QENS and SANS. SANS showed that the gels are highly branched structures with relatively large pore sizes (550 nm). Using QENS, it was possible to extract the diffusion coefficients for three solutes in the composite material that can be related to D_2O, benzoic acid, and glycerol. The lowest sodium benzoate concentration contributed ~50% of the elastic signal, indicating

that it will be possible to measure the kinetics of a drug at lower concentrations in carriers. This investigation demonstrates that a combination of QENS and SANS can be employed for characterization of drug delivery systems. In particular, it highlights how QENS can be used to calculate the diffusion coefficients of individual components in a complex environment. A manuscript is currently being prepared on this work.

The assembly and organization of a sol-gel material formed via an in vitro biomineralization reaction was investigated using a combination of electron microscopy and SANS. Lysozyme-templated precipitation of silica synthesized by sol-gel chemistry produces a composite material with antimicrobial properties. The aim of this study was to investigate the structural properties of the composite material that allow for retention of the native antimicrobial activity of lysozyme. Electron microscopy, both scanning (SEM) and transmission (TEM), revealed that the composite has a hierarchical structure composed of quasi-spherical structures, approximately 450 nm in diameter, which are in turn composed of closely packed spherical structures of approximately 8–10 nm in diameter. Using SANS with contrast variation, it was possible to separate the scattering signatures of the lysozyme and silica within the composite. It was determined that the lysozyme molecules are spatially correlated in the material and form clusters with colloidal silica particles. The size of the clusters determined by SANS agrees well with the structural architecture observed by TEM. BET analysis revealed that the surface area of the composite is relatively low (4.73 m^2/g). However, after removal of the protein by heating to 200°C, the surface area is increased by ~20%. In addition to demonstrating a well-organized sol-gel synthesis that generates a functional material with antimicrobial applications, the analysis and modeling approaches described herein can be used for characterizing a wide range of mesoporous and ultrastructural materials. This work was selected as the cover image for the September 23, 2010, issue of *Advanced Functional Materials.*

Information Shared

Cardoso, M. B., H. R. Luckarift, V. S. Urban, H. O'Neill, and G. R. Johnson. 2010. "Protein Localization in Silica Nanospheres Derived via Biomimetic Mineralization." *Adv. Functional Mater.* **18**(20), 3031–3038.

REACTOR AND NUCLEAR SYSTEMS DIVISION

00507

Advanced Variance Reduction Methods for Active Interrogation Modeling

Douglas E. Peplow, Thomas M. Miller, Bruce W. Patton, and John C. Wagner

Project Description

Active interrogation systems are designed to detect special nuclear material (SNM) (uranium and plutonium) hidden in cargo containers. Active interrogation involves exposing containers to radiation such that if SNM is present, secondary radiation from reactions (e.g., fission) within the SNM can be detected, thereby detecting the presence of SNM. Extensive radiation transport simulation is required to design these systems and analyze their effectiveness in different situations. Because of the large quantities of material in a cargo container (e.g., 55 gal drum, tractor trailer, or ocean-going vessel), these systems are very difficult (and sometimes impossible) to simulate with ordinary Monte Carlo codes. Advanced variance reduction can help speed up simulations via the use of an importance map. This project will develop a method for using multiple importance maps to cause source particles to first interact in the fissionable material and then move out towards a detector. This type of improvement should drastically reduce the simulation time and greatly increase the number of simulations possible.

Mission Relevance

Creating methods for performing rapid computer simulation of active interrogation systems will benefit a wide array of DOE National Nuclear Security Administration (NNSA) programs, particularly NA-22 (Nonproliferation Research & Development) and NA-24 (Nonproliferation & International Security). NA-22 currently funds efforts related to the development of active interrogation systems, hence, the ability to analyze and improve these systems through faster computation is of interest to that agency. The methods developed through this project are also expected to have relevance to other DOE/NNSA applications in which it is necessary to distinguish between individual components of radiation signals (e.g., direct and scattered radiation components). The Domestic Nuclear Detection Office of the Department of Homeland Security has programs to detect and prevent nuclear materials from entering the United States. The Defense Threat Reduction Agency of the Department of Defense also has responsibilities related to detection and prevention of the flow of illicit nuclear materials. Improved computer simulation capabilities would increase the ability of these agencies to design and evaluate proposed active interrogation systems.

Results and Accomplishments

A new multistep approach for applying variance reduction to active interrogation problems was developed. The basic concept is that the problem can be broken into steps and each step can be accelerated separately. For example, the interrogating particles can be biased to determine the fission

distribution and rate in the nuclear material. This then becomes the source in a second step—the transport of fission particles to the detector. More complex problems, where interrogating particles also cause reactions in structural materials, can be treated as well.

Three examples of scanning system problems were constructed that each contained a significant quantity of highly enriched uranium embedded in normal materials: (1) a neutron source and a neutron detector for water-filled 55 gal barrels, (2) a neutron source and both neutron and gamma detectors for a 40 ft shipping container, and (3) a bremsstrahlung photon source and two neutron detectors for a steel-hulled fishing trawler containing fish and ice in the main hold. New coding was added to the SCALE package to convert the reaction rates in one step into a source term for the next step.

The multistep approach worked well for each example problem, and significant speed-ups (compared to standard, analog calculations) were obtained. For the barrel scanning example, using the multistep hybrid variance reduction was 200 times faster than analog. For the 40 ft shipping container, speed-ups ranged from 5 to 100, depending on the materials inside the container (more attenuating materials gained more from the variance reduction). For the fishing trawler problem, the analog method was not attempted due to the difficulty of the problem. The multistep method computed the change in the detector responses due to the nuclear material within a single day on one central processing unit.

Information Shared

Peplow, D. E., T. M. Miller, and B.W. Patton. 2010. “Hybrid Monte Carlo/Deterministic Methods for Active Interrogation Modeling.” *Proceedings of the American Nuclear Society Joint Topical Meeting of the Radiation Protection and Shielding Division, Isotopes and Radiation Division, Biology and Medicine Division,* Las Vegas, Apr. 19–23.

00521

Development of a Machinable SiC-BN Ceramic Composite Compatible with High-Temperature Molten Fluoride Salts

David E. Holcomb, Steve Nunn, Dane Wilson, and David L. West

Project Description

The overall project task is to evaluate the mechanical and fluoride salt corrosion properties of a recently developed silicon carbide–boron nitride (SiC-BN) composite material. Key to the new composite material being useful for engineering applications is combining the high hardness and mechanical strength of silicon carbide with the ease of machinability of boron nitride while preserving their chemical inertness. If the new material performs as anticipated, this work will serve as leverage for ORNL to create a larger program focused on developing SiC-BN to the point where it can be used in engineered systems in support of high-temperature energy transfer processes.

The project methodology is to fabricate a set of SiC-BN composite samples and experimentally measure their molten fluoride salt corrosion performance. As a new composite material, the fabrication methodology for producing SiC-BN has several variants with unresolved performance differences—notably including corrosion properties. Two fabrication routes are being explored to create suitable material test coupons. The first fabrication method employs reaction synthesis followed by hot pressing. The second fabrication technique utilizes pressureless sintering instead of hot pressing, with the final porosity being removed from the material by impregnating with a carbon bearing liquid.

Mission Relevance

Effective high-temperature thermal energy exchange and delivery at temperatures over 600°C has the potential of significant national impact by reducing both capital and operating costs of energy conversion and transport systems. Today, no standard, commercially available, high-performance heat transfer systems exist for temperatures above 600°C. Liquid fluoride salts offer good heat transport properties at high temperatures with low vapor pressures, toxicities, and reactivity at reasonable costs and are, therefore, leading candidate fluids for increased heat transport efficiency. Both pure SiC and pure BN are compatible with high-temperature molten fluoride salts and high-temperature air exposure (up to 850°C).

Results and Accomplishments

Two approaches to producing machinable, high-density SiC-BN composite material were investigated. One of the processes resulted in dense samples when implemented with sintering aid additions or an elevated hot pressing temperature. The samples containing 20 wt % BN reached higher relative densities than samples containing similar sintering aid additions but having 30 wt % BN content. The 30 wt % BN samples, which showed good machinability and had a reasonably high density after hot pressing, were evaluated for compatibility with FLiNaK. Unfortunately, the presence of the sintering aids results in this material being readily attacked by the fluoride salt.

00523

Investigate the Feasibility of Increasing the Thermal Conductivity of UO_2 through the Addition of High Thermal Conducting Material to Improve the Performance of Nuclear Fuel

D. F. Hollenbach, L. J. Ott, J. W. Klett, T. M. Besmann and B. L. Armstrong

Project Description

The maximum power of a nuclear reactor is limited by the rate at which heat can be transferred from the fuel pellet to the coolant. UO_2 fuel is limited by its low thermal conductivity. The objective of this project is to investigate the feasibility of increasing the thermal conductivity of UO_2 fuel by including long thin fibers of highly ordered graphite in the UO_2. Polymerized graphite has a thermal conductivity of ~2000 W/m·K in the planar dimension and ~10 W/m·K in the transverse dimension. Graphite fibers in UO_2 fuel pellets should act as heat conduits, transferring the heat generated inside the pellet to the outer edge. To optimize heat transfer the fibers need to have a large aspect ratio (>200). Our current research uses 10 µm diameter fibers with a length of 2–5 mm. A protective silicon carbide (SiC) coating on the graphite will act as a protective layer, thus preventing interaction between the graphite and UO_2. This project examines the change in thermal conductivity of UO_2 with the addition of long thin graphite fibers.

Mission Relevance

The generation of electric power without greenhouse gases is of fundamental interest to the United States from national security and environmental standpoints. Nuclear reactors are a safe, reliable, proven technology for generating electricity without greenhouse gases. The maximum reactor power level is limited by the rate heat energy can be transferred from inside the fuel to the coolant. An increase in the thermal conductivity of the UO_2 fuel would enable both the maximum power level and safety margin to be increased, thus generating more electric power from existing reactors. It would also allow new reactors designs to have higher power levels. The DOE Office of Nuclear Energy (DOE NE) is currently funding several projects to assess the viability of advanced fuel concepts. The projects examine higher

enrichments, burn-up limits, and heat transfer rates. DOE NE has either provided or promised additional funding for this project as follows. The Advanced Fuels Campaign of the DOE NE Fuel Cycle Research and Development program has provided $100,000 to prepare a 3 year, $5 million proposal to continue this line of research. The LWR Sustainability Program has promised a minimum of $200,000 next fiscal year to continue this work. ORNL has also applied for a patent on this new type of fuel.

Results and Accomplishments

Significant progress has been made on the project tasks. After a slow start, which brought to light the safety and administrative limitations of working with UO_2, it was decided to do the initial work using CeO_2 as a surrogate material. CeO_2 is widely used in research as a surrogate for UO_2 because of its similar chemical and thermal conductivity properties. The initial work was divided into two parallel tasks: (1) developing a method for interacting a continuous SiC layer on graphite fibers and (2) developing a method of mixing CeO_2 particles and fibers in a homogeneous mixture without damaging the fibers.

Graphite interacts with both CeO_2 and UO_2 above 1000°C. To prevent this interaction both during sintering and reactor operations, a SiC layer is created on the outer surface of the graphite fibers. The SiC layer needs to be firmly bonded to the graphite fibers. Simply applying a coating of SiC particles will not provide a uniform continuous SiC layer or a tight bond with the graphite. A process was developed that interacts silicon into the outer layer of the graphite fiber by passing Ar–4% silane gas (SiH_4) over the graphite fibers in a reaction chamber at elevated temperatures. The method forms a fixed integral bond between the graphite and SiC of uniform depth that is continuous over the entire outer surface of the fiber.

To provide efficient heat conduction paths through the pellet, the fibers need to be homogeneously dispersed throughout the pellet with minimal clumping. Several UO_2 fiber mixing methods were investigated. Initial methods involved mixing the CeO_2 particles and fibers using a high shear blender. The fibers shattered using this method, exposing the graphite, which interacted with the CeO_2 during sintering. The method was attempted again using 10-µm-diameter, 5-mm-long tungsten wires in place of fibers. The wires did not disperse but instead twisted into a ball. Adding liquids of different densities and viscosities or reducing the mixing speed did not improve the results. A liquid mixing technique, which combined the oxide and fibers in a solution with dispersants, was developed. Interatomic forces prevented the fibers from clumping and allowed them to homogeneously mix with the oxide. The mixture was then dried, pressed, and sintered to form a pellet. Pellets of ~40% theoretical density have been formed. Forming a denser green pellet and sintering at higher temperatures should allow pellets to reach densities in excess of 90% theoretical density.

Information Shared

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Hollenbach, D. F., L. J. Ott, T. M. Bessman, J. W. Klett, and B. L. Armstrong. 2009. “Composite Nuclear Fuel Pellet.” U.S. Patent Application 13/489,118, filed July 30.

05886

Flaw Detection in Nuclear Fuel Pins Using Ultrasonic Torsional Guided Waves

Sacit M. Cetiner, David E. Holcomb, Roger A. Kisner, and Venugopal K. Varma

Project Description

The project suggests using ultrasonic torsional guided waves to detect flaws in cladding of nuclear fuel pins. Ultrasonic torsional guided waves have long been used successfully for damage inspection of metal tubes. This research aims at building upon existing know-how and applying it to surface flaw detection of fuel pins while they are in the spent fuel pool. A unique approach in the project is to employ a clamshell coupling to attach an ultrasonic rotor to fuel pins. This approach, if it works, offers the advantage of allowing fuel pin inspection without requiring disassembly of the fuel assembly. The ultrasonic waves launched by the rotor will traverse the mechanical coupling and will be reflected by surface flaws. The success of the project depends on the acoustic energy that can be generated by the transduction element, most of all on the accuracy of the detection system and the transmission efficiency of the mechanical coupling.

Mission Relevance

Timely detection of flaws in nuclear fuel pins is critically important in terms of economic as well as safe operation of the nuclear fleet. An undetected damaged pin may fail during operation in the subsequent cycle, resulting in premature abortion of reactor operation, which can be costly in terms of loss of generating capacity.

The project addresses certain mission areas of the DOE Light Water Reactor Sustainability (LWS) program, particularly LWS-4, “Advanced LWR Nuclear Fuel Development Pathway” and LWS-8, “Advanced Instrumentation, Control, and Information Systems Technologies Pathways.” The project is also highly relevant for the mission of the Nuclear Regulatory Commission.

Results and Accomplishments

The project started with the design of the mechanical coupler. In the concept phase, the mechanical coupler was considered as a transient attachment device that will engage with the fuel pin, provide interface to transmit acoustic signals, and, upon completion of the test, disengage from the pin without any damage to the tested component.

The transduction element used for the project was designed and manufactured during another project titled “In-Vessel, Magnetostrictive, Ultrasonic Level Measurement System Development” funded by the DOE Office of Nuclear Energy under the GEN-IV Nuclear Energy System program. This element used several magnetostrictive strips specially brazed onto an Inconel 600 waveguide body.

Magnetostriction is a physical phenomenon observed in certain metals that manifests as a change in physical dimensions in response to magnetic field in the environment. The strips were brazed onto the body at a 45-degree angle to create a torsional stress wave in the waveguide. We had two identical pieces of this transduction body.

The experimental setup in this project also resembled the setup for the aforementioned project. The same measurement electronics were used. The electronic setup included a National Instruments PXIE function generator, a preamplifier, a power amplifier, an impedance matching transformer, a two-stage filter

amplifier, a magnet bias power supply, and an analog digitizer. An isolation switch and an input protection module were designed at ORNL previously.

The body of the transduction element was first machined to prepare for welding to the mechanical coupler. The mechanical coupler was made of stainless steel primarily because of its welding compatibility with Inconel 600 as well as its high Young's modulus for efficient transmission of acoustic energy. The coupler was welded to the far end of the waveguide body.

The mechanical coupler consists of two components that are tightly screwed together to attach to a metal tubing in similar geometry as the conventional light water reactor fuel pin. A soft metal shim is placed between the metal tubing and the coupler to increase transmission of acoustic wave from the coupler to the tubing. The metal shim is wrapped around the tubing. They are sandwiched between the two pieces of the coupler, and then the whole thing is tightly screwed creating a good coupling for the sound waves to travel.

The soft metal shim is a critical component of this configuration. This material should "flow" for effective wave transfer. A number of material options were considered, but a quick down select based on practical considerations left 99.99% pure aluminum and 99.99% pure nickel as candidate materials. We chose high-purity annealed aluminum because of its price and availability. It is important to have an annealed material, because we anticipated that, though highly pure, stressed material will cause deterioration in transferring the stress waves.

The transducer body with the welded mechanical coupler was assembled and placed into its stainless steel container that included two magnet coils: one for creating bias magnetic field, the other for driving the magnetostrictive strips. The unit was connected to the measurement system. The electronic setup was tested and confirmed that a reference signal was generated and transmitted to the transducer, and was successfully read back.

An aluminum tubing with no defect was attached to the mechanical coupler as described previously. No proper signal was observed. Because of its finite length, reflections from the free end were expected.

The transduction casing was then disassembled. It was determined that the axial mounting stud on the waveguide body was not straight. It was also observed that the waveguide body did not freely rotate as it was designed. These observations claimed that the bearings that were supposed to mechanically isolate the waveguide body from the surrounding mass were not functioning. We tried to rectify the condition of the pieces within the resources we had, but no improvement was observed in the performance of the transducer.

The existing configuration required remanufacturing of the pieces. Because of the monetary limitations of the project, we decided to at least demonstrate the feasibility of the concept of detecting surface flaws with torsional waves, but without a transient coupler. A stainless steel tube of ~1 m was obtained and welded to the far end of the waveguide body. Stainless steel was chosen for material compatibility reasons for welding an Inconel solid piece to the interior of a metal cylinder. When connected, it was observed that a proper response was generated. The signals were being transmitted from the waveguide body through the welding to the test tubing. Reflection waves were observed separated from the original launched signal by approximately 600 μs, which confirmed our calculations based on the data on longitudinal velocity of shear waves in the literature.

First, measurements were taken with the metal tubing with no flaws introduced. The data was obtained and recorded. Because the tubing was welded to the waveguide body, we did not want to replace the tubing with another one to keep the first test specimen intact. The primary reason behind this was that

replacing the tubing would require removing the connected piece and welding the new piece, which would have introduced additional uncontrollable parameters, such as the condition of the new weld, which would in turn affect how the signal would be transmitted across.

With this limitation, we started to incrementally introduce flaws to the test specimen. First, we drilled a ~1.6 mm (1/16 in.) hole at 10 cm and acquired the data. Then, the same hole was enlarged to ~3.2 mm (1/8 in.). A second 1.6 mm (1/16 in.) hole was drilled at 50 cm, which was later enlarged to 3.2 mm (1/8 in.) diameter. For each case, a frequency scan was performed independently to find the band that gave the highest response. At each step, sufficient data was collected and recorded.

We observed that the experimental system—though not optimized for this purpose—was sensitive for detecting pinholes as small as 1.6 mm (1/16 in.) diameter. Irregular defects in real fuel pins are reported in the literature as being as large as approximately 50% of pin outer diameter—i.e., approximately 5 mm defect size—due primarily to fretting wear.

The results obtained in the experiments demonstrate that ultrasonic torsional guided waves are a promising methodology for detecting surface defects in nuclear fuel pins. More R&D funds are needed to mature this technique into a technology that can be deployed in an industrial setting. Seed and, later, programmatic funds will be sought to improve the technology.

PHYSICS DIVISION

05851

Solar-Wind Heavy Ion Sputtering of Lunar Regolith

Fred W. Meyer, Harry M. Meyer, III, Nasser F. Barghouty, and James 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

We have 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. Both are in the process of being tested in preparation for improved measurements planned for FY 2011.

Information Shared

Meyer, F. W., P. R. Harris, C. N. Taylor, H. M. Meyer III, A. F. Barghouty, and J. H. Adams, Jr. In press. "Sputtering of Lunar Regolith Simulant by Protons and Singly and Multicharged Ar Ions at Solar Wind Energies." *Nucl. Instrum. Phys. Res. B.*

05868

Irradiation Effects in Graphene-Based Electronics

Predrag S. Krstic and Fred W. Meyer

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 (mono- or multi-layer 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

We have accomplished the following in the few months since the project began.

- 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.

- Using tight-binding Density Functional Theory (DFT), the change in electronic structure was detected in the case of hydrogen molecules sticking to the graphehe sheet.

05869

Modeling of the Plasma-Material Interface

Predrag S. Krstic, Paul R. Kent, Jeffrey H. Harris, Donald Lee Hillis, Fred W. Meyer, and Carlos O. Reinhold

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 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 (due to the low electronegativity of lithium in comparison to carbon and hydrogen), which in addition to the short-range

covalent bnds 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” 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.

Information Shared

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RESEARCH ACCELERATOR DIVISION

00513

Study of Radio Frequency Critical Magnetic Fields of Superconducting Materials Using Microsecond-Long Pulses

Kevin W. Jones and John Galambos

Project Description

To date only a handful of data exists on the maximum critical fields that a few superconductors can reach when subject to microwave or radio frequency (RF) fields. The main reason for such lack of data is due to the complexity of manufacturing complete cavities out of known or new superconductors which can be operated successfully in continuous wave to fields high enough to be of interest to physics. The method in this project circumvents that problem by using microwave pulses shorter than the thermal relaxation times of those materials and allows one to rapidly test small samples of materials at various temperatures, thus selecting potential new materials for microwave applications and giving a better insight into non-equilibrium superconductivity. The results will be plentiful databases on the critical magnetic fields at microwave frequencies for many superconducting materials.

Mission Relevance

Better knowledge of the limiting fields in superconductors is of great importance to applications in superconducting particle accelerators, such as the Spallation Neutron Source for Basic Energy Sciences, the Continuous Electron Beam Accelerator Facility for Nuclear Physics, the future International Linear Collider or Project X at FermiLab, or other accelerators for high-energy physics. Moreover, the study of the microwave properties of superconductors can also lead to an improved physical understanding of their non-equilibrium properties, knowledge which benefits the superconducting materials science. A systematic study of the critical microwave fields in superconductors would constitute an exhaustive database never before available for all researchers to access. In particular the National Institute of Standards and Technology would be an obvious beneficiary, given its role of repository of materials.

Results and Accomplishments

The purpose of the study was to investigate superconducting RF properties of different materials under pulsed superconducting RF conditions by measurement. The study plan consisted of designing and fabricating an RF resonator and an instrumentation insert and a dewar assembly. These would be used in a suitable RF source (tens of gigahertz, microsecond pulse length, ~100 kW peak power) at cryogenic He temperature. Initial progress was good. The resonator and insert were fabricated, and test samples of lead, copper and yttrium-barium-copper-oxide were collected. Also a 16 GHz RF source was identified. Initial tests were performed with the 16 GHz RF source; however, the RF control proved to be unstable and the power levels not sufficient to meet test requirements. Efforts then focused on setting up an improved 18 GHz RF source. The new RF source was moved to the SNS RF Test Facility building, and efforts were

undertaken to provide proper electrical power and cooling. The dewar, resonator, and instrumentation insert were fabricated and the temperature instrumentation calibrated and tested. Some preliminary measurements were made with the new RF source at an undetermined RF power level, in April 2010, but progress stopped at this point. The work did not progress to the point of observing SRF effects in any of the prepared materials; no further effort was undertaken because the principal investigator and a second key member of the team left ORNL.

SUMMARIES OF PROJECTS SUPPORTED THROUGH LABORATORY-WIDE FELLOWSHIPS

WEINBERG FELLOWSHIP

05916

Development of a Novel In Situ Electron Microscopy Method to Study Interfaces in Li-Ion Batteries: Application towards Electrical Energy Storage Materials

Raymond R. Unocic, Nancy J. Dudney, and Karren L. More

Project Description

The accelerated design and development of the next-generation electrodes and electrolytes for electrical energy storage devices necessitate the development of unique in situ experimental methodologies that are aimed at providing a mechanistic insight into the nanometer-scaled, structural and chemical changes that occur during the electrochemical energy conversion process. In situ electron microscopy provides a viable means to investigate structure-property relationships of energy storage materials under electrochemical exposure such that the dynamically evolving processes can be studied in *real time* and at high temporal and spatial resolution. This is made feasible through the use of specialized in situ transmission electron microscope (TEM) holders in conjunction with the imaging, diffraction, and spectroscopy capabilities afforded within a high-resolution TEM.

In electrical energy storage (EES) systems, interfaces play an active role in controlling the electrochemical energy conversion process. A prime example is found in lithium-ion-based battery systems where a passive interfacial film, comprised of decomposed liquid electrolyte compounds, forms at the electrode/electrolyte interface. This layer is termed the solid electrolyte interphase (SEI), and there are two major SEI functions that are relevant for EES systems: (1) the SEI acts to protect the anode and cathode materials from degradation and (2) the SEI regulates the degree of Li^+ ion intercalation during electrochemical charge/discharge cycling. Due to the dynamically evolving nature of this *nm*-scaled interface, it has proven difficult to design experiments that will reveal details regarding SEI nucleation and growth and how the interface structure and chemistry evolves as a function of charge/discharge cycling. Therefore, the overarching goal of this research initiative is to develop and utilize advances in situ electron microscopy characterization methods to elucidate SEI growth mechanisms and to continuously monitor the SEI structural/chemical changes that occur during rapid charge/discharge cycles events. The outcome of these research activities will undoubtedly shed new light on the fundamental physical and chemical processes that control electrical energy storage and generation. This will in turn enable a cross-disciplinary team of researchers at ORNL to synergistically accelerate the development of more durable and efficient battery design through combinatorial materials research and computational materials modeling efforts.

Mission Relevance

Rechargeable lithium ion batteries represent a highly desirable class of electrical energy storage technology that has applications geared towards portable electronic devices and hybrid electric vehicles due to their high-energy density storage capacity. The accelerated design and development of the next-generation electrodes and electrolytes for electrical energy storage devices necessitate the development of unique in situ experimental methodologies that are aimed at providing a mechanistic insight into the nanometer-scaled, microstructural, and chemical changes that occur during the electrochemical energy conversion process. This research aligns well with the grand scientific challenge as outlined by the Basic Research Needs for Electrical Energy Storage. Although the prime focus of this research program has been on EES materials, it is recognized that the development and implementation of these versatile in situ TEM devices can be utilized in a variety of other research activities.

Results and Accomplishments

In this project an in situ electrochemical cell TEM holder was developed specifically for the characterization of electrochemical processes in EES systems. The holder was designed in collaboration with Hummingbird Scientific (a leading developer of in situ TEM devices). The electrochemical cell is comprised of biasing microchips (silicon chips with electron transparent SiN viewing windows and integrated biasing contacts), microfluidic delivery system, and electrical connections for interfacing the electrochemical cell to a potentiostat (for electrochemistry testing). A focused ion beam/scanning electron microscope (FIB-SEM) instrument is currently being used to fabricate and attach micrometer-scale electrodes onto the biasing contacts, which are imprinted on the biasing microchips. Once the electrodes are attached to the chips, the microchip assembly is placed into the tip of the custom-built liquid flow, electrochemical cell TEM holder. Preliminary results have shown that it is feasible to create on-chip microbatteries using this in situ platform and successfully perform in situ electrochemistry experiments. In situ dynamic observations during the electrochemical charging processes showed the formation and growth of the nanometer-scale SEI on the graphite anode within an electrolyte consisting of 1 *M* $LiCLO_4$ in EC:DEC. To gain a fundamental understanding of the dynamically evolving nature of the SEI, the in situ electrochemical flow-cell TEM holder developed in this program will be utilized in future studies to dynamically monitor the kinetics and growth mechanisms of the SEI during electrochemical exposure, study the influence of electrolyte/electrolyte additives on SEI formation and stability, and determine SEI breakdown degradation mechanisms.

05918

Extended Defect Chemistry and Optoelectronic Activity in Solar Photovoltaic CdTe Thin Films

Chad M. Parish

Project Description

Solar photovoltaics (PVs) will only be competitive to grid electricity if their cost can be significantly reduced and their efficiency improved. To achieve these goals, CdTe thin-film absorber layers deposited onto low-cost substrates such as metal foils or glass are an alternative to expensive silicon or GaAs-based solar cells. CdTe is a strong candidate because its bandgap of 1.5 eV is optimal for high-efficiency single-junction devices under solar irradiation, and CdTe can be grown by multiple low-cost methods. The current understanding of dopant behavior and interface activity in CdTe is incomplete and controversial. Understanding the relationship between doping and interface character will allow science-based design of

future materials with improved photovoltaic efficiency. Complementary electron microscopy and atom probe techniques were explored to characterize the structures in CdTe thin films and other energy-related materials in order to provide a more fundamental understanding of the doping effects and multidopant synergies at interfaces in CdTe absorber layers. By improving the basic understanding of how to characterize CdTe layers, future lower-cost, higher-efficiency solar cells can be enabled.

Mission Relevance

Solar energy is a domestic, non-carbon renewable energy source, and the development of low-cost, high-efficiency PV technologies will have a large impact on U.S. manufacturing. Improved efficiencies of PV cells and component absorber layers have relevance to the DOE Energy Efficiency and Renewable Energy (EERE) mission and improved manufacturability to the DOE Industrial Technologies mission. The primary thrust of this project is to develop a deeper understanding of defect behavior in compound semiconductor PV thin films, which is relevant to the Basic Energy Sciences (BES) Materials Science and Engineering (MSE) mission. The most immediate impact of this project was the development of experimental characterization techniques, relevant to both CdTe PVs and energy-related materials in general, and these techniques have been made available through the SHaRE BES-Scientific User Facilities Division (SUFD) program.

Results and Accomplishments

Studies on CdTe thin films allowed the proper experimental methodologies to be developed, yielding valuable information to enable future studies to produce science-based understandings of solar PV systems. First, CdTe is found to be highly sensitive to damage from electron or ion beams; therefore, focused ion beam (FIB) sample preparation methodologies were refined to allow preparation of beam-sensitive material on a highly insulating substrate and to prepare site-specific specimens for electron backscatter diffraction. Second, transmission electron microscopy (TEM) techniques were refined to allow high-resolution elemental mapping via X-ray spectrum imaging and energy-filtered TEM with minimal perturbation of the sample structure due to fast electron damage. These techniques were then applied to the CdTe/CdS active interface in PV device structures, where S-Te interdiffusion was characterized for relation to device performance. Te-S interdiffusion was found to be less than 10 nm, and small defective areas at the CdS/CdTe and CdS/substrate boundaries were found by MVSA despite being missed by standard analysis techniques.

In addition to experimental methodology refinements, mathematical techniques were developed. Experiments such as the X-ray spectrum imaging applied to the CdTe/CdS interface produce prodigious quantities of data, and unbiased statistically derived methods are needed to draw proper materials science and engineering conclusions from such experimental data. Mathematical methods and computer codes were developed to (1) use multivariate statistical analysis to produce an unbiased, low-noise description of atom probe tomography reconstructions and (2) resolve the contributions of embedded particles from the surrounding matrix in TEM X-ray spectrum imaging of thin samples using multivariate curve resolution mathematical techniques. These mathematical methods were tested by application to a diverse variety of different energy materials.

Information Shared

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05919

Investigation of Quinone-Containing Organic Molecules as Lithium Cathodes

Wyatt 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 deployed in plug-in hybrid and electric vehicles. While current technologies are adequate for many consumer applications, next-generation lithium-ion batteries need to be developed for large-scale production of “green” vehicles. The cathode is a critical component where significant advancements must be made to enable wider implementation of lithium ion batteries. Cathodes receiving the most attention by the battery research community are based on inorganic species containing transition metal elements. The abundance and cost of many of these elements will be an issue for commercial applications. Even for cathodes composed of abundant elements, such at $LiFePO_4$, the costs and pollution associated with cathode production 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. However, 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. This year, 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

The primary objective for the 2010 fiscal year was to develop vapor deposition techniques to synthesize thin film cathodes composed of 9,10-anthraquinone (9,10-AQ). A significant accomplishment was the development of a vacuum evaporation system to enable the deposition of 9,10-AQ. Much effort was required to optimize the system because 9,10-AQ has a low vapor pressure and high boiling point of 380°C, which makes controlled evaporation difficult. Currently, 9,10-AQ can be successfully deposited into crystalline structures. Also, the solubility of 9,10-AQ in organic solvents was studied; these data were not readily available in the literature. Understanding the organic solubility enabled the fabrication of traditional composite cathodes by slurry techniques. The composite cathodes consisted of 9,10-AQ as active material, carbon black, and binder. Now that these cathodes have been successfully fabricated, the performance of 9,10-AQ in a standard battery cell with a lithium anode and organic liquid electrolyte can be characterized. These results will be readily utilized by other researchers working on novel cathodes. Currently, the two remaining tasks of characterizing the electrochemical performance of 9,10-AQ and correlating structural parameters of 9,10-AQ to its performance have not been completed. Although 9,10-AQ can be vapor deposited, its resulting structure, consisting of needle-like crystallites, precludes electrochemical characterization. Future work will focus on modulating the deposition parameters to achieve smooth, continuous films of 9,10-AQ that are appropriate for characterization and then understanding how the structural parameters of the films influence performance.

05921

An Investigation into the Synthesis and Annealing of Iron-Based Superconductors under High Magnetic Fields

Orlando Rios, Athena Safa-Sefat, Gail M. Ludtka, and Michael 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 atom 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 are 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

In FY 2010, 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. A recently discovered iron-based SC ($Sr_4V_2O_6Fe_2As_2$) was also magnetically annealed with less promising results that were linked to the nucleation of metastable phases during thermal processing. 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.

In FY 2011 we plan a modified magnetic synthesis experiment on the $NdFeAsO_{0.88}F_{0.12}$ superconductor. This experiment will include controlled rapid cooling rates to kinetically limit the formation of lower temperature structures that form during slow cooling. Additionally the microstructures of the $LaFeAsO_{0.90}F_{0.10}$, $CeFeAsO_{0.88}F_{0.12}$, and $NdFeAsO_{0.88}F_{0.12}$ will be investigated by scanning electron microscopy (SEM) and energy filtered transmission electron microscopy (TEM) on selected areas of interest. Quantitative microscopy will be used to link the modified electronic and magnetic properties with the crystal structure, microstructure, and morphology. A beam time proposal will be submitted in FY 2011 to conduct neutron scattering powder diffraction experiments that will investigate the interrelation between the microstructure and the crystal/magnetic structural transformations through the superconducting transition temperature of materials reacted and annealed under extreme conditions.

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

Dongwon 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 are 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 2010 effort focused on the thermodynamic modeling of the Zn-S system and first-principles calculations on the binary sulfide phases in the Sn-S system. Gibbs free energy descriptions for the solid phases in Zn-S have been taken from the SGTE (Scientific Group Thermodata Europe) substance database, and that of the liquid phase has been evaluated to reproduce the experimental phase boundary data with an associates model. Total energies for tin sulfides have been obtained from first-principles calculations and used to evaluate formation enthalpies. First-principles thermochemical data will be used in the thermodynamic assessment to supplement scarce experimental data.

WIGNER FELLOWSHIP

05908

Low-Dimensional Multiferroicity

Xiaoshan 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 possible solar energy harvesting, due to 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 materials and improve their properties by tuning the chemical substitution, structure, and dimensionality. Among many means, tuning dimensionality provides great opportunities: (1) 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; and (3) nanoscale materials allow the possibility of manipulating the individual domains (domain walls), whose dynamics are critical for application. So far, there has not been much research on nanoscale physics of multiferroics because the former is mostly concentrated on a relatively simple system. Our objective is to grow high-quality epitaxial multiferroic thin film and tune/study their properties at low dimension. This will not only bring more insight into the mechanism of multiferroicity but will also help realize the desired material properties.

Mission Relevance

The field of multiferroics is of such interest in fundamental science and commercial applications 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 type 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 new candidates as solar energy harvesting materials with greater efficiency and tunabilities.

Results and Accomplishments

During FY 2010, $LuFe_2O_4$ (LFO) has been deposited on different substrates and orientations, including MgO (111), $SrTiO_3$ (111), Al_2O_3 (0001), ZnO (0001), etc. Characterization methods included reflectance high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray diffraction (XRD), superconducting quantum interference device (SQUID), and atomic force microscopy (AFM). Since there is no substrate that matches LFO within a 1%

difference, all the substrates we tried only have a super-cell match. The XRD and SQUID results show that on SrTiO3 and Al2O3, undesirable mixed phases (e.g., Fe_2O_3, Fe_3O_4 and LFO) are grown. We are able to grow single-phase LFO films on top of MgO (111) substrates according to XRD data, which is already a big step forward since no one has reported growth of single-phase LFO in the literature so far. The quality of the film depended strongly on the MgO substrate quality and the substrate temperature at the growth time (>900°C). Because MgO (111) surface is polar, it is unstable to surface reconstruction. The preparation of a MgO (111) atomically flat surface is a challenge. Nevertheless, we have been able to grow single-phase LFO films on MgO (111). The films had multiple preferred orientations, say (001) and (101), perpendicular to the substrate surface. Measurement of magnetization using SQUID shows promising high magnetic transition temperature (above room temperature) with strong anisotropy, indicating dimensionality dependence of LFO, which is desirable for application. Crystallization of LFO on a ZnO substrate is poor because the ZnO substrate decomposes at relatively lower temperature, which makes a high substrate temperature unobtainable. Our next step will be to grow single orientation films and characterize the magnetic and charge order. The preliminary results suggest that this approach is very promising.

Information Shared

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05914

Control of the Ionic Flux by Nanofluidic Diodes

Ivan 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 the living organism, 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 the current year we (1) built a setup for graphene growth by chemical vapor deposition, (2) developed a procedure for graphene transfer, and (3) fabricated various suspended graphene structures.

05915

Unlocking Emergent Phenomena in Complex Materials through Spatial Confinement

Thomas 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. Due to 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 project are laying the cornerstones for a paradigm shift in consumer electronics where chaos-driven materials replace existing devices.

Results and Accomplishments

In this project, my goal is to investigate new phenomena in complex materials under spatial confinement and take lessons learned from these studies to begin the task of actively controlling the desired characteristics in chaos-governed materials. To accomplish this, I have conducted studies on confined complex oxide manganite systems and introduced novel methods of strain and spin controls. These techniques have led to major progress in the form of tunability in the metal-insulator transition and critical temperatures.

By selectively tuning the energetic landscape that shapes the emergent formation of electronic phase separation, never before seen anisotropic transport properties were uncovered that promise new tunable device applications while answering fundamental questions on the role of electronic phase separation in manganites. It was found that we can selectively induce anisotropic electronic domain formation along one axis of a single crystal thin film by epitaxially locking it to an orthorhombic substrate. Simultaneous temperature-dependent resistivity measurements along the two perpendicular in-plane axes showed significant differences in the metal-insulator transition temperatures and extraordinarily high anisotropic resistive behaviors on macroscales. This work was published in *Nature Physics*.

In complementary work, it was discovered that applying ferromagnetic nanodots to the surface of a spin frustrated manganite film makes it possible to raise the metal-insulator transition temperature by over 200°C and increase the magnetoresistance by 5000%. These changes are observed to be tunable with nanodot density and offer exchange coupling across a film's surface as a new means to drive spin alignment in complex oxide systems. This manuscript is in review at *Physical Review Letters*.

The status of these findings was presented in the form of invited talks at the12th International Ceramics Congress (Montecatini, Italy) and the 2010 International Workshop on Nanomaterials and Nanodevices (Beijing, China).

Information Shared

Ward, T. Z., et al. 2009. "Elastically Driven Anisotropic Percolation in Electronic Phase Separated Manganites." *Nat. Phys.* **5,** 885.

INDEX OF PROJECT CONTRIBUTORS

INDEX OF PROJECT NUMBERS