OAK RIDGE
NATIONAL LABORATORY

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FOR THE DEPARTMENT OF ENERGY

ORNL/PAA-2007/1

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2006 ANNUAL REPORT

UT-BATTELLE

ORNL-27 (4-00)

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Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2006 ANNUAL REPORT

March 2007

Prepared by
OAK RIDGE NATIONAL LABORATORY
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managed by
UT-BATTELLE LLC
for the
U.S. DEPARTMENT OF ENERGY
under Contract DE-AC05-00OR22725

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INTRODUCTION

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

This report includes summaries all ORNL LDRD research activities supported during FY 2006. The associated *FY 2006 ORNL LDRD Self-Assessment* (ORNL/PPA-2007/2) provides financial data about the FY 2006 projects and an internal evaluation of the program's management process.

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

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

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

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

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

Table 1. ORNL LDRD Program

	Director's R&D Fund	**Seed Money Fund**
Purpose	Supports laboratory initiatives	Supports core competencies
Year established	1983	1974
Funding cycle	Annual	Continuous
Proposal review	Initiative review committees	Proposal review committee
Project budget	Typically < $1,200,000	< $175,000
Project duration	24–36 months	12–18 months
LDRD outlay	78%	22%

Director's R&D Fund

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

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

The initiatives and research priority areas for FY 2006 were as follows:

- *Advanced Energy Systems:* advanced technologies for the electric grid, alternative fuels, portable power (jointly with *National Security Initiative*), and nuclear and fusion energy technologies;
- *Advanced Materials:* nanoscale science, controlled synthesis of nanomaterials, nanobiotechnology, nanomaterials for energy applications, and new tools for molecular characterization at the nanoscale;
- *National Security*: application of mass spectrometry to homeland security and national defense; portable power (jointly with *Advanced Energy Systems Initiative*) and knowledge management (jointly with *Ultrascale Computing Initiative*);
- *Neutron Sciences:* novel applications of neutron scattering, neutron physics, novel instrumentation concepts, scientific challenges of power upgrades for spallation neutron sources, and biological applications of neutron scattering;
- *Systems Biology:* novel approaches for high-throughput isolation, identification, characterization, and application of molecular machines, molecular interactions, and

molecular networks; nanobiotechnology; detection and simulation of ecosystem response; and

- *Ultrascale Computing*: computing science (e.g., future computing architectures, multiscale mathematics, and high-speed networks), science applications (e.g., atomic- and molecular-scale modeling, application of computational modeling to problems in materials science, nuclear technology, climate science, and systems biology), and knowledge management (jointly with the *National Security Initiative*).

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

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 2006, $19.9 million was allocated to the Director's R&D Fund to support 71 projects, 33 of which were new starts (Table 2). About 90% of the fund's annual allocation is awarded to projects at the beginning of the fiscal year. The remainder, about 10%, is held in reserve primarily to support research projects of new R&D staff members being recruited to address strategic Laboratory needs. The levels of investment in each initiative are summarized in Fig. 1.

Table 2. ORNL LDRD by Fund

	Director's R&D Fund	**Seed Money Fund**
Costs	$19.892 million	$4.179 million
Number of projects	71	61
Number of new starts	33	35
Continuing (second year of funding)	38	26
Average total project budget (1–3 yr)	$569,356	$117,765
Average project duration	24 months	16 months

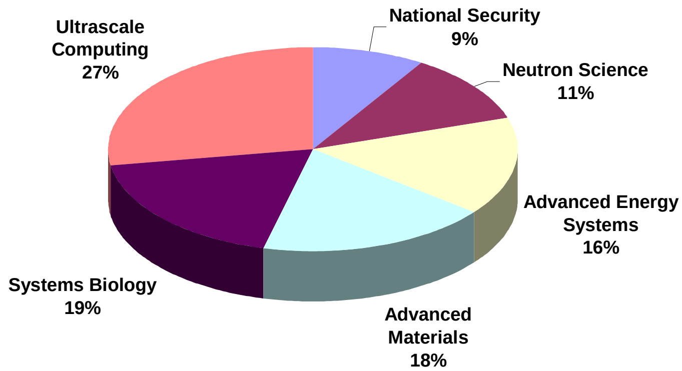

Fig. 1. Level of Director's R&D Fund investment in the Laboratory-wide initiatives for FY 2006.

Seed Money Fund

The Seed Money Fund complements the Director's R&D Fund by providing a source of funds for innovative ideas that have the potential of enhancing the Laboratory's core scientific and technical competencies. It also provides a path for funding new approaches that fall within the distinctive capabilities of ORNL but outside the more focused research priorities of the major Laboratory initiatives. Successful Seed Money Fund projects are expected to generate new DOE programmatic or Work-for-Others 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 ($175,000 is the maximum) are reviewed by the Proposal Review Committee (PRC), which is comprised of scientific and technical staff members representing each of the Laboratory's 13 research divisions and a member of the Office of Strategic Planning, who chairs the committee. To assist the committee, each proposal is also peer reviewed by two 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 2006, $4.3 million of the LDRD program was apportioned to the Seed Money Fund to support 61 projects, 35 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

Report Organization

This report, which provides a summary of all projects that were active during FY 2006, is divided into eight sections: one for each of the six Laboratory Initiatives discussed above, a General Category of projects funded through the Director's R&D Fund by the Deputy Director for Science and Technology, and the Seed Money Fund. This section is further categorized by the research division of the principal investigator. Each summary consists of three parts: project description, mission relevance, and accomplishments through the end of FY 2006. A list of publications is also provided, if the work has resulted in journal articles or conference presentations.

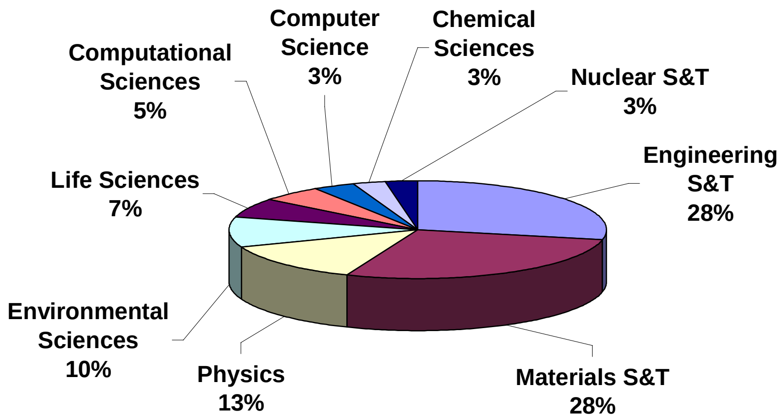

Fig. 2. Distribution of Seed Money Fund by science and technology area for FY 2006.

Advanced Energy Systems Initiative

Advanced Energy Systems Initiative

D05-015: Real-Time, Interconnection-Wide Power System Analysis and Visualization

Brendan Kirby, John Stovall, Budhendra Bhaduri, Alexandre Sorokine, Mallikarjun Shankar, Kalyan Perumalla, James Nutaro, Phani Nukala, Srdjan Simunovic, David Reister, Thomas Overby, and Robert Jeffers

Project Description

The objective of this project is to develop a wide-area analysis and visualization environment to monitor power systems larger in size than today's regional transmission operators with the goal of improving overall system reliability, situational awareness, and avoidance of widespread cascading outages. Around the world, the recent large-scale blackouts have dramatically demonstrated that even with modern energy management systems, cascading blackouts are still possible. Even today, a few untrimmed trees are still capable of putting tens of millions in the dark! In North America, a list of recommendations for reducing this possibility was included in the final report for the August 14, 2003 blackout entitled *Final Report on the August 14, 2003 Blackout in the United States and Canada: Causes and Recommendations*, U.S. Department of Energy (April 2004). These recommendations covered a wide range of topics, from institutional changes by government agencies to changes in protection system plans and practices. It is clear that a number of changes can be made in several different areas to decrease the risk of future blackouts.

Mission Relevance

The project is relevant to the DOE Office of Electricity Delivery and Reliability as part of their mandate to aid senior governmental decision makers in maintaining situational awareness of the state of the nation's electricity infrastructure. This ability to visualize and assess system conditions enables improved federal response during energy emergencies—such as hurricanes—and the identification of regional and local impacts of energy disruptions. As a result of this project, ORNL in partnership with TVA is developing a monitoring system to characterize the status of the electric transmission system infrastructure across the Southeast, including a wide-area visualization environment. The work is also relevant to the Federal Energy Regulatory Commission, Division of Reliability as part of their mandate to monitor the electric network in the country.

Results and Accomplishments

There are several key technical results. A software application for visualizing the electrical network and animating external events impacting the network has been developed and can utilize the ORNL EVEREST facility. EGIVAC (Electric Grid Interactive Visualization, Animation and Control) is a graphical user interface designed to help electric grid operators visualize, animate, and control the operation of the grid in a highly interactive fashion. The system has been designed with the objectives of interactivity of display/control and of reflecting geographical correspondence of electrical elements. The EGIVAC tool is also intended to serve as an intelligent front-end to control electrical network models, such as a rapid contingency analysis using parallel/distributed execution of multiple scenarios.

A public domain geographic information system (GIS) software application has been adapted to use the full capabilities of the ORNL large display wall called EVEREST. An analytical method of building a wide-area power steady-state model has been developed based upon combining state estimator's results from two or more utility networks. The method uses a linear algorithm to join the state estimates rather than combining the models and performing a second state estimate. A method analyzing cascading power system failures has been adapted based on existing methods and source code for analyzing the failure of discrete lattice model, quasi-brittle materials under stress developed at ORNL. The method was successful demonstrated on the Texas electrical network model. Software has been created and tested on the Texas electrical network model to perform steady-state power system analysis and contingency analysis.

Publication

Sorokine, A. "Implementation of a Parallel High-Performance Visualization Technique in GRASS GIS." *Comput. Geosci.* Submitted.

D05-034: A Novel Thermomechanical Process for Producing Fe–3%Si Magnetic Steel Sheet for Transformers

B. Radhakrishnan, G. Sarma, D. B. Reister, A. Goyal, and J. R. Thompson

Project Description

The current technology for making Fe–3%Si transformer core steel with a sharp Goss texture is based on particle-induced secondary recrystallization that requires critical heat treatment steps that are time and energy consuming. The particles are intentional additions that are precipitated, progressively dissolved, and finally removed from the matrix through these elaborate heat treatment steps. The resulting Goss grains are so large that they lead to energy loss during service in the form of micro-eddy currents. The material therefore undergoes a post-anneal laser scribing process in order to refine the size of the magnetic domains. The objective of the project is to develop an alternate thermo-mechanical processing route that can form a sharp Goss texture without the need for particle-induced secondary recrystallization. While such a process would result in considerable energy savings in the production of transformer core steels, it would also be more readily applicable to the processing of near-net shape cast hot bands that do not readily form the precipitates needed for the conventional process. The alternate process is based on applying deformation under specific combinations of shear and compression followed by annealing. The scientific issues involve predicting texture evolution during complex deformation paths and the formation and evolution of Goss nuclei during subsequent annealing, so that the process variables can be optimized for maximizing the Goss texture. From a technical standpoint, the project opens up many new avenues for processing sheets with specific textures that result in better mechanical properties for other non-magnetic applications, such as in the automotive sector.

Mission Relevance

By eliminating time and energy-intensive heat treatment steps, it is possible to save a significant amount of energy in the production of core steel, which is directly relevant to the mission of DOE Office of Energy Efficiency and Renewable Energy. Eliminating processing steps would result in significant cost savings and make high-quality steel more affordable to the transformer manufacturers, ultimately leading to better performance and security of the energy grid, a mission relevant to DOE Office of Electricity Delivery and Energy Reliability. Shear deformation processing to produce new textures in sheet products is of significant interest to DOE's Lightweight Materials Program, especially in the processing of magnesium sheets for automotive applications, as well as to DOD's basic materials research programs. Follow-on funding to continue this work has been obtained through DOE's Gridworks Program.

Results and Accomplishments

We have successfully performed mesoscale computations of texture evolution in Fe–3%Si steel to understand the influence of both microstructural variables and deformation path on the formation of Goss texture. Using the computational results, we were able to successfully identify critical microstructural and processing variables that lead to the formation of Goss texture during shear deformation. We developed a mesoscale model for predicting the formation of recrystallization nuclei during annealing of deformation substructures that consistently predict the formation-specific texture components during recrystallization of face-centered cubic (FCC) and body-centered cubic (BCC) polycrystals. We used the nucleation model in conjunction with a mesoscale simulation code to predict the evolution of recrystallization texture in Fe–3%Si subjected to complex deformation paths. Based on the model predictions, we were able to identify the deformation conditions for which the Goss texture would intensify during subsequent annealing. We performed extensive simulations of shear deformation by asymmetric rolling using finite-element modeling and identified the rolling conditions that maximize the through-thickness shear for a given compressive deformation. These simulations were mainly targeted for the reel-to-reel rolling facility at ORNL. Using Fe–2.6%Si hot band supplied by the industry, we successfully validated the predictions of the deformation model for symmetric rolling. Asymmetric rolling experiments and optimization are currently in progress and will be continued as part of the new projects generated through this LDRD. As part of the project, we also successfully set up an industry-standard test facility for measuring the magnetic properties of a transformer core steel sheet.

Publication

Radhakrishnan, B. and G. B. Sarma. "Texture Evolution during Shear Deformation and Annealing of Polycrystalline Iron." *TMS Annual Meeting 2007*, February 25 - March 1, 2007, Orlando, FL.

D05-054: Development of Lightweight Lead-Acid Batteries

Edgar Lara-Curzio, Ke An, Beth L. Armstrong, Frederick S. Baker, Cristian I. Contescu, Nancy J. Dudney, and Jim O. Kiggans

Project Description

The low specific energy of lead-acid batteries has limited their use in electric and hybrid-electric vehicles, as well as in other mobile and portable applications where the weight of the battery is critical to meeting efficiency goals. Major factors controlling the specific energy of lead-acid batteries include the weight of the main components (grid/current collector, active materials, electrolyte, and container) and the efficient utilization of the active materials. The potential weight savings to be gained by replacing the lead alloys currently used as grid/current collectors with graphite (carbon) materials has been widely recognized. In addition to its relatively low density, graphite has the advantage of being chemically stable in sulfuric acid and is a good thermal and electrical conductor. The objective of this project was to develop technologies that can be used for the production of durable, lightweight lead-acid batteries by (1) reducing the weight of the grid/current collectors through the use of graphite fibers, (2) designing layers of active materials that increase material utilization, and (3) engineering the interface between the graphite fibers and the active material to ensure long-term durability.

Mission Relevance

In his 2006 State of the Union address, the President outlined the Advanced Energy Initiative (AEI), which stresses the need to change how we power our automobiles in order to reduce the nation's dependence on oil. In the area of transportation, the AEI proposes significant new investments in advanced batteries, cellulosic ethanol, and hydrogen vehicles. Although the specific energy density that could be achieved with the technologies developed in this project is lower than that of lithium-ion batteries, the new technologies have the potential of providing comparable power density with greater durability and safety, at a significantly lower cost. In addition to potential uses in transportation, the technologies are relevant to the mission of DOE's Office of Electricity Delivery and Energy Reliability, which manages research, development, field testing, and demonstration projects for the next generation of electric delivery and infrastructure security technologies, including batteries for energy storage. The technologies developed in this project are also relevant to the mission of the Department of Defense in which reliable, durable, and safe lightweight batteries are required in mobile and portable applications.

Results and Accomplishments

Using powder-processing techniques, compounds of Ti, Pb, Si, and C (Ti_3SiC_2 and Ti_2PbC) were sintered in bulk form and as coatings on graphite fibers. These compounds were found to possess the required properties to serve as buffer layers between graphite fibers and active materials in lead-acid batteries. Buffer layers are necessary to ensure that active materials remain bonded to current collectors, because debonding of active materials is the most common mode of failure in lead-acid batteries that use carbon-based current collectors. Buffer layer materials must also possess good thermal and electrical conductivity to minimize ohmic losses. Transmission electron microscopy examination of the interfaces between graphite fibers and Ti_3SiC_2 (or Ti_2PbC) revealed that the buffer layers were strongly bonded to the fibers. Electrochemical tests demonstrated that positive and negative electrodes incorporating these buffer layers could operate reliably under cyclic loading/unloading conditions.

The feasibility of depositing thin layers of active materials (e.g., electrodeposited lead and lead dioxide) onto graphite fibers was demonstrated, indicating that it is possible to significantly improve active material utilization in this system. Furthermore, coupled with the large specific surface area of graphite fibers, the combined results indicate that it should be possible to fabricate durable lead-acid batteries with both high specific energy (≈100 Wh/kg) and high specific power (>1000 W/kg) and, furthermore, that this configuration should result in very rapid charging times. The feasibility of utilizing a slurry-based "paste" for application to electrode/support materials, and its long-term stability, was also demonstrated in this project.

D05-059: Advanced Overhead Transmission Conductors

Stephen D. Nunn, James O. Kiggans, and Vinod K. Sikka

Project Description

The United States has an ever-increasing need for electric power, which is transmitted from the generating source to the consumer primarily by overhead conductors. Increasing capacity by building new transmission corridors is inhibited by the cost of acquiring the necessary land for rights-of-way, concerns regarding environmental impact, and the general "not-in-my-back-yard" sentiment in many communities. Adding more power lines or higher voltage to existing rights-of-way is also limited by regulations and the capacity of existing support towers. The most viable approach to meeting future power needs is to increase the current-carrying capacity (the ampacity) of conductor lines. Until superconducting materials become readily available, significant increases in the fundamental conductivity of the conductors (primarily aluminum) is not expected. However, there are other material properties that can be exploited to increase the ampacity of power lines. One of the main limitations of power lines is controlling the amount of sag in the wires between support towers. The sag is temperature dependent and varies with the wire weight, its strength, and its thermal expansion coefficient. Improving these properties could significantly increase the conductor ampacity. This project will explore (1) increasing the strength and elastic modulus with reinforced aluminum that may eliminate the need for the high-strength steel core that is typically used in most conductor cables, (2) alternative cores with lower weight and/or improved electrical conductivity, and (3) use of high emissivity coatings to reduce the conductor temperature at a given electrical current level.

Mission Relevance

This project supports the mission of the recently created DOE Office of Electricity Delivery and Energy Reliability (OE). DOE recognizes the critical importance of providing adequate and reliable electrical power transmission and distribution to the nation both in terms of economic development and a secure energy future. Successful completion of this project will provide technology and understanding to help ensure that the growing electrical power demands of the country can be met with an advanced and dependable conductor system. This project is also relevant to DOE's Energy Efficiency and Renewable Energy program office, the Department of

Homeland Security, and to commercial developers in the power transmission industry. Southwire, a leading electrical conductor manufacturer based in Carrollton, Georgia, has provided $50,000 under a Work For Others contract for initial follow-on efforts to develop specialty steel alloys for conductor cores that can operate at temperatures approaching 250ºC, thus allowing higher electrical currents without increasing power line sag.

Results and Accomplishments

A major result of this project has been the laboratory demonstration of improved mechanical properties in carbon fiber-reinforced aluminum. Testing of sample composite materials showed an increase in tensile yield strength of as much as 200% for aluminum with 5–10 vol % carbon fiber reinforcement when compared to aluminum samples with no carbon fibers. It was found that copper-coated carbon fibers were more easily wet and incorporated in the aluminum matrix. These tests indicate that it may be possible to use a fiber-reinforced aluminum composite to replace the steel core found in most transmission conductor cables, thus reducing the weight while simultaneously increasing the electrical conductivity. Carbon fiber addition to aluminum also increases the elastic modulus and decreases the thermal expansion coefficient, both of which allow higher conductor ampacity. A second key accomplishment was the identification of a high emissivity coating for aluminum. In laboratory tests, it was shown that the coating increased the radiant heat loss of rod-shaped samples to reduce the metal temperature by 25ºC when compared to uncoated aluminum. Analysis shows that, with this increase in radiant heat loss, the electrical current in a coated conductor could be increased by 18% while operating at the same temperature as an uncoated conductor. This is a substantial potential increase in ampacity.

D06-088: Novel Carbon Materials for Advanced Energy Storage

David DePaoli, Sheng Dai, Nancy Dudney, Jim Kiggans, James Klett, Chengdu Liang, Huimin Luo, Sea Park, and Terry Tiegs

Project Description

This project is focused on devising innovative materials technology for electrochemical capacitors, including nanostructured carbon for electrodes and alternative electrolytes. Electrochemical capacitors are high-power energy storage devices that have performance capabilities somewhere between conventional capacitors and batteries and are attractive for a wide variety of applications, both as stand-alone energy storage devices and as a complement to batteries in hybrid power systems. Currently, application of electrochemical capacitors is limited by cost and performance issues associated with electrode and electrolyte materials. Novel mesoporous carbon materials synthesized at ORNL exhibit large accessible surface area and controllable pore size and thus present promise for exceptional energy-storage performance. Through the experimental synthesis, characterization, and performance testing conducted as part of this project, we expect to develop inexpensive materials that provide greater energy and power density than currently available systems and breakthrough frequency response. We aim to develop a unique capability for the tunable production of electrode materials and matching electrolytes that can deliver performance characteristics targeted for specific applications. This project, which transitions an ORNL nanoscience discovery into an energy-related nanotechnology, will provide opportunities for long-term fundamental research as well as multiple opportunities for grid, vehicle, renewable energy, and military applications.

Mission Relevance

Advanced energy storage is actively sought in a wide range of vital applications of concern to national security, including stability of the electrical grid, renewable energy production, portable power systems for military and homeland security applications, and the transition to alternative-fuel transportation systems through electric, and hybrid electric, and fuel-cell powered vehicles. This project is directly relevant to the Electricity Storage Program of the DOE Office of Electricity Delivery and Energy Reliability and multiple programs of the DOE Office of Energy Efficiency and Renewable Energy, including FreedomCAR and Vehicle Technologies; Industrial Technologies Solar Energy Technologies; Hydrogen, Fuel Cells and Infrastructure Technologies; and Wind and Hydropower Technologies. In addition, there are multiple potential applications for other federal missions, including those of the Department of Defense.

Results and Accomplishments

During the first year of this project in FY 2006, significant progress has been made in applying discoveries from basic science studies on the self-assembly of nanoscale carbon materials to energy-related materials technology. As a result of experimental synthesis studies, mesoporous carbon with controllable pore size can now be produced in two forms suitable for supercapacitor electrodes—as a film with excellent connection to a conductive substrate and as free-standing material. The synthesis of these carbon materials involves curing the self-assembling precursors at room temperature, followed by treatment at elevated temperature. The final products are carbon materials with controlled pore sizes, typically less than 10 nm. It was demonstrated that the nanostructured carbon materials can be synthesized using conventional manufacturing techniques. While the materials synthesized to date have been prepared from relatively expensive precursors, an approach using cheaper materials appears viable and is under investigation.

The evaluation of these mesoporous carbon materials as electrodes for electrochemical capacitors was performed using several electrochemistry techniques: cyclic voltammetry, chronopotentiometry, and electrochemical impedance spectrometry. Our results clearly show that the electrochemical performance is promising. Results obtained to date indicate that specific capacitance of untreated mesoporous carbon is ten times higher than commercially available activated carbons or carbon paper. With high-temperature treatment, the specific capacitance decreases, while the response time and equivalent series resistance improve.

During the next year, we plan to undertake additional tasks needed to span the gap between nanoscale science and viable energy technologies. The work will include studies of structure-performance relationships, long-term testing of chemical compatibility and degradation, and investigation of nanomanufacturing issues.

D06-094: Multi-Component Fuel Spray Simulation Tools for Alternative Fuels

Joanna McFarlane, Valmor de Almeida, Johney Green, Stuart Daw, Kalyan Chakravarthy, Sam Lewis, Scott Sluder, Bill Steele, Robert Wagner, and Rolf Reitz

Project Description

A new tool set is being developed for modeling combustion processes that combines knowledge of chemical physical properties, chemical kinetics, and computational fluid dynamics to simulate the performance of novel alternative fuels under realistic engine operating conditions. A database of chemical information on alternative fuels has been established from existing literature, computational analysis, and modeling. The project involves the integration of this chemical database with various existing software components for chemical kinetics and in-cylinder combustion (CHEMKIN III, KIVA-3-ERC), with the goal being to develop a simulation package of practical value for advanced engine research. A key aspect is the reduction of the chemical mechanism so that it can be incorporated into the engineering-scale simulation, and this will be accomplished using a new automated analysis tool (XChemKin). The simulations are being validated for advanced combustion modes by comparison with results obtained at the Fuels, Engines and Emissions Research Center (FEERC) on a multi-component, yet chemically simple fuel, biodiesel, burned in a Mercedes engine. In particular, emissions of small oxygenated organic molecules, soot, and nitrogen oxides are dependent on the formulation of the fuel. Successful completion of this project will provide a unique and powerful predictive modeling capability that can be used to evaluate engine performance with alternative fuel formulations such as oil sand fuels, heavy oils, and biofuels. Mechanisms and results from this project can be used to benchmark Scientific Discovery through Advanced Computing (SciDAC) combustion calculations to assist in the development of supercomputing for engineering applications.

Mission Relevance

The development of non-petroleum sources of transportation fuel is an emerging national priority aimed at reducing our dependence on foreign sources of petroleum. This project establishes a new research capability at ORNL of great interest to two subprograms—the DOE Energy Efficiency Renewable Energy (EERE)-Fuel Technology subprogram of the Office of FreedomCAR and Vehicle Technologies (OFCVT) and Fuels Combustion of the Office of Distributed Energy (DE). The current OFCVT R&D plan specifically references the need for a predictive tool for next-generation transportation vehicles operating in advanced combustion modes on fuels derived from biomass, oil sands, or synthetic formulations. The U.S. Department of Defense (DOD) also has interest in research focused on ensuring military fuel supplies and engine development. In addition, the next-generation multi-component fuel model developed here could be integrated into the companion terascale initiative project and yield an internationally competitive simulation suite running efficiently on the National Leadership Computing Facility (NLCF) computers.

Results and Accomplishments

Progress in FY 2006 focused on establishing the capability for combustion simulation at ORNL using KIVA-3-ERC that includes University of Wisconsin models for spray breakup and soot formation. Critical values of a prototypical alternative fuel, biodiesel, were calculated based on a group-additive algorithm, and subsequently used in an equation-of-state analysis for thermodynamic and transport properties. The combustion kinetics of an n-heptane/methyl butanoate/NO_x mixture was evaluated using the wrapper program XChemKin, written at ORNL specifically for this project. This flexible tool allows exploration of reaction-phase space, without requiring a priori reduction of reaction mechanisms, through the use of parallel computing and graphical analysis. Preliminary comparison of chemical kinetics simulations agreed with formaldehyde and olefin emission data collected at FEERC, analyzed in the exhaust of a Mercedes diesel engine. In particular, the use of biodiesel blends increases the amount of aldehyde formation in combustion over that produced by standard diesel fuel. However, the ignition timing, heat, and pressure release are not greatly affected by the use of biodiesel. Collaborations have been established with Dr. Rolf Reitz (University of Wisconsin ERC), whose group is performing KIVA simulations; David Torres (Los Alamos National Laboratory), the developer of KIVA4; and Dr. Jim Glimm (SUNY Stony Brook), developer of the FronTier interface tracking model for sprays, to broaden the project scope.

D06-100: Nanocomposite Dielectrics: New Smart Materials for Electric Power Applications and the Advanced Grid

Isidor Sauers, David R. James, Enis Tuncer, Mike J. Gouge, David Beach, Parans Paranthaman, Amit Goyal, Panos Datskos, and Nickolay Lavrik

Project Description

A new class of materials**,** nano composite dielectrics, is being developed by this project that can address the needs of the advanced power grid in the twenty-first century and beyond. These materials offer the possibility of engineering the precise properties needed for each application, thus improving performance, reliability, and overall life. In general, dielectric materials for grid applications should have high dielectric strength. Depending on the particular application dielectric materials should also exhibit high mechanical strength, thermal compatibility, high thermal conductivity, low losses, desired permittivity, or various combinations of the above. Therefore composites have been developed in which filler materials are used to effect a change in the various physical properties that are needed. The use of fillers normally results in a reduction of the dielectric strength. However, when particles are on the nanoscale (i.e., less than 100 nm), the effects of the interface are significantly reduced. The program plan is to examine various polymer (or epoxy)—particle filler combinations and compare the dielectric properties of these nanocomposites with the corresponding micro composite and with the base polymer.

Mission Relevance

Advanced materials are needed to improve the performance of electric supply and transmission equipment such as transmission lines, fault current limiters, transformers, bushings, standoffs, and capacitors. Virtually all of the grid technologies require dielectrics (i.e., electrical insulation) in one form or another to permit the continuous operation of high-voltage components and to prevent shorting to ground, leading to power failure and blackouts. Therefore, this research is relevant to the DOE Office of Electricity Delivery and Energy Reliability's (OE) Superconductivity Program and the OE Gridworks Program. Other programs of relevance include the Office of Naval Research for electric ship applications, Defense Advanced Research

Projects Agency (DARPA) cryocapacitor program, and the DOE Energy Efficiency and Renewable Energy's Freedom Car and Vehicle Technologies Program for hybrid vehicles and power electronics for the development of new materials for high-energy density capacitors.

Results and Accomplishments

In the first year of the project we have examined several combinations of nanoparticle filler and polymer/epoxy composites. Results were obtained for barium titanate (BTO) and calcium copper titanate (CCTO) in araldite epoxy and for titanium oxide (TiO_2) in polyvinyl alcohol (PVA). All show improved dielectric properties over samples with fillers that are in the micrometer size range. The latter combination, TiO_2 in PVA, has dielectric strengths that significantly exceed (by 40%) the unfilled PVA, marking a significant milestone and accomplishment in dielectric materials research and offering the possibility of tailoring dielectric materials for specific applications. We have also obtained breakdown data and other dielectric properties including permittivity and polarization/relaxation results for these samples. Further work will focus on improving mixing techniques with an emphasis on self-assembly. We will also look at other polymer/nanoparticle combinations including polyimide and will begin modeling the dielectric properties.

Publication

Tuncer, E., et al. 2007. "Electrical properties of epoxy resin based nano-composites." *Nanotechnology* **18**, 25703.

D06-138: Experimental Optimization of Advanced Stellarator Confinement

Jeffrey H. Harris

Project Description

Toroidal magnetic confinement of plasmas for fusion power production increasingly involves the exploitation of the three-dimensional character of toroidal magnetic geometry. Stellarators use external helical fields to provide stable, steady-state confinement at zero or greatly reduced plasma current, a major advantage for the achievement of practical fusion power. The most recent generation of large stellarator experiments, including the flagship Large Helical Device (LHD, Japan, still in operation), has demonstrated the viability of stellarator plasma confinement. The next generation of stellarators now being built [Wendelstein VII-X in Germany, the National Compact Stellarator Experiment (NCSX) at Princeton Plasma Physics Laboratory, and the Quasi Poloidal Stellarator (QPS) at ORNL, proposed] has been designed using massive computational techniques to develop optimal magnetic configurations for maximum plasma confinement performance appropriate for reactors. These devices represent a major conceptual advance and require long construction times—they will come into full operation in 2010–2014. Because of the long lead times, it is important to use existing experiments to verify as effectively as possible the underlying physics properties that are to be optimized in the new devices. In this project, we have developed specific experimental scenarios using magnetic configuration variation in the Japanese LHD and (1) the magneto-hydrodynamic stability of ballooning modes, which can rupture magnetic confinement, and (2) the role of flows in regulating turbulent radial transport of particles and heat.

Mission Relevance

This work contributes directly to the Office of Fusion Energy Science (OFES) program, DOE Office of Science. The OFES program is the national basic research effort to advance plasma science, fusion science, and fusion technology—the knowledge base needed for an economically and environmentally attractive fusion energy source. This program supports the goal of the President's American Competitiveness Initiative "to demonstrate the scientific and technological feasibility of fusion energy." More broadly, fusion research also contributes to the goals of programs in Science (SC), Electricity Delivery and Energy Reliability (OE), Energy Efficiency and Renewable Energy (EE), and Nuclear Energy, Science and Technology (NE). Fusion research also provides stimulus and opportunity for industrial innovation in electromagnetics, materials, instrumentation, and control. Fusion research generally, and this project in particular, makes significant use of international collaboration on large research facilities, and thus contributes to maintaining the nation's international scientific links and profile.

Results and Accomplishments

We are collaborating internationally on the key stellarator physics issues of ballooning stability and flows and working with the teams in Japan, at the LHD facility at the National Institute for Fusion Science in Toki and the Heliotron-J experiment at Kyoto University; in Spain, with the TJ-II experiment located in CIEMAT (Centro de Investigaciones EnergŽticas, Medioambientales y Tecnologicas) in Madrid; and in Australia, with the H-1 experiment at the Australian National University (Canberra). We have used ORNL's leading stellarator design codes (VMEC, STELLOPT, DKES, COBRA) to analyze the stability and flow behavior of different magnetic configurations, looking for key measurements that would prove/disprove physics ideas. We have determined that the LHD super dense core plasmas can become ballooning unstable in the outer plasma but are stable in the core. These stability properties may play a role in maintaining optimum plasma conditions. In 2007, we will participate in experiments on LHD to look for ballooning modes. We have developed similar scenarios in the TJ-II, Heliotron-J, and H-1 experiments and have developed a data mining technique on H-1 that will allow us to search for ballooning modes in very large data sets. We have analyzed the flow patterns for LHD and TJ-II and have found that configuration variation that significantly change and even reverse the flows, and thereby alter the turbulent transport of particles and energy. In 2007 we will be looking for experimental evidence of these effects, first on LHD, which will have new flow diagnostics.

Publication

Kumar, S., et al. "Wire tomography in the H-1NF heliac for investigation of fine structure of magnetic islands." *Rev. Sci. Instrum.* submitted.

D06-141: Theoretical and Computational Methodologies and Tools for Second-Generation Integrated Fusion Simulation

Raul Sanchez and Steven P. Hirshman

Project Description

Our project intends to lay the basis for achieving more accurate simulations of fusion experiments close to burning-plasma conditions in the near future. This predictive capability will be critical to support design decisions and to operate next-step experiments, such as ITER. Due to the large disparity of relevant scales present in the problem (over ten orders of magnitude in time scales; around six in spatial scales), direct simulation is simply impossible with present-day resources. Instead, the problem is broken down in smaller pieces that deal with reduced ranges of temporal and spatial scales that must be simulated by specialized codes. All these pieces must then be brought together, in order to perform a global simulation, in a self-consistent manner that requires the interchange of relevant information among the different codes in an iterative manner. Many of the codes presently available to attack the partial problems are not the most appropriate to play these roles within the integrated simulation framework just described. Also, determining how information must be passed among the different codes while preserving the essential physics is still the subject of active research. The current project aims at improving the present situation in both regards. First, we are attempting to lay the basis for the development of a new fast magneto-hydrodynamical (MHD) equilibrium code able to tackle the complex magnetic topologies (such as magnetic islands or open field lines) that will be relevant in these global simulations. Secondly, we are exploring several promising methods that may act as efficient interfaces among those pieces of the problem for which they are not presently available, namely, the interaction of fast scales (associated to wave-particle interactions and micro-turbulence) with the slower ones that determine the confinement properties of magnetic confinement devices.

Mission Relevance

The DOE Office of Fusion Energy Sciences (OFES) recognizes the need for accurate simulation capabilities with predictive power as one of its top priorities, from which major future initiatives should be expected. The development of a numerical framework such as the one described above—in which various specific codes calculate and efficiently transfer each piece of information relevant to carry out a global simulation—is the main objective of the Fusion Simulation Project (FSP), an ambitious 15-year program being proposed for funding by the DOE Office of Science. Indeed, the main goal of FSP is to “develop a fully integrated capability for predicting the performance of externally-controlled fusion systems, including turbulent transport, macroscopic stability, wave-particle physics and multi-phase interfaces.” If funded, FSP is expected to be a joint program between the OFES and the Office of Advanced Scientific Computing Research (OASCR).

Results and Accomplishments

During FY 2006, we started the process of identifying the main issues that need to be addressed to develop a fast MHD equilibrium solver that can deal with magnetic islands and stochastic field lines. Significant progress has been made in this regard. In particular, we have already identified which parts of the algorithms used in previously existent fast solvers (that assume instead closed magnetic surfaces) may be retained for the current problem and which ones must be substituted. We are currently testing several options for the latter. Initial coding of a test version of the code is also currently under way.

Regarding the investigation on new closure methods capable of capturing more effectively the effect of the fast/short scales on the slower/larger ones of interest for MHD simulations, we have successfully completed a renormalization process that allows us to derive effective expressions for turbulent fluxes in terms of fractional differential equations in simplified situations. This work, which was started while the principal investigator of this project was still a staff member of the Universidad Carlos III de Madrid (SPAIN), was finally completed during the first months of the current project.

Publications

Martin-Solis, J. R., et al. 2006. “Enhanced Production of Runaway Electrons during a Disruptive Termination of Discharges Heated with Lower Hybrid Power in the Frascati Tokamak Upgrade.” *Phys. Rev. Lett.* **97**, 165002.

Mier, J. A., et al. 2006. “Study of the interaction between diffusive and avalanche-like transport in near-critical dissipative-trapped-electron-mode turbulence.” *Phys. Plasmas* **13**, 102308.

Sanchez, R., et al. 2006. “Renormalization of tracer turbulence leading to fractional differential operators.” *Phys. Rev. E*. **74**, 16305.

Woodard, R., et al. 2007. “Persistent correlations in self-organized critical systems away of their critical point.” *Physica A*. **373**, 215.

Advanced Materials Initiative

Advanced Materials Initiative

D05-013: Nanostructured Superhydrophobic Materials

Brian R. D'Urso, John T. Simpson, and Phillip F. Britt

Project Description

We have been investigating superhydrophobic surfaces, which are hydrophobic materials enhanced by surface nanostructure. Energetically, water prefers to bind to itself instead of superhydrophobic surfaces so strongly that a layer of air separates most of the interface between water and a superhydrophobic surface. We have demonstrated a remarkable ordered superhydrophobic surface fabricated by drawing and etching glass, and other superhydrophobic surfaces based on differential etching of composite materials. Our goal for the second year of this project is to build on the foundation of capabilities and materials established during our first year. We will develop new and improved superhydrophobic materials, replicate some of those materials in polymers, and investigate potential high-payoff applications. This research will include investigating how to improve our techniques for producing high-aspect-ratio, nanoscale surface features for superhydrophobic surfaces, how to scale the fabrication to larger areas at reasonable cost, and how base material choice affects the superhydrophobic properties and surface durability. The most superhydrophobic, durable, and cost-effective materials developed will be further tested to explore potential applications in drag reduction, energy efficiency, and microfluidics.

Mission Relevance

Superhydrophobic materials are relevant to the Materials Science and Technology subprogram within the DOE Office of Science, particularly with respect to nanotechnology. Our proposed research is creating nanoscale materials with extraordinary properties and will establish new capabilities in producing nanostructured materials through glass fiber drawing at ORNL. Drag reduction with superhydrophobic materials could also contribute to national security by enabling new underwater weapons, defenses, or even fuel savings for watercraft. Our research into superhydrophobic materials is already contributing to other projects or leading to new projects, some of which extend into nanobiotechnology research. We have seen great interest from the Department of Defense, particularly through the Defense Advanced Research Project Agency.

Results and Accomplishments

During FY 2006, the project's second year, we made significant progress in four areas. (1) Polymer-based superhydrophobic materials, which have the highest durability of any superhydrophobic materials we have produced. This is a result of the flexibility of the polymer features and the lack of need of a hydrophobic surface coating which can easily wear. We have also improved the scalability of this process so that large areas can potentially be covered. (2) Inexpensive superhydrophobic powder in organic binder, which can be used to apply a conformal superhydrophobic coating to many surfaces. This material is also very scalable and easy to apply, although it is not as durable as the polymer-based materials. (3) More complex structures, such as electrically conductive superhydrophobic features, which can be used for microfluidic manipulations, such as by Electrowetting On Dielectric (EWOD). Features with a range of aspect ratios were also produced and demonstrate the transition from a normal hydrophobic surface to a superhydrophobic surface with increasing aspect ratio. (4) Initial evaluation of materials for applications, including evaluation of condensation resistance, optical transparency, and possible hydrodynamic drag reduction. The potential applications for condensation-resistant materials in energy efficiency applications will be a particularly strong motivator of future research into superhydrophobic materials.

Publication

D'Urso, B. R., et al. "Nanocone Array Glass." *Science*. Submitted.

D'Urso, B. R., et al. "The Emergence of Superhydrophobic Behavior on Vertically Aligned Nanocone Arrays." *Appl. Phys. Lett.* Submitted.

D05-056: Effects of Confinement on the Statistical Physics of Nanoparticles—From Idealized Models to Real Materials: Application to Antiferromagnetic Oxides

G. Malcolm Stocks, Markus Eisenbach, Baohua Gu, Wei Wang, and Jian Shen

Project Description

The realization of nanostructured electronic and magnetic devices will require a deep understanding of the effects of confinement on the statistical physics of real materials. Recently it has been discovered that the magnetic properties of a wide range of antiferromagnetic (AFM) nanoparticles shows indications of thermoinduced (*ferro*) magnetism (TiM) that are not explainable using theories of the bulk. In this project, we used nanoparticles of antiferromagnetic transition metal oxides (AF-TMO) as prototype systems for developing a fundamental understanding of the effects of confinement on their statistical physics. We used an integrated experimental and theoretical approach in order to distinguish between the canonical effects of confinement and materials specific behavior.

Mission Relevance

This work is directly relevant to DOE's research portfolio in basic science. It is particularly relevant to DOE initiatives in materials science, nano-science, computational science, and high-performance computing as well as neutron sciences. At ORNL this work is particularly relevant to stated goals of the Center for Nanophase Materials Sciences (CNMS), the Leadership Computing Facility (LCF), and the Spallation Neutron Source (SNS).

Results and Accomplishments

We established that long-range order is essential for TiM through numerical calculations on linear arrangements of spins, for which long-range order does not occur in the absence of anisotropy. We also found that TiM occurs only at temperatures low enough for the anisotropy to establish long-range ordering. In addition, we found in the strong-anisotropy limit that TiM is related to the fluctuations of individual spins away from this long-range order. Neither result is explained by current theories of TiM. In addition, we developed a version of self-interaction correction (SIC) to local density approximation (LDA) that will enable its natural implementation in the framework of full-potential and relativistic multiple scattering theory, to be able to treat strongly correlated TMO nanoparticles.

We developed a method to synthesize pure-phase hematite α-Fe_2O_3 nanocrystals with a controlled size of 5–400 nm and a narrow size distribution of <15%. Structures and morphologies were characterized by dynamic light scattering, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (TEM), and X-ray diffraction (XRD). We discovered an unusual amorphous-hematite-phase transformation by Raman spectroscopic analysis. We also explored synthesis methods to produce other oxide nanoparticles, such as chromium oxide (α-Cr_2O_3), nickel oxide (NiO), and manganese dioxide (MnO_2) nanoparticles. A series of α-Cr_2O_3 nanocrystals 20 to 200 nm in size were produced. These nanoparticles are coated with surfactants or a thin shell of SiO_2 to protect them from agglomeration.

We have successfully measured the properties of hematite (α-Fe_2O_3) particles with diameters from 65+ nm down to 5 nm. A SQUID magnetometer was used to measure the magnetic moment of these α-Fe_2O_3 nanoparticles as a function of temperature and size. We observed that all AFM particle assemblies show *strong* evidence of an anomalous increasing moment, indicative of TiM, and we successfully grew AFM metallic nanoparticles (Cr) using a cluster beam source that has a very narrow size distribution (<5%), ideal for studying TiM.

Publication

Zhai, H., et al. 2006. “Giant Discrete Steps in Metal-Insulator Transition in Perovskite Manganite Wires.” Phys. Rev. Lett. 97, 167201.

D05-075: Radioimmunotherapy Using Oxide Nanoparticles: Complete Radionuclide Containment and Mitigation of Normal Tissue Toxicity

Adam J. Rondinone, Sheng Dai, Saed Mirzadeh, and Steve Kennel

Project Description

Radioimmunotherapy (RIT) is an important FDA-approved treatment for several non-solid tumor cancers. The basic strategy of RIT is to couple a radionuclide to a monoclonal antibody. The antibody is specific to cancerous tissue and guides the radionuclide to the treatment site, where radiation therapy occurs. RIT has shown high success rates in treating B-cell lymphomas, including non-Hodgkin’s lymphoma, in several clinical trials but is dose limited by the unintentional release of the radionuclide or daughter products into normal tissues, causing radiotoxicity. This project focuses on fundamental research into the in vivo behavior of nanoparticles coupled to targeting antibodies and the potential leaching of the isotope from the nanoparticles with the objective of developing novel nanoparticle-based radionuclide delivery agents for RIT. The nanoparticle provides an insoluble, robust delivery medium that safely sequesters the radioisotope and the daughter products. The nanoparticle is linked to a monoclonal antibody specific for cancerous tissue, in the same manner as current approaches. This nanoparticle-based approach will mitigate the uncontrolled release of radionuclides that occurs with the typical organic-chelator delivery agents.

Mission Relevance

This project supports the missions of two federal agencies: the Department of Energy (DOE) and the National Institutes of Health (NIH). The project is relevant to DOE's mission because it offers, potentially, an improvement over current radiotherapy treatments. Nuclear medicine was borne out of DOE research, and DOE remains a primary source of isotopes for the pharmaceutical industry. This project is also relevant to NIH because it can potentially improve on current cancer therapies. Because it is cutting-edge nanotechnology, this project is relevant to both agencies. DOE has been made steward of five nanoscience centers for the advancement of nanotechnology in the public interest, and NIH has committed resources to the advancement of nanotechnology-based therapies such as drug delivery.

Results and Accomplishments

This project has been successful in the demonstration and quantitative measurement of in vivo targeting of nanoparticles to an anatomical site. Specifically, time-resolved and quantitative data on the targeting of a nanoparticle to an anatomical site (termed *biodistribution*) has never been collected prior to this study. However, as with any potential pharmaceutical (or pharmaceutical approach), biodistribution data is crucial. This data was collected by loading CdTe/ZnS nanoparticles with radioactive tellurium and linking the nanoparticles to a monoclonal antibody specific for mouse lung. The conjugates were injected into a large set of live mice, and the fate of the nanoparticles was measured over the next 6 days. The experiment proved that a large percentage of the nanoparticles may be targeted to a site. The experiment also measured the rate of clearance, and the fate of untargeted nanoparticles. This data will be useful to any type of nanoparticles-based therapy, whether radioactive or not.

The original proposal listed two other types of nanoparticles that would be investigated: yttrium oxide (Y_2O_3) and lanthanum phosphate ($LaPO_4$). We have also collected targeting data on yttrium oxide and determined that technical problems will prevent its use as a radionuclide delivery medium. We are still investigating lanthanum phosphate and have so far worked out the chemical approach necessary to bind the nanoparticle to a targeting antibody. We are currently awaiting radionuclides from an off-site reactor to test targeting efficacy.

Publication

Woodward, J., et al. "Biodistribution of radioactive $Cd^{125m}Te/ZnS$ nanoparticles targeted with antibody to murine lung endothelium." *Science*. Submitted.

D05-092: Interfacial Solids: Functionality from Atomic-Scale Charge Transfer at Stacked Interfaces

Hans M. Christen, Ho Nyung Lee, Matthew F. Chisholm, Maria Varela del Arco, Claudia Cantoni, Leon Petit, Thomas Schulthess, and Walter Temmerman

Project Description

This project was motivated by the desire to design and create three-dimensional materials with strongly anisotropic, functional physical properties resulting entirely from atomic-scale charge transfer at repeatedly stacked, two-dimensional interfaces. To this end, the work focused on the synthesis, experimental properties determination, and theoretical/modeling analysis of specific interfaces between dissimilar perovskite materials. This approach thus goes far beyond previous superlattice studies, in which the effects of fields originating within one entire layer on the properties of adjacent layers were investigated.

The approach focused on correlating the macroscopic properties of such "interfacial solids" with computational results and atomic-scale imaging, laying the foundation for the ultimate miniaturization of devices using materials comprised of a few interfaces, and leading to the design of materials with properties beyond the possibilities of incremental optimization of known materials. The resulting broader understanding of the limits and possibilities of this "bottom-up" approach to materials synthesis is expected to have a strong impact on functional materials for sensors, non-linear optics and electro-optics, spintronics, photovoltaics, ionic conductors, storage devices, and switches.

Mission Relevance

This work is relevant to the Materials Science and Technology subprogram within the DOE Office of Science, Basic Energy Science Program, as it supports the goal of developing new materials based on a fundamental insight into the relevant mechanisms at the atomic scale. In particular, the explored "bottom-up" approach to analyzing, understanding, and synthesizing materials based on interfacial properties will allow us to create entirely artificial materials with properties that are not seen as a simple combination of those of the constituents. This approach is believed to be a future component of a large number of DOE's materials efforts in numerous energy-related applications. It also strengthens the Laboratory's scientific visibility, thus contributing to the attractiveness of user facilities such as the Center for Nanophase Materials Sciences.

Results and Accomplishments

In FY 2005, the first-year effort, we have obtained experimental results that illustrate the potential of using interfacial effects to fundamentally modify a perovskite oxide material's properties on a length scale of several unit cells. Using single interfaces between $SrTiO_3$ and $LaMnO_3$, synthesized by pulsed-laser deposition, we have demonstrated the ability to compute the valency of transition metal ions in a complex chemical environment, including complex interfacial solids, to the point where theory and modeling will be able to guide our effort in synthesizing new nanophased materials with interesting properties. The numerical work was performed using the self-interaction-corrected local spin density approximation. The combination of these results from synthesis, atomic-scale characterization, and theory/modeling demonstrated the promise that such interfaces could be integrated into large stacks to form three-dimensional materials with properties defined at the local scale and in two dimensions.

In the project's second year, FY 2006, we synthesized superlattices with unprecedented quality (again using $LaMnO_3$ and $SrTiO_3$), as well as interfaces with other test systems (including a newly developed lattice-matched alloy, $La(Al_xSc_{1-x})O_3$). Further analysis of the electron energy loss spectroscopy data obtained in the scanning transmission electron microscope pointed towards subtleties of this analysis not previously understood—pointing towards unexpected (but theoretically understood) additional electronic changes, particularly core-level effects, at the interfaces.

D05-096: Confocal Scanning Transmission Electron Microscopy for Three-Dimensional, Atomic-Resolution, In-Situ Imaging

Stephen J. Pennycook, Andrew R. Lupini, Albina Y. Borisevich, Matthew F. Chisholm, Maria Varela, Klaus van Benthem, Yiping Peng, and Tim Gosnell

Project Description

Aberration correction has revolutionized electron microscopy over the past 5 years, and ORNL has been at the forefront of several developments. We were the first national laboratory to install a working aberration corrector which led to the current position of holding two world records: the highest resolution direct image and the highest sensitivity spectroscopic analysis, a single atom. Besides resolution improvements, aberration correction has resulted in other beneficial effects, including detection of light atoms (imaging of oxygen columns in perovskites, manganites and high-temperature superconductors), sensitivity to single atoms on surfaces or within the bulk, and sensitivity to single atoms embedded in grain boundaries and interfaces. A direct consequence of aberration correction is that the larger imaging aperture results in a reduced depth of field. A through-focal image series in aberration-corrected scanning transmission electron microscopy (STEM) thereby provides a means of depth sectioning. Our aim in this project was to explore and develop the potential of this revolutionary new technique for 3D electron microscopy. Confocal microscopy has revolutionized biological imaging, and the ability to perform 3D imaging with the higher resolution of the electron microscope could also be a revolutionary development for materials, chemical, and biological sciences and nanosciences.

Mission Relevance

This work is relevant to the Materials Science and Technology subprogram within the DOE Office of Science, Basic Energy Science Program, and supports the goal of the President's American Competitiveness Initiative to develop "chemical, biological, optical, and electronic materials breakthroughs." We expect that the success of this project will initiate a new effort in atomic-level characterization of major importance, leading to new initiatives in many areas of science. It may also initiate a grand challenge for the 3D mapping of subsurface electronic and atomic structure. With further development, this technique could represent the equivalent of the scanning tunneling microscope for surface studies, but instead probing the bulk. Such a capability would represent the ultimate goal in materials characterization, with relevance to all areas of the DOE mission.

Results and Accomplishments

During FY 2005, the project's first year, we tested the depth sectioning technique with a range of different samples. We succeeded in demonstrating the 3D location of individual Hf atoms within a nm-wide SiO_2 layer in a next-generation high dielectric constant (K) device structure. Such capability was on the semiconductor industry road map as a critical requirement with no known solution. It has generated immense interest and large numbers of invited talks. During FY 2006 we performed extensive simulations to determine the expected depth resolution. Experiments with Pt atoms on carbon supports gave complete agreement with the theoretical predictions, and a new definition of vertical resolution was proposed based on the well-known Rayleigh criterion for lateral resolution. We demonstrated the difference between resolution, around 7 nm in depth, and precision, which was to sub-Ångstrom level for atoms that were separated in depth by greater than the resolution. Precision requires locating the peak of the visibility and is sensitive to the background in the image. Results were published in the Proceedings of the National Academy of Science and other journals and reported at many meetings and invited talks.

Publications

Becher, P. F., et al. 2006. "Influence of Additives on Anisotropic Grain Growth in Silicon Nitride Ceramics." *Mater. Sci. Eng. A.* **422**, 85.

Cosgriff, E. C., et al. 2005. "The Spatial Resolution of Imaging Using Core-Loss Spectroscopy in the Scanning Transmittion Electron Microscope." *Ultramicroscopy* **102**, 317.

Shibata, N., et al. 2005. "Rare-Earth Adsorption at Intergranular Interfaces in Silicon Nitride Ceramics: Subnanometer Observations and Theory." *Phys. Rev. B.* **72**, 140101.

van Benthem, K., et al. 2005. "Tomographic Imaging of Nanocrystals by Aberration-Corrected Scanning Transmission Electron Microscopy." *2004 MRS Fall Meeting*, November 29–December 1, 2004, Boston, MA, USA.

D05-101: Imaging Molecules, Active Sites, and Reactions on Nanocatalysts

S. H. Overbury**,** A. P. Baddorf, Sergei V. Kalinin, Vincent Meunier, David R. Mullins, and Jing Zhou

Project Description

The objective of this project was to demonstrate and develop at ORNL the capability for imaging and modeling molecular processes at surfaces. Molecular processes at surfaces are of crucial importance to understanding heterogeneous catalysis, and the scientific goal was to learn about the active sites, reaction pathways, and energetics of catalytic processes occurring on oxide-supported catalysts. Scanning tunneling microscopy (STM) holds the greatest promise for direct imaging the elementary steps that occur on a heterogeneous catalyst surface: adsorption, migration, bonding, and reaction. An ultrahigh-vacuum-based, variable-temperature STM (Omicron) was used to obtain all molecular images. Other techniques were used to characterize desorption products and the chemical nature of surface species. Interpretation of the images obtained using this instrumentation was expanded through the use of computational modeling via first-principles density functional theory. All computations made use of the Vienna ab initio simulation package, VASP, and with this, first-principles total energy and electronic structure calculations were performed using the pseudopotential plane wave method within the local density approximation (LDA). Computations were performed at ORNL's supercomputing center and the Nanoscience Theory Institute. We combined these two elements, experimentation and modeling, and probed their abilities and current limitations for the study of adsorption and reaction of benzene, formic acid, and phenol on a $TiO_2(110)$ surface and on palladium metal clusters supported on the TiO_2 .

Mission Relevance

Catalysis is a core technology for of all chemical and fuel processing. Recognizing this, catalysis is a major research focus area of the Chemical Sciences, Geosciences and Biological Sciences Division of the Office of Basic Energy Sciences (BES) at DOE. Since the effectiveness of catalysts depends upon high surface area, and therefore small particle size, catalysts were part of the materials that were originally at the forefront of the development of nanoscience. Recent advances in the preparation and synthesis of nanoscopic materials (i.e., nanocatalysts) have brought about new opportunities for catalysis. Therefore, catalysis by nanoscaled materials is relevant to the mission of BES's nanoscale science research centers including ORNL's Center for Nanophase Materials Sciences and has now been incorporated as a theme area of this new facility. Similarly with rapid improvements in imaging capabilities and computational power, there is now the possibility to observe and model individual molecules on single clusters of a supported catalyst. Molecular imaging was the subject of a recent new DOE initiative entitled Basic Research for Chemical Imaging, and the principal investigators on this project have submitted a pre-proposal to this initiative.

Results and Accomplishments

This work has led to three publications, two manuscripts in preparation, and several presentations at conferences. The first work, now published in *Physical Review Letters*, concentrated on learning how to prepare a defect-free TiO_2 (110) surface but led to the discovery of a new type of defect on the $TiO_2(110)$ surface and surface reconstructions driven by titanium interstitials. The images were explained by use of discrete Fourier transform (DFT) calculations of the structures and energetics of interstitial strands of titanium atoms on the surface. Work then proceeded to molecular adsorption on nearly defect-free TiO_2 surfaces. A paper published in *Physical Review B* describes benzene reactions on these surfaces. It was found that benzene adsorption could not be imaged stably by STM above 40 K, due to the high mobility of the molecules on the surface. Comparison of low-temperature images showed that benzene interacts weakly the TiO_2 (computed adsorption energy of 670 meV) and lies flat with the aromatic ring parallel to the surface. The bonding site was also determined. In the presence of co-deposited catalytic palladium metal particles, a portion of the benzene was observed to decompose to CO and H_2, although STM could not resolve molecular adsorbates on the surfaces of the palladium islands. Benzene adsorption adjacent to palladium particles was observed, suggesting that the clusters did not capture benzene at low temperatures. Since benzene interacts weakly with the oxide surface, molecules that are expected to bond more strongly were studied. Phenol and formic acid might be expected to interact through the –OH functionality on these molecules, therefore anchoring them to the surface more tightly. Formates were imaged on defect-free TiO_2 and on TiO_2 with titanium strands and were found to adsorb most stably at step edges. At high coverage, a well-ordered overlayer of formate is observed. A manuscript describing this work is in progress along with computational work to better understand these structures.

Publications

Park, K. T., et al. 2006. "Surface Reconstructions of TiO_2(110) Driven by Suboxides." *Phys. Rev. Lett.* **96**, 226105-1.

Park, K. T., et al. 2005. "Surface Defect-Mediated Reactivity of Au/TiO_2(110)." *Materials Research Society Spring Meeting*, March 28–April 1, 2005, San Francisco, CA, USA.

Zhou, J., et al. 2006. "Adsorption, Desorption, and Dissociation of Benzene on TiO_2(110) and Pd/TiO_2(110)." *Phys. Rev. B.* **74**, 125318-1.

D05-106: Deformation Mechanisms in Nanocrystalline Metals

T. G. Nieh, Easo George, Bing Yang, and Ming Zhang

Project Description

Advances in material synthesis and process have recently resulted in the production of materials with grain sizes in the nanometer range. The large interfacial area-to-volume ratio poses challenges for the design of nanostructured and interfacial materials, and for the characterization or assessment of their mechanical response, performance, and thermal stability under complex conditions. For instance, nanostructured materials appear not to follow the traditional rules; the classical Hall-Petch relationship breaks down and the solid solution mechanism ceases to operate at a length scale of about 10 nm. Available data indicate that nanostructured materials have excellent properties, such as high strength and good wear resistance, which are technologically important. However, despite its importance to understanding and further controlling the performance of these materials, little is known about the mechanisms involved in the deformation of nanocrystalline materials. Diffusional creep and grain boundary sliding/grain rotation have been proposed to be the key deformation mechanisms for nanocrystalline solids with a grain size less than about 50 nm, but the existence of diffusional creep is fiercely debated in the scientific community. We will, therefore, conduct critical experiments to address this controversy. An answer regarding the existence of diffusional creep is important to understanding of nanocrystalline materials, and for the construction of a deformation map for refractory alloys to correctly predict their creep life for space nuclear power application. This project seeks to develop a robust scientific framework for the mechanistic understanding of nanocrystalline and interfacial materials.

Mission Relevance

Nanoscience and nanotechnology are currently major thrust areas for DOE and the nation. There is an extensive nationwide effort to explore new science in nanostructured materials and develop new technology for structural and functional applications. Our work is directly relevant to such efforts. One of the beneficiaries of this project is the Office of Basic Energy Sciences (OBES). In fact, we are now preparing the research results from this project to respond to the recent OBES call for Basic Research for Advanced New Energy Systems (ANES), which is also an area of secondary emphasis for the ORNL Center for Nanophase Materials Sciences (CNMS). Successful development of a sound scientific program as outlined in our proposal would greatly strengthen the ties between CNMS and ORNL's Materials Science and Technology Division.

Results and Accomplishments

During FY 2006, the project's second year, we made significant progress in four areas. (1) We prepared nanocrystalline tantalum by radio frequency magnetron sputtering and subsequently showed that the sample is remarkably hard at a grain size of 76.5 nm, about one order of magnitude harder than that of conventional bulk tantalum. We also demonstrated that body-centered cubic metals are structurally more efficient than face-centered cubic metals. (2) We employed a multi-step load-unload nanoindentation technique to demonstrate that grain growth can occur in nanocrystalline nickel under stresses even at room temperature. Previously, it was believed that grain growth is a thermally activated process. (3) In the area of understanding the deformation behavior of metastable amorphous alloys, based upon the analogy between mechanical and thermal energy, we proposed a deformation model and successfully predicted the temperature rise in localized shear bands and derived a unified equation to describe the fracture strength of bulk metallic glasses. (4) Finally, in an effort to resolve the controversy as to whether diffusional creep exists, we have now generated some preliminary creep data from gold wires with a bamboo structure crept at very high temperatures and low stresses. The available data indicate that the creep rate is linearly dependent upon stress, as suggested in diffusional creep, but the rates are about 100 times lower than the model predictions. We will further evaluate the grain-size dependence and examine the denuded zones, because they also provide evidence of diffusional creep.

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D05-107: High-Resolution Imaging of Biological Samples in a Wet Environment

Niels de Jonge

Description of Project

We are developing a new high-resolution scanning transmission electron microscopy (STEM) technique to image individual proteins and cells in their native liquid environment with a resolution down to 1 nm. We include the means to control and change this environment and conduct time-resolved measurements to observe structural changes. In our in situ STEM technique, samples in liquid are imaged in an electron microscope by using a specially designed flow cell with electron-transparent windows. Biological samples, such as membrane proteins and whole cells, are immobilized, grown on a window of the flow cell, and maintained under life, or close to life, conditions.

Mission Relevance

This project is relevant to DOE's Biological Sciences, Chemical Sciences, and Nanoscale Science and Technology programs. In situ STEM could revolutionize imaging of biological systems on a molecular level. The project supports the DOE goal of renewable and alternative energy sources and the first goal of the Genomics to Life program, to identify and characterize the molecular machines of life on a molecular level.

This project will benefit other federal agencies as well. It will provide a new tool to image biological structures in their native environment that will benefit all agencies involved in biological sciences, medicine, and drug design. Specific calls include the National Institutes of Health (NIH) institute, National Institute of General Medical Sciences, call for the development of high-resolution probes for cellular imaging. The aim of this call is to develop probes that improve detection schemes by a factor of 10 to 100. The ultimate goal is to develop probes that can be used to routinely achieve single-molecule sensitivity for imaging dynamic processes in living cells.

The National Science Foundation (NSF) has issued a call on instrument development for biological research. This program supports the development of novel or of substantially improved instrumentation likely to have a significant impact on the study of biological systems at any level. Proposals aimed at concept or proof-of-concept development for entirely novel instrumentation are encouraged.

Results and Accomplishments

During FY 2006, a special flow cell was constructed for STEM imaging of biological samples in liquid. The flow cell consists of two ultra-thin windows of silicon nitride which are electron transparent. A sample in liquid is enclosed by these windows and placed in the vacuum of the microscope. The parts of the flow cell were designed and constructed in collaboration with the company Protochips in North Carolina. A sample cartridge for placing the flow cell in the microscope was designed and constructed with the help of Shular Tools, a local company. A STEM dedicated to in situ work was also installed and upgraded. We performed experiments on osmium-stained and epoxy-embedded 3T3 cells obtained from the NIH. Focal series of these samples were recorded, and 3D data sets were reconstructed by deconvolution. These 3D images provided the proof of concept of 3D STEM on conventional thin sections. Chinese hamster ovarian (CHO) cells were immobilized on one of the windows of the flow cell. For the local attachment of cells, a layer of poly-L lysine was made on a defined position on the window using a micro-droplet provided by a pico-pump system.

D06-014: Probing the Boundary between Imaging Microscopy and Spectroscopy: Toward the Exploration of Single Particles by Nuclear Magnetic Resonance Spectroscopy

Edward Hagaman, Dave Geohegan, Gyula Eres, and Tony Moore

Project Description

Spectroscopic resolution on the nanoscale using nuclear magnetic resonance (NMR) is explored in this project by implementing small detector coils. Microcoils already exist that allow the successful detection of protons in 1 fL. This corresponds to a proton density on the order of 10^{12} protons—on the way to a truly countable number. The goal in this project is to build an NMR probe which incorporates a 30-µm-diameter coil which should allow more than an order-of-magnitude decrease in the nuclear spin concentration. The maintenance of NMR sensitivity through better coupling of the nuclear spins to the coil and the size restrictions of the coil diameter itself conspire to allow the NMR analysis of single particles, (e.g., catalyst particles). In addition to lowering to the minimum concentration of spins required for NMR detection, we will test the probe for its ability to generate intense radiofrequency field strengths for use in new solid state NMR experiments.

Mission Relevance

This work is relevant to the DOE, the National Institutes of Health (NIH), and other agencies that fund both NMR development and applications. The microcoil NMR probe will be of interest to Chemical Sciences within Basic Energy Sciences (BES) through their program development in chemical imaging. In addition, the National Institute of Biomedical Imaging and Bioengineering (NIBIB) within NIH supports fundamental discoveries, design, and development of technological capabilities in biomedical engineering. The microcoil probe of this work is directly relevant to many facets of selective NMR analysis in living tissues.

Results and Accomplishments

In FY 2006 we made significant progress in the fabrication on the microcoils. One strategy for this work, fabrication via e-beam lithography, was explored at the Cornell Nanofabrication Facility (CNF). The final microcoil dimensions present significant scale problems for lithography that have resulted in interest at CNF to develop the requisite lithography protocols for fabrication. Simultaneous effort at ORNL using micromanipulation techniques have succeeded in mechanically producing the needed coils. These have been incorporated into an L/C circuit design and shown to tune correctly.

D06-017: Synthesis and Neutron Scattering Characterization of Ordered Self-Assembled Polymer Nanostructures and Biomembranes

Volker S. Urban, Kunlun Hong, Phillip F. Britt, Jimmy W. Mays, and Alexander Boeker

Project Description

This proposal will establish new capabilities at ORNL for synthesis and neutron scattering analysis of nanostructures with controlled orientation and long-range order over macroscopic mono-domains. Block copolymer nanophases in organic solutions will be aligned in electric fields, and small-angle neutron scattering (SANS) will discern structural details in these field-aligned systems. The technique will also be applied to lipid bilayer membranes, which emulate the native biological environment of intact, functional membrane protein complexes. The knowledge generated from this project will advance our understanding of nanoscale science, enhance the technological capabilities at the Center for Nanophase Materials Sciences (CNMS), and highlight novel applications of neutron scattering in field-oriented systems with flag-ship experiments using the new ORNL SANS instruments. With alternating and crossed fields, two- and three-dimensional orientational order could be induced, enhancing the information from SANS in a manner similar to the way single-crystal diffraction is compared to powder diffraction.

Mission Relevance

This work is relevant to the Materials Science and Technology subprogram within the DOE Office of Science, Basic Energy Science Program, and supports the goals of the President's American Competitiveness Initiative to develop "chemical, biological, optical, and electronic materials breakthroughs" and to overcome "technological barriers to efficient and economic use of hydrogen, nuclear, and solar energy through new basic research approaches in materials science." The project implements unique research capabilities and addresses key issues in molecular self-assembly of nanostructured and bio-inspired materials. The project will generate knowledge of molecular interactions and develop a field-alignment technology for nanophase materials with in situ structural characterization by neutron scattering. By addressing central challenges in nanomaterials and membranes, benefits will be generated in a range of highly important research programs of the DOE, the Department of Defense (Defense Advanced Research Project Agency, Air Force, Army), the National Science Foundation, and the National Institutes of Health.

Results and Accomplishments

During FY 2006, the project's first year, we made significant progress in several areas. We hired a postdoctoral researcher with expertise in X-ray reflectivity studies of liquid/liquid interfaces in electric fields and experience with key software that is essential to our project. We designed, built, assembled, and tested a setup that includes a capacitor cell, high-voltage generator, safety enclosure with interlock system, and computer control program that can apply static electric fields to liquid samples with a field strength of 5 kV/mm. The system can be operated in situ in a small-angle X-ray or neutron scattering experiment. We analyzed small-angle neutron scattering data of deuterium-labeled, symmetric polystyrene-*b*-polyisoprene block copolymers that were dissolved in deuterated toluene and aligned in an external electric field of up to 3 kV/mm. The experiments show that the polymer chains undergo a small degree of stretching, and we communicated our results at the Deutsche Physikalische Gesellschaft (German physics society) spring meeting and at the 19th International Symposium on Polymer Analysis and Characterization.

D06-037: Taming Electronic Spins in Conjugated Polymers for Photovoltaic and Solid-State Lighting Applications

Jian Shen, Sheng Dai, Kunlun Hong, Bin Hu, Phillip F. Britt, and An-Ping Li

Project Description

Conjugated polymers are a new class of semiconducting materials that are revolutionizing many technologies including energy-related applications such as solar cells, large-area flexible solid-state lighting, and lasers. The grand challenge of conjugated polymer research is to tailor the formation and dissociation of singlet and triplet excitons to maximize the efficiency of photovoltaic response and electroluminescence. We propose to meet this challenge by taking a radically new approach, namely, introducing and controlling the electronic-spin degree of freedom in the polymers. Specifically, we will dope the polymers with magnetic nanowires and use spin-polarized charge transfer, spin injection, and spin-orbital coupling to tune the singlet and triplet exciton density in conjugated polymers. Building on this concept, we plan to carry out an interdisciplinary research effort which will include (1) synthesis of conjugated polymers with electron-withdrawing side groups and surface-functionalized magnetic nanowires, (2) control of polymer/nanomaterial interface, (3) advanced characterization of optoelectronic, magnetic, and spin-dependent transport properties of the polymer/nanomaterial composites with high spatial and time resolution, and (4) fabrication of photovoltaic and light-emitting devices.

Mission Relevance

This work is relevant to the Materials Science and Technology subprogram within the DOE Office of Science, Basic Energy Science Program, and supports the goal of the President's American Competitiveness Initiative to develop "chemical, biological, optical, and electronic materials breakthroughs." If successful, we expect that this project will initiate a new effort in using magnetically tunable polymer/nanomaterial composites, which is also high on DOE's Science-to-Energy agenda. While this project has its focus on providing a fundamental understanding, we fully anticipate that it will grow into a much broader program that will impact diverse technologies under development at the Department of Defense (Defense Advanced Research Projects Agency, Air Force, Army) and the National Aeronautics and Space Administration.

Results and Accomplishments

During FY 2006, the project's first year, we made significant progress in four areas. (1) We used ferromagnetic cobalt nanodots as spin injectors to efficiently inject spin-polarized charge carriers into organic semiconducting materials. More importantly, this spin injection breaks the theoretical limit of the singlet/triplet exciton ratio of 1/3, increasing the singlet fraction from 25 to 30% at the magnetic field of 450 Oe in organic semiconducting materials. (2) We successfully modified the effective spin-orbital coupling by mixing two soluble organic semiconducting materials. We found that increasing the triplets can lead to an enhancement of the photovoltaic efficiency in an advanced organic solar cell. (3) On the chemical synthesis side, we have developed seeded growth of nickel and CoPt nanowires with solvothermal synthesis and enhanced the dispersion of CoPt nanowires in organic solvents. (4) Finally, we have exploited various approaches to synthesize poly[2-methoxy-5-(2-ethylhexyloxy)xylene] (MEH-PPV) and found that a method which starts with 4-methoxyphenol works better. The as-synthesized MEHPPV is soluble in chloroform, and NMR spectra confirmed the structure.

D06-119: Nanocrystalline/Amorphous Silicon Thin-Film Composite for Stable, High-Efficiency Photovoltaic Applications

R. D. Ott, A. S. Sabau, R. B. Dinwiddie, J. E. Jellison, and M. J. Lance

Project Description

The research project involves a thermal annealing process in order to introduce a nanocrystalline phase within a hydrogenated amorphous silicon phase for thin-film photovoltaics (PV). The presence of the nanocrystalline phase has shown near 100% increase in the collection efficiency of such PV devices. The ultimate goal is to introduce this nanocrystalline phase for improved PV collection efficiency while utilizing low-cost, low-temperature polymer substrates. By doing so it may be possible to drive the cost per peak watt of the thin-film PV system to the range of DOE's goal of $0.5/Watt. The annealing process will be performed utilizing ORNL's unique high-density plasma-arc lamp with power densities approaching those of lasers but able to process broad areas. ORNL is in a unique position since it is the only place in the world this technology can be used for research purposes.

Mission Relevance

Approximately 0.02% of annual energy consumption in the United States is met by PV, equating to about 0.02 Quads or 0.67 Gigawatt-year. Realizing the potential of this revolutionary processing capability could have a significant impact on U.S. energy production in the years to come. Approximately 10% of U.S. energy production could be based on PV, equating to approximately 10 Quads or 335 Gigawatt-year by the year 2030 based on low-cost high-efficiency PV systems. The impact of developing such a low-cost high-efficiency solar cell would mean the United States would have abundant, secure, and reliable domestic power and a more stable power grid in the future. Not only would DOE benefit from such a technology breakthrough, but the Department of Homeland Security would benefit as well, given the fact that PV systems can reliably produce the same electricity cost for 30 years. Also the ability to decentralize solar power will dramatically reduce the vulnerability of the U.S. electrical system.

Results and Accomplishments

To date we have established a close working relationship with United Solar, a world leader in thin film amorphous silicon photovoltaics. United Solar is providing specimens for this project, and we have developed a process scenario/sequence related to specimen geometry and deposition. The thermophysical data specific to these specimens has been generated so that the process thermal model can be refined to achieve more precise processing parameters. The high-density plasma arc lamp was updated so that higher power densities can be achieved in shorter processing times, thus allowing more transient thermal processing to occur, which will lead to better microstructural control at the nanoscale. Amorphous silicon specimens have been successfully crystallized with the high-density plasma arc lamp, thus setting the stage for next fiscal year where the focus will be on optimizing processing conditions to achieve high collection efficiencies.

National Security Initiative

National Security Initiative

D04-103: Advanced Plasmonic Sensor Array for Homeland Security

Tuan Vo Dinh, Guy Griffin, Arpad Vass, Alan Wintenberg, Fei Yan, and Musundi Wabuyele

Project Description

The goal of this project was to develop a novel sensing technology based on an advanced plasmonic sensor array (APSA) concept for rapid and sensitive detection of spectral signatures for chemical and biological warfare (CBW) agents. Plasmonics refers to the enhanced electromagnetic properties of metallic nanostructures from plasmons, quanta associated with longitudinal waves propagating in matter through the collective motion of large numbers of electrons. Light irradiating these nanostructures excites conduction electrons in the metal and induces excitation of surface plasmons, leading to enormous electromagnetic enhancement of spectral signatures such as surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF). The novel features of the APSA technology include an array of sensors based on nanostructured probes capable of producing plasmonics and a combination of bioreceptor recognition and enhanced spectral signatures for detection. With our novel, selective, plasmonics-enhancement approach, the molecular interactions between the adsorption layer molecules and the plasmonics substrate depends on the chemical nature of the analyte molecules and the adsorption layers—a feature that enables sensitive detection of CBW agents.

Mission Relevance

This project fits the DOE mission in protecting its workers and the general public from health effects associated with exposure to chemical and biological agents and toxicants. The plasmonics sensor technology developed in this project can also be used to monitor a wide variety of environmental pollutants, such as the compounds associated with energy production technologies (e.g., petroleum industry, coal gasification, and liquefaction industries). This project will also benefit other federal agencies such as the Department of Homeland Security (chem-bio sensors), the Department of Defense (sensors for defense applications), the Department of Justice (forensic monitors), the National Institutes of Health (biomedical diagnostics sensor programs), and the National Science Foundation (optical sensor research programs).

Results and Accomplishments

We initially investigated deposition methods for producing nanostructures that would permit enhanced field detection (Raman, fluorescence) of model compounds of interest to CBW detection. These methods included deposition of metal-island films on smooth surfaces and metal on nanoparticle arrays and evaporation of a thin silver layer (~100-nm thickness or less) directly onto a solid support. Under optimal conditions, the silver layer develops into a uniform plasmonic array of isolated metal islands on the support. We successfully demonstrated that these structures could detect various CBW simulants.

In the second phase of this project, we developed an optical waveguide-based multispectral imaging system to record the entire two-dimensional image of the plasmonic probe array. These sensor arrays are based on polymer-coated APSA sensors and data processing using pattern recognition and chemometric techniques. Our experiments demonstrated the potential of the plasmonics array for multi-analyte detection capability. Following laser excitation and imaging, the location of specific SERS peaks on the image could be correlated to a specific agent, based upon the absorptive properties of the polymer. Alternatively, different plasmonic-active receptors could be spotted at different sites on the plasmonics array, and following selective reaction with individual CBW agents, the alterations in spectral properties of the various receptors could be correlated with the presence of specific threat agents.

In the last phase of this project, we developed and evaluated an integrated APSA sensor using CW simulants and biomarkers of pathogenic agents and successfully demonstrated that both SERS and SEF, which are two complementary plasmonic detection modalities, could be combined into a single platform for sensing of Raman-active, dye-labeled biomolecules. Our preliminary study suggested that the surface density of the underlying silver islands, the sampling procedures for CW simulants and biomarkers of pathogenic agents, and the experimental configurations, etc., could be the main factors for both better SEF and SERS enhancement.

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D05-074: Mass Spectrometry Beyond 100 Kilodaltons: A New Generation of Mass Spectrometers to Solve a New Generation of Problems

Peter T. A. Reilly, William B. Whitten, and Robert S. Foote

Project Description

The current, realistic range of mass spectrometers is limited to roughly 100 kilodaltons (KDa). Though there have been mass measurements made beyond this limit, they are not routine and their resolution is generally poor. There are two fundamental problems that set this limit—the tremendous kinetic energy imparted to high-mass species upon moving them into vacuum and the inability to detect large ions. This project has demonstrated the solutions to these problems. A reverse jet–based inlet was developed to reduce the expansion-induced kinetic energy so that the massive slow-moving charged species can be delivered to a mass spectrometer for analysis. A detector that thermally vaporizes and fragments the massive charged species into many small molecules and fragments for subsequent ionization and detection “on the fly” was also developed. We have integrated these technological advances with a frequency-variable digital quadrupole mass spectrometer to create a mass spectrometer with an essentially unlimited mass range. This instrument was demonstrated by mass measurement of singly charged particles of up to 550 nm in diameter at a mass-to-charge ratio (m/z) of 7×10^{10} Da and a resolution of approximately 10 m/Δm. The work is still ongoing to increase the mass range and resolution of the measurements. Once this technology is fully developed, it will change the paradigm for studying biological systems by mass spectrometry by enabling the direct identification and quantitation of large, intact biological species such as whole proteins, protein complexes, whole RNA, DNA, and viruses.

Mission Relevance

Increasing the working range of mass spectrometry will change the paradigm for the mass spectrometry–based study of biological systems and benefit many programs at DOE, DHS, DoD, and NIH. Large biological molecules and systems will no longer need to be broken apart and charged until their mass-to-charge ratios are within the working range of the mass spectrometer (currently ~ <10 KDa). This advance will drastically simplify and accelerate the procedures used for biological mass spectrometric analysis. Once fully developed, this technology will permit the direct study of viruses, disease, and biological functions and mechanisms. For example, it should promote the rate of vaccine and drug discovery.

Results and Accomplishments

During the first year, FY 2005, we developed the reverse jet–based inlet to reduce the expansion-induced kinetic energy so that massive charged species can be delivered to a mass spectrometer for analysis without their kinetic energy overwhelming the applied fields. We also developed a detector that thermally vaporizes and fragments the massive charged species into many small molecules and fragments that are subsequently ionized and detected "on the fly" by conventional detectors. During the second year, FY 2006, these advances were integrated with a digital quadrupole mass filter to produce a mass spectrometer with an essentially unlimited mass range. This spectrometer was used to demonstrate mass measurement of singly charged particles up to 550 nm in diameter or 67 GDa. Our results demonstrate the feasibility of mass measurement of essentially any mass-to-charge ratio ion. They show that the working range of mass spectrometers can be extended far beyond the current value of approximately 10 KDa. This work marks the beginning of a paradigm shift in the methods used for biosystems analysis by mass spectrometry and will open the door to quantitative analysis of biomolecules by direct mass measurement in much the same way we currently perform these analyses on small molecules. Large biological species will no longer need to be broken up to enable mass analysis.

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D05-082: Fog Vortices with Electrospray Mass Spectrometry for Detection of Chemical and Biological Agents

Peter J. Todd, Henry S. McKown, and Dave Sree

Project Description

Fog formation is a familiar phenomenon. Technically, fog is a suspension of water droplets. A typical droplet size of wet fog is about 3–20 μm. These droplets have a high surface-area-to-volume ratio and serve as a viable medium for collecting micron and submicron (biological/chemical) particles present in the atmosphere. Traditionally, air sampling has been done using standard filters which involves thermodynamic PΔV work to push air containing particles through the filter—the smaller the particles, the finer the filter, and the greater the power required for sampling. Air sampling via fog collection requires minimal PΔV work, mainly because the volume of water contained in fog is significantly less than the volume of air suspending the water as fog. Power is required to generate fog, and to mix air and fog, however, so the relative power consumption for the amount of air sampled is a figure of merit. Instruments have been developed and utilized to collect *natural* fog and cloud-water samples. Furthermore, fog collection has been used to study atmospheric science, air quality, and industrial pollutants; in some remote, dry areas, fog collection is being used as a means of freshwater supply. It is the intent of the authors to design and evaluate a self-contained fog generation and collection system for sampling air. The goal of this project is to minimize the amount of power and water used and, at the same time, to maximize the collection efficiency of the system.

Mission Relevance

Air sampling–collection of airborne biological and chemical agents is a key barrier to their detection and identification. Mass spectrometers and other analytical devices are quite able to identify such agents with a sensitivity approaching that of a single cell. However, at present, roughly 50% of the power budget of systems used for agent detection is devoted to sampling. We believe that using fog as a collection medium will substantially reduce this power requirement. Such improved efficiency will add substantially to the success of the missions of the Departments of Defense and Homeland Security in protecting soldiers and civilians from chemical and biological attack.

Results and Accomplishments

During FY 2006, we demonstrated the proof of principle that artificial fog is an efficient means of collecting airborne agents. In particular, we can show a 90% agent collection efficiency, sampling 1 m^3/min of air, with a power consumption of about 50 W, that is, about 5% of the conventional sampling power requirement. Patent protection for details of the operation and design of this system is pending.

D06-016: Detection and Identification of Bacteria and Viruses Including Stealth and Genetically Modified Organisms

W. Hayes McDonald, Loren Hauser, Anthony V. Palumbo, Christopher W. Schadt, and Kevin J. Hart

Project Description

The ability to detect genetically modified threat agents is an emerging requirement for both defense and homeland security applications. ORNL has played a critical role in developing the current generation of systems for the detection of threat agents and is in a position to lead the development of the next generation of detectors, which must be faster, more sensitive, and address broader threat spectra. Genetic engineering of bacteria to either enhance the pathogenicity of non-threat agents or disguise the identity of threat agents should leave signatures that we are targeting for identification. These targets include virulence factors, toxin genes, insertion elements, and antibiotic resistance markers. In the first phase of this work, we have used surrogate organisms that can be handled at biosafety level (BSL) 1 or 2 (e.g., genetically engineered non-pathogenic bacteria) to develop protocols and strategies for detecting their genetic modification. These measurements are essential not only to determine sensitivity and specificity, but also to ascertain the knowledge base required to characterize the nature of these emerging threat agents. As part of the process, we are beginning to build databases of target genes and gene products using both publicly available and newly acquired information.

Mission Relevance

This work is relevant to solving a significant defense/homeland security challenge facing our country in the coming years—detecting genetically engineered biothreat agents. This project and its context within a broader system-of-systems approach to the next generation(s) of chemical and biological detectors lay the groundwork for rapidly detecting these and other threats.

Results and Accomplishments

We have made substantial progress on several of our originally outlined goals. In sample preparation, we are taking a two-pronged approach for developing new strategies for protein biomarker detection. One is a scaled-down version of a standard trypsin-based proteomic digestion strategy. The second is a much more rapid, non-enzyme based, microwave-assisted acid hydrolysis protocol. Coupling these sample preparation protocols with multidimensional separation strategies that can be used with our newly acquired high-performance mass spectrometry platform, LTQ-Orbitrap, has provided additional challenges for us to meet. To enhance the quality of data collected using this new instrument, we have explored a variety of data acquisition strategies that are unique to this platform. During this first year, we have demonstrated the ability to detect genetically modified elements using both of our sample preparation protocols. While we chose to focus our initial efforts on the longer-lead-time developments, we are now also ramping up our microarray and computational simulation tasks. These include the design of a prototype array that should allow for the detection of a range of possible genetic modifications and the development of software to determine which peptide sequence with a particular family of proteins would make an appropriate candidate biomarker and to evaluate the degree of conservation of a peptide that we detect in our survey experiments.

D06-020: Design and Synthesis of Novel Infrared-Active Nanophosphors

Linda Lewis, Lynn Boatner, Bob Smithwick, and Steve Allison

Project Description

Numerous federal agencies have identified a need for nanomaterials that emit infrared (IR) radiation with high fluorescent yields. Nanostructured materials are required for several reasons, including ink-jet printing tags for tagging, tracking, and locating; covertly marking and tracking materials of interest (e.g., nuclear components, combat ID, vehicles, illegal transactions); studying internal combustion in various engines to identify processes that increase fuel efficiency; enhancing luminescent light output due to increased surface-area-to-activator ratios for portable photovoltaic batteries; and combat-support applications. Rare-earth-doped inorganic phosphors were targeted due to their inherent properties including chemical, optical/UV, and radiation stability. Specifically, double-doped rare-earth nanophosphors, known to increase luminescence output as a result of energy-transfer processes on a macro scale, were studied on a nanoscale and found in some cases to possess higher quantum efficiencies than their macro-sized counterparts. During the FY 2006 phase of this project, the luminescent properties of rare-earth-doped phosphors and glasses were evaluated with regard to doping levels, host matrix, and, to some extent, particle size. Systems activated by UV (solar), energetic electron, and optical interactions that result in the emission of IR at the desired wavelengths are in progress. The first-year goal was to design nanomaterials that support the needs identified above, while planning to concentrate on nano-sized production and sensor applications the second year.

Mission Relevance

This work is relevant to programs within the DOE Applied Technologies Program and DoD. The Office of the Secretary of Defense Counter Narcoterrorism Technology Program Office is interested in materials based upon the near- and mid-IR glass phosphers. A fact sheet is being disseminated throughout DoD that has generated a tremendous amount of interest in our nanophosphers. The materials being developed in this project have application to such areas as detection of improvised explosive devices and long-life photovoltaic batteries.

Results and Accomplishments

Differences between matrix compositions and dopant configurations (surface or embedded) in inorganic nano-phosphors may significantly influence quantum-level properties, thus influencing electronic and optical characteristics. Therefore, an array of solid-state materials was prepared through a variety of methods with various host matrices, dopant mixtures, sizes, surface/entrapped treatments, and distributions to study the effect of these variables on fluorescence-emission characteristics. Differences between matrix compositions and dopant configurations were initially screened on a nano to micron scale through combustions and sol-gel synthesis, a micro scale through crystal growth, and macro scale through glass melting. Rare-earth elements active in the near- and mid-IR region were substituted into solid state as well as amorphous host matrices, including rare-earth orthophosphates, YAG, alumina, complex aluminates, yttrium oxides, silicates, oxysulfides, garnets, and glass. A partial list of the materials prepared during this fiscal year this FY include the following:

Sol Gel Synthesis: $CaAl_2O_4$:Nd (1%); $CaAl_2O_4$:Yb (1%); Y_2O_3:Yb(3%); Al_2O_3:Yb(3%); SiO_2:Cr (1%); SiO_2:Mn (1%); and an array of complex strontium aluminates triple doped with Er, Dy, and Cr

Combustion Synthesis: Al_2O_3:Yb(3%); Al_2O_3:Yb, Cr(3%); Al_2O_3:Yb, Mn (0.25–3%); Al_2O_3:Nd (0.5-3%); Al_2O_3:Cr (0.25–3%); Al_2O_3:Nd,Cr (0.5–5%); an array of doping combinations for Al_2O_3: Ti, Cr; $CaAl_2O_3$:Nd, Cr; Y_2O_2S:Yb (3%); $Er_{0.08}Gd_{1.92}O_2S$:,Ti (2%); Al_2O_3:Eu (1–2%); and array of $SrAl_2O_4$:Eu, Nd; etc.

Glass: $PbScPO_4$ with Er (1, 2, 4, 8, 12%); $PbInPO_4$ with Er (1–8%); $PbScPO_4$ with an array of Nd and Ce doping levels

Crystals: $LuPO_4$: Er (2,4,8%); YPO_4: Er (2,4,8%); 60g $PbHPO_4$ + 3.5g Lu_2O_3 + 0.14 g Er_2O_3(4%) + 0.35 g Dy_2O_3(1%); 60 g $PbHPO_4$ + 3.5 g Lu_2O_3 + 0.14 g Er_2O_3 (4%) + 0.035 g Tm_2O_3(1%)

Activation by solar radiation was one of the methods targeted for investigation. Unique materials have been prepared via combustion synthesis that holds promise for fulfilling the need for solar-activated tags. Activation efficiency by energetic electrons, cathodoluminescence, and radioluminescence will soon be investigated on these new materials.

Publication

Goedeke, S., et al. "Cathodoluminescence Emission Studies for Selected Phosphor-Based Sensor Materials." *IEEE Trans. Nucl. Sci.* Submitted.

D06-128: Combustion of Nanostructured Metal Fuels: Towards Designing Optimized Combustion Chambers

M. P. Paranthaman, B. G. Sumpter, A. L. Qualls, and S. D. Labinov

Project Description

This project directly addresses the need for novel, high-energy-density fuels for use in civilian transportation technology, high-performance military vehicles, portable power sources, and particularly those for anaerobic applications. This work is based on ORNL's original concept of the solid-state combustion of engineered fuel clusters consisting of metallic nanoparticles. Our objectives are to develop the optimal metal nanofuel and the working model of the combustion chamber for utilization of this safe and renewable high-energy-density carrier. Our initial combustion chamber will be focused on external combustion such as a closed-cycle gas turbine or a Sterling-cycle engine. An experimental study and a detailed mathematical model that directly takes into account the unique properties of the nanostructured metal fuel will be used to determine optimal parameters of a combustion chamber and its dynamic characteristics as applied to an engine with both static and variable loading.

Mission Relevance

DOE's overarching mission is to advance the national, economic, and energy security of the United States and minimize dependence on imported oil, which requires alternative energy sources and carriers. This project opens the possibility of an energy carrier and heat engines more powerful than both gasoline and internal combustion, and independent of the carbon cycle. While the project focuses on high-performance military applications of interest to DoD and NASA, the follow-on implications for civil applications are enormous. While military designs may not be recyclable, civil ones could be done easily. Just as electricity moves energy from generation to point of use, nanostructured metal fuels can carry energy from centralized reduction facilities (using nuclear, coal, solar, geothermic, or water energy) to where transportation and portable power are needed. As an alternative to fossil fuels, metal fuels would be safer, potentially easier to store and transport, have much greater power density, not pollute the environment during combustion, and be less costly to produce from metal ores than gasoline is from crude oil. This project addresses unfilled technology requirements for propulsion engines that have more power and energy density than those currently available so as to enable development of specific classes of unmanned vehicles, in particular anaerobic engines where either the induction of air or the exhaust of hot gas is foreclosed by either mission requirements or the operating environment.

Results and Accomplishments

During FY 2006, we have made significant progress in the following four tasks:

1. The temperature of self-ignition has been determined experimentally for nanoparticles of boron, aluminum, and iron during the solid state combustion. It has been shown that these temperatures are substantially less than those for micron-size particles. The time of combustion was on the order of microseconds. These results demonstrate the proof-of-concept of the ORNL's new solid state combustion and open the door for practical applications of the nano metal fuel.
2. Theoretically, it has been predicted and experimentally confirmed that a nanometallic fuel can absorb the oxygen on the particle's surface. These results show that the combustion of such fuels without any additional oxidizer is possible and that an anaerobic engine can be developed.
3. A mathematical model of the combustion chamber for a nanometallic fuel has been developed, and an experimental set for a working model of the combustion chamber has been proposed.
4. The combustion behavior of iron nanoparticles has been tested in experiments using a reciprocal engine. No mechanical damage was observed inside the walls of the engine cylinder.

Neutron Sciences Initiative

Neutron Sciences Initiative

D04-107: H-Laser Stripping Proof-of-Principle Experiment for the Spallation Neutron Source Power-Upgrade Proposal

Yehuda Braiman, Stuart Henderson, Alexander Aleksandrov, Saeed Assadi, Jacob Barhen, Viatcheslav Danilov, Warren Grice, and Yun Liu

Project Description

We developed a novel approach for laser stripping of a 1-GeV H^- beam, which uses a three-step method employing a narrowband laser. In the first step, the beam traverses a strong magnetic field in which the H^- ions are stripped to H^0 ($H^- \rightarrow H^0 + e^-$) by the Lorentz-stripping mechanism (arising from the strong electric field generated in the H^- rest frame from the Lorentz transformation of the magnetic field). In the second step, the H^0 beam is excited to the $n = 3$ state by colliding a laser beam with the neutral hydrogen beam at an angle chosen to provide the necessary transition frequency in the hydrogen atom's rest frame. In the final step, the excited hydrogen is readily stripped ($H^{0*} \rightarrow p + e^-$) in a second high-field magnet due to the small electron binding energy of the excited atomic state.

Mission Relevance

As the beam power of the Spallation Neutron Source (SNS) is increased from the 1.44-MW baseline design to more than 3 MW as envisioned in the SNS Power Upgrade Proposal, the traditional stripping scheme utilizing foils will become a severe limitation for two primary reasons. First, carbon foil lifetime tests show rapid degradation of performance at power deposition corresponding to beam powers in the multi-MW range due to the extreme temperatures reached on the foil. We expect peak foil temperatures of 2000, 2500, and 3100 K for intensities corresponding to 1.44-, 3-, and 5-MW SNS operation, respectively. Rapid reduction in foil lifetimes was reported at peak temperatures above 2500 K. A second limitation arises from beam scattering in the foil due to multiple traversals of the foil by stored protons. Each proton accumulated in the ring passes through the foil 6–10 times, increasing the probability of large-angle coulomb or nuclear scattering, which results in the loss of the scattered proton in an uncontrolled manner on the accelerator vacuum chamber. For the SNS, this uncontrolled beam loss is a central issue, since it may lead to activation of the accelerator components, thus complicating routine maintenance of the facility. For these reasons, it is essential that an improved multi-MW, charge-exchange injection scheme be developed in the next several years for the SNS Power Upgrade.

Results and Accomplishments

The main goal of the project was to design and implement a proof-of-principle experiment, as there were a number of challenging aspects of the method that had to be studied and successfully demonstrated. Chief among these challenges were (1) design of the stripping magnets, (2) control of the magnetic fields, (3) achievement of good spatial and spectral laser beam quality, (4) control of the laser beam parameters, and (5) demonstration of high stripping efficiency in the real accelerator environment.

The first substantial (about 50%) stripping was observed at SNS on March 23, 2006. In August, we repeated our experiments, and 90% efficiency laser stripping was observed over the duration of the laser pulse (~7 ns). The number is close to that for conventional foils. Therefore, we believe that the feasibility of replacing the graphite foils with a laser has been demonstrated. We believe these results are of the most important and impressive achievements in accelerator physics and technology over last few years and are very promising not only for SNS but for other projects as well.

D05-001: Neutron Reflectometry Studies of the Structure of Polyelectrolyte Thin Films Subject to Shear

G. S. Smith, J. Mays, W. A. Hamilton, J.-H. Cho, W. Holley, and T. L. Kuhl

Project Description

In this project, we aim to investigate the static and sheared structures formed by confined, opposing polyelectrolyte monolayers using neutron reflectometry. Knowledge of the conformations that adsorbed or terminally anchored chain molecules adopt when subjected to confinement and shear flow is essential for predicting the interaction forces, and tribological and rheological properties of such coated surfaces. When densely packed polymers attached to a substrate are placed in a good solvent (for the unbound end of the polymer), the polymer-free energy consists of a competition between the osmotic forces which want the chains to dissolve in solution and the energy cost of stretching the coiled chain. The resulting carpet-like molecular structure is referred to as a polymer "brush." When opposing polymer brushes are brought into contact, two processes may occur simultaneously: interpenetration and compression, which determines their lubrication and adhesive properties. These interactions can be further modified by using a charged polymer (polyelectrolyte) to modify the surface. In this project, our approach was to measure the effects of shear on the structure of neutral diblock copolymers previously studied under static confinement. The diblock consisted of an insoluble anchor polymer (polyvinyl pyridine, PVP) covalently bound to a soluble polymer (polystyrene, PS) in toluene. In parallel, we explored ways of creating an analogous tethered polyelectrolyte diblock (PS-NaPSS, where NaPSS is polystyrene sulfonate with a sodium counterion). In water, the PS acts as an anchor and the NaPSS dissolves and the charge.

Mission Relevance

Several benefits are expected upon the successful completion of this project. We have developed new techniques for studying materials in confinement, which will benefit both neutron scattering and nanoscience programs in basic soft matter research at several BES laboratories. The confinement/shear apparatus will be available for users at the Spallation Neutron Source and the HFIR, which will strengthen the user programs at both facilities. Having developed a new cell and sample prep techniques, they will continue to be used in support of the in-house BES-funded neutron scattering research at SNS and HFIR. This work will not only have applicability in polymer science but will be relevant to molecular biology and nanoscience given that biomaterials such as proteins are charged polymers.

Results and Accomplishments

Using state-of-the-art polymerization techniques, we synthesized controlled model architectures to elucidate the structure of these complex systems at interfaces under confinement and shear. These molecules consisted of diblock copolymers which had a charge-neutral (poly)tertbutylstyrene molecule covalently bound to a water-soluble polyelectrolyte (poly)styrenesulfonate (PS-PSS). We performed the first-ever shear experiments on a neutral PS-PVP diblock analogs in confined/sheared geometry. We found that the polymer structure changes dramatically after a shear force has been applied and stopped and that the resulting polymer structure continues to change over several weeks with increased overlap between the opposing polymer chains. When we tried to prepare the PS-PSS diblocks on solid substrates, however, we found that the same techniques used to deposit neutral films did not produce PS-PSS bilayers with the PS next to the substrate. Henceforth, the project focused on developing methods of preparing films for reflectivity experiments using spin coating and physisorption on bare and modified substrates. Polymers with a range of molecular weights and different solvents were explored. Four sets of neutron scattering experiments were performed to examine the basic architecture of the films. The most promising films were found to consist of a silicon wafer coated with a homo-polymer PVP with the polyelectrolyte physisorbed from solution. Finally, we designed and built a new generation of confinement cell which has a fine force adjustment and is lighter weight than the original version. This cell was recently tested on the SPEAR reflectometer at LANSCE.

Publication

Smith, G. S., et al. "Structure of Confined Polymer Thin Films Subject to Shear." *Physica B*. submitted.

D05-002: Small-Angle Neutron Scattering Investigation of the Mechanism and Kinetics of Membrane Protein Crystallization in Self-Assembled Surfactant Mesophases

William A. Hamilton, Gary W. Lynn, Divya Singh, William T. Heller, Dean A. A. Myles, Lionel Porcar, Ursula Perez-Salas, and P. D. Butler

Project Description

Membrane proteins play a critical role in signal passage and chemical transport across the walls of living cells and are coded by a substantial fraction of the genome. However, only a very few of the ~26,000 known protein structures are those of membrane proteins because they are difficult to dissolve and crystallize in the quantity required for high-resolution X-ray and neutron diffraction studies. Membrane mesophase "in meso" templating of crystallization has had some success, but the mechanism remains conjectural, which makes improving the process difficult.

We are using neutron-scattering contrast techniques to reveal the exact structural evolution of proteins in these mesophases to determine the parameters governing crystallization. While bulk surfactant solutions have been used to mediate hydrophobic interactions as an aid to crystallization, the paucity of structures determined to date indicates only limited success by this means alone. Among the numerous approaches involving surfactant-based systems exploiting the spontaneously self-assembling properties of lipids, one crystallization technique that has recently attracted considerable attention due to some promising initial results is the so-called "bicelle method." The bicelle method consists of using as an incubator a discotic micelle. While the mechanism is as yet poorly understood, it has been speculated that the mesophase provides periodic nucleation sites and supports crystal growth by lateral diffusion of protein molecules within the surfactant membrane. The identity of the structure or phase that feeds the growing crystal surface is still unknown; however, through our experiments we hope to gain an understanding of this mechanism.

Mission Relevance

A basic understanding of the mechanisms of "in meso" protein crystallization and their dependence on process variables will allow faster and more efficient production of the crystals that are essential for atomic-scale-resolution, X-ray, or neutron diffraction studies. The structures so derived will contribute initially to our understanding the operation of proteins as machines in life processes and ultimately to the engineering of protein functionality in technological applications ranging from bioweapon detection and defense [Department of Defense (DOD) and Department of Homeland Security] to hazardous waste cleanup (DOD and DOE) and healthcare therapies and biosensors [National Institutes of Health (NIH)].

Results and Accomplishments

Solutions of mixed long and short (detergent-like) phospholipids, referred to as "bicelle" mixtures in the literature, are known to form a variety of morphologies based on their total lipid composition and temperature in a complex phase diagram. In this work, we studied the low-temperature phase, where there is agreement on the discoid structures but where molecular packing models are still being contested. We characterized the isotropic fluid phase formed by these mixtures in a range of measured molar ratio q (q = [DMPC]/[DHPC]) values, q = 2–5, and concentrations of the lipids, 0.5–10% at 10°C. Using data from small-angle neutron scattering (SANS) experiments, we showed how the radius of the planar domain of the disks is governed by the effective molar ratio q_{eff} of lipids in aggregate and not the measured molar ratio q, as had been previously thought. Using a model first proposed by Clint for surfactant mixtures, we propose a quantitative packing model and show that in this self-assembly scheme, q_{eff} is the real determinant of disk sizes. Based on q_{eff}, a master equation can then scale the radii of disks from mixtures with varying q and total lipid concentration. Further, we have shown that at low temperatures the bicelles show segregation but appear to start mixing as temperature increases.

D05-053: In-Situ Time-Resolved Neutron Diffraction Study of Materials Behavior under Severe Thermomechanical Deformation

Zhili Feng, Wan C. Woo, Xun-Li Wang, Camden R. Hubbard, Stan A. David, B. Radhakrishnan, and Gorti Sarma

Project Description

The microstructure evolution of materials under rapid and severe thermomechanical deformation is one of the most important yet least understood areas in materials science and engineering. A major contributing factor has been the lack of direct in situ observation and determination of the temperature, stress, and microstructure changes as they evolve rapidly under complex thermomechanical material synthesis environment. This project is aimed at addressing this challenge by developing a novel neutron-scattering measurement and data analysis approach that would enable unique in situ, time-resolved measurement of material behavior under severe thermomechanical loading conditions, a completely new area of application for neutron scattering in materials science and engineering. The program builds upon the following key technical tasks: (1) a novel in situ data collection technique that would drastically improve the temporal resolution of neutron scattering, thereby allowing for time-resolved material studies; (2) a portable thermomechanical processing system that can be used as a platform for controlled severe thermomechanical conditioning of materials; (3) new data processing and interpretation techniques to decode the temperature, stress, and microstructure information embedded in the neutron scattering data; and (4) in situ measurement of stress, temperature, and microstructure changes in aluminum alloys.

We have successfully demonstrated the novel neutron scattering approach for in situ, time-resolved neutron measurement. The new measurement methodology has attracted considerable attentions in the materials science and neutron scattering community.

Mission Relevance

This project is relevant to DOE BES Neutron Science and Materials Science and Engineering programs, as it leads to novel use of neutron scattering to understand the fundamentals of materials behavior. Our technique will provide a better understanding of the intricate interplay of stresses, temperature, and microstructures in complex metal processing and synthesis, which would be important to a wide range of advanced structural and functional materials for DOE Energy Efficiency, Fusion Energy, and Fossil Energy programs. Successful demonstration of the in situ neutron scattering capability would also enable us to enhance materials research and development being conducted by other federal agencies and U.S. industry. We expect (1) a new and active academic and industrial user base for in situ, time-resolved neutron scattering studies of material behavior, (2) basic materials science research programs to develop the theoretical basis for novel approaches to produce unique microstructures in structural and functional materials, and (3) applied research programs from U.S. industry where thermomechanical processing of materials is critical to their business.

Results and Accomplishments

Significant progress has been made. We confirmed the existence of the quasi-steady-state condition in our experiments. We demonstrated that, under the quasi-steady-state condition, neutron collection time is independent of the rate of change of material behavior during the transient. This makes it possible to select the neutron collection time based purely on the neutron flux and sampling volume requirement of a test, thereby circumventing the neutron flux limitations for studying fast transient material behaviors. We developed a neutron diffraction data analysis methodology to allow for simultaneous decoding the transient temperature and stress from the neutron measurement data for a two-dimensional case, without the need for additional auxiliary measurement.

We have developed a completely new in situ neutron scattering approach in which the temporal resolution actually increases as the neutron scattering volume decreases—a breakthrough in neutron diffraction. Using this new approach, we obtained the fast transient thermal stress and temperature behavior "inside" a bulk aluminum alloy subjected to a "real-world" material thermomechanical process (the friction stir process)—a first in materials science. This project has demonstrated the feasibility of using neutron scattering to simultaneous measure temperature, bulk stress, strain, recrystallization, and other phase transformations of microstructures that are essential to understanding how a material responds under complex processing and synthesis conditions.

Publications

Feng, Z., et al. "In-situ neutron diffraction measurements of temperature and stresses during friction stir welding of 6061-T6 aluminum alloy." *Sci. Technol. Weld. Joining*. Submitted.

Woo, W., et al. 2006. "Feasibility of thermal strain measurements during quasi-steady state using neutron diffraction." *ECRS7*, September 13–17, 2006, Berlin, Germany.

Woo, W., et al. "In-situ neutorn difraction measurement of transient temperature and stress fields in a thin plate." *ECRS7 Conference*, September 13, 2006, Berlin, Germany.

Woo, W., et al. 2006. "In-situ neutron diffraction measurement of transient temperature and stress fields in a thin plate." *Appl. Phys. Lett.* **88**, 1.

D05-073: A Deuteration Facility for in vivo H-D Isotopic Labeling of Biological Macromolecules for Neutron Structural Biology and Soft Matter Science

Dean A. A. Myles and Dale Pelletier

Project Description

The purpose of this project was to establish a pilot-phase bio-deuteration laboratory for in vivo production of H/D bio-macromolecules to support the development of neutron structural biology research and user programs at ORNL's neutron scattering facilities. Neutron scattering provides a unique nondestructive tool that is able to probe delicate macromolecule complexes and higher order assemblies over a wide range of length and time scales and can provide key insights into the structure and dynamics of complex systems. These studies are enhanced by the design and production of specific, random, and uniform H/D-labeled biological macromolecules that permit selected parts of macromolecular structures to be highlighted and analyzed in situ. The development of a bio-deuteration laboratory for D-labeled macromolecules will have a significant strategic impact on neutron scattering at ORNL and will provide benefits not just in higher quality and throughput of experiments but also in extending the range, scale, and complexity of strategic biological problems that can be addressed.

The objectives of our project were as follows:

- To establish and exploit a bio-deuteration laboratory to enable the efficient production of H/D-labeled proteins/nucleic acids and other bio-molecules for the user community
- To develop and implement robust, reliable, and efficient technologies for the production of deuterium-labeled biomacromolecules
- To evaluate and exploit these reagents in improved downstream applications, including data collection and interpretation for neutron scattering at the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS)
- To train researchers from academia and industry in using these powerful techniques, thus ensuring broader access and innovative use of our neutron scattering facilities
- To expand our user base at ORNL by providing a critical "point of entry" that will attract and support users from the wider biology community

Mission Relevance

As a central training and user facility, the Deuteration Laboratory will provide a critical "point of entry" and interface that will make neutron scattering visible and accessible to a broader community, including DOE and other government laboratories, academia, and industry. Programmatic benefits will include new competencies and capabilities in labeling technologies that will bring synergy and added value to the neutron scattering programs of HFIR and SNS, will complement the development of nanoscale technologies at the Center for Nanophase Materials Sciences (CNMS), and will provide a critical resource for the analysis of biological complexes and assemblies that are of interest to programs at NIH and the DOE Genomics:GTL program. Where advanced labeling strategies are required, the bio-deuteration laboratory will team with individual scientists on proposals to their respective funding agencies, such as DOE, NIH, and NSF.

Results and Accomplishments

Providing access to the methods and tools needed to produce H/D-labeled materials at the bio-deuteration laboratory will ensure broader access and innovative use of ORNL's neutron scattering facilities. The range of materials that can be labeled in vivo extends from individual amino acid residues, to signaling peptides and hormones, and through individual proteins up to multimeric protein complexes and multi-component systems, including protein/protein and protein/RNA/DNA complexes and functional molecular motors and machines. Work in the pilot project focused specifically on the expression of deuterated recombinant proteins that have been selected for analysis by small-angle neutron scattering (SANS), reflectometry, or neutron protein crystallography. The technical approach in the pilot phase was to (1) establish protein labeling and production facilities, (2) import and implement baseline technologies and scale-up procedures for overexpression of H/D-labeled proteins in commonly used microbial (*E. coli)* systems, and (3) demonstrate the use of these materials in downstream neutron applications. A number of test and demonstration projects have been identified with collaborators who will become the future users of the bio-deuteration laboratory, the Center for Structural Molecular Biology (CSMB), HFIR, and SNS. The documented and centralized procedures for producing deuterated proteins in large quantities will be made available to all potential users of infrastructures at ORNL.

Publications

Lynn, G. W., et al. 2005. "Bio-SANS—a dedicated facility for neutron structural biology at Oak Ridge National Laboratory." *Physica B*. Submitted.

Mason, T., et al. 2005. "The Spallation Neutron Source: A powerful tool for materials research." *Physica B*. Submitted.

D06-004: Time-Resolved Analyses of Microstructure in Advanced Materials under High Magnetic Fields Using Neutrons

Gerard M. Ludtka, Frank R. Klose, Roger A. Kisner, Jaime A. Fernandez-Baca,
Gail Mackiewicz-Ludtka, John B. Wilgen, Roger A. Jaramillo, Louis J. Santodonato,
Xun-Li Wang, and Camden. R. Hubbard

Project Description

Fundamental science breakthroughs are being facilitated by high-magnetic-field studies in a broad spectrum of research disciplines. Furthermore, processing of materials under high magnetic fields is a novel technique with very high science and technological potential. However, there did not exist the capability to do in situ time-resolved neutron scattering at very high (>10 T) magnetic field strengths and at elevated temperatures. Therefore prior measurements were performed ex situ and did not capture the microstructural evolution of the samples during high-field exposure. To address this deficiency, we are establishing a high-field magnet processing and analyses system at the HFIR (High Flux Isotope Reactor) and SNS (Spallation Neutron Science) which will link the analytical capabilities inherent in neutron science to the needs of magnetic processing research. To achieve the research initiative goals, we are designing, developing, and testing high-magnetic-field instrument inserts that would provide the thermal processing and auxiliary instrumentation environment needed to run ultrahigh-magnetic-field processing experiments initially at the HFIR and subsequently at the SNS. Our goal is to be the first team to apply advanced neutron scattering to explore time-resolved characterizations of magnetically driven alloy-phase transformations and to determine ordering and magnetic moments in an alloy under transient conditions. The enhanced, in situ time-resolved materials characterization capability will be an enabler of basic science research opportunities. This work will also establish the research instrument for international community users at the HFIR and SNS.

Mission Relevance

Successful accomplishment of this research will provide unique, world-leading neutron scattering instrument environmental systems at the HFIR and SNS, thus facilitating high-magnetic-field research that will result in major scientific breakthroughs in understanding fundamental material behavior, in advancing magnetic-field-based energy-saving processing methods, and in developing the materials systems of the future across a broad range of scientific disciplines. This endeavor will establish the environmental system at the HFIR and the beamline at the SNS totally dedicated to high-magnetic-field research and therefore will become a critical component of the HFIR and SNS user programs for collaborative neutron science research. Hence, very basic through applied research programs utilizing this unique capability are anticipated to be funded through the DOE Office of Science, Energy Programs, DARPA, NIH, NASA, NSF, and industry through the many research opportunities that high-magnetic-field processing coupled with neutron science will spawn.

Results and Accomplishments

This project has accomplished several significant milestones to date. These include (1) the design and fabrication of a sample environment system for the 5-Tesla magnet at HFIR, (2) neutron scattering experiments at HFIR to develop the analysis methodology for steel alloys at ambient magnetic fields and temperature, and (3) acquisition and metallographic characterization of very-high-purity Fe-C alloys. Specifically, a sample insert was developed that provides the capability for inductively heating steel samples to 1000°C while limiting the heat load to the magnet cryostat. To minimize deleterious interactions of the neutron beam with the sample insert, an air-cooled induction coil is used to heat the sample. To facilitate the process of changing out samples rapidly, the thermally insulated steel samples are enclosed in a quartz tube that can be readily withdrawn from the magnet, which is relatively inaccessible as deployed during neutron scattering measurements. Initial neutron diffraction experiments were performed at the HFIR in the December 2005 beam cycle using steel specimens at ambient temperature. This specific accomplishment provided scoping data for developing and refining the diffraction pattern analysis methodology and lays the foundation for future elevated-temperature experiments in FY 2007. Finally, very-high-purity elemental iron and iron-carbon binary alloys were obtained and metallographic characterization performed on the as-received microstructures. The acquisition of these very-high-purity bulk samples represents a key accomplishment as the high purity represents a fundamental requirement for accurately investigating high-magnetic-field effects on shifting phase equilibria using neutron science methods.

D06-015: Infrastructure Development for Neutron Scattering for Biomembranes and Biomimetic Membranes

William T. Heller, Yiming Mo, Dean A. A. Myles, Greg S. Smith, and John F. Ankner

Project Description

Biological membranes and biomimetic systems are topologically complex and incredibly dynamic systems where function is largely effected through complex interactions between components of the system, such as lipids and proteins in biological membranes. The study of biological membranes and biomimetic systems is important to a variety of scientific disciplines, and it is an area of key strategic interest to the Department of Energy (DOE) and National Institutes of Health (NIH). Oak Ridge National Laboratory (ORNL) currently lacks the infrastructure to effectively support this science at its two neutron sources. We propose to develop the preparative capabilities, sample environments, analytic and modeling tools, and the core expertise required to support a strategic program of biomembrane, membrane protein, and biomimetic membrane research at ORNL and facilitate user community science at the Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR). Specifically, we will establish facilities and expertise for the expression and purification of membrane proteins and sample preparation for neutron reflectometry experiments. Additionally, sample environments for the neutron reflectometers will be developed that are optimized for investigations of the structure and function of biological membranes and biomimetic systems. Data analysis and modeling tools needed to interpret the data collected from these complex systems will be identified. We will demonstrate these capabilities by studying the association of specific lipids with the membrane-integral protein porin. Establishing this platform and capability at ORNL will leave us optimally positioned to contribute to the programmatic goals of DOE and NIH in this exciting field of science.

Mission Relevance

The project addresses mission goals of the DOE Office of Biological and Environmental Research's Genomics: Genomes to Life by developing the sample preparation and neutron scattering infrastructure needed to develop a molecular-level understanding of biomembranes, a critical and complex system possessed by every living cell, and biomimetic systems having technological applications. The work is also relevant to the missions of the NIH. The NIH's Structural Biology Roadmap resulted in the programs Membrane Protein Production and Structure Determination (RM-04-026) and Centers for Innovation in Membrane Protein Production (RFA-RM-04-009). The NIH program call (PA-06-119) for studies of the structural biology of membrane proteins is a continuation of a long-running program announcement serving several institutes of the NIH. By providing the infrastructure that researchers need, we will make it possible to use neutron scattering as another structural characterization tool for studying these challenging systems.

Results and Accomplishments

Good progress was made during FY 2006. User community input was solicited regarding sample environments for biomembranes and biomimetic systems. The main requirements are that the sample environments have stable and accurate temperature and relative humidity control. References to existing sample environments were supplied by the user community in response to the call. A concept design was presented to the SNS Instrument Support Group's sample environment team leader for further development. Assembling the infrastructure needed for membrane protein expression and purification, as well as for neutron reflectometry sample preparation, was driven by Dr. Yiming Mo, a postdoctoral research associate who started work in April 2006. His addition to the group provides the production and purification expertise on membrane proteins that is needed to support a user community at the ORNL neutron sources. He identified and acquired materials and equipment needed to produce membrane proteins. A number of tools needed for the analysis and modeling of neutron reflectometry data have been identified, including methods suggested by the user community. Dr. Mo led the efforts of the demonstration project. He obtained clones of two membrane proteins from researchers at the Universities of Houston and Connecticut. Expression and purification of the membrane protein porin was successful. A proposal was submitted by the project team to the National Institute of Standards and Technology's Center for Neutron Research's user program. The proposal was awarded three days of instrument time in late 2006 or early 2007.

D06-061: Small-Angle Neutron Scattering Investigations and Computational Modeling of Creep Cavitation in Nanoparticle-Strengthened Materials

G. Muralidharan, M. Agamalian, R. L. Klueh, Weiju Ren, J. P. Shingledecker, M. L. Santella, B. Radhakrishnan, and G. B. Sarma

Project Description

Ferritic/martensitic steels such as P22, P91, P92, and P122 are typically strengthened by nano-sized precipitate particles that include carbides and carbo-nitrides. Creep void formation (cavitation) occurs at prior austenite grain boundaries and precipitate interfaces during service; this phenomenon eventually leads to cracking in the fine-grained heat-affected zone (HAZ) of weldments of these steels and in the base metal and can severely limit their service lifetimes. Hence, there is a critical need to understand the role of various microstructural features that clearly affect cavitation. Small-angle neutron scattering (SANS), combined with electron microscopy and computational modeling, has the potential to develop the much-needed understanding of the process of cavity nucleation and growth. SANS and ultra-small-angle scattering (USANS) are powerful techniques suitable for the study of the nucleation, growth, and evolution of nanoscale second phases (i.e., precipitates) and voids. Computational modeling that incorporates the effects of grain and precipitate structure, as well as the spatial distribution of cavity nucleation (from the loading history), will enable interpretation of results obtained from the SANS measurements. The purpose of this project is to develop SANS and USANS techniques and supporting computational modeling approaches to help understand creep cavitation and to establish a broadly integrated capability to conduct research on a number of other important problems requiring intimate knowledge of microstructural processes.

Mission Relevance

Ferritic-martensitic steels are candidate materials for use in various energy systems, including Generation IV nuclear reactors, ultra-supercritical (USC) steam boilers, fusion reactor first-wall and blanket structures, heat-recovery steam generators, turbines, and fuel cells. This research project emphasizes the application of SANS and computational modeling in solving problems relevant to these next-generation energy sources and is consistent with the DOE missions in energy resources and science. DOE's nuclear reactor, industrial technologies, fossil energy, and hydrogen programs and the Office of Science are expected to benefit from this research. Success in the synergistic approach proposed to address fundamental aspects of materials performance controlled by phenomena that span multiple length scales will enable the Laboratory to actively pursue many areas of materials research and development related to processes that involve high temperatures and/or fine-scale structures. Materials-related programs that are part of other federal agencies, such as the DOD, also are likely to benefit from the results from this work.

Results and Accomplishments

In the first year of the project, USANS and SANS measurements were performed on an experimental grade of Fe-9Cr ferritic-martensitic steel that had been subjected to several heat-treatments but had not developed creep cavities. These heat treatments were designed to result in different (but typical microstructures) observable in these steels. USANS and SANS data from the same sample were combined to obtain a complete scattering curve that characterized the microstructure over multiple length scales, ranging from about 5 nm to 5 μm. The combined USANS/SANS work performed in this study is the first demonstration of such experiments in ferritic-martensitic steels. It was observed that the USANS and SANS data obtained from the samples varied as a function of heat treatment and, hence, the microstructural changes in the sample. Based on the potentially strong scattering expected from creep cavities, it was concluded that it would be feasible to identify scattering from such cavities. A finite-element, elasto-viscoplastic model coupled with crystal plasticity has been developed to model deformation at the mesoscale. The model is capable of computing the mean stress and the plastic strain distribution at various microstructural locations, such as grain boundaries and particle-matrix boundaries. Based on the assumption that the probability of cavitation is proportional to the product of the mean stress and the effective plastic strain, the computations were able to capture the presence of enhanced cavitation probability at certain grain boundaries.

Publication

Sarma, G. B. and B. Radhakrishnan. "Modeling the Effect of Microstructural Features on the Nucleation of Creep Cavities." *2007 TMS Annual Meeting & Exhibition*, February 25–March 1, 2007, Orlando, FL.

D06-143: Use of Small-Angle Neutron Scattering to Study Complex Systems

Kenneth C. Littrell

Project Description

Many different systems exhibit changes to structure and order on length scales ranging from nanometers to microns. Examples of such systems include complex fluids, catalytic materials, nanocomposites, coals and oil-bearing shales, metallic alloys, and novel magnetic materials. These systems are important in medicine and food science, energy and environmental remediation, and industry and engineering. SANS (small-angle neutron scattering) provides information that is complementary to and not readily measured by other techniques. We propose to develop the techniques, ancillary equipment, and software necessary to utilize the SANS1 small-angle neutron scattering instrument at the High Flux Isotope Reactor (HFIR) to probe the formation, morphology, and interactions of the nanoscale structures present in complex systems in tunable environments. In particular, we will study the phase diagram of actinide solvent-extraction systems related to the PUREX (Plutonium and URanium Extraction) process by

SANS, develop data analysis software for this and related systems, develop high-speed, high-accuracy approximations to numerically integrated SANS scattering models of cylinders and similar structures derived from them. We will also develop and test expressions for the resolution function for a lens SANS instrument, both single-axis and anisotropic 2D, including the effects of gravity, lens thickness, and lens-sample separation, and design ancillary equipment for the SANS instrument to accommodate these experiments.

Mission Relevance

The solvent extraction work directly addresses DOE missions in energy resources, nuclear security, and environmental quality by helping close the circle in the nuclear fuel cycle. Other aspects of the project support this work and DOE missions in providing top-quality scientific service to the user community in neutron science. The developments that result from this program will substantially enhance the benefits of the availability of SANS to the Scaling of Structure and Properties Research Focus Area in the Center for Nanoscale Materials Science (CNMS) for probing structures on nanometer to micron length scales on site and of experiments that would not be possible or practical at other domestic facilities due to flux limitations. The form factor calculations will also benefit DOE synchrotron (and lab instrument)–based SAXS (small-angle X-ray scattering) user program and science initiatives.

Results and Accomplishments

During FY 2006, the project's first year, we made significant progress in several areas.

1. We developed the theory describing the anticipated performance of and completed the analysis of the data measured on the one-dimensional magnetic neutron lens. We demonstrated both that the test lens performed to the theoretical expectations and that a device is possible on practical scales. We have received an expression of interest from researchers at a sister facility (ISIS at Rutherford Appleton Laboratory in the United Kingdom) for collaboration in further developments.
2. The cylindrical form factor results have been tested over a wide range of input parameters. Collaborators at the Advanced Photon Source have integrated these results into their own data analysis package.
3. We have calculated the lens resolution function for anisotropic Cartesian data.
4. Finally, we have developed a reader that will allow us to input a SANS1 data file and its associated metadata into Igor Pro for reduction and analysis using existing software packages that are familiar to the general U.S. small-angle neutron and X-ray scattering community.

Systems Biology for Energy, Environment, and Health Initiative

Systems Biology for Energy, Environment, and Health Initiative

D05-066: An Integrated Experimental and Modeling Approach for the Study of Microbial Biofilm Communities

Anthony V. Palumbo, Craig C. Brandt, Steven D. Brown, Jennifer L. Morrell-Falvey, and Mitchel J. Doktycz

Project Description

The development of new imaging and microarray techniques has enabled examination of the interactions among members of microbial communities, and this type of research is of interest to several DOE programs and outside agencies. Biofilm communities offer a spatially structured community in which we are applying these techniques to obtain data on their spatial structure and on expression of unique genes (e.g., those expressed in response to the presence of other bacteria or to growth in a biofilm). The objective of the research was to develop a foundation for the examination of microbial communities based on ORNL strengths in imaging and measurement of gene expression. We focused our attention on assessing gene expression in S*hewanella oneidensis* biofilms (with and without exposure to chromium) and in co-culturing of S*hewanella* and *Desulfovibrio*.

Mission Relevance

This research is relevant to DOE's interests in bioremediation, carbon sequestration, energy production, and bioproduct manufacturing. The methods being developed for biofilm, and mixed culture studies in this project will be applicable to DOE and several National Science Foundation (NSF) and National Institutes of Health (NIH) programs. For example, the DOE Genomes to Life Program has identified mixed cultures and communities as areas of studies in mission areas such as bioremediation and energy production. Bioremediation in sediments will take place primarily by attached bacteria that have aspects of biofilm formation. In all natural environments, the interactions of bacteria are critical so that even fully identifying the functions of genes that are present in bacteria that have been sequenced by DOE or metagenomic sequencing efforts cannot be completed without the mixed culture studies for which we developed methods in this project.

Results and Accomplishments

We have obtained data to compare gene expression in biofilms of S*hewanella oneidensis* MR-1 with stationary and exponential-phase planktonic systems. The data suggested that biofilms may have distinctive patterns of gene expression when compared with planktonic bacteria. Cytochrome genes such as mtrA-B and omcA-B were more highly expressed in biofilms. This expression is indicative of oxygen limitation, and the degree of differential expression of these genes was greatest compared with stationary-phase bacteria. In contrast, transcripts from iron-uptake genes were less abundant in biofilm cultures, and the greatest degree of differential expression was in comparison to stationary-phase bacteria. We monitored biofilms of *Shewanella oneidensis* cells expressing GFP (green fluorescent protein) with a confocal laser scanning a progressive aggradation of the community in the flow cell. The average size of contiguously occupied areas increased in all dimensions, suggesting the formation of larger and more interconnected blocks of cells. We also completed experiments comparing gene expression of *Shewanella oneidensis* MR-1 exposed to chromium in a biofilm to unexposed cells. The effects in biofilms will be compared to published data on the effect of chromium on planktonic cells. In addition, we have completed a set of experiments on co-culturing of *Shewanella oneidensis* and *Desulfovibrio* in batch cultures. We used quantitative polymerase chain reaction (QPCR) to determine the relative levels of each bacterium at various stages of growth. We harvested mRNA at different growth phases (exponential, stationary) for microarray gene expression studies. The gene expression under these conditions will be compared with gene expression for cells grown in pure culture.

D05-069: Inhalation Exposure of Processed Nanoparticles: Exploring Nanotechnology and Biological Links

Meng-Dawn Cheng, Brynn J. Voy, David B. Geohegan, and Dabney L. Johnson

Project Description

Nanotechnology and nanoscience are expected to enable the production of smart, autonomous, and reliable materials and products to be used in our daily lives in the 21st century. However, if we have learned anything from human history, it is that history repeats itself. For example, while we are developing new nanomaterials across the globe on a daily basis, there is a lot we do not understand about the effects of these new materials on human health and the environment. To avoid unanticipated impacts, as has happened with the introduction of other new technologies (e.g., nuclear energy, pesticides), it would be wise to gain an understanding of the behavior of nanoparticles in the human body and environmental systems.

This project explored how nanoparticles interact with biological systems associated with nanometer-scale materials and structures by asking the following questions:

- What aspects of nanomaterials/nanostructures contribute to biological effects?
- How would these attributes change in the environmental and/or physiological conditions?
- What are the health consequences of surface modification on nanomaterials (e.g., material synthesis, decoration, air chemistry, environmental processing, and so on)?
- What are the cellular and physiological mechanisms of health effects of the nanomaterials (biological responses)?

Our 2-year efforts have been directed toward the following sub-projects:

- Conduct an investigative survey of current techniques for nanotoxicology evaluation and risk assessment

- Probe physiological, immunological, and genetic responses to exposure of precisely fabricated metal oxides (passivated aluminum nanoparticles, CdSe Qdots, and NiO nanoparticles) and carbon nanoparticles (carbon nanotubes and carbon nanohorns)
- Develop new and novel methods for controlled generation of aerosol aggregates for inhalation exposure experiments
- Test a novel air-cell interface device for nanoparticle exposure and establish a protocol for nose-only animal nanomaterial inhalation experiment
- Advance our understanding of carbon nanoparticle formation during nanomanufacturing production processes

Mission Relevance

Upon the completion, we expect this project will initiate a new frontier of science on how nanomaterials/nanostructures interact with biological systems. This science is of tremendous importance to the biocompatibility and safety of the nanomaterials that DOE centers across the country and commercial sectors are developing. The improved knowledge will also enable DOE to protect workers from exposure to possible nanomaterial toxicity as well as to unwanted nanoscale by-products and wastes. The accumulated knowledge could assist in minimization of potential environmental impacts caused by the new materials. To other federal agencies, this work could advance areas of biomedical diagnosis, medicine, and the environmental research that support to the missions of the NIH, FDA, and EPA.

Results and Accomplishments

Lack of information regarding possible toxicity of nanomaterials has hampered a clear distinction of ultrafine nanoparticles (as in waste products) from engineered nanoparticles (as in commodity). This knowledge vacuum is caused by plethora of technical problems associated with producing, handling, and evaluating nanoparticles and nanoparticle aggregates. Nanoparticle aggregation alters the properties of nanoparticles and hinders precise toxicological experimentation unless the state of aggregation can be controlled. Techniques to produce well-controlled aggregates were developed via an aerosol route using ultrasonic and electrospray generation principles suitable for cellular or animal studies employed in the project. The bioavailable toxicity of metal oxides such as NiO, TiO_2, and aluminum nanoparticles was reduced when the surfaces of these materials were coated by surfactants such as PEG and PLG. The protective coating was damaged readily in an oxidizing environment, leading to an enhanced toxicity of these nanoscale metal oxides. Pure carbon nanostructures (nanohorns) were found to be benign at concentrations realistic to actual exposure; however, when they were modified by ozone, the benign nanomaterials triggered severe biological responses. Free radicals and peroxides were identified on oxidized carbon nanostructures; the oxidants (measured by ROS) invoke cellular inflammatory responses (measured by multiple cytokines) and cellular apoptosis. Genomic profiling shows multiple active regulations (up or down) of mouse cell lines upon short-term exposure to undecorated CNH aggregates; however, a link to phenotype is yet to be established.

Publications

Chen, D. and M. Cheng. “Using a Fast-Scanning Electrical Nanoparticle Sizer to Characterize Nanoparticles from Laser Ablation.” J. Aer. Air Qual. Res. Submitted.

Cheng, M., et al. "Study of Formation and Production of Carbon Nanohorns Using Continuous In-Situ Characterization Techniques." Nanotechnology. Submitted.
Mahurin, S. M. and M. Cheng. "Generating nanoscale aggregates from colloidal nanoparticles by various aerosol spray techniques." Nanotoxicology. Submitted.

D05-071: Genome-Enabled Detection of Differential Mortality in a Northern Temperate Forest Ecosystem

Gerald A. Tuskan, Stephen P. DiFazio, and Tongming Yin

Project Description

The primary purpose of this investigation was to determine the relative age of the existing aspen stands within Rocky Mountain National Park (RMNP) and Yellowstone National Park (YNP). We have successfully designed microsatellite (SSR) markers for the characterization of somatic mutations. We have sampled populations of aspen (*Populus tremuloides*) in RMNP and YNP that were used to develop SSR marker sets for application to archived aspen samples from YNP. In addition, we estimated the degree of linkage disequilibrium in the sampled RMNP population. We have also characterized the clonal structure of the existing aspen stands in both parks and have derived estimates of mutations rates that will be applied to estimates of clone age.

Mission Relevance

This work is relevant to the Environmental Science and Molecular Ecology subprogram within the DOE Office of Science. By employing population-level systems biology approaches, we are exploring the possibility that variation at the DNA level is associated with natural variation in intact wild populations of *Populus*. We are attempting to reconstruct the process of adaptation by examining the genome over time and space. If successful, we will use this molecular signal of adaptation to ultimately build a predictive model of ecosystem-level changes as affected by global climate change.

Results and Accomplishments

We tested over 2000 primer pairs, screened out 47 pairs, and amplified the most variable microsatellite loci within the genome. The average number of alleles revealed per primer pairs was 12.5. These selected primer pairs were intensively screened, thus providing a valuable resource for population genetics studies in natural aspen stands. We genotyped 2495 samples (1 sample was amplified as consensus genotype control; the other four samples from the same tree were pooled to detect mutation) from 499 trees collected at 12 stands from RMNP. We collected 2400 new samples on 490 trees from YNP and processed the DNA extraction from these samples. Thirty-nine microsatellites were investigated. We increased the resolution of the MicroCat scanner to 8 microns, producing a high-resolution image useful in determining the transaction age of the sampled trees. Our findings also indicate this ecosystem is delicate as triploids are incapable of sexual reproduction, and the disappearance of one genotype is irreversible loss of adaptive genes from the gene pool. This result has important ramifications on how to protect this ecosystem. Finally, 18 somatic mutations were detected among the 2495 leaf samples. Twelve occurred among ramets in single clones and six were found within trees. The mutation rate (0.7%) is significantly higher than the expected rate (0.1~0.001%).

D05-098: A Systems-Biology Framework for Post-Genomic Microbiology

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Project Description

The purpose of this project was to develop a computational framework for the integration and systems modeling of key *R. palustris* pathways using available experimental and computational information. This activity has been used to advance our system-level understanding of *R. palustris* cellular machinery and provide the basis for potential applications such as hydrogen production using nitrogenase pathways. The major thrusts of the project have been focused on regulatory interactions as well as codifying the necessary metabolic pathways and their parameters. These are a necessary foundation for approaching quantitative models. One successful goal of the project was to build an active collaboration with ORNL experimental efforts devoted to the protein interactions elucidation. During the project, we (1) developed a version of the microbial encyclopedia for storage and processing of *R. palustris* interaction and pathway information utilizing various data sources; (2) estimated protein function and interactions based on protein structure predictions with PROSPECT and other tools; (3) installed a database for storing and managing network pathway systems and models and predicted *R. palustris* metabolic systems; (4) reconstructed initial carbon-nitrogen fixation pathways in *R. palustris*. We followed these activities with a targeted effort to utilize the collected information for regulatory flux balance modeling of selected pathways (e.g., the nitrogenase metabolic pathways and their regulation). These should eventually be suitable for systems simulations in key application areas for *R. palustris*.

Mission Relevance

This effort is addressing the goals of the Office of Biological and Environmental Research (OBER) Genomics:GTL Program. Our research focuses, in particular, on pathway and network systems that can eventually be utilized in the production of hydrogen as an energy fuel and, more generally, on elucidating systems and molecular machines which carry out such functions in environmental microbes. The Genomics:GTL program seeks to achieve a systems-level understanding of microbes (including fungi) directly relevant to DOE mission needs in energy (cleaner energy, biomass conversion, carbon sequestration) or the environment (cleanup of metals and radionuclides at DOE sites). Our work is also relevant to the hydrogen fuel initiative of 2003, which encourages research and development of carbon-neutral hydrogen production technologies geared towards supplying the needs of a future hydrogen economy. In some specific cases, details of the biological processes linked to hydrogen metabolism and of the enzymes involved as essential catalysts have been investigated and are reasonably well known. However, efforts to understand the variety of organisms and the diversity of biochemical mechanisms that participate in this extensive biological hydrogen economy are still at an early stage. The emergence of tools for genomic analysis of microorganisms and for dissecting their interlocking metabolic functions presents an opportunity for extremely rapid progress in this promising area of research.

Results and Accomplishments

The project has made progress in three tightly connected tasks: (1) create a comprehensive annotated map of protein-protein interactions in *R. palustris* using the whole set of available predictive algorithms, public databases, and data mining tools; (2) devise a feedback loop between the implemented map of protein-protein interactions and ongoing pull-down and whole proteome experiments at ORNL; (3) build a capability for integration of regulatory and metabolic information, with the goal of supporting regulatory-metabolic flux balance analysis models and other large-scale simulations of reconstructed constructed systems. These elements are summarized as follows:

R. pal data integration. A microbial encyclopedia database has been constructed for *R. palustris* as an integrated data infrastructure with advanced querying capabilities across a large and diverse set of data sources, including sequence, structure, and protein interaction databases. We have significantly extended the capabilities to accommodate storage and processing of the protein interaction information. Incorporation of the KEGG pathways for *R. palustris* forms the basis for our efforts to systematically reconstruct the selected group of pathways, preparing ground for the predictive simulations of *R. palustris* systems biology such as flux models and flux models with transcriptional regulation.

Data sources and algorithms. Seven data sources have been integrated into the *R. palustris* microbial encyclopedia to build evidence for protein-protein interactions important for *R. pal* system modeling. Additionally, complete datasets based on COGs, Pfam, and BLAST homologies have been produced and loaded for two bacteria: *E. coli* and *R. palustris*.

*Genome-wide structure predictions and function estimates***.** We comprehensively used PROSPECT and ROSETTA to build structure models for *R. palustris* proteins to assist in assigning function (a histogram of best Z-scores for each gene). About half (1804) of the genes have significantly confident matches, with a Z-score > 10. Overall, more than 70% of the *R. palustris* proteins studied had template-based structure models that are expected to be accurate for these genes, thus providing valuable clues to functional class.

*Analysis of the selected complexes***.** We have used a non-redundant and verified dataset of 1173 PDB complexes to identify protein complexes in *R. palustris*. Sequence profiles built by a PSI-BLAST search of the NCBI NR database were used to align *R. palustris* protein sequences to the proteins in the PDB complexes dataset. Significant hits were found for subunits in 55 different PDB complexes. The predictions not only identify proteins that co-occur in the same complex but give direct clues about the proteins in the direct physical interactions. The results of this analysis form the basis for experimental validations. In this analysis, multiple *R. palustris* complexes were predicted for nitrogenases, which are a focus of our effort. These enzymes catalyze the reduction of dinitrogen to ammonia through the transient association of an a2b2 heterotetrameric MoFe protein and a homodimeric Fe protein. They also produce molecular hydrogen as a by-product. Numerous homologs were found for each of the three distinct subunits of an *A. vinelandii* Mo-Fe nitrogenase complex. A total of 21 *R. palustris* proteins matched the MoFe component a and b chains and 14 proteins matched the iron component. Most matching proteins were annotated as nitrogenases, but some were not. It is clear that experiments are necessary in order to determine which of these candidate subunits associate into a functional nitrogenase complex. The elucidation of the structure and function of nitrogenase molecular machines is critical for both an understanding of the ecologically important process of nitrogen fixation and engineering of *R. palustris* for hydrogen production as a potential fuel.

D05-099: Molecular and Cellular Imaging

Jennifer L. Morrell-Falvey, Mitchel J. Doktycz, and David C. Joy

Project Description

Imaging technologies that complement DNA sequencing, gene expression, and proteomics studies are needed to provide a comprehensive description of molecular function at the cellular level. These imaging techniques need to validate bioinformatic predictions as well as illustrate how genomic instructions are executed across spatial and temporal dimensions. The objective of this project is to develop advanced approaches to access biochemical pathways in the live cell using a combination of confocal laser scanning microscopy, atomic force microscopy, electron microscopy, and automated image analysis. We have applied these methods to the study of carbohydrate metabolism in *Escherichia coli* and surface elasticity in enteroaggregative *E. coli.* We have also developed automated image analysis for the study of rotavirus particles.

Mission Relevance

The project addresses mission goals of the DOE Office of Biological and Environmental Research, Genomics:Genomes to Life program by observing molecular processes and interactions in live cells in order to understand the principles underlying the structural and functional design of living systems and ultimately to develop the capability to model, predict, and engineer optimized microorganisms. The work is also relevant to the missions of the National Institutes of Health (NIH). In particular, the National Institute of General Medical Sciences (NIGMS) is interested in promoting the development of materials/methods for imaging subcellular structures at the nanoscale in living cells (PAR-07-270). The development of approaches to access biochemical pathways in live cells using a combination of modalities will help meet these goals.

Results and Accomplishments

To monitor the distribution and dynamics of the *E. coli* glucose transporter $IICB^{Glc}$ (encoded by *ptsG*) and the transcriptional repressor Mlc, we genetically modified *ptsG* and *mlc* to encode GFP-tagged proteins expressed from their native promoters. In the presence of glucose, $IICB^{Glc}$-GFP was localized to the cell membrane using confocal laser scanning microscopy. We confirmed its localization to the cytoplasmic membrane by detection of $IICB^{Glc}$-GFP in *E. coli* cells in which the outer cell walls had been removed. Mlc-GFP, on the other hand, was detected in the cellular region containing the nucleoid. These tagged proteins were also determined to be fully functional by a variety of genomic and physiological methods. In addition, we also used atomic force microscopy (AFM) to measure the cell surface elasticity of enteroaggregative *E. coli*, which is pathogenic and produces severe diarrhea in humans. A mutant strain which does not produce the cell surface protein dispersin is not pathogenic. We compared the cell surface elasticity of wild type and dispersin mutants using AFM force-distance spectroscopy as an initial step to understand the role of the dispersin protein in pathogenocity. In an attempt to facilitate quantitative AFM imaging, we also developed an automated image analysis routine to extract data from AFM images. As a test case, we imaged viral particles and developed an automated algorithm to extract average dimensional characteristics of the particles. This algorithm can be further extended for analysis of other biological samples imaged by AFM.

Publications

Beckmann, M., et al. 2006. "Measuring cell wall elasticity on enteroaggregative Escherichia coli wild type and dispersin mutant by AFM." *Ultramicroscopy* **106**, 695.

Venkataraman, S., et al. 2006. "Automated image analysis of atomic force microscopy images of rotavirus particles." *Ultramicroscopy* **106**, 829.

D06-028: Biomass Ethanol from *Clostridium thermocellum*: Linking Bioprocessing with Systems Biology for Bioenergy

Jonathan Mielenz, Babu Raman, Catherine McKeown, Steve Brown, and Shuba Ireland

Project Description

The technology to produce ethanol from lignocellulosic biomass has been known for years, but concerns regarding the cost and efficiency of the process have limited its use. A game-changing microbe is *Clostridium thermocellum*, which is capable of both very rapidly hydrolyzing cellulose with its own cellulases and producing ethanol and other products by fermentation. This combining of unit operations, called consolidated bioprocessing, will significantly reduce the cost of producing ethanol from cellulose-containing material such as plant biomass. However, more information regarding the basic metabolism of *C. thermocellum* is needed before its use to produce ethanol can be further developed. Filling this information gap will lead to more efficient production of ethanol by *C. thermocellum* at a lower cost. Integrated, modern systems biology tools are being used to better understand the biology of *C. thermocellum* using whole-genome microarrays generated from available genome sequence data. The organism's transcriptome, proteome, and fermentation end products are being examined at selected times during fermentation of either cellobiose or cellulose to dissect the regulatory networks and molecular mechanisms involved during ethanol fermentation. This will be a first combined demonstration of the full capabilities of ORNL's system biology potential applied to fermentation.

Mission Relevance

The DOE Office of Biomass Program (OBP) has actively supported biomass ethanol technology research, development, and demonstration (RD&D) for over 25 years. Its multi-year program plan included such work within the advanced technology development section. Technical management at OBP supports the mission of this project. In addition, the concept of consolidated bioprocessing, which this fermentation system represents, has been mentioned as an important bioengineering concept by senior management in the Office of Science. The primary outcome of this research will be building a stronger foundation for lower-cost biomass ethanol fermentation, thus improving national security, our environment, and our rural economy. In addition, this research will directly support efforts to reduce the cost of biomass ethanol production needed to meet the President's Advanced Energy Initiative goal of replacing 30% of the nation's gasoline use with biofuels by 2030.

Results and Accomplishments

We met all our goals for this year, which included growth and maintenance of *C. thermocellum* on cellobiose and cellulose, testing RNA and protein isolates from these cells, constructing a whole-genome microarray for 3163 predicted protein-encoding genes, testing the quality of the microarray, conducting 2-L fermentations with cellobiose, and pilot testing the microarray. Initial challenges were growth of *C. thermocellum*, a thermophilic strict anaerobe, in a highly reproducible manner critical for consistent fermentations and eventual expression data analysis. This was accomplished by the development of a set protocol for culture growth, storage, and controlled regrowth to start the fermentations. Microarray hybridization conditions were improved to better suit the G + C of *C. thermocellum* genes, resulting in a higher-quality-array hybridization. The initial cellobiose fermentation microarray analysis has been completed as well. Protein analysis clearly detected distinct difference in the proteins present in cellobiose-vs-cellulose fermentations, and these results will serve as the foundation for further proteomic analysis during the project's second year. In addition, the decision was made to accelerate the cellulose fermentation development into third quarter of the project's first year to provide earlier differential microarray data. Reproducible cellulose fermentations were developed along with isolation of intact RNA from these fermentor samples. Finally, with the closure of the genome sequence for *C. thermocellum* (no longer draft sequence), additional genes were sought and new microarray gene oligonucleotides were obtained to update the microarray for the final genome sequence from the Joint Genome Institute.

D06-033: A Model System for Analyzing Whole-Body Toxicity of Toxic Industrial Chemicals (TICs), Toxic Industrial Materials (TIMs), and Chemical Warfare Agents

Brynn H. Voy, Elissa J. Chesler, Jennifer Sedowski, and Wayne H. Griest

Project Description

There is great concern by the United States military and homeland security organizations that unguarded stockpiles of industrial process chemicals can be used as highly effective chemical warfare agents. An example is methyl isocyanate (MIC), which killed and injured thousands following its accidental release at a Bhopal, India, Union Carbide plant in 1984. The extent of toxicity among Bhopal survivors varied widely across the exposed population; part of the variation was attributed to genetic susceptibility. The Bhopal accident is one of countless examples of how an individual's genetic background impacts his/her response to environmental factors. Our goal is to establish ORNL expertise in systems biology approaches to gene-environment interactions while taking advantage of mouse genetic reference populations maintained at ORNL. Environmental factors include a diverse spectrum of potential exposure agents; we have chosen MIC because of its potential relevance to homeland security. The genetic reference population in use is a panel of BXD (C57BL/6J X DBA/2J) recombinant inbred (RI) strains. Our strategy for this project is to identify phenotypic traits that respond to MIC in a predictable manner and then use these measures as the basis for a survey of MIC response across a genetically diverse BXD RI strain population. Integration of these meaningful physiological endpoints with gene expression profiling in a relevant target tissue and with existing genotype data forms the basis for our strategy to identify molecular networks of MIC response and genetic susceptibility.

Mission Relevance

The long-term benefit to military and homeland security agencies will be twofold; first, we can identify those genetic variants that will tend to make individual soldiers particularly sensitive to chemical exposures, and second, we can point the way to molecular mediators of response that might make good therapeutic targets. In particular, our results from using BXD strains as a model for gene-environment interactions should benefit the Genes and Environment Initiative recently launched by the National Institute of Environmental Health Sciences and the Counter-measures against Chemical Threats Program at the National Institutes of Health.

Results and Accomplishments

We have accomplished the following during the first year of this project: (1) established consistent MIC delivery in mice by subcutaneous injection; (2) identified informative physiological measures that can be used to monitor the MIC response in mice and that can be made with the necessary throughput; (3) identified and acquired the instrumentation necessary for phenotype collection; (4) performed a dose and time course analysis of MIC response; (5) initiated a survey of a panel of RI BXD mouse strains, including profiling changes in blood chemistry and body temperature and collecting tissues for RNA and transcriptomic analyses; and (6) performed an initial screen for changes in the expression of DNA damage response genes in blood as potential biomarkers of MIC exposure.

D06-034: Systems Biology of the Mammalian Cilium: A Cellular Organelle Essential for Human Health and Development

Edward J. Michaud, Cymbeline T. Culiat, Mitchell L. Klebig, and Bradley K. Yoder

Project Description

Primary cilia are microtubule-based organelles that project from the surface of cells in organisms as diverse as green algae and humans. Primary cilia function as biochemical and mechanical sensors for the cell, receiving information from neighboring cells and from the environment. Cilia play critical roles in human development and physiology, as evident from numerous genetic disease syndromes arising from defects in cilia. Symptoms of these diseases include abnormalities in left-right sidedness, retinal degeneration, hydrocephaly, infertility, obesity, respiratory distress, and cystic lesions in the kidney, liver, and pancreas. Recent comparative genomics and proteomics studies revealed that the primary cilium is composed of about 300 to 500 proteins, but most of their functions are unknown. We are using *Caenorhabditis elegans* (worms) and *Mus musculus* (mice) as model organisms to determine the biological functions and interactions of highly conserved cilia proteins. The major focus of this project is on generating mutations in orthologous mouse cilia genes with a state-of-the-art, high-throughput, and cost-effective mutagenesis strategy developed here at Oak Ridge National Laboratory. The phenotypes of mutant mice will be examined at the molecular, cellular, and whole-animal levels, which will provide insights into the assembly and function of cilia. This work may also facilitate the development of new methods for the diagnosis, treatment, and prevention of cilia diseases.

Mission Relevance

The DOE initiated the Human Genome Project and played a major role in the completion of the human genome sequence. The DOE, through the Joint Genome Institute, continues to provide the scientific community with DNA sequences of many other prokaryotic and eukaryotic organisms. These sequenced genomes are facilitating innumerable comparative genomics and proteomics approaches, including the identification of the "cilia proteome," which would otherwise have been impossible without these sequences. This project will help annotate the conserved cilia proteome in humans by initiating a systems-biology-based understanding of cilia assembly and function through mutagenesis of the homologous genes in mice. This work also benefits the National Institutes of Health (NIH). Symptoms of cilia diseases in humans include abnormalities in left-right sidedness, retinal degeneration, hydrocephaly, infertility, obesity, respiratory distress, and cystic lesions in the kidney, liver, and pancreas. Therefore, many institutes within the NIH will be potential sources of follow-on funding, including the NCI, NEI, NIA, NIAMS, NIBIB, NICHD, NIDCR, NIDDK, NIGMS, and NINDS.

Results and Accomplishments

Major research accomplishments in FY 2006, the first year of this project, included the following five areas. (1) We constructed multiple translational green fluorescent protein vectors for the localization of candidate cilia proteins in *C. elegans* and produced multiple transgenic lines of *C. elegans*. (2) We obtained multiple mouse gene-trap embryonic stem-cell lines for cilia genes and generated chimeric mice harboring mouse gene-trap mutations. (3) We completed a conditional knockout vector for one cilia gene and generated chimeric mice. (4) We are screening 22 mouse cilia genes in the Cryopreserved Mutant Mouse Bank (CMMB) resource for ethylnitrosourea(ENU)-induced genetic mutations. (5) Finally, we identified six ENU-induced point mutations in three mouse genes in the CMMB and are using frozen sperm to recover live mutant mice.

Publications

Michaud III, E. J., et al. 2005. "Efficient gene-driven germ-line point mutagenesis of C57BL/6J mice." *BMC Genom.* **6**, 1.

Michaud III, E. J., et al. 2005. "Gli2 and Gli3 Localize to Cilia and Require the Intraflagellar Transport Protein Polaris for Processing and Function." *PLoS Genetics*. **1**, 480.

Michaud III, E. J. and B. Yoder. 2006. "The Primary Cilium in Cell Signaling and Cancer." *Cancer Research*. **66**, 6463.

D06-071: Accelerated Domestication in *Populus*: Harnessing the Recently Sequenced Genome for Bioenergy Crop Production

Timothy J. Tschaplinski, Tongming Yin, Xinye Zhang, Xiaohan Yang, Lee Gunter, David Weston, Nancy Engle, Sara Jawdy, Maud Hinchee, and Don Kaczmarek

Project Description

The recent sequencing of the poplar (*Populus* sp.) genome provides a tremendous opportunity to harness this genetic resource for the purpose of increasing bioenergy crop production by identifying the fundamental constraints on productivity and addressing those constraints using modern genomic tools. The goals of this project are to identify candidate genes for drought (dehydration) tolerance in *Populus* using a comparative genomics approach and to determine the function and potential economic value of these candidate genes via transgenesis. The rationale for the study is based on our previous identification of quantitative trait loci (QTL) in a three-generation inbred *Populus trichocarpa x deltoides* (TxD) family 822 at Corvallis, OR, including 364 F_2 progeny. After sampling over 1400 trees, two large-effect QTL for osmotic potential were detected that explained 43.6% and 32.1% of F_2 phenotypic variance. Specifically, we are

1. identifying candidate genes associated with large-effect QTL for dehydration tolerance in two hybrid poplar pedigrees,
2. cloning the homologs of candidate genes that are transcription factors for dehydration tolerance from other species,
3. engineering the poplar candidate genes for up- and down-regulation for transgenesis,
4. producing multiple lines with which to create a range of phenotypic variation, and
5. validating early phenotypic expression using metabolomics.

Our goal is to transform highly productive, albeit drought sensitive, TxD hybrids to create drought-tolerant clones that remain productive under limited water availability. Increasing dehydration tolerance will increase stand productivity, improve overall feedstock uniformity, and reduce production risk and the cost of supplying biomass feedstocks for the production of alternative fuels.

Mission Relevance

This work benefits the Office of Biological and Environmental Research (OBER) by testing the concept of accelerated domestication and leverages the Office of Science's efforts to sequence the *Populus* genome. OBER currently funds research in the Carbon Sequestration Using the Poplar Genome program and has created a new program targeting genomic research in *Populus*, which can benefit from this project. Similar genomic approaches for accelerated domestication will apply to herbaceous energy crops that are of interest to the U.S. Department of Agriculture Agricultural Research Service (USDA-ARS). The Energy Policy Act of 2005 and the resulting national biomass initiative are specifically aimed at improving biomass technologies and increasing the amount of biopower, biofuels, and bioproducts used. The research will contribute to the President's goal for the nation of producing 30% of its transportation fuel from biomass. Responsible agencies include the Environmental Protection Agency, USDA, DOE, and the National Science Foundation.

Results and Accomplishments

A large genetic marker linkage map for TxD family 822 was created by screening 568 simple sequence repeat primer pairs selected from the poplar consensus map. Of the 471 primer pairs that generated segregating loci in one or both parents, 196 primer pairs were selected based on their consensus position and were amplified in 93 F2 progeny to build the framework map for family 822. This map was used in conjunction with osmotic potential data to reidentify two large-effect QTL for drought tolerance. The annotated gene sequence was then aligned with the target QTL regions (for both TxD families 331 and 822) to produce a list of six candidate dehydration tolerance genes in *Populus* for further functional analysis following transformation by ArborGen LLC (Summerville, SC) to produce poplar clones with constructs containing up- and down-regulated candidate genes. Two DREB genes were identified from the poplar gene sequence that have a high similarity match with Arabidopsis DREBs that are known drought-tolerant transcription factors (TF). *Populus* DREB2A is located in the large-effect QTL marker interval on linkage group (LG) X. Our best candidate gene associated with the large-effect QTL identified in family 331 is the poplar ortholog of AREB1/ABF2, which is located on LG II and is another known drought TF. Constructs with up- and down-regulated function were prepared and sent to ArborGen for transformation of a pure eastern cottonwood (*P. deltoides*) clone. We forwarded our concept of accelerated domestication at four meetings, and prepared four papers, including a *Science* publication.

Publications

Tschaplinski, T. J., et al. 2007. "Identification of QTLs associated with biomass production in hybrid poplar. I. Heterosis and the stability of QTLs across contrasting environments." *Tree Genetics & Genomes*. Submitted.

Tschaplinski, T. J., et al. "Identification of QTLs associated with biomass production in hybrid poplar. II. Relationship among QTLs for crown architecture and stem growth." *Tree Genetics & Genomes*. Submitted.

Tschaplinski, T. J., et al. 2006. "Phenotypic variation and quantitative trait locus identification for osmotic potential in an interspecific hybrid inbred F_2 poplar pedigree grown in contrasting environments." *Tree Physiol.* **26**, 595.

D06-136: Disentangling Soil Respiration Using Genomic Techniques

Aimee Classen, Christopher Schadt, and Richard Norby

Project Description

Soil respiration (R_{Soil}) is an integrator of ecosystem metabolism and a key component of the interaction between the terrestrial biosphere and the atmosphere. Separation of R_{Soil} into component fluxes is an important research priority, but no extant techniques can unambiguously separate plant from microbial respiration. We hypothesize that processes measured at the level of gene transcripts will be predictive of organismal respiration, which in turn can be used to estimate ecosystem-scale respiration. We propose to devise a new approach for predicting the effects of environmental change on the integrated metabolism (as represented by R_{Soil}) of a diverse old-field ecosystem. We will use quantitative, real-time polymerase chain reaction (PCR) to assay portions of the ecosystem transcriptome that we predict will be indicative of plant and microbial respiratory activity. We will also develop and validate our methods using controlled incubations and then apply the approach to analysis of R_{Soil} in a complex old-field environment.

Mission Relevance

This project will directly benefit research programs in the DOE Office of Biological and Environmental Research (OBER). The primary goal of the Program for Ecosystem Research (PER) is to understand, and be able to predict, the effects of environmental changes associated with energy production on the structure and functioning of terrestrial ecosystems. PER has specifically encouraged explorations into the transfer of information across levels of biological organization and has encouraged the use of genomics in ecological research. Thus, our goal of using genomic tools to understand process response and enable ecosystem monitoring is consistent with the overall goals of the OBER.

Results and Accomplishments

We have successfully accomplished the following:

1. tested and optimized nucleic acid (DNA and RNA) extraction protocols from old-field plants and soil, resulting in good quantity and quality DNA that is amplifiable with primers designed for this project
2. assayed microbial diversity in old-field soils by constructing clone libraries targeting ribosomal genes for both bacterial and fungal communities
3. assessed and selected two target enzymes, citrate synthase for the tricarboxylic-acid cycle and enolase within the glycolytic pathway, completing the initial design, and initiated laboratory testing of degenerate primers targeting these two genes
4. targeted citrate synthase of the dominant soil bacterial group the Proteobacteria
5. validated the proposed assay using ribosomal primers targeting ribosomal ribonucleic acids (16S rRNA for bacteria, 18S rRNA for fungi, and 26S rRNA for plant)
6. hired Aimee Classen, an ecosystem ecologist, in October 2005 and Hector Castro (post-doctoral fellow), a microbial ecologist, on January 30, 2005

D06-137: Photoregulated Peptide–Protein Interaction Systems for Bionanotechnology Applications

Robert F. Standaert

Project Description

This project centers on a combined chemical and biochemical approach to developing light-responsive peptide–protein interaction pairs that have light-tunable affinity and can be coupled to other systems of interest. The peptide partner in each case is modified by the installation of a photoresponsive amino acid that isomerizes reversibly upon irradiation. Key challenges include the design and synthesis of the amino acids, identification of effective sites for their installation, and protein affinity measurements for photoisomeric forms of the peptides. The methodology is in principle broadly applicable, but this project is focused on two specific peptide/protein pairs selected for their versatility and ready applicability to bionanotechnology applications.

There are two major long-term objectives driving the development of light-regulated interaction systems. The first is remote control of biological systems. Controlled molecular association is a fundamental process governing the structure and function of cells. Tools that enable the extracellular manipulation of molecular association within cells will enable both the dissection of complex signaling pathways and the non-invasive manipulation of cell functions, with applications ranging from basic biology to tissue engineering. The second is light-directed patterning and assembly of peptide- and protein-based materials under biocompatible, aqueous conditions. Use of light to regulate the assembly of these materials would provide exquisite spatial resolution as well as precise temporal control and the ability to create dynamic structures that can be reconfigured in real time for diverse applications.

Mission Relevance

This work is relevant to a number of programs within DOE and other major federal agencies. With regard to DOE, the methods being developed are particularly well suited to the Genomics:GTL program (DOE, Office of Biological and Environmental Research) and projects within the Center for Nanophase Materials Sciences (CNMS, sponsored by the DOE Office of Basic Energy Sciences). Our methods will have broad applicability in life science and materials research and are thus also of interest to other agencies, particularly the National Institutes of Health (NIH) and Department of Defense (DOD). Proposals based on the work described here have been submitted to the National Cancer Institute (NCI), National Institute for Biomedical Imaging and BioEngineering (NIBIB), and the Defense Threat Reduction Agency (DTRA).

Results and Accomplishments

The goals of the project have been broken down into two major tasks, the first associated with the remote control of cells and the second with light-regulated materials assembly. Good progress was made during the first year of the project. For both tasks, a central requirement is the availability of suitable photoresponsive amino acids. A major accomplishment has been to prepare stocks of such compounds in forms suitable for use in solid-phase peptide synthesis, to study the photochemical behavior of selected examples, and to publish a paper on findings pertaining to several new photoresponsive amino acids developed. One important finding is that the new amino acids have photochemical properties (good photochemical interconversion of isomeric forms and slow dark interconversion) well suited for application to the project. A second accomplishment has been the preparation of fluorescently labeled control peptides, acquisition and setup of instrumentation for peptid-protein binding measurements, and pilot binding experiments with a target protein. Several candidate peptides incorporating the photoresponsive amino acids have been prepared and are pending evaluation. A third accomplishment has been the identification of a new class of ligand for the $GABA_C$ r1 receptor, a protein of central importance in vision and one of the targets for achieving remote control of cellular function.

Publication

Standaert, R. F. and D. S. B. Park. 2006. "Abc Amino Acids: Design, Synthesis, and Properties of New Photoelastic Amino Acids." *J. Org. Chem.* **71**, 7952.

D06-139: Functional Analysis of the Role of microRNAs in Cancer

Yisong Wang, Mitchell Klebig, Edward J. Michaud, Yun You, and Dabney Johnson

Project Description

MicroRNAs (miRs), a class of the non-coding small regulatory RNA family, have recently been shown to regulate gene expression during embryonic development, tumorigenesis, virus infection, cell proliferation, and apoptosis. More than 400 miRs have been identified experimentally in humans. Expression profiling analysis has identified about 30 miRs that are deregulated in cancer cells so far, but none of them have been functionally characterized. We propose to generate mutations that disrupt the function of some selected miRs to see if these alterations change the cancer outcome in mice. Gene disruptions will be accomplished in the following ways, depending on the known or suspected biological role of the miR genes in promoting cancer. Mutations that knock out the function of a miR gene in a specific tissue at a specific time will be made for those miRs in cases where the absence of miR expression appears to cause cancer. For cases where overexpression of a miR causes cancer, transgenic constructs that add expression to the cellular system will be made. In all cases, mutant mice will be made and aged to assess changes in cancer phenotypes. We hope this study will allow us to identify miRs as new targets for anti-cancer therapeutics specifically for cancers caused by miR gene mutations in humans.

Mission Relevance

It is not overstating the case to say that every human disease and every human health state will have miR components. Every NIH institute will potentially support mutant mice for miRs of their interest, bringing income and publicity to our Mouse Genetics Research User Facility. Our results and resources generated in this project will position us at the forefront for the study of non-coding RNA biology and enable us to pursue R01 and R21 funds from NCI and to secure our funding petition for several NIH calls, such as ID#: PA-06-003, PA-06-314; RFA-MH-07-040. In the future, crossing our cancer-susceptible miR mutant mice to Collaborative Cross strains will enable us to identify genetic quantitative trait loci (QTL) that modify the cancer effect of the miR mutation (and therefore that may be targets for new therapeutic intervention). An experimental demonstration of a causal effect of cancer by miR knockouts or transgenics will also provide a rationale for using the collaborative cross to look for more subtle linkages between miR genes and cancer [e.g., miR single-nucleotide polymorphisms (SNPs) associated with variable susceptibilities to cancer]. This will also provide data to justify funding for our long-term Collaborative Cross Program/Mouse User Facility Center through, for example, an NIH U54 center grant, which will serve as the major operating grant for our Collaborative Cross Program in place of our current FWP (DOE OBS) 4 years from now.

Results and Accomplishments

During our project's first year (FY 2006), we engineered mouse conditional and non-conditional knockout cassettes for the simultaneous deletion of both miR-15 and -16, respectively; conditional knockout cassettes for miR-145 and miR-32; and a transgenic construct for the overexpression of the mouse miR-17/18/19a/20/19b-1 polycistronic transgene cluster under the control of a K14 keratinocyte-specific promoter in skin epidermis. Some of these cassettes or constructs have been introduced into mouse embryonic stem (ES) cells. In all these cases, mutant mice will be made from the validated ES clones. In addition, transgenic mice with skin-specific expression of the miR-17/18/19a/20/19b-1 polycistron will be made by pronuclear microinjection of the transgene. These miR mutant mice will be valuable resources to explore not only the importance of miRs in cancer development and progression but also the discovery of new targets for anti-cancer therapies.

Publications

Gomez, M. V., et al. 2006. "PARP1 is a TRF2-associated poly(ADP-ribose) polymerase and protects eroded telomeres." *Mol. Biol. Cell.* **17**, 1686.

Wang, Y. and Y. Liu. 2006. "Msh2 deficiency leads to chromosomal abnormalities, centrosome amplification, and telomere capping defect." *Oncogene*. **25**, 2531.

D06-142: Novel Approaches for Uncovering Total Environmental Gene Expression Patterns

Martin Keller

Project Description

DOE has ambitious goals in its bioremediation and bioenergy production mission areas that will require isolation and development of new strains of bacteria. In an effort to gain greater access to uncultivated microorganisms (up to 99% of all bacterial species) and their genes, proteins, and biochemistries, we propose using a technology based on encapsulation of a single cell or a small number of cells within individual gel microdroplets (GMDs). We will use this high-throughput cultivation method, which is based on the random encapsulation of individual cells in millions of individual agarose beads, followed by high-speed flow sorting based on light scattering changes (sort speed of 5000 events per second) to detect bacterial growth. In this technology, the microbial community is reconstituted by loading the GMDs into a growth column. The community is grown in the column under very low-nutrient-flux conditions using basal medium supplemented with low concentrations of nutrients extracted from the sampling site. Over time, each cell capable of growth under the conditions in the column forms a microcolony within its GMD. The high-throughput nature of this technology is the simultaneously parallel growth of microorganisms in 10 million agarose beads and the use of a high-speed flow cytometer and cell sorter to identify GMDs containing microcolonies of >20 cells which are sorted (one positive GMD per microtiter well) for further analysis.

Mission Relevance

Our goals are to (1) demonstrate these novel methods in direct application to DOE mission areas and (2) isolate novel strains of bacteria that can be applied to DOE mission areas in bioremediation (uranium reduction) and bioenergy (e.g., ethanol and hydrogen production).

Results and Accomplishments

Because the project started late in the year, most of the effort was directed at implementing the technology discussed above in preparation for conducting the experimental plan. We purchased a new state-of-the-art flow cytometer from Cytpea which will be delivered in October. In addition, we established an controlled fermentation facility with six small glass vessel fermentors with integrated GC-MS measuring capability. This facility will be used for downstream characterization of newly isolated microorganisms and will allow us to rapidly characterize novel microorganisms for desired trades such as ethanol production, ethanol tolerance, and metabolic turnover rates.

Ultrascale Computing Initiative

Ultrascale Computing Initiative

D05-022: Multiscale Mathematics on Massively Parallel Computers: New Tools for Computational End Stations on the Cray X1E, Red-Storm, and the IBM Blue Gene

George Fann, William Shelton, Bobby Sumpter, Srdjan Simunovic, Sreekanth Pannala, and Ahmed Khamayseh

Project Description

Multiscale mathematics and fast computational algorithms are being derived and developed that will benefit chemical physics, climate dynamics, fusion, computational materials, and computational nano-biology. General and cross-cutting mathematics and their associated algorithms for multiscale decomposition, fast summation, and associated sampling theory are also being developed with an emphasis on accurate assessment of multiscale multi-particle interactions (e.g., Green function) and numerical models with particle and continuum interactions. These tools will form the basis of a general multiscale tool set. In this project, we applied these techniques to fast sampling and summation methods to combine a classical density functional theory/molecular dynamics method and a kinetic Monte Carlo/Lattice Boltzmann method.

Mission Relevance

This work is relevant to the mathematics subprogram within the DOE Office of Science, Office of Advanced Scientific Computing Research (OASCR) and supports the goals of multiscale mathematics, Scientific Discovery through Advanced Computing (SciDAC) program and associated collaborations (e.g., Global Nuclear Energy Partnership). We expect that this project will initiate new efforts in the development and application of new multiscale mathematical methods to large scientific simulations in multiple disciplines. While this project has its main focus on providing fundamental mathematical methods, we anticipate that they can be applied to much broader programs that will impact diverse technologies under development by other agencies.

Results and Accomplishments

The collaborative efforts of computational scientists, mathematicians, and computer scientists were applied in developing new methods. In summary, fast summation techniques were developed and applied to upscale from discrete simulations to continuum simulations. We also conceptualized a procedure for coupling mesoscopic methods with microscopic methods for heterogeneous chemical reacting flow and investigated a new application of adaptive mesh refinement for climate dynamics models. Our accomplishments are as follows:

Mathematical Techniques: We derived a sampling technique for a more accurate interpolation of multivariable functions involving discrete models and continuum models related by integro-partial differential equations. This technique was used to integrate the molecular dynamics/classical density functional code through a secondary auxiliary equation. Accurate, conservative multiresolution remapping in field simulation requires the periodic remapping of conserved quantities such as mass, momentum, and energy from an existing mesh to some other arbitrarily defined mesh. This procedure is a type of interpolation which is usually constrained to be conservative and monotone. We developed an integral form of this method in mapping the earth's surface orography field from initial logical mesh resolution to an arbitrary hybrid mesh resolution in two and three dimensions. This technique can be applied to climate dynamics and multi-physics-based simulations, computational chemistry, computational biology, computational materials, fusion, and environmental sciences.

Multiscale Density Functional Theory: We have implemented a fully parallel Brownian Dynamics (BD) code based on several high-performance architectures located at ORNL for simulating polymers in solution. Using traditional approaches, it is often very difficult to simulate the solvent along with the polymer to the appropriate time scale needed to obtain equilibrium quantities (gyration radius, etc.). However, by using BD, one can accelerate the dynamics by approximating the interaction of the solvent by a stochastic forcing term. The mathematical formulation of this dynamic process produces the well-known Langevin equation. The following list of features incorporated in this code includes flexible and semi-flexible polymers, Lennard-Jones interaction, Debye-Huckel interaction, and Ewald summation for treating long-range interactions. In addition, hard-wall, Lennard-Jones wall, and spheres can be included, and a variety of boundary conditions have been incorporated. Preliminary validation of this code was performed for several simulations of polymer and biosystems.

Lattice-Boltzmann Methods: A prototype Lattice-Boltzmann code was implemented and validated. We applied a new sampling technique to facilitate the integration of a kinetic Monte Carlo code with the Lattice Boltzmann code and conceptualized a procedure for coupling mesoscopic methods with microscopic methods for heterogeneous chemical reacting flow.

Publication

Sumpter, B. G., et al. "An Electronic Structure and Inelastic Neutron Scattering Investigation of Surface-Adsorbate and Adsorbate-Adsorbate Interactions in Multilayers of CH_4 on MgO(100)." *J. Phys. Chem. B.* submitted.

D05-023: Exploring Alternative Technologies for Next-Generation Leadership-Class Computing

J. S. Vetter, J. Barhen, N. Imam, K. Roche, M. C. Smith, M. Vose, and S. Alam

Project Description

This project was aimed at extending ORNL's strong evaluation project in leadership-class computing to explore potential disruptive and alternative core technologies for next-generation computer architectures. Several trends motivate the need for exploration of alternative and possibly disruptive technologies for next-generation computational systems. First, the

International Technology Roadmap for Semiconductors (www.itrs.net) and other reports predict that without significant technological breakthroughs, Moore's Law will come to an end in the 2012–2015 time frame. Second, practical considerations, such as power and cooling of large-scale systems, are forcing computer architects to redesign their upcoming systems. Introduction of multicore processors in mainstream computing is a result of these limitations. Third, the increasing differences in the performance of microprocessors and their memory subsystems, sometimes labeled "the Memory Wall," have resulted in low sustained performance for important applications on many contemporary architectures. These three trends combined require the exploration of new technologies and algorithms for nontraditional computational systems. In this effort, we explored core technologies that address fundamental limitations of existing high-end computing systems, namely, reconfigurable computing, optical processors, and heterogeneous multicore processors. At the highest level, we performed the following tasks:(1) exploration of computational opportunities for emerging technologies; (2) algorithm development for these new technologies; (3) performance assessment of each technology in terms of speed, accuracy, efficiency, and robustness and evaluation of its potential for future development; and (4) development of pathways to petascale architectures.

Mission Relevance

Within DOE, this work is relevant to the Basic Energy Sciences (BES), Biological and Environmental Research (BER), and Nuclear Physics (NP) programs. As a result of the progress made during this project, the Office of Naval Research (ONR) and the Defense Advanced Research Projects Agency (DARPA) through its High-Productivity Computing Systems (HPCS) project, where the goal is to build a petascale computer by 2010, are sponsoring follow-on work. The current HPCS vendors (IBM, Cray, and Sun) and mainstream processor vendors, Intel and AMD, have proposed many ideas that have been explored and investigated during this project. Hence, our feedback could be invaluable in shaping the next generation of computing technology to meet DOE needs.

Results and Accomplishments

During FY 2006, the project's second year, we made significant progress in the six areas.

1. We continued to work with scientific applications and kernels that are representative of our mission applications on the reconfigurable computing architectures. With the addition of the Mitrion software development kit (SDK), we also began looking at implementations on the Cray XD1 system as well as those originally targeted for the SRC computer system. Results were presented at various international conferences and workshops.

2. We accelerated a full-scale scientific application called AMBER using its native high-level programming language interface, Fortran 90, on the SRC-6E FPGA devices in collaboration with the SRC Computers Inc. AMBER is a molecular dynamics (MD) framework for biomolecular and biochemical systems simulations that has been used extensively by computational biologists and chemists at the DOE laboratories and academia.

3. We explored the performance potential of an emerging heterogeneous multi-core system by IBM called the Cell Broadband Engine (BE), which combines a general-purpose POWER architecture core with eight independent single-instruction-multiple-data (SIMD) cores. Each

core is capable of very high performance; however, users must explicitly manage data movement, scheduling, and synchronization. While these attributes provide some of the cell processor's greatest performance strengths, they also form its greatest weaknesses in terms of developer productivity, code portability, and initial performance efficiencies. We evaluated several of these factors by adapting and optimizing a diverse set of kernels and applications to a Cell BE system.

4. We evaluated the speedup of giant Fourier transforms (80,000 complex samples) arising in matched filter algorithms on the EnLight optical core processor. In FY 2006, our goal was to demonstrate orders-of-magnitude speedup for the large-scale Fourier transforms underlying the above matched filter paradigms. The EnLight-64α prototype hardware achieved a speedup factor in excess of 13,000 (i.e., 6,826 × 2) over a single Xeon processor. The implementation on the EnLight-256 simulator yielded a projected speedup factor in excess of 113,000.

5. We obtained preliminary estimates of speedup of singular value decomposition (SVD) on the IBM Cell (BE) multicore processor; SVD is at the core of replica processing and thus essential for real-time underwater target tracking. Timings for a single Cell BE are compared to those obtained from an Intel Pentium D (dual core operating at 2 GHz). The Cell BE implementation was based on an SPE-centric paradigm. For large matrices (1024 × 1024), we achieved a speedup factor exceeding 100.

6. Finally, an iterative method was developed for computing-tomography imaging-spectrometer (CTIS) image reconstruction in the presence of both photon noise in the image and post-detection Gaussian system noise. The new algorithm, which assumes the transfer matrix of the system has a particular structure, was evaluated through computer simulations which demonstrate that, for larger problems, it is several orders of magnitude better than both the multiplicative algebraic reconstruction technique (MART) and the mixed-expectation image-reconstruction technique (MERT) with respect to accuracy and computation time.

Publications

Barhen, J. and N. Imam. "Implementation of an Active Sonar Matched Filter Algorithm for Broadband Doppler-Sensitive Waveforms on the EnLight Terascale Optical Core Processor." *IEEE Trans. Signal Proces.* Submitted.

Vetter, J. S., et al. 2005. "Capturing Petascale Application Characteristics with the Sequoia Toolkit." *ParCo: Parallel Computing*, September 13–16, 2005, Malaga, Spain.

D05-028: A Chemistry End Station for the Leadership Computing Facility (Chemical Catalysis at the Nanoscale)

Robert Harrison, William Shelton, Bryan Hathorn, David Bernholdt, Edward Valeev,
A. C. Buchanan III, Phillip Britt, and Steven Overbury

Project Description

We have been developing a chemistry end station (ChemES) with an initial focus on chemical catalysis at the nanoscale. The eventual end station will comprise a nationwide community of developers and end users, and an integrated software suite optimized for execution of capability-class simulations on the computers planned for the Leadership Computing Facility (LCF), notably the Cray X1/2 and Red Storm/Ranier. Activities include research into scalable parallel-vector algorithms and software architecture, prototyping of end-station infrastructure, selecting, porting, and optimizing existing packages (e.g., NWChem) to the Cray-X1, applying this capability to provide early scientific results and to guide future activities, development of a national user/developer community, and establishment of requirements for end-station design and functionality. The selection of nanoscale catalysis as the initial focus area reflects its strategic importance to chemistry within ORNL and DOE as a whole and its economic value to the nation. The resulting tools will have broad application, including to hydrogen storage, fuel cell technologies, nano-bio molecular models, combustion, and environmental chemistry.

Mission Relevance

As a result of the recent development of new theories and algorithms and with the advent of petascale computers, chemical simulation promises the solution to chemical problems that are central to the strategic, economic, and environmental future of our nation. These include problems of special interest to DOE including chemical catalysis as it relates to clean energy production and biological systems and the chemistry of heavy elements, including that required to model advanced nuclear fuels and design new separations processes. These capabilities are broadly applicable and highly relevant to other agencies such as the National Science Foundation, the Department of Defense, the Department of Homeland Security, and the National Institutes of Health. The cost and complexity of developing computational chemistry software for petascale computers have passed beyond the resources of individual research groups and must now become a communal endeavor. We at ORNL are leading the international effort to form such a community and to develop the associated tools and standards. Pending review is a proposal to DOE for initial funding of this long-term effort with a collaboration that involves five national laboratories and eight universities.

Results and Accomplishments

In this last year, we have focused upon deploying capability on the resources of the LCF, in particular to enable early scientific results from these computers. Since major future growth of the LCF will be in the Cray XT3 line of products rather than the Cray X1, we have focused on that resource. The ESPRESSO and VASP programs were tuned for the system, and scalability analyses were performed. Calculations in catalytic chemistry and pyrolysis were performed to demonstrate and apply the new capability. The Common Component Architecture (CCA) is being recommended to the community as the best choice for integration of our applications, and a team member is now the principal investigator of the recently renewed CCA project. The main design discussions have focused on portability and performance, appropriate granularity at which to deploy the CCA, and availability of the CCA on the Cray XT3.

Publication

Hathorn, B. C. and S. Schlamp. "Molecular orientation and angular momentum alignment in a supersonic shock front." *J. Phys. Chem.* Submitted.

D05-033: Computational Mechanics End Station: Parallel Implementation of Finite-Element Software on Ultrascale Computers and Its Application on Modeling of Human Joints

Phani K. Nukala, Srdjan Simunovic, Richard D. Komistek, Mohamed R. Mahfouz, and Michael Puso

Project Description

General-purpose finite-element (FE) software is widely used in many engineering and industrial applications. Since the inception of high-performance computing initiatives such as the Accelerated Strategic Computing Initiative, Scientific Discovery through the Advanced Computing, and Advanced Simulation and Computing, there have been significant efforts to develop high-performance parallel finite-element codes at DOE laboratories. Currently, using ParaDyn, explicit finite-element simulations of up to 10 million degrees-of-freedom are routinely performed on the ASCI-White computer (12.3 Tflops) at Lawrence Livermore National Laboratory. However, large-scale implicit finite-element simulations are still limited to only a few million degrees of freedom due to the memory constraints imposed by the fill-in during factorization using sparse direct solvers and the necessity of solving the large system of linear equations during each nonlinear iteration. The majority of computational effort in an implicit code is in solving the linearized system of equations, and the overall performance of an implicit code is significantly influenced by the performance of the equation solver.

In this proposal, we ported and developed a high-performance, implicit finite-element computational toolkit using a hierarchical domain decomposition method with balancing domain decomposition–style iterative algorithms and a domain-wise multi-frontal sparse direct solver approach suitable for national leadership–class computer architectures. The application base of the proposed work spans materials science, engineering, and industrial applications. The basic idea is to divide the FE domain into a number of non-overlapping subdomains, wherein parallel domain-wise sparse direct solvers are used to solve the fine scale problem (Schur problem which eliminates the degrees-of-freedom internal to each of the subdomains) and use a parallel iterative solver based on a balancing domain decomposition method to solve the coarse problem.

Mission Relevance

The proposed work develops a high-performance, implicit finite-element computational toolkit that would enhance the existing capability to simulate large-scale, finite-element problems. The project is relevant to DOE's Mathematical, Information, and Computational Sciences Program. In addition, the project is relevant to DOE's Global Nuclear Energy Partnership and Basic Energy Sciences and Energy Efficiency and Renewable Energy programs in terms of its use in simulating large-scale nuclear fuel rod, materials science, and thermomechanical/structural applications. Furthermore, our high-performance implicit-FE toolkit is applicable to many scientific areas involving biomedical and biomechanical simulations.

Results and Accomplishments

In FY 2005, we completed two essential tasks, namely, (1) porting, performance tuning/optimizing, and benchmarking the NIKE3D code on Cray-X1 (Phoenix) and (2) implementing and interfacing vectorized sparse direct solvers with NIKE3D suitable for use on Cray-X1. In terms of benchmarking, we tested a variety of nonlinear benchmarking problems, and a large Boussinesq problem of a million degrees of freedom. We accomplished vector processing and multi-streaming (performance tuning) by using pat_build and loopmark listings. Performance comparison of sparse solvers (SSPOTRF/SSPOTRS) of Cray-X1 Scientific Library (SciLib), SuperLU, MUMPS, and Vectorized Sparse Solver (VSS) has been completed. Using the VSS (which is the best on Cray-X1 even in comparison with Cray-X1 SciLib Sparse solvers) on Cray-X1, the NIKE3D code currently runs at 5 Gflops (Giga Floating Point operations per second) per MSP (Multi-Streaming Processor) (out of 12.8 Gflops) and at 2.5 Gflops per SSP (Single Streaming Processor) in SSP mode (out of 3.2 Gflops) at an impressive 3.79 Floating Point operations per load, and at an average vector length of 62. The total number of translation lookaside buffer (TLB) misses are at an impressively low rate of 20/sec.

During FY 2006, we ported ADVENTURE code onto Cray-XT3 (Jaguar) and IBM-SP4 (Cheetah). ADVENTURE code is based on a hierarchical domain decomposition method, wherein the finite-element domain is decomposed into smaller subdomains so as to reduce the original large set of system of equations to a smaller set of equations expressed only in terms of the interface degrees-of-freedom (coarse problem). Subsequently, the smaller set (still of the order of a few million degrees-of-freedom) of linear system of equations is solved using either a parallel preconditioned iterative solver or an efficient parallel vectorized sparse direct solver that is best suitable for the ultra-scale architecture. The fine problem on each subdomain is solved using a sparse direct solver. Using the ADVENTURE code on 2000 cores of Cray-XT3, we simulated a huge 100 million degrees-of-freedom problem at a phenomenal 20% efficiency, achieving more than a 2-Tflops speedup.

Publication

Nukala, P. K. and S. Simunovic. 2006. "Comment on Finite Element Mapping for Spring Network Representations of the Mechanics of Solids." *Phys. Rev. Lett.* **96**, 199401.

D05-035: Advanced Network Capabilities for Terascale Computations on Leadership-Class Computers

Nageswara S. Rao, William R. Wing, Steven M. Carter, Qishi Wu, Anthony Mezzacappa, and John Blondin

Project Description

As the scale of computations enabled by the leading-edge supercomputers continues to increase, so does the need for network capabilities that can match their computational speeds and data rates. The ability to strategically and remotely steer large-scale computations and data movements to and from supercomputers is vital to their effective utilization. This project addressed technologies to achieve (i) efficient realization of data paths between the internal nodes and edges of supercomputers, (ii) effective interconnections between the supercomputer and external networks, (iii) protocols to sustain high-performance data and control streams, and (iv) end-to-end optimization of control flows. The overall objective of this project is to develop the technologies and expertise needed to provide dedicated network connections between the applications running on Cray X-class supercomputers and remote users. Due to the multi-faceted nature of this project, this task has been divided into a number of component areas: (a) system architecture design and optimization, (b) design, analysis, and testing of data path hardware and transport protocols, (c) application and transport module installation and experimentation, and (d) coordination and collaboration with Cray Inc. Dedicated hardware cross-connects and wide-area network connections were established between the ORNL Cray X1(E) supercomputer and remote hosts. Special-purpose transport protocols were tuned and tested over these dedicated configurations, which achieved some of the highest network throughputs. These experiments also contributed to the identification and diagnosis of performance bottlenecks in this class of high-performance, wide-area connections to supercomputers.

Mission Relevance

This project provides networking technologies and expertise for making facilities, such as the DOE Office of Science Leadership Computing Facility, available to scientists at national laboratories and universities. There has been a surge in the procurement of supercomputers by federal agencies, including National Science Foundation (NSF), Department of Defense (DOD), and the National Aeronautics and Space Administration (NASA). Providing suitable network access to such machines is vital to their effective utilization. Particularly for open research projects envisioned on NSF and NASA supercomputers, the users are distributed across the country at various institutions and universities. Our project can contribute technologies and expertise in providing the high-performance network capabilities to these supercomputers to make them accessible to users and also achieve their effective utilization. Our methods can also provide an additional level of security for DOD supercomputers by isolating these flows from other network flows.

Results and Accomplishments

We performed a detailed analysis of the internal data paths of Cray X1 to identify methods to improve the performance of network transport to remote clients. We optimized the existing bbcp protocol to achieve 250–400 Mbps from Cray X1 to North Carolina State University (NCSU) compared with the default throughput of 50 Mbps. We developed the Hurricane protocol that achieved stable 400 Mbps using a single stream between Cray X1 and NCSU. These are the highest speeds achieved between Cray X1 and a remote site. We designed an interconnect by utilizing a linux host, which is connected to Cray X1 via four 2-Gbps FC connections. Under this configuration, we achieved a 2-Gbps file transfer rate using multiple bbcp streams between Cray X1 and a host located at ORNL, and also achieved 1.4 Gbps using single flow using Hurricane. These were the highest file transfer rates achieved over Ethernet connections from a supercomputer to an external host for both multiple and single streams. We then configured a dedicated 1-Gbps connection from Cray X1E (an upgraded version of X1) to a host at NCSU. Performance tests revealed significantly degraded throughputs; the default method achieved 5 Mbps, bbcp achieved 40 Mbps, and Hurricane achieved 200 Mbps. These tests were then repeated with no other applications running on X1E, and Hurricane's throughput reached 400 Mbps. Through detailed experimentation, the performance problem was diagnosed to be within the service nodes, and these results provided us valuable insights for ensuring high network throughputs for supercomputing systems.

Publication

Wu, Q., et al. "System Design for On-line Distributed Computational Visualization and Steering." *International Conference on E-learning and Games*, April 16–19, 2006, Hangzhou, China.

D05-036: Computational Modeling of Alloy Deformation Based on a Novel Statistical Mechanics Approach

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Project Description

Deformation of structural alloys, such as those incurred during thermo-mechanical processing or stress-induced failure, is characterized by complex dislocation structures that depend strongly on the crystal structure and alloy chemistry. Because of its scientific and technological importance, the prediction of alloy deformation and microstructure evolution remains a central research topic in metallurgy and continuum mechanics. Recent advances in parallel computing capabilities have led to much progress in the development of advanced models for structure evolution. However, current models at the microstructural length scale (mesoscale models) based on crystal plasticity rely on empirical constitutive laws that lack sufficient rigor, while models at the scale of individual dislocations (discrete dislocation simulations) are limited to small strains and low dislocation densities. The main objective of this project is to develop a computational capability to predict the evolution of complex dislocation densities and other mesoscale structures in alloys at large plastic strains by combining a statistical mechanics theory of dislocations with the crystal plasticity models. The statistical mechanics formalism captures both the basic dislocation mechanisms and their collective behavior during large plastic deformations and is described by a set of nonlinearly coupled kinetic equations for the dislocation density functions. These kinetic equations must be solved in conjunction with the conventional finite deformation kinematics and stress equilibrium functions to model the microstructure evolution.

Mission Relevance

The proposed computational capability is of direct relevance to many aspects of materials research within various DOE programs as well as within other agencies. A fundamental understanding of the microstructure evolution under different thermo-mechanical processing conditions is essential to develop a predictive capability for tailoring properties of materials for optimum performance during service, to develop novel processing routes that can reduce energy consumption, and to aid in the design of new and advanced alloys. Many DOE programs, such as the Basic Energy Sciences Materials Division, Industrial Technologies Program, would benefit from such a capability, which would enable not only detailed and fundamental studies on the evolution of dislocation structures during thermo-mechanical processing but would also provide an advanced computational tool for alloy design.

Results and Accomplishments

Accomplishments during the first year include (1) completion of the theoretical development of expressions for the source terms in the kinetic equations, (2) development of a numerical scheme to solve the evolution equations for the dislocation densities, and (3) parallel implementation of a finite-element formulation based on an elasto-viscoplastic crystal plasticity model to compute the deformation and elastic stress field in the material. The source terms for the dislocation model include contributions from cross slip and from short-range interactions, such as annihilation, sessile junction formation, and Burgers vector reactions. Accomplishments during the second year include (1) implementation of the numerical scheme based on the first-order system least-squares variational formulation to solve the continuity equations for the dislocation density field and (2) testing of the implementation for some simple cases with and without the presence of source terms. The solution of the continuity equations in 3D space requires additional discretization of the orientation parameter, leading to a system of equations that depends on four independent variables and time and requiring special considerations in developing the finite-element scheme to solve for the discretized density field. Progress has been made in developing solutions for a few specific simplified cases, but some challenges have been identified in extending the scheme to more general problems.

D05-040: Toward Systematic Computational Instrumentation for Nanoscale, Condensed Matter, and Materials Science

Thomas Schulthess, Michael Summers, Paul Kent, Peter Cummings, Malcolm Stocks, and Tom Swain

Project Description

In this project we developed a community software repository for computational nanoscience with the following three distinguishing features: (1) it consists of loosely coupled tools that are optimized for leadership computing platforms; (2) the tools are coupled by a common input/output (I/O) system and data structure representation that allow real users as well as software frameworks to interface with the software in the repository; and (3) software quality processes are implemented to ensure rigorous configuration management and quantitative certification. This software repository comprises the *computational instrumentation*, from which integrated simulation frameworks for nanosciences will be built. We have chosen not to specify or develop a specific simulation framework. Rather, by supporting the interfaces with existing frameworks, we give the various user communities of the repository the choice of selecting the most appropriate framework for their needs.

Task I of the project was concerned with the development of a SourceForge-like software repository for computational science that supports all commonly used software development tools (revision control, bug tracking, content management, WIKI, etc.) and is compliant with the Department of Energy’s cyber security requirements. In task II, we focused on developing optimized kernels of applications used on the leadership computing platforms that scale to the full scale of these computers. In task III, we developed the software layers required to incorporate existing computational science codes into an XML-based I/O system.

Mission Relevance

With the Leadership Computing Facility at the National Center for Computational Sciences, the Nanomaterials Theory Institutes of the Center for Nanophase Materials Sciences (CNMS), and the clearly stated intent to support advanced data analysis for neutron sciences at the Spallation Neutron Sources (SNS), ORNL is becoming the focal point in computational nanoscale, condensed matter, and materials sciences. For these three DOE user facilities to function coherently from a computational sciences point of view, there is an urgent need to systematize the computational instrumentation in the field, allowing the integration of high-performance computing with the established user programs at CNMS and SNS.

Results and Accomplishments

The main accomplishments of this project are (1) launch of the collaboration server SciCompForge.org, where follow-on funding has been obtained from the Scientific Discovery through Advanced Computing program to complete and maintain this server; (2) development of a prototype XML subsystem (see http://scicompforge.org/xmldir), which is currently being incorporated into two electronic structure codes that are written in Fortran; (3) port and optimization of the VASP code to the Cray X1 (the acquired expertise is presently being encapsulated into a wave function module that will be usable in other plane wave pseudo potential–based electronic structure packages); (4) implementation of quality control procedures, including an automated documentation system for generic toolkits (see http://psimag.org).

The software repository SciCompForge.org (see http://scicompforge.org) is similar to SourceForge with the following distinguishing characteristics: (1) projects can be hidden from the public as is often required in scientific software development; (2) users do not need computer accounts as all components of the repository support web-based solutions (e.g., Subversion for the revision control system); (3) the user management system is custom built and can be configured to work with any external authentication system.

XMLDir is a software system that gives easy access to Fortran, C, and C++ programmers to XML-based technology, including XML Schemas. It supports parsing and validation of input files. The system is a thin software layer that provides Fortran, C, and C++ application program interfaces to the Xerxes and XAlan libraries of the Apache project. Special attention has been given to portability, compatibility with high-performance computing platforms, and long-term maintainability.

D05-041: Reliability, Availability, and Serviceability for Terascale Computing

Stephen L. Scott, Arthur S. Bland, Kasidit Chanchio, Christian Engelmann, Xiaosong Ma, and Sudharshan Vazhkudai

Project Description

Commercial information technology (IT) organizations have long provided service-level agreements to deliver measurable support metrics including, but not limited to, application performance, response time, and system availability. These organizations are held to the highest levels of reliability, availability, and serviceability (RAS) even in the face of catastrophic failures of critical hardware components such as a disk, central processing unit (CPU), or network interface. Downtime of commercial IT systems, while measured in hours and minutes, are counted as dollars lost through revenue loss via lost opportunities and dissatisfied customers. With the tens of millions of dollars invested in computing equipment and significantly more in researchers' time, why is it acceptable today in the high-end computing (HEC) community to suffer through hours of unplanned resource downtime when a system failure occurs? While most high-performance computing (HPC) sites have sufficient redundancy at the compute node level to ignore a peer's failure, there are some systems where the loss of any single component will render the entire system unusable. The worst-case scenario is when the "gateway," or head of a larger system, fails, as this single failure will, in many cases, idle thousands of healthy processors as they are cut off from the outside world and the users they serve. Therefore, this effort will work toward a general solution to enable a high-level of RAS for terascale HEC resources. The goal of this work is to produce a proof-of-concept implementation that will enable the removal of the numerous single points of failure in large systems while improving scalability and access to systems and data.

Mission Relevance

This work is relevant to the DOE Office of Science program for operating/runtime systems for extreme-scale scientific computing. It also benefits the National Science Foundation's Directorate for Computer and Information Science and Engineering program for software and tools for high-end computing and the Defense Advanced Research Projects Agency's Information Processing Technology Office.

Results and Accomplishments

Our research effort focused on efficient redundancy strategies for head and service nodes, as well as on a distributed storage infrastructure. We developed two replication mechanisms (internal and external) for providing symmetric active/active high availability for services running on head and service nodes in order to offer the highest level of availability without significantly impacting performance. We implemented proof-of-concept prototypes for the batch job management system, Torque, and the parallel virtual file system (PVFS) metadata server. Both solutions offer 99.9997% service uptime using just three redundant nodes. Moreover, the PVFS metadata server solution utilizes load balancing, thus improving performance. After gaining further maturity, the developed technology is expected to be deployed in production-type systems though vendor collaborations. For distributed data storage, the developed FreeLoader solution is built on a contributed desktop storage substrate. We developed parallel I/O mechanisms to store/access data to/from network workstations. Furthermore, we developed mechanisms such that the distributed storage infrastructure can be treated as a cache to store more recently used datasets. This may be positioned as a storage cache that complements current storage offerings in the supercomputer centers in order to improve availability of and access to data. Our results indicate that FreeLoader can offer high data retrieval rates for large datasets using novel striping strategies. Furthermore, FreeLoader may be utilized as a virtual cache, storing only prefixes of datasets and yet delivering the entire dataset by masking the suffix patching. We anticipate FreeLoader evolving into an alternative for transient supercomputer datasets.

Publications

Engelmann, C. and S. L. Scott. 2005. "Concepts for High Availability in Scientific High-End Computing." *High Availability and Performance Workshop (HAPCW) 2005*, October 11, 2005, Santa Fe, NM, USA.

He, X., et al. "A Unified Multiple-Level Cache for High Performance Storage Systems." *Int. J. High Performance Com. Net.* Submitted.

Ma, X., et al. 2006. "Coupling Prefix Caching and Collective Downloads for Remote Data Access." *20th ACM International Conference on Supercomputing*, June 28, 2006, Cairns, Australia.

Okunbor, D. I., et al. 2006. "Exploring Process Groups for Reliability, Availability and Serviceability of Terascale Computing Systems." *2nd International Conference on Computer Science and Information Systems 2006*, June 19–21, 2006, Athens, Greece.

Uhlemann, K., et al. 2006. "JOSHUA: Symmetric Active/Active Replication for Highly Available HPC Job and Resource Management." *IEEE International Conference on Cluster Computing (Cluster) 2006*, September 25–28, 2006, Barcelona, Spain.

Vazhkudai, S. S., et al. 2005. "FreeLoader:Scavenging Desktop Storage Resources for Scientific Data." *Supercomputing 2005 (SC'05): International Conference on High Performance Computing, Networking and Storage*, September 12, 2005, Seattle, WA, USA.

Vazhkudai, S. S., et al. 2006. "Constructing Collaborative Desktop Storage Caches for Large Scientific Datasets." *ACM Trans. Storage*. **2**, 1.

D05-051: Terascale Computations of Multiscale Magnetohydrodynamics for Fusion Plasmas

D. A. Spong, E. A. D'Azevedo, D. del-Castillo-Negrete, M. Fahey, S. P. Hirshman, and R. T. Mills

Project Description

Production of self-sustained burning fusion plasmas in future devices such as the ITER project requires stable, stationary plasmas with good confinement properties. However, high-temperature tokamak plasmas develop slowly growing instabilities, known as neoclassical tearing modes (NTMs), that reconnect magnetic field lines, resulting in enhanced transport. These instabilities are driven by localized "holes" in the plasma current associated with magnetic islands, which are small-scale defects in the confining magnetic field structure. It has been demonstrated that use of localized ECH (electron cyclotron heating) can fill in these current holes and remove the NTMs. Reliable control and suppression of these instabilities requires an integrated plasma simulation capability that involves coupling continuum MHD (magneto-hydrodynamics) with kinetic particle-based closure relations. To achieve this goal, we have carried out research that (1) improves the performance of the MHD codes on the Leadership Computing Facility (LCF) computers at ORNL; (2) provides efficient data compression techniques for passing the MHD field data to the particle model; (3) develops a new, more self-consistent particle closure relation methodology; and (4) provides efficient noise reduction methods for passing the particle-based closure relations back to the MHD model.

Mission Relevance

This work is relevant to the Office of Fusion Energy Science (OFES) within the DOE Office of Science and supports the ITER (Latin for "the way") project. ITER is the top-ranked project in "Facilities for the Future of Science: A Twenty-Year Outlook," the DOE prioritized roadmap of new facilities. This work also supports the second DOE roadmap priority of ultra-scale scientific computing capability. In connection with this goal, the DOE Offices of Advanced Scientific Computing and Fusion Energy Science have been funding a number of SciDAC (Scientific Discovery through Advanced Computing) projects that will eventually lead to an integrated Fusion Simulation Project (FSP). This LDRD project has allowed us to participate in a successful SciDAC proposal: "Center for Simulation of Wave Interactions with Magnetohydrodynamics."

Results and Accomplishments

During FY 2006, this project's second year, we made significant progress in (1) developing efficient compression and noise reduction methods for transferring three-dimensional data back and forth between MHD and particle codes; (2) constructing closure relations for the MHD equations; and (3) calculating the effects of magnetic islands on neoclassical viscosity coefficients. The data compression techniques were developed using the generalized low-rank approximation method, which relies on iterative use of SVD (singular value decomposition) steps. This method is well suited to three-dimensional data from MHD codes that typically have slowly varying, periodic data in one of the dimensions (toroidal). We found that compression factors of up to 35 can be obtained for typical MHD data without significant loss of information.

This degree of compression can allow more rapid gather/scatter operations between processors and improve the efficiency of the particle calculations by allowing them to more readily fit into cache memory. Particle-distribution-function partitioning methods were developed for closure relations that consistently preserve the flow velocities contained in the macroscopic MHD equations. This avoids unnecessary redundancy between the MHD and particle models and will lead to improved implicit differencing in the MHD equations, potentially allowing larger time steps. Using these methods with data from the MHD code, the dependence of the viscous stress tensor components (which provide the closure relation) on magnetic island size was studied, indicating that viscosities increase up to a certain island width and then decrease. This will influence the degree of current deficit within the island.

Publications

Del-Castillo-Negrete, D. B., et al. 2006. "Compression of Magnetohydrodynamic Simulation Data Using Singular Value Decomposition." *J. Comput. Phys.* Submitted.

Spong, D. A. and K. C. Shaing. 2006. "Magnetic Island Induced Bootstrap Current on Island Dynamics in Tokamaks." *Phys. Plasmas*. **13**, 022501-1.

D05-089: Petascale Computation in Condensed Matter Physics

Elbio Dagotto, Randy Fishman, Adriana Moreo, Thomas Maier, Thomas Schulthess, and Ross Toedte

Project Description

The study of complex oxides is among the most important areas of research in condensed matter physics. These materials present a variety of exotic phenomena such as high-temperature superconductivity and colossal magneto-resistance. It is widely accepted that a theoretical understanding of these interesting properties requires the simultaneous consideration of several degrees of freedom such as charge, spin, lattice, and orbital. Such a formidable task can only be achieved with the help of large-scale computer simulations. The proposed task in this project was to use state-of-the-art algorithms in combination with the vast computational resources of ORNL to carry out the most detailed computer simulation ever conducted of models for copper and manganese oxides. Moreover, technically the methodology to be followed is similar to that needed to handle other materials known as diluted magnetic semiconductors (DMS), of relevance in spintronics. Then, our computational effort also developed a component in that direction, which also included important analytic work. Achieving a deep understanding of complex oxides and DMS materials will lead us to the next level: the design of artificially engineered heterostructures of these materials for the purpose of achieving functionalities similar to those reached with semiconductor-based electronics.

Mission Relevance

Since this work deals with materials with interesting physical properties of potential technological importance, the effort is clearly of relevance to the Materials Science and

Technology subprogram within the DOE Office of Science, Basic Energy Science Program in the context of functionalities of complex materials and diluted magnetic semiconductors.

Results and Accomplishments

During FY 2005 and FY 2006, we achieved most of our goals. In recently finalized computer simulations, the large changes in the resistance of manganese oxides under the influence of small magnetic fields were properly reproduced. The effect was found to originate in the existence of nano-scale domains of competing phases in the state that has the colossal magneto-resistance effect. Moreover, the numerical studies also allowed us to address the physics of the high-critical-temperature superconductors, clarifying the origin of the charge-pairing tendencies in Hubbard models, widely believed to represent at least a considerable portion of the physics of the cuprates. This understanding opens the way toward further progress in a variety of other materials with similar complex behavior. These efforts would have never been possible without the computational resources of ORNL. In addition to the numerical work, the current effort benefited from analytic calculations based on the dynamical cluster approximation (DCA) that allowed the proper study of the influence of impurities in DMS materials, improving on the local dynamical mean-field approximation.

Publications

Alvarez, G. "Computational Study of Colossal Magnetoresistive Manganites." *Fall Creek Falls 2005*, October 16–18, 2005, Fall Creek Falls, TN, USA.

Alvarez, G., et al. 2006. "Fragility of the A-type AF and CE Phases of Manganites: An Exotic Insulator-to-Metal Transition Induced by Quenched Disorder." *Phys. Rev. B.* **73**, 224426.

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Moreno, J., et al. 2006. "Transition Temperature of a Magnetic Semiconductor with Angular Momentum *j*." *Phys. Rev. Lett.* **96**, 237204.

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Sen, C., et al. 2006. "Study of One- and Two-band Models for Colossal Magnetoresistive Manganites Using the Truncated Polynomial Expansion Method." *Phys. Rev. B.* **73**, 224430.

D06-005: Enhanced Cognizance of Evolving Threat Situations via Knowledge Discovery from Disparate Data

Auroop R. Ganguly, Vladimir Protopopescu, and George Ostrouchov

Project Description

The objective of this project is to develop new methodologies for knowledge discovery (KD) from disparate, dynamic data for adaptive predictive analysis and decision-making in evolving threat situations. The premise of our approach is that (i) evolving threat situations are often accompanied by signatures of abnormal, rare, and/or unusual events and (ii) abrupt (unexpected) changes may be forewarned by hidden patterns in observables that can be built from continually refined models of "normal behavior" and statistical deviations therefrom. To implement this idea, we envisaged a coordinated offline-online KD framework. The offline part is a closed loop comprising disparate data integration, data analysis and unusual pattern detection, and process modeling where process-dynamical simulations are selected according to their outcomes. In this loop, disparate data are used to establish "normality" in patterns and behaviors, which in turn can be utilized for detecting "abnormality," and subsequently coordinated with event-based analysis of real-time, dynamic data for online detection of anomalies, abnormalities, or change. The off-line loop is coupled with an online decision support loop that provides information to and receives feedback from analysts and end users. The developed methodologies are tested on simulated data and applied to real data. Due to the ubiquitous and consequential nature of highway transportation, the application focus is on truck weigh-station data with the aim of facilitating faster and more reliable end-user decisions on whether a new truck at a weigh station represents a plausible security or safety hazard and hence should be held for manual inspection.

Mission Relevance

Every federal agency is facing a huge stream of data which has to be distilled—sometimes very fast —into consequential decisions. For instance, DOE deals with very complex problems ranging from climate change to the security of its physical and cyber infrastructure. DOD (e.g., JFCOM, ARL), DHS (e.g., S&T, DNDO), and the intelligence community are facing similar challenges. Large sets of data gathered from remote or in situ sensors, simulations, and network traffic need to be processed into actionable knowledge, and provided to decision-makers for accurate, timely, and reliable decisions. Sometimes, like in climate change, a threatening situation may evolve over decades, with changes difficult to notice as they happen. In some other cases, such as transporting hazardous material on interstates, the evolving threat develops more rapidly. In either case, to ensure adequate response, proper threat detection and quantification mechanisms are needed. The exponential growth of data prevents routine human analysis, while the importance and complexity of the questions preclude a purely automated decision making. The present LDRD is addressing several of these important issues. The tools developed within this project will benefit DOE, DOD, DHS, and the intelligence community.

Results and Accomplishments

We have developed novel capabilities in all four areas targeted in the off-line loop, namely, off-line data integration, pattern detection, and process modeling, and a rigorous statistical framework for online anomaly detection and decision support. These methodologies have been applied to both simulated data and real data collected from weigh-station sensors or remote sensing observations.

A suite of specific KD approaches have been developed, which include: (i) automatic entity extraction from text-based graph stripping; (ii) extensible data base architecture for multimodal information integration; (iii) new measures of “closeness’’ based on nonlinear manifold embedding and dimensionality reduction; (iv) dynamic process modeling based on data acquired from cyber-physical sensor networks; (v) new goodness-of-fit and adaptive threshold measures for pattern classification and deviation detection; and (vi) online change and anomaly detection from dynamic data. These approaches have been validated with various functions in analytic form and realistic model simulations, and applied to real data collected from weigh-station sensors and other related applications.

Upon applying these methods, new results and insights have been gained, specifically the following:

- Improved precision, recall, and computational efficiency of extracting named entities and their relationships from text data
- Faster and more user friendly queries on disparate knowledge bases
- Possibility of behavior detection and discrimination from blog and e-mail data in simple dynamical social models
- Improved discrimination between normal and abnormal truck profiles from static-scale weigh-station data
- Discovery of a new fundamental finding, namely, a universal power law behavior in truck speed distribution
- More accurate anomaly and change point detection and alarm generation based on adaptive thresholds in an online mode

Publication

Fang, Y., et al. “Online change detection: Monitoring land cover from remotely sensed data.” *The 2006 IEEE International Conference on Data Mining (ICDM)*, December 18–22, 2006, Hong Kong (China).

D06-075: Development of a Global Biogeochemistry Capability for Enhanced Climate Simulation and Earth System Modeling

W. Post, J. Drake, D. Erickson, F. Hoffman, A. Sandu, A. Mirin, and A. King

Project Description

The purpose of this project is to develop a quantitatively rigorous method for initialization of biogeochemistry-model components for coupled carbon cycle–climate simulation models that employ parameter and initial condition estimation using optimization techniques and efficient data-assimilation algorithms. The proposed work is divided into three tasks:

1. Identify canonical components of current and near future land-surface/terrestrial models and associated geographic information system layers
2. Define equilibrium benchmarks and objective functionals and develop optimization methods to adjust parameters and initial conditions for biogeochemistry models to be consistent with current climate conditions simulations
3. Develop optimization/data assimilation schemes to handle nonequilibrium conditions that are required for changing climate–terrestrial interactions over the past 200 years with changing atmosphere land-use change. Our intent is to integrate these methods into the National Center for Atmospheric Research (NCAR)/DOE Community Climate System Model (CCSM)

Mission Relevance

A major objective of DOE's climate change research is to "deliver improved climate data and models for policy makers to determine safe levels of greenhouse gases for the Earth system" by 2015. The Scientific Discovery through Advanced Computing (SciDAC) programs of DOE will support this endeavor by contributing to the Climate Change Science Program (CCSP), in particular their role in the development of the CCSM. The Climate Change Research Division contributes to this deliverable through Terrestrial Carbon Processes (TCP), Ocean Science (OS), and the National Institute for Climatic Change Research (NICCR), through research on coupled carbon cycle–climate research. This project will develop new capabilities for integration of carbon cycle and climate models. The National Aeronautical and Space Administration (NASA) is also committed to the development of earth system models that make use of remote-sensing products. Remote-sensing data streams will become important benchmarks that our enabling technology will use.

Results and Accomplishments

We are developing a method of adjusting the initial terrestrial carbon pools with different turnover times so that the ensuing model simulations are close to the observed seasonal and interannual shifts in atmospheric CO_2 concentrations. CCSM was recently coupled to the Integrated Biosphere System (IBIS) model. Progress for task 1 involved recoding IBIS to report output fields in a common approach used by CCSM3 so that they can be compared to data. We are now using these to develop standard restart files that are used to initialize the compartment states of each forward simulation. Regarding task 2, assembly of benchmark data sets for use in the construction of cost functions has been completed. For task 3, the variational approach to adjusting the initial condition to find optimal values was attempted. This involved generating the adjoint of our cost functional for the land-surface model using the Tangent linear and Adjoint Model Compiler (TAMC). This proved to be very difficult. TAMC was unable to generate the adjoint code for the model in its initial state due to source code restrictions and the size and complexity of the model. Because the sequential approach does not require development of an adjoint, we are shifting to this method for the other models. Completing the ensembles for using the sequential approach will require considerable additional computational time.

D06-087: Terascale Simulation Tools for Next-Generation Nuclear Energy Systems

Kevin T. Clarno, Valmor F. de Almeida, Eduardo F. d'Azevedo, Ahmed Khamayseh, and Cassiano R. E. de Oliveira

Project Description

A multilaboratory, multiuniversity collaboration (CANS: Collaboration for Advanced Nuclear Simulation) has been formed to advance the state of the art in high-fidelity, coupled-physics simulation of nuclear energy systems. Through LDRD funding from Idaho National Laboratory (INL) and Oak Ridge National Laboratory (ORNL), along with a grant from the Science Alliance at the University of Tennessee, we are embarking on the first phase in the development of a new suite of simulation tools dedicated to the advancement of nuclear science and engineering technologies. The computational challenges associated with high-fidelity, multiphysics simulations of these complex systems require the use of terascale, parallel supercomputers.

The primary goals of this LDRD project are to develop and demonstrate a state-of-the-art computational tool for high-fidelity heat-generation (neutronics) simulation in nuclear reactors and formulate the computational science infrastructure for coupled physics simulation within CANS. The primary software development is focused on the creation of a new high-fidelity radiation transport solver that is designed specifically for terascale computing architectures; the resulting software will provide extensive and accurate details of all relevant quantities (isotopic distributions, radiation fields, activation products, heat generation, etc.) on an unsurpassed differential level, yet with full-system interaction, as needed for other multiphysics simulation codes. This includes superior information about heat sources, resulting from the fission of nuclear fuels, and corresponding gamma-radiation heating, needed for heat transfer, fluid flow, and structural mechanics calculations. The computational science infrastructure will enable a single mesh-handling interface, solver coupling strategy, and data analysis and visualization mechanism for all associated physics within CANS.

The three major ORNL objectives of this project are as follows: (1) develop a high-fidelity radiation transport code for terascale parallel computing, (2) develop and assemble the computational infrastructure for efficiency and interoperability, and (3) demonstrate a radiation transport simulation coupled with nonisothermal fluid flow.

Mission Relevance

The Global Nuclear Energy Partnership (GNEP) is a primary objective of the DOE for the advancement of nuclear energy and closing the nuclear fuel cycle. The development of an applied high-fidelity neutronics solver and coupled physics reactor simulation is critical to the DOE Office of Nuclear Energy for the optimized design and safety analysis of advanced nuclear reactors proposed within GNEP and the Generation IV program. The DOE Office of Advanced Scientific Computing Research (ASCR) is also interested in the advancement of ultrascale computing simulation of nuclear energy systems for GNEP. Because of its university connection, this project is also addressing the DOE goal of training the next generation of leaders in nuclear engineering and computing simulation.

CANS is demonstrating the effectiveness of a multi-institution collaboration for high-fidelity simulation of nuclear energy systems, a project that is critical to a major presidential initiative (GNEP). NEWTRNX and GMAS are critical elements to the success of CANS, and their development is on track with respect to both time and budget.

Results and Accomplishments

During the initial year of the project, significant progress was made in four areas.

1. The infrastructure for a multiphysics simulation suite was developed. This infrastructure is based on the Common Component Architecture (CCA) developed within the SciDAC (Scientific Discovery through Advanced Computing) program of ASCR.
2. A module was adapted from a driver for the SCALE (Standardized Computer Analysis for Licensing Evaluation) nuclear data processing software to incorporate and utilize accurate nuclear data within a high-performance computing environment.
3. A new parallel three-dimensional radiation transport solver (NEWTRNX) for simulation of nuclear systems was designed and developed specifically for high-performance computing architectures. The NEWTRNX solver is based on the Slice-Balance Approach and incorporates parallelization strategies developed within the Advanced Simulation and Computing program of the National Nuclear Security Administration.
4. A module for geometry and mesh handling, the Geometry and Mesh Adaptivity Server (GMAS), which will coordinate all meshing challenges of the multi-institution collaboration, was developed. GMAS presently reads a mesh file and is coupled with modules for nuclear data handing and calculating the neutron distribution.

Publication

Clarno, K. T., et al. "GNES-R: Global Nuclear Energy Simulator for Reactors Task 1: High-Fidelity Neutron Transport." *PHYSOR-2006:* American Nuclear Society, Reactor Physics Division Topical Meeting, September 10–14, 2006, Vancouver, BC, Canada.

D06-101: Multiscale Modeling: Application to Hydrogen and Helium in Steels

D. M. Nicholson, P. K. Nukala, Yu. N. Osetskiy, R. E. Stoller, and M. N. Guddati

Project Description

We propose to build a multiscale framework for the modeling of dislocations in iron alloys containing small impurity atoms, hydrogen, and/or helium. This framework will immediately have a much broader range of application, provide better understanding of the role of interstitial solutes such as carbon, and promote growth in other areas of materials modeling. However, we take the very pragmatic view in that the urgency of the scientific and energy relevance of this research requires us to focus on realistic models rather than toy systems and to go directly after the science issues. Those issues are the mechanical properties of steels to be employed in advanced nuclear (fission and fusion) energy systems, in the pipelines and tanks required for a hydrogen economy, and in the target at the Spallation Neutron Source. Mechanical failure in any of these applications could render them unviable. The goal of this proposal is to ultimately link nanoscale structural evolution and mechanical properties in a predictive way.

Mission Relevance

This work is relevant to structural materials research within the U.S. Department of Energy in the areas of transportation, energy production, and energy delivery. We will advance the ability to model mechanical properties of metals, thereby benefiting a large cross section of industries. In particular, the mechanical properties of iron alloys in the presence of hydrogen and helium are important to the delivery and storage of hydrogen for the "hydrogen economy" and for the next generation of nuclear reactors.

Results and Accomplishments

Advances have been made in software, computed results, and formalism. We have incorporated molecular dynamics into the parallel finite-element code Nike3D. This implementation uses a finite-element (FE) mesh refined to the atomic scale in a handshaking region with a corresponding Hamiltonian (introduced by Vashishta) that determines dynamics. The design is such that other molecular dynamics (MD) codes in use at ORNL and elsewhere can easily utilize FE boundary conditions in our FE-MD-Nike3D code as an alternative to more restrictive periodic boundary conditions. A new multiscale formalism based on correlation functions has been introduced and is available in a draft manuscript. It will be implemented in our FeMD software. In addition, a one-dimensional (1-D) MD code was written with absorbing boundary conditions, which had originally been studied for a 1-D elastic continuum. Studies of wave reflection at a scale-changing interface and correlation including the direct correlation function were carried out. Absorbing boundary conditions were implemented in a three-dimensional MD code and tested for a transverse pulse.

The Greens function boundary method was implemented for quasi-static, that is, Newtonian, dynamics followed by relaxation via the Greens function. Results were obtained for an edge dislocation interacting with a 2-nm void in bcc iron. Favorable comparisons were made to calculations using the Periodic Array of Dislocations (PAD) procedure introduced by Baskes and Daw. The Green function boundary condition (GFBC) removes unphysical forces between dislocations and their periodic images that occur in the PAD method. PAD calculations are made with very large numbers of atoms in the cell to reduce the effect of image forces resulting from periodic boundary conditions. GFBC calculations give results similar to PAD simulations using much larger cells. Both give the same Peierls stress of 24 MPa and similar critical strain [0.033% (GFBC) and 0.035% (PAD)].

Several hundred density functional results of atomic forces and energetics of defects in iron with or without hydrogen were used to quantify the energy and magnetization landscape of the FeH. The first-principles calculations are to be used for developing embedded atom classical force fields.

We have proposed a global Hamiltonian that describes an atomistic region representing a single event such as a moving dislocation that is embedded in a thermally averaged coarse grained region. The formalism is based in part on classical density functional theory but at a higher order than was typically used. We have formulated the functional to be applicable to a MD region embedded in a FE region. The central quantity in this formalism is the pair distribution function, which is usually thought of as isotropic.

Our work on absorbing boundary conditions started with a theory for outgoing waves in a system described by partial differential equations. Our initial code was for a transverse elastic wave in one dimension; however, our real interest is in the interface of MD with FE in 3-d. We wrote a 1-d MD code in which we implemented absorbing boundary conditions. A number of analytic and simulated results have been obtained for the 1-d with nearest-neighbor harmonic interactions.

D06-105: Exploring Performance Tools for Petascale Systems with Lightweight Compute Node Kernels

Philip C. Roth, Richard F. Barrett, and Jeffrey S. Vetter

Project Description

A fundamental part of the Office of Science's leadership-class computing strategy is the use of systems like the Cray XT3 with a large number of simple compute nodes, each running a lightweight operating system kernel (LWK). Such systems are attractive for large-scale scientific computing because their lightweight kernels enable application scalability and performance predictability. However, these systems present a challenging target for performance, correctness, and system administration tools. Large numbers of application processes stress tool scalability, and lightweight kernels lack higher-level operating system services used by tools to monitor and control application processes. We propose to investigate petascale performance tools in the context of LWK systems like the Cray XT3 system deployed at Oak Ridge National Laboratory (ORNL). First, we will examine the feasibility of dynamic software-based instrumentation techniques on such systems. This type of instrumentation can adapt its behavior to the performance phenomena of the application and system, enabling a user to gain performance insight as the application executes. Second, we will explore the use of hierarchical communication and data aggregation techniques for tools on LWK systems. Our earlier work with the MRNet tool infrastructure explored such techniques on systems running full-operating-system kernels, but their use on LWK systems remains unexplored. Finally, we will investigate the automation of performance analysis techniques like multivariate statistical analysis on systems with lightweight compute node kernels. Automated techniques enable users to distill insight from their application's behavior without requiring them to become performance analysis experts.

Mission Relevance

This research addresses ORNL's long-term objectives in the Terascale Computing and Simulation Science initiative by investigating techniques for analyzing the performance of scientific codes at scale. The work responds to the programmatic opportunity for establishing ORNL as a world leader in capability computing and in scalable performance tools. Because the techniques we will investigate can also be used on systems with traditional compute node kernels and in correctness (e.g., debugging) and system administration tools, our results will generalize to a wider class of tools and systems to support ORNL's leadership computing strategy. Successful pursuit of this project will also benefit other agencies with significant interest in petascale computing, including the Department of Defense (Defense Advanced Research Project Agency, High Performance Computing Modernization Program), the National Security Agency, and the National Aeronautics and Space Administration.

Results and Accomplishments

During FY 2006, the project's first year, we made significant progress in two areas: petascale performance tool infrastructure and scalable performance analysis results visualization techniques. In the first research area, we made progress in developing a prototype tool infrastructure to support the investigation of scalable techniques for diagnosing performance problems in scientific programs running on large-scale systems such as the systems slated for deployment at the National Leadership Computing Facility at ORNL. The target of our work has been the ORNL Cray XT3, a large-scale system with a lightweight compute node kernel called Catamount. We prototyped the support for launching a tool and a parallel application as part of the same XT3 batch queue job, necessary for monitoring parallel applications with on-line tools that share the compute nodes of a parallel computing system. We also made progress adapting our MRNet hierarchical overlay network software, initially developed for compute cluster systems running the full-featured Linux operating system, to the Portals high-performance data transfer software used by the XT3. In the second research area, we implemented and evaluated a visualization technique called the Sub-Graph Folding Algorithm (SGFA) for making scalable graph-based presentations of the results of a performance diagnosis technique that automatically searches through a space of potential performance problems to identify the problems afflicting a parallel program. For one of our test programs with 1024 processes, the SGFA reduced a performance diagnosis results graph with over 30,000 nodes to a composite graph with 44 nodes showing the same qualitative problem diagnosis information.

Publication

Roth, P. C. 2006. "On-line Automated Performance Diagnosis on Thousands of Processes." *2006 ACM SIGPLAN Symposium on Principles and Practice of Parallel Programming (PPoPP'06)*, May 29–31, 2006, Manhattan, NY.

D06-116: Ensuring Dynamic Power Grid Stability: Integrated Electric and Information Grid Modeling

Mallikarjun Shankar, James Nutaro, Phani Teja Kuruganti, Kalyan Perumalla, and John Stovall

Project Description

The electric power systems industry is increasingly deploying modern information technology and algorithmic techniques to solve management and control problems in the distributed electric power grid. The transient dynamics and information processing mechanisms of the complex interconnected electric grid need greater understanding, while current state-of-the-art modeling for cascading failures and distributed behaviors considers only smaller systems or simplified steady-state network models. This project claims that computational techniques can help ensure the dynamic power grid's stability. While computational techniques to support integrated information and electric grid modeling and analysis are enabled by the advent of ubiquitous computational infrastructures, developing an integrated information and electric grid modeling method is a major challenge which requires a combined modeling, simulation, and analysis approach. The joint representation of the electric grid (analog and continuous) and the computational infrastructure (digital and discrete) requires information and control to cross the dividing line between the two infrastructures. We approach this problem by treating both infrastructures as network graphs in which the power network is mirrored by a distributed sensor network that carries sensor and actuation information (i.e., we consider the electric grid as a distributed network of physical devices, sensors, communication networks, and compute nodes). This approach allows us to use traditional computational techniques. By formulating electrical-grid-stability concerns such as frequency control during load-loss recovery as a distributed sense-response problem, we employ and evaluate algorithms that can prevent system degradation and collapse. We also support the computational approach by incorporating a user-directed discovery process based on data analysis and visualization. By compiling data sets from advertised outage databases, we are applying classification techniques to identify patterns in outage (and response) behavior. For the user-directed discovery process, we are developing geo-spatial visualizations of power system state and of the outage data sets.

Mission Relevance

New federal and industry initiatives for distributed power generation, distributed power storage, and demand-response-based market participation in power grid control make it increasingly urgent to examine the interaction between the power grid and its information backplane, and their consequent impacts on stability. Major power-generation companies and transmission and distribution operators are attempting to make the case for increased infrastructure investment and analysis directed at antiquated grid components following the Energy Policy Act (EPACT) of 2005. A set of arguments that justifies and highlights the importance of the infrastructure investment will emerge from this project. The research is relevant to the DOE offices of Electricity Delivery and Energy Reliability (e.g., the Visualization and Controls thrust, GridWise-ModernGrid and its follow-on efforts) and Energy Efficiency and Renewable Energy. The results emerging from this project also have implications for critical infrastructure protection and assurance under the Department of Homeland Security. Recent research opportunity notices from state energy commissions (e.g., California Energy Commission) and from DOE suggest that our proposed research is well aligned with strategic agency requirements.

Results and Accomplishments

In 2005–2006 we made significant strides as evidenced by the following activity summary:

- *Modeling and Simulation*: hybrid modeling—we developed scenarios for joint continuous and discrete event modeling; we have created an initial tool platform for hybrid simulations.
- *Data-Analysis*: construction of outage data set for analysis—we reviewed the Disturbance Analysis Working Group data advertised by North-American Electric Reliability Council and created a scrubbed data set for analysis along two main axes. The first is to use well-known data-mining and visualization methods to identify anomalous or unexpected behavior. The second is to analyze the behavioral effects embedded in the outage data as extremes in the larger context of system faults.
- *Algorithmic formulation*: distributed agent based response—we have formulated the distributed response mechanism on the electric grid as a set of software modules (or agents). These agents will respond to sharp load variations (due to frequency excursion caused generator shutdown or restart) by locally reacting to loads. We have reproduced the models generated by leading researchers in the field and are currently applying different algorithmic strategies to assess distributed software's response efficiencies.
- *User-Oriented Discovery*: targeted contingency analysis and visualization—we have developed software modules that enable situational awareness of the electric grid and enable targeted contingency analysis of regional failures (e.g., due to hurricanes).

Publications

Nutaro, J. J. "An optimistic simulation algorithm for DEVS models and its correctness proof." *Trans. Soc. Comput. Simul.* Submitted.

Nutaro, J. J. 2005. "Constructing Multi-point Discrete Event Integration Schemes." Winter Simulation Conference, December 4–7, 2005, Orlando, FL, USA.

Nutaro, J. J., et al. "A Technique for Integrating Hybrid System Simulation Models and Discrete Event Simulation Software Packages." 40th Annual Simulation Symposium (ANSS), March 25, 2007, Norfolk, VA, USA.

Nutaro, J. J., et al. 2006. "Integrated modeling of the electric grid, communications, and control." ORMMES'06, September 6, 2006, Coimbra, Portugal.

Nutaro, J. J., et al. "Hybrid power system modeling with DEVS." *Discrete Event Dynam. Syst.* Submitted.

Nutaro, J. J. and B. P. Zeigler. "A Stability Theory for Discrete Event Solutions of Differential Equations using Quantization." *J. Comput. Phys.* Submitted.

D06-117: Automated Code Transformations in Support of Ultrascale Code Migration

Wael R. Elwasif, David E. Bernholdt, Robert Harrison, Richard T. Mills, Michael Summers, Christian Y. Cardall, and Anthony Mezzacappa

Project Description

The success of the ORNL Leadership Computing Facility (LCF) depends, in large measure, on the ability of computational science software to effectively utilize LCF resources for petascale simulation. Historically, porting of codes to new architectures and tuning them for high performance has been a time-consuming process, in which performance problems are isolated and remedied one at a time. Where code motifs that perform poorly on the target platform are used extensively, tedious changes are required to replace them throughout the code, generally by hand. This project investigates the use of "source-to-source" (S2S) transformation technologies to capture and apply the changes required to adapt codes to new platforms, allowing those transformations to be systematically and quickly applied throughout the code.

Mission Relevance

This project is relevant to the Computer Science and Leadership Class Computing thrust areas within the DOE Office of Science, Advanced Scientific Computing Research Program. This project supports the President's American Competitiveness Initiative to develop a "world-leading, high-end computing capability (at the petascale) and capacity." If successful, this project would streamline the process of migrating scientific codes to novel high-end computing platforms and programming paradigms and enable the acquisition of the expertise of porting and optimization experts in an automated and reusable form. This project also ties into the Defense Advanced Research Project Agency (DARPA) High-Productivity Computing Systems (HPCS) goal, as it looks into the possibility of introducing automation to facilitate the migration towards novel programming paradigms similar to those envisioned in the HPCS project.

Results and Accomplishments

We successfully developed pilot source-to-source transforms using the ROSE compiler infrastructure developed at Lawrence Livermore National Laboratory (LLNL) to facilitate the porting of code that uses the vector component of the Portable, Extensible Toolkit for Scientific Computation (PETSc) math library developed at Argonne National Laboratory (ANL) from version 2.2.1 to version 2.3.0 and applied those transforms to the PETSc example suite to validate their correctness. We also developed transforms to convert scientific codes written in the C programming language that use the *arrays-of-structs* data structure to an equivalent code using the *struct-of-arrays* data structure. This change should lead to improved performance in code fragments that have a sequential access pattern to entries in the aforementioned data structures. Finally, we developed a tool to enable the development and deployment of source-to-source transforms for scientific codes written in the Fortran programming language, which dominates the scientific programming universe. This tool, named *Fortran Smart*, is being used to deploy Fortran S2S transforms to sample codes.

D06-133: Large-Scale Exploration of Protein Models for System Biology Applications

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Project Description

The elucidation of functional roles for hypothetical proteins is one of the most important and interesting problems in modern biology. Even partial characterization of the hypotheticals will give a tremendous boost to our ability to reconstruct cellular networks and put together predictive models in the bacterial organisms central to energy production and bioremediation efforts. For this class of problems, computational modeling provides a truly unique value, as a few biological experimental techniques can be used without at least an initial hypothesis about the function. We propose to build high-performance computing implementation of the ROSETTA program—a leading ab initio folding platform—and apply it to system-wide studies of the organisms targeted by the DOE bioenergy program. The proposed algorithmic innovations are targeting two main research directions: (1) improve the prediction quality through more efficient and comprehensive sampling of the conformational space and (2) find new ways to discriminate successfully folded models and translate their structures into biological insights.

Mission Relevance

Our approach is aimed at providing significant impact to the DOE system biology effort through the extensive structure modeling of the bacterial proteins targeted by large research efforts for their energy production potential within the DOE Office of Science, Biology and Environmental Research Program. The most relevant efforts are the Genomics:GTL research initiative and the planned DOE biofuel centers. The determined structure will provide multiple opportunities for further analysis and may immediately point to the range of possible functional roles for the sequence in question. The proposal is focused on modeling the hypothetical proteins by engaging petascale computer power, and the corresponding technology advances the research agenda of the Office of Advanced Scientific Computing. The acquired technology may be used in the biological networks in other organisms, and the broader impact is relevant to research efforts at the National Institutes of Health (in NIH Centers of High Accuracy Protein Modeling), Department of Defense (DOD) Defense Advanced Research Projects Agency (DARPA), for designing protein with new properties, and Department of Homeland Security (DHS) bio-defense initiatives.

Results and Accomplishments

During FY 2006, we implemented the Parallel Monte-Carlo ROSETTA platform and conducted several types of folding experiments on ~500 functionally important protein domains. It was shown that the Parallel ROSETTA has a unique capability to cross high potential energy barriers and is incomparably better in the exploration of the possible chain conformations than the previous implementations of this algorithm. For the first time, we have demonstrated that longer simulations do produce qualitatively new effects, indicating the possibility of reaching full Monte-Carlo convergence at least for the shortest protein domains. These technological breakthroughs led to a significant increase in the model quality across the whole investigated benchmark. In the subset of the shortest domains, the achieved improvements have crossed a crucial threshold, as high-quality structures were obtained for 75–88% of all tested sequences. With this success rate, it is feasible to apply this technology to system biology problems, such as an annotation of the hypothetical proteins in the targeted genomes. In addition, the enormous volume of the conducted simulations (over 500 protein domains) and significantly improved ability to search conformational space led to much better understanding of the folding simulation themselves. One of the main remaining obstacles is the situation when all Monte-Carlo trajectories are passing too far (beyond 4A root mean square deviation) from the native structure. Further improvements in the fragment libraries and experiments with quantum mechanics–derived energy functions are two possible ways to resolve this problem and further extend the set of protein structures for which predictions can be reliably made.

D06-140: Exploring Reconfigurable Computing Programming Models to Accelerate High-Performance Computing Applications

Olaf O. Storaasli

Project Description

High-performance computer (HPC) vendors see field-programmable gate array (FPGA)–based computing as their next major performance advance. Silicon Graphics Inc. predicts FPGAs will “accelerate mission-critical applications by over 100×.” Cray selected DRC FPGA co-processors for future supercomputers, as they offer “the greatest opportunity for application acceleration,” enabling new scientific breakthroughs to solve hitherto intractable problems.

New algorithms are needed to effectively exploit FPGAs for large-scale scientific codes, a challenge requiring bottom-up FPGA expertise and a top-down HPC application developer/user perspective. This research proposes a computational framework to speed scientific codes used by DOE by placing their computation kernels (floating point, fast Fourier transforms, matrix and linear algebra, etc.) on FPGAs via appropriate tools/languages. This research leverages close collaboration with the HPC group at Xilinx (main FPGA vendor), Cray, Mitrion, University of Tennessee (UT), the National Science Foundation Center for High-Performance Reconfigurable Computing at the University of Florida, SRC Computers, OpenFPGA.org, and others.

Mission Relevance

This research supports DOE’s Office of Science Ultrascale Computing Initiative and the President's Information Technology Advisory Committee (PITAC May 2005) as being “critical to scientific leadership, economic competitiveness, and national security.” It is anticipated to grow into a broader program impacting diverse technologies supporting the Defense Advanced Research Projects Agency (DARPA), the Air Force, Army, Department of Homeland Security, National Security Agency, and National Aeronautics and Space Administration (NASA). This research should demonstrate how key DOE codes (climate/weather, bioinformatics, and matrix equation solution) can achieve major performance gains by harnessing FPGAs, leading the way for other codes to follow. FPGA acceleration may prove attractive for Oak Ridge National

Laboratory (ORNL) application performance to exceed 1 PetaFLOP, enabling major application speedups and scientific breakthroughs.

Results and Accomplishments

Since our February 2006 start, we have made significant progress. All tasks are progressing well and have been expanded and accelerated with no-cost additions of Xilinx's HPC team, a UT professor and full-time Ph.D. student, Mitrion programmer, plus hardware and software donations. C-to-FPGA compilers (Xilinx, DSPlogic, and Mitrion) speed our FPGA code development over traditional coding methods. Already, weather/meteorology and bioinformatics codes have been ported to FPGAs and different tools evaluated. This rapidly moving research benefits from experts participating in biweekly OpenFPGA steering committee meetings. Initial results using ORNL's FPGA-equipped Cray XD1 using Mitrion-C were compared with other HPC systems (SRC, Starbridge's Viva). It appears FPGA acceleration of 5× is possible for initial applications with kernel speedups up to 10–15×.

General

D05-009: Applications of Ultrafast, Ultraintense Lasers to Radioactive Ion Beam Production and Diagnostics

David R. Schultz, Charles R. Vane, James R. Beene, Daniel W. Stracener, Charles C. Havener, Herbert F. Krause, Junjien Liang, Robert W. Shaw, Warren P. Grice, Anatoly Maksimchuk, and Donald P. Umstadter

Project Description

Enabled by extremely rapid advances in ultrafast, ultraintense laser (UUL) technology, we are pursuing development of innovative methods for laser acceleration of charged particles, particularly electrons, to relativistic energies as a means for producing radioactive ions for nuclear physics research and other applications. Specifically, we are investigating and developing the necessary stages of proof-of-concept to produce neutron-rich ion beams and diagnostics for those beams, utilizing UUL pulses. In addition, many novel features of these high-power-density light pulses are being explored with respect to enabling applications aiding other key ORNL objectives, such as providing a compact, ultrafast X-ray light source complementing neutron-scattering capabilities for nanophase, chemical, biological, and material sciences.

Mission Relevance

This work is particularly relevant to the DOE Office of Nuclear Physics, specifically to a program of upgrades to the ORNL Holifield Radioactive Ion Beam Facility (HRIBF) that will continue until an alternative successor to the Rare Isotope Accelerator project takes shape. The addition of a second unstable nucleus production accelerator would significantly expand HRIBF capabilities, and a compact, laser-driven photofission source would fit particularly well as a crucial component of the upgrade plan. The DOE, the Nuclear Science Advisory Committee, and various review committees have endorsed upgrading HRIBF, and the photofission driver could substantially extend the lifetime of HRIBF as a world-leading facility. UUL-based technology can also be applied to homeland security as a compact tool for photofission-based interrogation of shipping containers, to the production of isotopes of interest to the National Nuclear Security Administration (NNSA), and for use in radiotherapy and medical diagnostics. Finally, having built a core UUL science and applications team and established laser-driven electron acceleration capability at ORNL, the basis will exist for further spin-off development work to create an ultrafast Thomson X-ray scattering light source that will provide new opportunities for our nanophase, biological, chemical, material, and physical sciences programs supported by the DOE Office of Basic Energy Sciences.

Results and Accomplishments

During FY 2006, the project's second year, we made significant progress in three areas. (1) We completed data analysis and submitted two papers based on the results of measurements taken at the University of Michigan of nuclear photo-excitation of carbon and copper and uranium photofission induced by bremsstrahlung from laser-accelerated 100- to 150-MeV electrons. These results were the first of their kind to employ a new, more efficient regime of laser plasma wake-field acceleration and showed an enhancement of 10–100 in radioisotope production yields over previous measurements at other laboratories. One paper has been accepted for publication in

Applied Physics Letters. (2) We designed, constructed, and tested a new pulsed, high-helium-density, high-repetition-rate-capable gas jet target apparatus, which has been shipped to the DIOCLES laser facility at the University of Nebraska at Lincoln, Nebraska. This apparatus is currently being installed there and will be used for electron acceleration and radioisotope production experiments this year, which at full design capability will be the highest time-average power ultrafast laser in the country. (3) We developed a new gas target time- and spatial-profiling capability for use with the new pulsed gas jet target apparatus based on elastic scattering of electrons. This will be used at DIOCLES to optimize the time and spatial overlap of the laser pulses with the dynamics of the pulsed supersonic jet target.

D05-108: Optimization Studies for ISOL-Type High-Powered Targets

Igor Remec, Tony Gabriel, Kenneth Childs, Mark Wendel, Georg Bollen, Reginald Ronningen, and Martin Grossbeck

Project Description

At present, several radioactive ion beam facilities (RIBFs) are operational; these include the Isotope Separator and Accelerator (ISAC) [TRI-University Meson Facility (TRIUMF), http://www.triumf.ca/], Argonne Tandem Linac Accelerator System (ATLAS) [Argonne National Laboratory (ANL), http://www.phy.anl.gov/atlas/], the National Superconducting Cyclotron Laboratory (NSCL) [Michigan State University (MSU), http://www.nscl.msu.edu/], and the Holifield Radioactive Ion Beam Facility (HRIBF) [ORNL, http://www.phy.ornl.gov/hribf/]. Research on short-lived nuclei (rare isotopes) that are far from the band of stable nuclei is focused on seeking answers to some of the most fundamental questions of nuclear science: those about the beginnings of matter and, ultimately, life. Progress in this science, however, requires the development of a new generation of RIBFs, capable of producing radioactive beams with intensities far exceeding present capabilities. This research will require the use of high-intensity primary beams. The heating and radiation damage rates in these new facilities will far exceed those encountered at the Spallation Neutron Source or at ISAC and will be a source of major concern regarding the design and operation of high-powered targets. The purpose of this research is to initiate the investigation and optimization of isotope separation on line (ISOL) targets for future RIBFs through advanced computer simulations. In an ISOL target, a high-energy (e.g., GeV) light-ion beam (e.g., proton) from an accelerator produces a wide range of rare isotopes by either the spallation and/or fission processes in the primary target, or by fission induced in a secondary target that contains fissionable material and surrounds the primary target. Rare isotopes migrate through diffusion/effusion processes into an ion extraction source where they are ionized, extracted, accelerated, and used for experiments. Detailed calculations of primary beam interactions with the target, combined with computational fluid dynamics simulations and thermal analyses, were used to study the one- and two-step ISOL targets.

Mission Relevance

This work is relevant to the DOE, Office of Science, Office of Nuclear Physics programs geared towards the development of a new-generation radioactive ion beam facility. The line item project, Rare Isotope Accelerator (RIA), was given Critical Decision-0 status in 2005. From 2004 to 2006 most of the authors of this LDRD project participated in a multi-institution collaboration involving Michigan State University, Oak Ridge National Laboratory, Lawrence Livermore National Laboratory, Lawrence Berkeley National Laboratory, Argonne National Laboratory, and Los Alamos National Laboratory, which performed preconceptual research and design for the RIA ISOL and fragmentation target areas and other related components, such as beam dumps and second-ion-beam stripping regions. In October 2006, these collaborators submitted several proposals in response to the Office of Nuclear Physics program's request for proposals on research and development of rare isotope beam capabilities. This collaboration's proposal entitled "Optimization Studies for ISOL-Type High-Powered Targets," if successful, will allow us to continue and expand the work started by this LDRD project.

Results and Accomplishments

We investigated one-step (direct) uranium carbide (UC) targets and two-step ISOL targets with UC_x secondary targets. Operation of both types of targets is limited by the requirement to maintain the maximum temperature of UC_x below ~2200°C so that the UC_x dissociation rate remains sufficiently low. The one-step target, consisting of UC (natural U) and cooled by thermal radiation, appears to be able to produce up to ~2.8×10^{13} fissions per second (f/s), with 1-GeV proton-beam power of 19 kW. A two-step target with a mercury and water-cooled-tungsten primary target shows about equal performance in terms of fission rate in the secondary target. About 20% by volume of water is needed for adequate cooling of tungsten at the primary-beam power of 400 kW. Heavy-water coolant shows no advantage over ordinary water. A two-step target can operate at the beam power of ~140 kW and produce ~3.7×10^{14} f/s without active cooling of the secondary UCx target. A secondary target actively cooled with helium can produce ~5.3×10^{14} f/s at a beam power of ~200 kW, while cooling with sodium allows up to ~300 kW of primary beam power and 7.7×10^{14} f/s. Using adiabatic conditions on the outer surface of the secondary target near the target ends results in a more uniform temperature profile, and the resulting penalty on the beam power is only about 5%. Comparison of the beam results of 1-GeV proton, 622-MeV/u deuterium, and 777-MeV/u He-3 indicates that the proton beam gives the best performance. This performance is based on the fission rate in the secondary target and the energy deposition in the primary target.

Publication

Remec, I., et al. 2006. "Particle and Radiation Simulations for the Proposed Rare Isotope Accelerator Facility." *Nucl. Instrum. Methods Phys. Res. A.* **562**, 896.

Seed Money Fund

S05-064: Identification of Protein-DNA Interaction and Protein-Protein Interaction in Single Living Cells Using Optical Nanosensors

Yisong Wang, Yie Liu, and Tuan Vo-Dinh

Project Description

Characterizing molecular interactions in the context of a live cell is a significant challenge for postgenomic studies. This proposal aims to develop DNA- and protein-based optical nanobiosensors and methods to detect protein-protein and protein-DNA interactions in single living cells. We are investigating the use of unique optical nanobiosensors that can be inserted into single living cells to detect molecular interactions without disrupting normal cellular processes. The new method will involve DNA- or protein-based nanobiosensor with a direct in vivo sensing capacity. We are also studying molecular interactions with a special emphasis on developing new detection systems in a single living cell. Our objectives are (1) development and application of optical nanobiosensor technology to protein-DNA interactions and (2) development and application of optical nanobiosensor technology to protein-protein interactions. This work will greatly enhance and benefit interdisciplinary approaches to biological research and current nanotechnology programs at ORNL.

Mission Relevance

This work will benefit programs of DOE, the Department of Homeland Security (DHS), the Department of Defense (DoD) [Defense Threat Reduction Agency (DTRA), Defense Advanced Research Projects Agency (DARPA)], the Department of Justice (DOJ), and the National Institutes of Health (NIH). The NIH has recently started several initiatives and issued a call for proposals focused on optical technologies for minimally invasive diagnostics of diseases. The NIH has also established a National Institute for Biomedical Imaging and Bioengineering (NIBIB), with biosensor technologies being one of its top funding priorities. The proposed research fits very well with these NIH initiatives. Finally we will also pursue technology transfer opportunities with commercial companies working in sensor technologies.

Results and Accomplishments

This proposal aims to develop optical nanobiosensors to detect protein-protein and protein-DNA interactions in single living cells. This will allow, for the first time, studies of molecular interaction in the context of functional cell architecture. Since protein-DNA interaction and some of the biologically critical protein-protein interaction take place in the nucleus of a cell, we are focusing our attention on the detection of these molecular interactions in the nucleus. We have devoted extensive effort to investigate methods to improve the reproducibility of nanofibers. The nanofibers were covalently bound with molecules, such as short telomere repeats, that are selective to target analyte fluorescent molecules in the nucleus. We have explored the use of these treated fibers in several types of mammalian cells and are currently modifying and improving our nanofibers, covalent binding procedures, and nanofiber insertion techniques. The protocol we have established is currently being tested in the detection of single molecular interactions in the nuclei of living cells.

S06-010: Generation of Mouse Embryonic Stem Cell Lines to Study the MicroRNA Functions through Conditional and Cell Lineage–Specific shRNA Knockdown Approaches

Yisong Wang

Project Description

MicroRNAs, a member of the noncoding small regulatory RNA family, have recently been shown to regulate gene expression during embryonic development, tumorigenesis, virus infection, cell proliferation, death, and angiogenesis. There are more than 400 microRNAs identified experimentally in humans so far, and only a few of them have been functionally characterized. Recent findings suggest that specifically designed small hairpin RNA (shRNA) can be used to knock down genes of interest. We propose to use a novel vector-based shRNA knockdown strategy to conditionally and cell lineage–specifically deplete the expression of specific microRNAs in mouse embryonic stem (ES) cells. Validated ES cell clones deficient in specific microRNA expression will be used to study the effects of these microRNAs on cell proliferation, differentiation, death, and tumorigenesis. This work will pave the way for the functional annotation of microRNAs in mammalian cells and thus will facilitate our understanding toward the development of cancer and related diseases.

Mission Relevance

It is calculated that more than half of protein-coding genes in the human genome are regulated by microRNAs, and thus every human disease may have microRNA components. Every health-funding agency, including NIH, will benefit from our studies. Demonstration of success in our complete experimental pipeline in shRNA cloning and mutant embryonic cell line production and verification of expression of the targeted microRNAs in embryonic stem cells will benefit NIH programs. The microRNA mutant embryonic stem cells generated in this study may be used to generate mutant microRNA-deficient mice in the future, some of which could be useful as unique animal models to study the mechanistic effects of biohazardous or bioterror materials for DOE-sponsored national security programs. This work will also benefit the DOE-sponsored Collaborative Cross Program/Mouse User Facility at ORNL.

Results and Accomplishments

During our project’s first year (FY 2006), we have engineered doxycycline-regulatable shRNA cassettes for five target microRNA genes (miR-145, 192, 218-1, 218-2, and 224), as well as constitutive and doxycycline-regulatable transgenic rescuing vectors for four microRNA genes (miR-192, 218-1, 218-2, and 224). We have introduced both the specifically designed shRNA and transgenes into mouse embryonic stem cells by stable transfection and obtained stable mouse embryonic stem cell lines. Our preliminary screen indicated that two out of five targeted microRNAs were significantly knock downed by the shRNA approach in a total of ten isolated stable stem cell clones, and all four transgenic stem cell clones expressed the introduced transgenes. We are currently isolating more shRNA clones that show significant downregulation of three more targeted microRNAs and investigating the effect of microRNA knockdown on cell proliferation, apoptosis, differentiation, and tumorigenesis in those mouse embryonic stem cells with mutant microRNAs.

Publications

Gomez, M. V., et al. 2006. "PARP1 is a TRF2-associated poly(ADP-ribose) polymerase and protects eroded telomeres." *Mol. Biol. Cell.* **17**, 1686.

Wang, Y. and Y. Liu. 2006. "Msh2 deficiency leads to chromosomal abnormalities, centrosome amplification, and telomere capping defect." *Oncogene* **25**, 2531.

S06-031: A Genomic Analysis of Microbial-Mediated Metal Transformation

Antony V. Palumbo, Steven D. Brown, and Craig C. Brandt

Project Description

Anaerobic sulfate–reducing bacteria (SRB) are a diverse group of microorganisms that participate in a wide variety of important environmental processes. In addition to their role in the sulfur cycle, SRB are key organisms in several processes that have significant consequences for humans, including production of monomethylmercury (a potent human neurotoxin), bioremediation of metals such uranium, and corrosion of buried iron tanks and pipelines. Unfortunately, the molecular mechanisms of these processes are not well known. To address this problem, as part of this project we have constructed a whole genome microarray for *Desulfovibrio desulfuricans* G20, a representative member of the SRB and an organism whose genome has been sequenced by the DOE. Microarray technology is an important tool that allows researchers to obtain insights into cellular processes by examining gene expression under various physiological states. Using the new microarray and one for *Desulfovibrio vulgaris* that is currently available at ORNL, we will study the molecular mechanisms of mercury methylation. Our research will (i) characterize mercury methylation capabilities in *D. desulfuricans* and *D. vulgaris*; (ii) construct a whole-genome microarray for *D. desulfuricans*; and (iii) conduct baseline gene expression experiments on *D. desulfuricans* and *D. vulgaris*.

Mission Relevance

This research supports the DOE Genomics:GTL and Environmental Remediation Sciences Program (ERSP) programs. Both of these programs are concerned with metal contamination. The fundamental science and physiology of metal transformations is a focus of the GTL program. The environmental transformations and remediation of metals are the major focus of the ERSP program. Both mercury and uranium are of concern to ERSP. Since *D. desulfuricans* G20 reduces uranium and presumably methylates mercury, it is relevant to the focus of the ERSP program.

Results and Accomplishments

We have obtained and grown a number of *Desulfovibrio* strains from the American Type Culture Collection (ATCC) and conducted preliminary mercury methylation assays in *D. desulfuricans*, *D. vulgaris*, and control strains (Task i). The results from these preliminary assays will become available in FY 2007 and guide gene expression studies that will be conducted in FY 2007 (Task iii). We designed a whole genome microarray for strain G20 that contained 3532 unique gene probes, and a further 151 genes were able to be represented by group probes, which represent more than one gene. This was made possible as the 3.7 Mb *D. desulfuricans* G20 genome was sequenced and predicted to contain 3775 candidate protein-encoding genes (http://genome.jgi-psf.org/finished_microbes/desde/desde.home.html). We designed the oligonucleotide probes for the array using ORNL designed software and had the probes synthesized. A total of 3683 genes were represented on the microarray, or 97.6% of the genome (Task ii, completed).

Preliminary whole-genome microarray hybridizations with *D. desulfuricans* G20 genomic were conducted to test the quality of the constructed array. G20 genomic DNA was labeled with either the Cy5 or Cy3 dye and co-hybridized on the G20 array. The normalized data points grouped closely together and all were within the two-fold bounds, indicating that the array did detect genomic DNA and is not biased. The array will be used to give a preliminary snapshot of genes involved in mercury methylation.

S06-059: Establishing a Targeted Mutagenesis System in *Clostridium cellulolyticum*

Yunfeng (David) Yang and Zamin Yang

Project Description

Clostridium cellulolyticum is a model organism for the mesophilic degradation of cellulose, which is critical for bioethanol production since it is the most abundant organic polymer in nature and largest component of all plant biomass. Cellulose has the potential to be fermented into useful products such as ethanol, butanol, and hydrogen, making it appealing for the production of biofuels. Although it is known that *Clostridium cellulolyticum* digests cellulose by secretion of a cellulosome, protein complex, industrial utilization of the bacterium has been greatly impeded by a lack of fundamental biological knowledge. To address this gap, ORNL is currently working with the DOE Joint Genome Institute to sequence and annotate the bacterial genome. The next challenge is to develop a genetic system for mutagenesis so that the sequence information can be leveraged and the key proteins involved in cellulose degradation be identified and characterized. In this study, we will establish a targeted mutagenesis method in *Clostridium cellulolyticum*. Suicide vectors available in other related bacteria will be engineered to carry appropriate antibiotic markers for *Clostridium cellulolyticum* and to incorporate DNA fragment(s) of the targeted gene. After transforming the manipulated DNA into bacterial cells, it will be forced into the genome by homologous recombination, resulting in disruption of the targeted gene. The successful accomplishment of this project will make it possible to study genes implicated in biofuel production in the native host *Clostridium cellulolyticum*.

Mission Relevance

This research directly addresses the national need to develop biofuels as a major secure energy source. Currently, basic research of bioenergy production is one of the top priorities of the DOE Office of Science. The Genomics:GTL facility plans have in fact recently been modified to reflect an emphasis on biofuels.

Results and Accomplishments

During FY 2006, we have tested and compared several defined media (CC-C modified, HEPES, and GS medium) in which to grow the obligate anaerobic bacterium *C. cellulolyticum*. GS medium was selected because it allows for highest yield of the bacterium [O.D. (600 nm) of >0.1 in defined medium and ~0.5 after adding yeast extract]. We also installed an electroporator in the anaerobic chamber and obtained by purchase/request several strains and plasmids relevant to our molecular biology work. We are currently testing the transformation efficiency using pSOS95. Genomic DNA of *C. cellulolyticum* has been prepared and used as template to PCR amplify the target genes. We are currently engineering two plasmids, pSOS95 and pKNOCK, to insert target genes Cel8C and Cel9E. pKNOCK will be used as suicide vector for insertional mutagenesis, and expression vector pSOS95 will be used as a control for mutagenesis. In addition, expressing a small piece of the ORFs of the target genes on pSOS95 enables antisense RNA silencing of the target genes, which is an excellent alternative strategy and should be compared to insertional mutagenesis in parallel.

S04-020: Creation of Photosystem II Designer Alga for Hydrogen Production

James W. Lee

Project Description

This project focused on a proof-of-principle study to control the expression of photosystem II (PSII) oxygen evolution activity through an innovative application of the latest RNA-interference technique. We hoped to create a PSII designer alga that could be used to produce photosynthetic hydrogen without the three problems associated with oxygen evolution: (1) the drainage of electrons by oxygen, (2) the poisoning of hydrogenase by oxygen, and (3) the mixed hydrogen and oxygen gas-product separation and safety issues. The fundamental question (hypothesis) is whether this RNA-interference technique can be used to selectively (and switchably) suppress the expression of the PSII oxygen-evolving complex so that all three oxygen-related problems can be eliminated under hydrogen-producing conditions. We tested the hypothesis by synthesis and application of designer OEE1 RNA-interference genes to selectively (and switchably) suppress the expression of the OEE1 subunit of the PSII oxygen-evolving complex.

Mission Relevance

This work is directly relevant to DOE national energy security objectives in that it supports the development of a clean and renewable algal hydrogen energy resource. It also supports the President's Hydrogen Initiative and is in line with the goals of the DOE EERE and BES Hydrogen Programs. Successful development of this new approach to control the evolution of oxygen could have a significant impact (a 10-fold improvement) on technology development in the field of renewable hydrogen research.

Results and Accomplishments

Significant progress was made in FY 2006. Two more synthetic genes with improved promoter sequences were designed, physically synthesized, and successfully delivered into the algal host organism *Chlamydomonas reinhardtii* to encode for an interference iRNA that could suppress the expression of a photosystem II gene OEE1. The synthesis of the two designer genes was accomplished in collaboration with Bioclone Inc. The delivery of the designer genes into the alga was done in our laboratory using electroporation gene transformation. We successfully generated a number of algal transformants that contain the OEE1-iRNA designer genes, as confirmed by DNA PCR experiments. Our recent assays of photosynthetic oxygen evolution, carbon dioxide fixation, and hydrogen production demonstrated that transformants such as O12-2 and O12-16 indeed manifest the predicted suppression of PSII oxygen evolution activity upon expression of the designer OEE1-iRNA genes induced under anaerobic (hydrogen-producing) conditions. Our latest reverse transcriptase PCR assays of mRNA showed that the designer genes were expressed selectively only under anaerobic conductions as expected. The objective of this project has therefore been achieved, and the results demonstrate that it is indeed possible to use designer iRNA genes to control the expression of PSII oxygen evolution activity for enhanced photobiological hydrogen production.

Publication

Zhao, B., et al. "Calvin-cycle activity inhibits photobiological hydrogen production: a study with Rubisco-deficient mutants of Chlamydomonas reinhardtii." *Int. J. Hydrogen. Energ.* submitted.

S06-005: A Proposed Material for Use in Combat Identification for the Department of Defense

Linda Lewis, David Glasgow, and Ralph Dinwiddie

Project Description

The Department of Defense (DoD) Battlespace Awareness and Battle Command Construct has identified passive and tunable combat identification marking systems (CID) that can be embedded into a soldier's uniform and function at long distances using a weapon-mounted low-signature active illuminator as a DoD critical-needs item. Under a recent DoD-sponsored initiative, a novel radiation-based method of generating self-illuminated infrared (IR) materials was developed for use with GEN-III Plus night-vision goggles without the need for active, long-range illumination. The development of this material allowed for marked objects to be tracked through the emissions of near-infrared (NIR) radiation between 700–900 nm. This material requires no batteries for operation and is directly applicable to CID needs if the wavelength region is extended past 900 nm. The purpose of this project was to prepare a series of samples expected to be radioluminescent in the wavelength range of interest and provide the "proof of concept" needed to prove applicability in the wavelength region identified by DoD as essential. Once prepared, the material detection characteristics were evaluated by forward-looking infrared (FLIR).

Mission Relevance

This project is relevant to several material science and technology needs, including combat identification and long-life photovoltaic batteries. During a recent visit to the Army's Special Products and Prototyping Division (SPPD) of the Night Vision and Electronic Sensors Directorate, a demonstration of the ORNL technology was given. The ORNL technology was embraced by SPPD. These samples prepared in this project provided a proof of concept for applications in a wavelength region required to address the CID needs. Currently, DoD is awaiting the results of a human and environmental safety assessment currently being sponsored by DoD at ORNL for the Nuclear Regulatory Commission. Additionally, a DOE IN-1 project for battery research based upon the findings of this LDRD project has recently been funded in FY 2007.

Results and Accomplishments

Single and double-doped crystalline and amorphous phosphors, known to emit at desired wavelengths between 900 and 1700 nm via optical excitation, were activated by the ORNL-developed radioluminescence method. The samples were coated with a low-energy pure-beta emitter, sealed in glass ampoules, and decontaminated for subsequent analysis as sealed sources. The samples were assessed for NIR radioluminescent emissions using both night-vision and NIR FLIR systems. Additionally, the samples were assessed for short-wave infrared (SWIR) emissions between 900 and 1700 nm. Not all phosphors emitted light through this radioluminescent excitation mechanism. Of the materials that were active, emission intensities were recorded and compared. The host matrix and crystalline properties were found to be critical parameters in excitation efficiency. Amorphous samples were found not to be effective host matrices for the radioluminescent system. During this assessment, we determined that phosphors capable of emitting at wavelengths beyond the NIR region into the SWIR region were compatible with the self-sustained IR source concept. This finding is significant to the SSIR program and has direct applications to numerous military and surveillance needs within DoD and the intelligence community.

S06-012: Development of ZnO Light-Emitting Diodes Utilizing Pulse Thermal Processing

Jun Xu, Zhengwei Pan, Ronald D. Ott, and David Norton

Project Description

The Department of Energy (DOE) has outlined the roadmap for reducing the cost and increasing the performance of light-emitting-diode (LED) solid-state-lighting (SSL) technology. In response to these needs, we propose to utilize a unique pulse thermal processing (PTP) technique available at ORNL in a novel method for doping of p-type carriers into ZnO to develop a homojunction LED. The objective of this project is to demonstrate that the prerequisite p/n junctions can be produced by the PTP method. The tasks include (1) generation and characterization of p-type ZnO layers using PTP, (2) growth and characterization of p/n junctions ZnO, and (3) demonstration of electroluminescence. Successfully demonstrating p-type ZnO generation would enable us to present a major breakthrough in developing ZnO nanowire–based LED, which is a key step for achieving high-performance LED’s for general illumination.

Mission Relevance

Solid state lighting is a focus area in the DOE Energy Efficiency and Renewable Energy (EERE) Building Technologies Program. One of goals is to increase performance of LEDs to 150 Lumen/Watt by 2025. We intend to contribute to this goal by developing new and better technology in SSL devices based on ZnO LEDs. Other federal agencies that are interested in high-efficient LEDs include the Defense Advanced Research Projects Agency (DARPA) and the National Institute of Standards and Technology (NIST).

Results and Accomplishments

During FY 2006 we generated and characterized p-type ZnO layers using pulse thermal processing (PTP) techniques available at ORNL. Two nitrogen-mixed ZnO films have been grown on alumina substrates in collaboration with Professor D. Norton at the University of Florida. The growth was carried out at a temperature lower than that for nitrogen activation, aiming to maintain nitrogen in the films. Photoluminescence spectra of an un-doped ZnO film show typical features associated with the near-band transition of ZnO. These features will be compared with photoluminescence spectra of p-type ZnO. Currently, we are tuning the PTP equipment to a desired power. After such a power is reached, we will apply the thermal pulses to the nitrogen-mixed ZnO films so that nitrogen can be activated as p-type carriers. Then the PTP-applied ZnO films will be characterized with photoluminescence. If the p-type signatures are identified, we will pursue tasks 2 and 3 of this project.

S06-041: Selective Electrochemical Oxidation of Water for Treatment of Ischemic Diseases and Other Applications

Elias Greenbaum, Charlene A. Sanders, Barbara R. Evans, Hugh O'Neill, Vilmos Kertesz, and Mark S. Humayun

Project Description

Diabetic retinopathy is a disease characterized by deprivation of oxygen (ischemia) to the retina, resulting in impaired retinal function and eventual retinal photoreceptor loss. Clinical studies have shown that oxygenation of the retina can have therapeutic use in retinal vascular occlusive diseases. This project proposes the electrochemical oxidation of saline solution for the production of oxygen (O_2), deliverable to anoxic tissue, without the formation of potentially toxic-free chlorine. The strategy to accomplish this goal will be approached in three ways: (1) design and construct apparatus to measure levels of free chlorine and oxygen in saline solutions charged with anodic electrical pulses from platinum (Pt) sphere electrodes; (2) optimize chlorine suppression by selective application of kinetic pulse profiles, varying amplitude, dwell time, and repetition rate, or rapid pulse phase reversal; (3) test the effects of surface modified Pt electrodes and PAN (polyacrylonitrile) carbon electrodes on O_2 production efficiency. Proof of principle in this project is the avoidance of chlorine formation when salt solution is electrolyzed to form physiologically significant concentrations of oxygen. If this objective is realized, it will have important implications for the treatment of retinal ischemia, applicable to all forms of systemic ischemic vascular disease.

Mission Relevance

This work falls within the scope of the Advanced Biomedical Technology Research Program at the DOE Office of Biological and Environmental Research. It reflects the goal of DOE to utilize national laboratory expertise and facilities to develop sophisticated and sensitive biomimetic devices for medical applications. This work also benefits the Defense Advanced Research Projects Agency (DARPA), the National Institutes of Health (NIH), and private agencies interested in biomedical research and applications.

Results and Accomplishments

We made considerable progress in this project during FY 2006. A closed-system gas flow electrolysis apparatus has been constructed and is fully operational. Nitrogen carrier gas sparges through phosphate buffered saline (PBS) in a water-jacketed electrolysis flow cell, removing gaseous products of electrolysis downstream to an oxygen galvanic sensor and a hydrogen Figaro sensor. A Multichannel Systems stimulus generator drives the Pt sphere electrodes in the flow cell. An assay for free chlorine, involving spectrophotometric analysis of the oxidation of ascorbate by chlorine, has been used to monitor thresholds of chlorine production in the cell during pulse stimulation. An 800-µA anodic pulse, 400-µsec dwell time, produced 0.25 ± 0.01 µmol O_2/hr and 0.05 ± 0.008 µmol chlorine/hr over the 4-hr stimulation period. Decreasing the dwell time from 400 µsec to 300 and 200 µsec decreased O_2 and chlorine incrementally. At 160 and 100 µsec, chlorine was entirely absent from the PBS but O_2 was measurable at 0.09 ± 0.01 and 0.06 ± 0.003 µmol/hr, respectively. This presents first-stage proof of principle that stimulation pulse profile can be manipulated to oxidize water at the anode before negatively charged chlorine ions can reach the charge exclusion zone at the negatively charged metal electrode. The partitioning of oxidizing equivalents between oxygen and chlorine formation is subject to electrochemical control.

These results have far-reaching implications for applications in neural electrode science and biomedical engineering research. In artificial sight experiments, electrodes have been implanted on the retina to activate retinal neuronal cells without accumulation of harmful electrochemical reaction by-products. This demonstrates the feasibility of electrode-driven O_2 production in the eye for treatment of ischemic retinopathy.

S05-040: Multivariate Dependence in Climate Extremes

Auroop R. Ganguly, David J. Erickson III, and George Ostrouchov

Project Description

The objective of this project was to develop novel methodologies to expand our understanding of extreme values and nonlinear processes from disparate real-world data and to apply these methodologies to climate and geophysical data, including real observations from remote and/or in situ sensors, as well as simulations from state-of-the-art climate or geophysical models. We investigated the linear or nonlinear dependence among the usual and the extreme values from time series, spatial, space-time, and geographic data in the presence of noise resulting from model or measurement errors, in the context of both large and limited data sizes. In particular, we focused on hydrologic extremes and the climate-hydrology connections. Our specific interest was to determine the impact of climate anomalies on precipitation extremes and river flows, as well as the spatio-temporal trends of, and relationships among, precipitation extremes. The advantages of this specific application area are threefold.

(1) Climate and geophysical extremes are important areas of scientific research and societal concerns.

(2) Climate and geophysical data are relatively easily available from the public domain or from ORNL sources, both for observations as well as for model simulations.

(3) The results are relatively easy to understand, interpret, and disseminate, even to an audience without a deep understanding of the domain, especially because the impacts of climate and geophysical extremes are wide and far-reaching.

The methodologies that we developed or adapted can be utilized in domains ranging from sensor networks, logistics, transportation security, and geographic information systems to statistical inference in neutron scattering.

Mission Relevance

This work is relevant to DOE and several federal agencies. The methodologies that we developed relate to offices and agencies within DOD (e.g., DARPA, the Army Research Laboratory, the Logistics Innovation Agency, and the Joint Forces Command) and DHS (Science and Technology Directorate and Domestic Nuclear Detection Office). The climate aspect of the research is aligned with the DOE Office of Science, NASA (Earth Sciences), the EPA (Office of Research), and the NSF (Computer and Information Science and Engineering, Geophysics). Our preliminary presentations and demonstrations have generated significant interest among these agencies, and we believe we have only scratched the surface in terms of realizing the true benefits from this project. In terms of generic methodologies, we have only begun to explore their use in domains like sensor networks and transportation security. Regarding the science of climate extremes, we believe that the true benefits from this project will be realized when we utilize the tools developed as part of this project for predictions and confidence bounds of future climate and hydrologic phenomena.

Results and Accomplishments

We developed new methodologies for nonlinear correlation of noisy and short data and dependence among extreme values in geospatial-temporal data. These methodologies will have wide application to (1) emerging techniques for mutual information computations to real-world data, (2) existing extreme value theory to large volumes of time series data, (3) existing extreme value theory to large volumes of spatio-temporal data and development of a measure for applicability of the theory on real data, (4) robust rank-based correlation measure for geospatial-temporal data, and (5) new geo-referenced index for extreme volatility, or the degree of surprise on the average from future extremes, with relations to risks from natural disasters.

New scientific insights in climate and hydrology that were gained using the methodologies developed in this project can be summarized as follows:

- We discovered stronger connections between the inter-annual climate phenomena called El Nino and the hydrology of the tropics as evident from the flow of major rivers around the world such as the Amazon, Ganges, Congo, Nile, and Parana. The connection was found to be 20 to 70 percent higher than those found by previous researchers from cross-spectrum studies or linear correlation analysis. This scientific evidence can have significant impacts on inter-annual river flow predictabilities and, hence, on water resources and agricultural planning.
- We also gained insights into the spatio-temporal variability of precipitation extremes that exist in South America. For example, the intensity of extremes in weekly time series of precipitation maxima, quantified through the 500-yr and 50-yr RLs, is the highest in the Amazon basin and Paraguay and exhibits an upward trend from 1970–2004 in Venezuela, Paraguay, and north Argentina.
- We gained new insights regarding the spatio-temporal dependence among precipitation extremes from observations and model simulations in the past, the trends in the dependence from successive time windows, and the evolution of the dependence structure in the future from climate model simulation for the future.
- We discovered new insights in precipitation extremes in the area around Chicago, Illinois, from observations and model simulation in the past and model predictions in the future.

Publications

Khan, S., et al. "Nonlinear statistics reveals stronger ties between ENSO and tropical hydrological cycle." *Science*. Submitted.

S06-001: Discrete Event–Based Simulation of Electromagnetic Wave Propagation in Highly Cluttered Environments

James Nutaro and Phani Teja Kuruganti

Project Description

We propose to develop and validate a computationally efficient, accurate, and site-configurable radio channel model that is based on discrete-event simulation of waveguide networks. This approach promises a computationally efficient discrete-event approximation of the wave equation that can be used to rapidly and accurately simulate propagating waves in cluttered environments with available site description data (e.g., DEM or DTED data, VRML, or other CAD models). This research project will develop and validate this modeling and simulation technology for use in performance studies of wireless networks.

Wireless network performance in cluttered environments cannot be accurately predicted using empirical models of the network's radio channels. Unlike wired channels that are stationary and predictable, wireless radio channels interact in complex ways with the environment and, consequently, are very difficult to analyze. However, crude empirical models continue to be used in network performance studies because more accurate and computationally feasible alternatives do not exist. The model that will be developed as part of this research project could replace empirical approaches that are presently used in wireless network simulations with a mathematically accurate, computationally feasible, and site-specific model.

Mission Relevance

Radio network modeling is recognized as a critical shortcoming in the Army's modeling and simulation programs for the Future Combat System and Military Operations in Urban Terrain. The outcome of this research project will be an accurate, site-specific, and computationally efficient model for predicting radio performance in urban areas. The model will provide a foundation on which new wireless network simulation technology can be built to fill this critical gap. The outcome of this research can be immediately integrated into packet-level simulators, such as OPNET and QualNet, and with war-gaming visualization tools in order to significantly enhance Department of Defense capabilities in this area.

Results and Accomplishments

In FY 2006, we made progress in three key areas. First, experiments showed that signal propagation through materials is not a significant factor in determining the received signal strength for high-frequency (MHz to GHz) communications signals. We were able to exploit this fact and thereby significantly reduce the time required for simulator execution. Second, a mathematical theory was developed that appears to explain two primary sources of numerical error in the simulation model. This theory points to three possible improvements to the underlying approximation: the use of octahedral scattering junctions, "best" selection for the algorithm's cutoff thresholds, and a scheme for selecting optimal grid space resolution given the relative importance of speed over accuracy. Third, the algorithm was expanded to allow for parallel computing using cluster computers. This parallel algorithm was implemented using the

Oak Ridge Institutional Cluster, and it allowed the simulation engine to scale to problems on the order of 10^7–10^8 grid points.

Publications

Kuruganti, P. "Validation of a Radio Wave Propagation Model." IEEE Radio and Wireless Symposium, January 2, 2007, San Jose, CA.

Nutaro, J. J. "An optimistic simulation algorithm for DEVS models and its correctness proof." *Trans. Soc. Comput. Simul.* Submitted.

S05-023: Modeling and Computational Platform for Architecture Design of Phase-Locked High-Power Semiconductor Laser Arrays

Yun Liu, Yehuda Braiman, Jacob Barhen, and Amir Fijany

Project Description

Semiconductor lasers have achieved a record power conversion efficiency of more than 70%, which is an order of magnitude higher than most other lasers. Such compact and extraordinary energy-efficient devices have attracted increasing attention in the fields of laser radar, laser imaging, optical space communication, and optical pumping. Due to the output power limitation from a single semiconductor laser, semiconductor laser arrays are currently considered to be the sole semiconductor device able to generate high-power, coherent light. However, the large number of coupled laser diodes leads to complex spatial laser interactions and to the formation of multiple spatial modes. The analysis of the influence of the array architecture (individual laser structure and spatial coupling scheme) on the quality of the combined beam is thus of crucial importance.

The project aimed at the development of a computational platform for high-power laser array architecture design. The computational tool is based on our modeling for the high-power semiconductor laser arrays with external optical feedback, which create coupling among lasers and lead to the synchronization of the entire laser array. The modeling included, for the first time, both laser structure (stripe width, optical-mode confinement factor) and spatial coupling configuration (coupling type and strength) features of the high-power laser array. A computational algorithm was implemented to include large number ($\sim 10^3$) of laser emitters. Such a platform would allow for a continuous parameter adjustment for phase-locking performance optimization.

Mission Relevance

Research to combine beams from arrays of high-power lasers is currently supported by a number of the U.S. Department of Defense agencies, including the Joint Technology Office within the Office of the Secretary of Defense, Defense Advanced Research Project Agency, and the Office of Naval Research (ONR). Innovative research proposals in the area of high-energy laser system architectures with an emphasis on combining the beams from laser arrays have been solicited on a regular basis. The novel modeling and computational platform developed in this project will provide a unique tool for optimizing and verifying phase-locked laser array designs. As a result of this project, our work on coherent beam combining from semiconductor laser arrays will continue under a grant from the Office of Naval Research.

Results and Accomplishments

We developed a theoretical model for broad-area lasers based on partial differential equations and set the parameter ranges by using experimental results. Beam propagation, shooting algorithm, and Fresnel integral methods have been applied to solve laser field evolution inside laser cavity, the carrier diffusion equation, and laser beam transmission in external cavity. Computer codes (C++) have been implemented for the algorithms and integrated to carry out calculations of a variety of laser structures from single solitary broad-area laser to a coupled array of high-power semiconductor lasers.

Our numerical work has brought about important findings in the field of beam combining from high-power semiconductor laser arrays. Primary results include (1) optical field distribution inside laser cavities with stripe widths ranging from 10 to 100 μm has been simulated, and the results revealed the evolution of lateral mode as functions of the stripe width and pumping level; (2) spatial laser coupling through external optical feedback has been investigated, which quantitatively characterized the relationship between the coupling strength and array structures; and (3) an optimization algorithm of phase correction has been derived for coherent beam summation from phase-locked laser beams. In addition to the numerical work, experiments on laser array synchronization were also carried out using special coating/packing of high-power broad-area laser arrays in collaboration with laser manufacturers. Using the coupling scheme derived from our numerical modeling, we have successfully achieved phase-locked laser array operation from a 37-emitter laser array.

S05-059: Smart Tunneling Barriers: A New Concept for Ferroelectric-Based Nonvolatile Random Access Memory

Vincent Meunier, Marco Buongiorno Nardelli, William A. Shelton, Hans Christen, Ho Nyung Lee, and Sergei V. Kalinin

Project Description

While computer technology has developed at a tremendous pace, it is not obvious to all users that many important technological developments—including critical changes of technological paradigms—have been needed to achieve current performance. In particular, entering the digital age would not have been possible without huge breakthroughs in the design of random access memory (RAM) chips. RAM is a memory that can be accessed or written to randomly (i.e., any byte or piece of memory can be used without accessing the other bytes or pieces of memory). Until recently, there were two basic types of RAM: dynamic and static. The problem is that both types of RAM are volatile, and there is, at present, no viable technology available for an affordable, high-speed, non-volatile memory. In this project, we are investigating a new paradigm for non-volatile memory: the asymmetric ferroelectric tunneling element (AFTE). It will be affordable and provide a viable and more efficient alternative to current technology. We propose to provide a proof of concept using state-of-the-art theoretical and computational methods. We will combine ab initio electronic structure calculation methods that can adequately access the electronic structure of complex oxide material and heterostructures with the non-equilibrium Green's function approach developed at ORNL to address for the first time finite-bias transport properties of asymmetric oxide heterostructures and, particularly, to extract polarization current-voltage characteristics. During this theoretical effort, we will be in constant communication with experimental groups, which will open the road to explicit implementation of the concept.

Mission Relevance

This work will benefit the DOE Office of Science in the areas of nanoscale science and technology. This research will provide a much needed link between the first-principles theory and materials preparation, providing clear guidelines for the prediction, design, and synthesis of materials with desired properties. With successful implementation of asymmetric ferroelectric tunneling element heterostructures, the same approach can be used for other multifunctional oxide structures, including ferroelectric field effect transistors and superconductive heterostructures. The results of the study coupled with ORNL's strong program in the growth of multifunctional oxide thin films and heterostructures will also benefit programs of the Office of Naval Research and the Defense Advanced Research Projects Agency.

Results and Accomplishments

We made significant progress during FY 2006. We looked systematically at a number of heterostructures between metallic and ferroelectric layered materials. The calculations are very promising since they clearly show a stable phase for the heterostructure and intriguing charge redistribution at the interface, in agreement with our initial idea to use an asymmetric barrier for a memory device. At the same time, it came to our attention that a new type of non-volatile memory element (based in this case on the reorientation of an organic molecule inside a metallic carbon nanotube) could be designed on the principle of confinement at the nanoscale. In that context, we developed a full theoretical understanding of the functioning of the switching device by introducing the concept of molecular gating. A molecular gate is similar to a conventional gate in a transistor device but differs in the fact that it is not coupled to an external battery. Instead, the gating amplitude is solely governed by the position of the molecule relative to the conducting host (the ends of one-dimensional conducting host constitute the source and the drain of the transistor).

S04-048: Alzheimer's Disease Detection via Nonlinear Analysis of EEG

Nancy B. Munro, Lee M. Hively, Charles D. Smith, Yang Jiang, and William R. Markesbery

Project Description

We wish to enable pre-symptomatic diagnosis and early treatment of Alzheimer's disease (AD). Thus, we proposed analysis of human scalp electroencephalogram (EEG) data by ORNL's novel phase-space dissimilarity measures (PSDM), coupled with novel applications of analysis of variability in an attribute of the discrete distribution function and also statistical network characterization. The goal is determination of dynamical signatures to distinguish among the following four groups of aged patients: (i) normal; (ii) mild cognitive impairment (MCI); early AD; and dementia with diffuse Lewy body disease (DLB). The objective of this project, which is being conducted in collaboration with the University of Kentucky (UK), Chandler College of Medicine's Sanders-Brown Center on Aging/Alzheimer's Disease Research Center, is to show proof of concept for early detection of Alzheimer's disease and possibly even the pre-Alzheimer's changes evidenced in MCI patients as well as early detection of DLB. The earlier cognitive decline can be detected and treatment started, the more effective the treatment is in slowing brain deterioration.

Mission Relevance

The technology developed under this project will be novel, general, patentable, and applicable to predictive maintenance of machines using electrical power including critical infrastructure in nuclear power plants and other energy production facilities. The success of this project will be of great interest to the NIH's Institute of Aging (NIA) according to Dr. Susan Molchan of the NIA, both as a biomarker for early Alzheimer's diagnosis and also in the context of their program on biomarkers of aging. Success is also of interest to NIH's Institute of Bioimaging and Bioengineering (NIBIB), according to Dr. Grace Peng of that institute.

Results and Accomplishments

In FY 2006, the second year of this project, work continued on mathematical methods development for data analysis using surrogate EEG data. The UK furnished 14 data sets, 13 of which were usable. Problems with the pace of subject scheduling and subsequent appearance for data acquisition were identified and addressed by UK by adding a $50 reimbursement for fuel costs and inconvenience and by changing the responsibility for scheduling to the staff in Dr. Jiang's laboratory. An additional cognitive task was added to the protocol which should significantly strengthen the value of the data obtained as preliminary results for an NIH proposal. A collaboration with UK and Dr. William R. Shankle of UC-Irvine was established. The success of this project will support other related research on neurodegenerative diseases, other dynamical brain disorders, susceptibility to addiction, and a variety of additional biomedical diagnostic applications (e.g., brain biometric and voice signature analyses).

S05-005: Metabolic Profiling of Phosphorylated and Coenzyme-Bound Metabolites Using Pressure-Assisted Capillary Electrophoresis Mass Spectrometry

Timothy J. Tschaplinski, Gary J. Van Berkel, Bruce A. Tomkins, and Marija Mentinova

Project Description

Metabolic profiling of phosphorylated carbon intermediates of the respiratory pathways, adenylates, nucleotides, and other highly charged metabolites, such as coenzyme-bound metabolites, is critically important, given their involvement in redox balance and energy transduction. These pathways have proved challenging to study directly. Our goal was to assemble a hybrid instrument that could separate and quantify low concentrations of highly charged metabolites by interfacing a Beckman Coulter P/ACE electrophoresis system with a Finnigan/Thermo LCQ DECA ion trap mass spectrometer (MS), and to optimize the electrophoresis and MS settings for reproducible nanogram-level detection. The research priorities were to (1) separate and quantify low-concentration, highly charged metabolites; (2) establish protocols for metabolite separation, including the limits of detection of key metabolites involved in redox balance; (3) establish a database of metabolites that can be detected and the characteristics of their detection (key mass-to-charge ratios and retention time) for subsequent data analysis; and (4) conduct analyses on test samples of leaf extracts or microbial cultures.

Mission Relevance

The research products will benefit DOE's Genomics:GTL program, where characterization of the concentrations of energetic metabolites allows an assessment of the health/status of microbial cultures (i.e., pinpointing the growth phase and energy utilization status). The rapid detection and analysis of phosphorylated and co-enzyme bound metabolites is currently a major gap in Genomics:GTL studies that require metabolomic analyses or analysis of challenging anaerobic pathways involving coenzyme-bound metabolites. Given that such metabolites are involved in the energy transduction pathways, their accurate quantification will be of interest to NIH to determine how cellular homeostasis is perturbed by disease or zenobiotic agents. The sequencing of the numerous microbial and plant genomes by a number of agencies, including NSF's Plant Genomics Research Program, will require metabolite profiling as a tool for gene discovery. The class of metabolites targeted in this project is not currently well addressed.

Results and Accomplishments

A Beckman Coulter P/ACE electrophoresis unit was initially operated in a stand-alone mode and optimized for the standard separation of two angiotensin isomers. The P/ACE unit was then interfaced with a Finnigan/Thermo LCQ DECA mass spectrometer and configured according to the manufacturer's instructions and optimized. Electrophoresis parameters considered included injection pressure and duration, separation voltage, and pressure "assistance" for the run buffer. MS parameters included the exact positioning of the electrophoresis capillary within the electrospray ionization (ESI) "needle," composition and flow of the ESI sheath liquid and gas, quality of the "spray" produced by the sample and sheath liquid, and ionization voltage. The ESI needle was modified to produce a finer and more consistent spray than that achieved using the standard needle. The separation of simple mixtures consisting of the target metabolites, adenosine polyphosphates (AMP, ADP, and ATP) and the reduced/oxidized forms of β-nicotanamide adenine dinucleotide phosphate, was achieved, but the separating power of the capillary electrophoresis (CE) columns was well below that reported in the literature (N ~ 20,000), and the method sensitivity was not satisfactory. Extensive instrumental cleaning and modifications improved the observed sensitivity somewhat, but not the number of theoretical plates. The method was used to evaluate the composition of two plant extracts; however, it was very difficult to determine the presence of typical components using the CE-MS procedure described. We anticipated that interfacing the P/ACE with a Sciex QToF-MS would result in markedly improved performance, but the latter MS was not available before the end of the study.

S05-011: Integrating Hydrologic and Economic Data for Water-Energy Nexus Assessment

G. A. Oladosu, S. W. Hadley, D. P. Vogt, and T. J. Wilbanks

Project Description

The hypothesis underlying much of the discussion on the water-energy nexus is that water stresses will have significant impacts on energy security in the United States. Despite the abundance of qualitative evidence, there is a dearth of quantitative estimates needed to both validate this hypothesis and to serve as the basis for addressing the important issues that it generates. An objective of this project was to attempt a quantitative validation of this hypothesis. Furthermore, the regulatory, technological, spatial, and policy issues associated with the water-energy nexus are complex. An adequate assessment of these issues requires an integration of research techniques spanning different disciplinary frameworks. Therefore, an additional objective of the project was to demonstrate, as a proof-of-concept, an integrated approach for water-energy nexus assessment. The above objectives called for three main steps: (1) estimation of water-supply characteristics at the county level; (2) modeling of state-level economic activities, with particular attention to energy; and (3) linkage of county-level water-supply measures to state-level energy and economic activities.

Mission Relevance

This work is relevant to the Energy Security and Assurance and Technical/Economic Analysis programs of DOE, which is in the preliminary phase of establishing an Energy-Water program under the Energy Policy Act of 2005 related to "research, development, demonstration and commercial application to, among others, address water-related issues associated with the provision of adequate supplies, optimal managements and efficient use of energy." We expect that the outcome of this research will provide useful initial information and approaches towards meeting this objective. In addition, the water issues being addressed under this project are relevant to a number of other public and private agencies, such as the Environmental Protection Agency (EPA), Army Corps of Engineers (ACE), and energy utilities.

Results and Accomplishments

The first two parts of this project were largely accomplished in FY 2005, with necessary modifications and improvements as implementation of the final step continued in FY 2006. In particular we re-specified our model of electricity generation, replacing the water withdrawal term with three separate measures that explicitly capture the different aspects of water use in this industry (i.e., plant design water flow rates, water availability, and cooling technologies). Estimation and statistical tests on parameters of these three terms show that while only a few parameters of the first two variables are significant, cooling technologies are highly significant determinants of plant competitiveness. This new approach and our findings are major differences from current models of the electricity industry where plant competitiveness and costs are based almost entirely on fuel and prime mover characteristics. We also devised an approach for incorporating our monthly electricity generation model into an annual model of the regional economy that would enable estimates of the economy-wide impacts of changes in water-related variables. An immediate policy-relevant application of our work is an evaluation of the electricity generation impacts of cooling technology changes under section 316(b) of the Clean Water Act. We will be seeking support from relevant agencies to extend application of our approach to assessments of policy and technology options being considered for addressing energy-water nexus issues, as well as to other regions of the United States.

S05-024: Exploring New Pathways in the Impact of Aerosols on Terrestrial Carbon and Hydrological Cycles

Lianhong Gu, Mengdawn Cheng, Mac Post, Qing Liu, Roger A. Pielke Sr., and Dev S. Niyogi

Project Description

Aerosols are a critical component of the atmosphere. Through their effects on atmospheric radiative transfer, formation, and properties of clouds and precipitation processes, aerosols play a fundamental role in the dynamics of the climate system. Prediction of climatic responses to increasing atmospheric greenhouse gas concentrations requires concerted understanding of the roles of atmospheric aerosols, terrestrial carbon, and water cycles in our earth climate system. However, the scientific community has been studying them as isolated individual processes and relevant federal programs have been operating independently. This practice has hindered our understanding of the dynamics of the earth climate system. The objective of this project was to demonstrate the necessity of an integrated research approach by examining the interactive effects of aerosols, carbon, and water cycles and identifying crucial processes that must be represented in the next generation of coupled climate–carbon models. Our main modeling tools were the Regional Atmospheric Modeling System (RAMS) and the terrestrial Fluxes and Pools Integrated Simulator (FAPIS). Through close collaborations of the team members who consist of climatologists, atmospheric scientists, and ecosystem modelers from Colorado State University, Purdue University, and ORNL, we have made a series of interesting scientific findings that benefited several DOE Biological and Environmental Research (BER) programs.

Mission Relevance

This study cuts across the three key areas in the U.S. Climate Change Research Initiative: (1) developing reliable representations of the climate forcing resulting from atmospheric aerosols, (2) improving understanding of the global carbon cycle (sources and sinks), and (3) increasing knowledge of climate feedback processes. The progress achieved through this project directly benefits the DOE Atmospheric Science Program, which focuses on research on atmospheric aerosols, and the DOE Terrestrial Carbon Process Program, which sponsors research on terrestrial carbon cycles. We wrote a white paper entitled “Integrating advanced land surface modeling with complementary atmospheric and ecological measurements to understand cloud–aerosol–carbon–water interactions” for the DOE Biological and Environmental Research Program in early 2006. We also helped with the planning of the Southern Great Plains Cloud and Land Surface Interaction Campaign under the DOE Atmospheric Radiation Measurement program.

Results and Accomplishments

The following scientific findings were made:

1. Surface albedo (when diffuse radiation and direct beam radiation are combined) over vegetated areas is not a constant and depends on aerosol optical depth. This is because diffuse radiation and direct beam radiation have different reflectance over plant canopies. For a given leaf area index, surface albedo increases with aerosol optical depth.
2. Aerosols have significant impacts on land–atmosphere interactions. We have found this in a model analysis over the Indian monsoon region and expect a similar feedback process irrespective of the geographical location. Aerosols affect radiation distribution and quality, which in turn affect the surface energy balance, boundary layer evolution, and mesoscale convection and precipitation.
3. In a field analysis, the effect of diffuse radiation change is to alter the leaf scale energy portioning with the more diffuse radiation environments, causing the plants to have higher photosynthesis rates and higher net primary productivity and yield. The NPP relocation was to the woody part of the canopy and not to the leaf area. This has implications for the dynamical vegetation growth models.
4. Using FAPIS, we found that biomass heat and biochemical energy storages are an integral and substantial part of the surface energy budget and play a significant role in modulating land surface temperatures and energy exchanges with the atmosphere. Without these processes represented, land surface models overestimate daytime surface temperatures and underestimate nighttime temperatures. Therefore it is concluded that biomass heat and biochemical energy storages must be considered in studies of land-atmosphere interactions and climate modeling.

S06-033: Determining Relative Value of Ecosystem Services

Rebecca Efroymson, Henriette Jager, Gbadebo Oladosu, and Victoria D'Urso

Project Description

Ecological valuation is the combination of methods by which dollar values or other value metrics are assigned to components of the environment, such as wildlife populations, individual animals, and forest communities, as well as processes termed "ecosystem functions" or "services" such as decomposition, pollination, water purification, provision of habitat, photosynthesis, nitrogen fixation, and carbon sequestration. Existing methods for valuing ecological functions or services fail to value related functions or services consistently or completely. Most applications are based on surveys of human preferences. We are developing a proof-of-principle methodology for analyzing the concept that established dollar values (or other metrics) of ecological entities can be extended to other ecological entities through models of ecological relationships. Our work addresses several scientific problems:

- How can ecological valuation, which reflects human preferences, also be anchored in ecological relationships?
- How can economic models incorporate simple and complex ecological relationships that control supplies of raw materials?
- What is the most effective case study or studies to demonstrate the incorporation of ecological algorithms in valuation of ecological services?

To answer these questions, our project aims to (1) review the existing use of ecological relationships in relative valuation, (2) illustrate how these relationships and more complex models could be used in relative valuation, and (3) describe and begin to demonstrate potential applications of relative valuation.

Mission Relevance

Various federal agencies and utilities (EPA, DoD, DOE, USDA, NOAA, Electric Power Research Institute) are converging on the need to develop reliable and rigorous methods for valuation of ecological populations, communities, functions, and scenarios involving ecological change. Examples of potential applications of this approach include the selection of contaminant remediation alternatives, the evaluation of environmental benefits of research programs, the quantification of appropriate damages to compensate for natural resource injuries, the valuation of natural disaster mitigation services of ecosystems, and the quantification of appropriate incentives for conservation. For example, the DOE Office of Legacy Management might benefit from this research as methods developed here may be used to prioritize long-term stewardship needs. Offices of DoD have expressed interest in the development of environmental benefit indicators to quantify ecological services of the natural resources of military installations.

Results and Accomplishments

Our research has highlighted some of the limitations of existing methods of ecological valuation. We have identified classes of benefits transfer that we plan to address in this project, some through case studies and others in a more theoretical way. These types of value transfers include

(1) ecosystem to ecosystem, (2) organisms to habitat, (3) predator to prey, (4) population of size 1 to population of size 2, (5) population to individual, and (6) commodity to ecological service provider (e.g., crops to honey bees). We have reviewed the use of ecological models and other ecological relationships in ascribing relative value to some of these ecological entities. Through this review, we have identified specific additions to Habitat Equivalency Analysis, an ecosystem-to-ecosystem benefits transfer method, that would address the ecological limitations of the methodology. Our research has also emphasized the use of population viability analysis models and thresholds derived from them in accomplishing transfers of value from a population to an individual and the use of predator-prey relationships in transferring value between trophic levels.

S06-040: Effects of Groundwater Chemistry on the Distribution of Soil Microorganisms in Natural Media

Philip M. Jardine, Tracy L. Bank, and Matthew Fields

Project Description

Our research will determine the effects of groundwater chemistry on the distribution of bacterial communities between the aqueous and solid phases in natural sediments using a novel, bench-top study. These investigations will use contaminated and non-contaminated intact sediment samples from the Field Research Center (FRC) at ORNL. Previous studies have suggested that changing groundwater chemistry, which resulted from legacy waste burial, leads to changes in the microbial communities present in contaminated-versus-uncontaminated groundwater at the FRC. We will characterize the microbial communities present in aqueous and solid-phase sediment samples from three areas of the FRC with similar geology but vastly different groundwater chemistry. We will simulate changing groundwater conditions and determine if the distribution of bacteria between the solid and aqueous phases changes using intact sediment column experiments. We will use atomic force microscopy (AFM) to measure the nanoscale forces of adhesion between the aqueous-phase bacteria and mineral phases present in the sediment. Our experiments will determine if bacterial stickiness to mineral surfaces can explain the distribution of cells between the aqueous and solid phases in natural sediment.

Mission Relevance

The project is directly relevant to DOE’s environmental quality and science missions. Our project uses nanotechnology and molecular biology tools to characterize complex microbial communities in natural soils for environmental use. It also provides an innovative application of AFM that will be of interest to a wide range of scientists involved in nanoscale research. If successful, we expect that this project will lead to broader applications within the subsurface biogeochemistry and microbial ecology elements of the Environmental Remediation Science Program and the Genomics:GTL Program. In our study we introduce a new and controversial approach to studying biodiversity using geochemical tactics rather than a classical microbial approach, which may provide new insight into microbial diversity at the Field Research Center and related contaminated sites. Results from our study may also be relevant to studies of bacterial and colloidal transport in porous media.

Results and Accomplishments

We were funded for 3 months during FY 2006 and completed two of the four major tasks described in the research proposal. Discussions with FRC staff led to improved sampling strategies, and intact sediment columns collected from three areas within the ORNL Intact core samples were acquired from low-, medium-, and high-ionic-strength environments using Geoprobe technology developed by the ORNL FRC staff. Samples were stored anaerobic and aseptic until use in miscible displacement experiments. Experiments designed to measure the distribution of bacteria between the solid and aqueous phases of sediment columns using simulated groundwater were initiated and have been completed. These experiments involved packing the various sediments into glass columns, purging with CO_2, and leaching the soils with solutions of similar ionic strength and solute composition as that observed in situ. Effluent was collected as a function of time, and microbial biomass was collected and stored at -80^{o}C until further use in the remaining research tasks. The samples are now ready for the remaining two tasks of the project, which will encompass the most difficult and time-consuming portion of the research. Microbial community analyses will be completed on solid and aqueous samples by microbiologist Dr. Matthew Field of Montana State University. Matthew, a former ORNL employee, is ideally suited for this task. Bacterial adhesion of aqueous samples will be measured using AFM at Virginia Tech by Tracy Bank, former ORNL post-doc, who is currently an assistant professor of geochemistry at SUNY, Buffalo. The project is on track to be completed in FY 2007.

S06-055: Multivariate Statistical Analysis Technique to Locate Ecological Observation Sites within Regional Landscapes

William Hargrove, Patrick Mulholland, and Latha Baskaran

Project Description

The objective of this project is to test a multivariate statistical technique that will produce landscape maps of biophysical similarity for regional assessment. Specifically, we are evaluating how a multivariate geographic clustering approach can be applied to locate observation sites in the National Ecological Observatory Network (NEON) Domain centered on East Tennessee (Southern Appalachians/Cumberland Plateau region) and demonstrate the robust nature of this approach for site selection for regional and continental-scale landscape analysis and monitoring. We are conducting three groups of within-domain “representativeness” analyses, based on groups of input map layers representing (1) soil variables, (2) vegetation variables, and (3) ecosystem process variables. The new analyses we are now engaged in will help ORNL to identify regionally representative observation sites that satisfy the NEON goals. The analyses will also guide us in the identification and selection of critical institutional partners associated with the observation sites identified. The information generated will strengthen our design prospectus for NEON measurement sites within the Appalachian/Cumberland Domain that includes East Tennessee. The regional analysis methods will also be valuable for other programmatic site-selection activities.

Mission Relevance

This project benefits the DOE mission of monitoring and improving environmental quality. In addition to the immediate value to DOE and ORNL, this work will also benefit the NSF as it designs and constructs new national Ecological Observatories. The project may also benefit other federal agencies that have monitoring networks, like United States Department of the Interior National Park Service, and may also help the United States Department of Agriculture to find locations appropriate for growing new crop varieties and to ensure that representative germ plasm has been stockpiled and preserved.

Results and Accomplishments

A combination of multivariate analysis of nine climatic variables and ecological expertise was initially used to create 20 national National Ecological Observatory Network (NEON) Domains. Each climatic variable is itself a map at 1-km^2 resolution over the conterminous United States, consisting of nearly 8 million cells. The same multivariate tools that were used to help create the 20 NEON Domains were then used to develop representativeness maps for each regional domain based on other variables (variables other than climate characteristics). Separate maps were developed based on gross primary productivity and respiration data, soil and topography data, and vegetation characteristics data (http://research.esd.ornl.gov/~hnw/neon/withindomainrep2/). These maps will be used in subsequent analyses to determine regional variability in ecological characteristics and aide in the potential deployment of instrumentation across ecological gradients. The maps represent non-climatic gradients in several key ecological characteristics grouped together and thus differ from the single-variable mapping that is commonly used to identify ecological gradients. This grouping of several ecological characteristics into a rigorous and quantitative digital database offers a more sophisticated basis on which to make decisions on locations for ecological sampling and analysis.

S06-073: Characterization of a Potentially New Si:TiO_2 Nanocrystal

Baohua Gu

Project Description

In a recent study of a solvent-induced nanoparticle growth process, we unexpectedly discovered that Si atoms could be introduced into TiO_2 single-crystalline phases. In this project, our aim was to prove that this newly synthesized nanomaterial is truly a single Si–substituted TiO_2 nanocrystal. If proven, this would be a new crystal phase that has not yet been documented. More importantly, we anticipate its potentially wide application to solar energy conversion and environmental and industrial catalysis because, in principle, the Si-substituted TiO_2 single crystal can lower the band-gap energy of TiO_2. This in turn will greatly increase the light absorption efficiency and energy conversion efficiency of TiO_2 because TiO_2 itself has a large band-gap energy and hence absorbs light or solar energy only in the ultra-violet (UV) spectral range (<3%

of solar energy). We proposed to use micro-Raman, X-ray diffraction (XRD), high-resolution transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) spectroscopy to provide detailed a characterization of this new material.

Mission Relevance

This work is relevant to the new nanomaterials development mission of DOE and fits DOE's Science-to-Energy agenda. If successful, we anticipate that the new Si:TiO_2 nanocrystal potentially has wide applications in solar cells for energy conversion and in environmental and industrial catalysis because the new material is expected to have a lower band-gap energy than that of TiO_2.

Results and Accomplishments

Results indicate that the newly formed crystal contains about 8.9% Si and about 39.4% Ti and thus demonstrate the incorporation of Si in TiO_2 materials. Raman spectra provided additional evidence of the newly synthesized Si:TiO_2 nanocrystals (as compared with pure anatase and quartz SiO_2). Raman spectra of Si:TiO_2 and TiO_2 resemble each other regarding basic characteristics of anatase; however, the synthesized Si:TiO_2 nanocrystals exhibit two new bands at 936 and 1080 cm^{-1}, which are attributed to stretching vibrational modes of Si-O-Ti bond. These results suggest a direct incorporation of Si atom into the TiO_2 nanostructure by chemical bonding. Additionally, the band shifts at 405 and 636 cm^{-1} for synthesized Si:TiO_2 nanocrystals also demonstrate modification of the anatase structure by Si doping. However, XRD data indicate that the synthesized nanocrystals predominantly exhibit the characteristics of anatase structure. The structures of neither Si:TiO_2 nor SiO_2 could be distinguished clearly. These observations are likely attributed to the fact that the Si-O-Ti bonds in synthesized nanocrystals may have localized amorphous structures and thus could not be detected in the XRD pattern. This argument is supported by the HR-TEM image, which showed pockets of well-crystalline nanostructures that appear to be surrounded by amorphous structures.

S04-050: No-Moving-Parts Pump and Preconcentrator

R. J. Warmack, C. L. Britton, J. E. Hardy, P. F. Britt, and T. Thundat

Project Description

Sensing of toxic materials at low concentrations presently requires bulky, power-hungry instrumentation not amenable to widespread use in portable applications. A breakthrough technology is being developed and tested that would enable real-time sampling and pumping of concentrated vapors in a 1-cm^3 package and using very low power. The technique uses a microfabricated device that absorbs and pumps selected analytes to a variety of detectors or analyzers. Demonstration of the device should lead to research programs to produce truly compact, low-power, highly selective detectors for trace analysis. Such detectors should be more reliable than those employing traditional pump designs and also have greatly improved chemical selectivity over that of single-stage analyzers, more closely approaching that of laboratory analytical instrumentation. The long-term objective is to develop a small, low-power sampling stage that will extend detection limits of existing detectors by a factor 100 to 1000 times while greatly improving the overall chemical selectivity and real-time response. The specific objective of this project was to fabricate and test a demonstration device to validate the concept experimentally.

Mission Relevance

Measurement science and technology is essential for monitoring and controlling processes to achieve better energy efficiency or to generate fewer waste products. Both of these outcomes are important parameters to DOE's mission and numerous programs including the Science-to-Energy agenda. Applications for low-cost, low-power microsensors and preconcentrators include buildings, transportation, and energy conversion. The demonstration of a preconcentrator and pump that has no moving parts (high reliability) and that has the potential to rival laboratory analytical instrumentation should prove to be very attractive to DOE to allow sensors for environmental, industrial, and personnel monitoring where size, power, and real-time detection of low levels of analytes are important. The implications for homeland security and the military are obvious for a toxic-agent monitor that can be reliably produced at low cost in high-volume quantities.

Results and Accomplishments

Extensive work was performed to select appropriate materials and determine methods for fabricating test microelectromechanical system (MEMS) structures. A 14-step microfabrication process was developed that successfully produced a number of preconcentrators in both individual die and 4-in. wafer formats. The completed die was mounted and wire bonded on a printed circuit platform with a custom circuit to drive and monitor the operation of the preconcentrator. A pulse power of 400 mW over only 10 ms provided a temperature rise of about 200°C, which should be sufficient to rapidly desorb anticipated analytes. A complete preconcentration cycle should then require less than about 100 mJ. Compared to the energy storage of a typical AA battery (10^4 J), about 100,000 cycles could be expected, which validates the low-power objective of this study. A thermal conductivity detector inserted adjacent to the device verified its ability to pump vapors. The tested device is now ready to be integrated with sensor arrays to enable environmental, industrial, and personnel monitoring using small, low-power devices.

S04-051: Three-Dimensional Imaging of Multiple Fluorophores

Jeffery R. Price and John P. Biggerstaff

Project Description

Three-dimensional (3D) optical microscopy, such as wide-field deconvolution and various confocal systems, are particularly useful for the study of many biological phenomena, ranging from the visualization and characterization of sub-cellular structures to the analysis of multi-species microbial communities. Current techniques, however, are limited in the number of parameters (e.g., fluorescent probe colors) that can be analyzed at one time. Although there exist some technologies that can resolve up to 10 probes, these technologies suffer sensitivity and photo-bleaching issues and can be prohibitively expensive for many laboratories. The goal of this project is to develop new algorithms and microscopy techniques to enable the resolution of many fluorescent probes in 3D at low cost using novel deconvolution algorithms and spectral unmixing in conjunction with commercially available 2D intereferometric microscopy equipment.

Mission Relevance

The technologies that will result from the work begun by this project will have applications to all biological and environmental problems in which multi-color fluorescence microscopy is employed. The work is relevant to the Environmental Remediation Sciences Program under the Biological and Environmental Research Program of the DOE Office of Science. In this capacity, the developed technologies will assist scientists in imaging and understanding the spatial distribution of individual microbes in microbial communities. Furthermore, the work in this project is relevant to numerous programs managed by the National Institutes of Health since multi-species microbial communities are involved in several disease mechanisms and health issues. This work is also relevant to the Environmental Protection Agency, as well as state and local governments, in protecting the public water supply, where multi-species microbial biofilms play roles in corrosion and infection risks.

Results and Accomplishments

During FY 2006, we accomplished three important goals. (1) We demonstrated the utility of the proposed methods in allowing rapid, specific, and simultaneous identification in suspension of five opportunistic pathogens relevant to public health. (2) We developed computational models to enable the application of hyperspectral unmixing algorithms to the spectral microscopy problem. (3) We developed a computational model for deconvolution that incorporates unmixing and will be applicable to any 3D fluorescence microscopy technology where fluorescent probes with overlapping spectra are employed.

Publication

Le Puil, M., et al. 2006. "A novel fluorescence imaging technique combining deconvolution microscopy and spectral analysis for quantitative detection of opportunistic pathogens." *J. Microbiol. Meth.* Submitted.

S05-003: "Nano/Microelectromechanical Systems Tools for Retinal Surgery

C. L. Britton, R. J. Warmack, J. Simpson, B. D'Urso, E. Chaum, S. Baba, and M. N. Ericson

Project Description

The ability to design and fabricate mechanical structures in both microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) processes creates the possibility of very small surgery-specific tools that will enable the physician to perform faster, safer, and more effective surgical procedures. We propose to create a tool that will "hook into" scar tissue that has grown on the retina and pull it off in a smooth peeling motion. This surgery is presently done with single picks and forceps, but our approach will enable the surgeon to apply a micro- or nano-version of a very large array of needles or spikes (surgical Velcro) that would greatly increase the efficacy and speed of the surgery. This project will be conducted in collaboration with Dr. Edward Chaum of the University of Tennessee Health Science Center.

Mission Relevance

As a result of this work and collaboration with Dr. Chaum, we hope to first produce a surgical tool and then focus on developing a program in this area (not just this instrument). Proliferative vitreoretinopathy remains an important clinical and surgical problem, and better approaches to prevention and treatment are a priority for the National Eye Institute of the National Institutes of Health. This work is also relevant to the U.S. Army Advanced Technology Research Center, which is interested in technologies that would advance the Operating Room of the Future concept.

Results and Accomplishments

We have fabricated and tested several of the "Velcro" pads using both carbon nanofibers and pulled-glass structures. Variations in results were observed that are due to a number of confounding factors associated with proper fixturing of both the membrane and probes. Furthermore, variations in the membrane shape, fibrous content and orientation, and surface wetness also affected measurement repeatability. We conducted experiments to confirm this using collagen-based gels and chicken allantonic membranes. In addition, a number of experiments were repeated using larger probes (at least ~1 cm × 1 cm) to eliminate frictional forces associated with the probe edges. The structures were also tested by Dr. Chaum.

S05-050: Preliminary Study of Phosphor-Based Tracer Rounds

Michael Cates, Shawn Goedeke, William Hollerman, and Noah Bergeron

Project Description

Conventional tracers consist of a projectile that contains a pyrotechnic composition in a hollow base that is ignited during firing. This pyrotechnic charge gives off light in the visible range, allowing the operator of a firearm to observe the path of the tracer projectile. When the pyrotechnic composition burns, it decreases the mass of the bullet and changes its aerodynamic properties. This burning limits the effectiveness of the tracer, particularly as the distance from the muzzle to the target increases. Also, the tracer charge leaves behind it a narrow cloud of burning material that is almost a meter long. While this increases the visibility of the tracer, it also makes it visible to the target and the surrounding area. In military scenarios, this is potentially dangerous to the shooter. The use of phosphors for novel constant-mass low-field-of-view tracer ammunition has the potential to solve many of these problems. The materials used for this application are long persistence phosphors (LPP) that are excited by visible light. In this case, it is anticipated that burning of the powder in the chamber will produce enough light to charge the phosphor and allow it to glow as it travels downrange. An added advantage of using phosphor is that many of these materials produce light upon impact. This would provide a means to locate where the tracer rounds are hitting and can be used for targeting.

Mission Relevance

This project applied ORNL's expertise in phosphor-based sensors to the development of more effective tracer ammunition. It was initially believed that the greatest challenge to the success of the phosphor-based tracer would be the coating durability. The results of this study showed the potential feasibility of the phosphor tracer concept. With this technology, it is conceivable that every round could be a tracer. The added bonus of this technology is that it will make it safer and more environmentally friendly to produce and transfer tracer ammunition. This concept has the potential to benefit every branch of the military.

Results and Accomplishments

The first task was to determine the survivability and viability of LPP in paint configuration. Task 1 was completed in collaboration with researchers from the University of Louisiana at Lafayette at Southern Shooting Center in Thibodaux, Louisiana. To determine the survivability of a phosphor binder combination, commercially available ammunition was modified. This modification was initiated by removing bullets from commercially available rounds. The pulled bullets are then coated with phosphor and reinstalled in the casings. The rounds had to be fired in a darkened environment, and some portion of the rounds recovered. Several of the recovered rounds had coatings that survived.

The second test was to determine the amount of energy needed to produce triboluminescence (TL). For this we used the outdoor range at ORNL's Central Training Facility (CTF) using a fixed test stand barrel. Targets consisted of 5/16-in. aluminum plate, 1/4- and 3/8-in. steel plate coated with poly phenl methyl siloxane (PPMS) binder mixed with ZnS:Mn in a 1:4 phosphor:binder mass ratio. The target holder consisted of a metal frame designed for 12- ×12-

in. sample targets. A plastic and aluminum box placed before the target holder functioned as a bullet trap, and a Shooting Chrony™ Model F1 chronograph recorded impact velocities. The TL was detected using a photodiode facing the coated backside of the target in a similar fashion to the approach used to measure hypervelocity impacts. These tests determined the survivability of the coating and provided a qualitative indication that our concept is feasible, but further research is needed.

S05-053: Doped-Carbon-Nanostructure Field-Emitter-Array Infrared Imager: A New Concept for Fast, Sensitive and Inexpensive Microbolometric Infrared Cameras

Kofi Korsah, Roger Kisner, Larry Baylor, John Caughman, and Philip Rack

Project Description

There is a continuing need for a sensitive and inexpensive infrared camera that operates without cryogenic cooling, is capable of high-speed performance (>100 KHz), and can be synchronized externally. Such a device would be unique and would revolutionize the infrared camera market in much the same way as the development of the uncooled microbolometer camera has over the last 10 years. In this project, we proposed to develop a novel, infrared imaging system based on an array of doped carbon nanostructures in which the field emission current of each nanostructure is modulated by the incident infrared photon energy. Back-of-the-envelop calculations showed that modulation currents on the order of fractions of microamps could be obtained with infrared energies around 3 μm with a responsivity approaching that of wavelength-responsive, cryogenically cooled systems. Signal strength of this magnitude could easily be used to obtain imaging information. Finally, the ease of producing small-diameter (< 5-μm) carbon-based devices implied that pixel sizes that are much smaller than that of current IR cameras (typical sizes are ~50 μm) could be fabricated, enabling the manufacture of much higher resolution cameras. If proof of concept could be demonstrated, the long-term objective of this project was to develop a sensitive, low-cost, uncooled infrared camera with a sensitivity and resolution approaching that of current high-end systems.

Mission Relevance

Measurement science and technology is essential for monitoring and controlling processes to achieve better energy efficiency or to improve performance of systems in several critical application areas (e.g., defense). Both of these outcomes are important parameters to the DOE mission and to numerous programs, including the Science-to-Energy agenda. In addition, infrared imaging is a cornerstone technology for a variety of national and homeland security applications, including security surveillance, night vision systems, border patrol, law enforcement, and search and rescue, as well as monitoring the movement of container ships in and through ports. The demonstration of a sensitive, low-cost, uncooled infrared camera with a sensitivity and resolution approaching that of current high-end systems should prove to be very attractive to DoD and DHS.

Results and Accomplishments

Extensive work was performed to fabricate doped-carbon nanostructures as low-work-function field emitters in which the incoming infrared energy is used to modulate the emitted field current. Two physical effects are being exploited to develop this idea: (1) the reduction in work function when a more electropositive material is used to coat a material and (2) the reduction in the surface barrier as a function of electric field. We were successful in demonstrating that field emission current can be modulated by photon energy, providing significant response. Results to date indicate that our current doping strategy needs to be refined to achieve the concentrations required for high-quality response in the infrared region of interest. In addition, noise characteristics of the modulated current are voltage dependent.

S05-054: Estimating Economic Impacts Due to Service Interruptions in Transportation Systems

Shih-Miao Chin and Ho-Ling Hwang

Project Description

Transportation is such a fundamental element in today's environment that many of us overlook its overwhelming importance in our daily lives. Practically everything we use in homes, offices, and schools is transported via a large and complex transportation network. Occasionally, unexpected incidents occur and some parts of this transportation network system fail, causing transportation services to be interrupted. Consequently, the flow of commodities and the movement of people are stopped or diverted.

The Center for Transportation Analysis (CTA) has extensive knowledge on how commodities and people are moved through the comprehensive network, and on how transportation infrastructure failures and shutdowns can impact traffic. However, the economic impact these disruptions might cause, particularly on the state and local levels, is not fully understood. The objective of this project was to advance the analytical capability of CTA in estimating economic impacts due to major transportation service interruption events.

This project involved the development of national freight demand models for 27 industry sectors covered by the 2002 Commodity Flow Survey. It postulated that national freight demands are consistent with the business patterns. Furthermore, the study hypothesized that the flow of goods which make up the national production processes of industries is consistent with the information described in the 2002 Annual Input-Output Accounts developed by the Bureau of Economic Analysis (BEA). The model estimation framework hinged largely on the assumption that a relatively simple relationship exists between freight production/consumption and the business patterns of each industry, as defined by the three-digit North American Industry Classification System (NAICS) industry codes.

Mission Relevance

This project is relevant to the mission of the DOE Office of Electricity Delivery and Energy Reliability. The developed system should be able to help decision makers and transportation analysts to understand the inner workings of energy-generating commodity flows such as coal by rail and petroleum products by non-pipeline modes. Furthermore, the system should enable transportation analysts to estimate the economic impacts of the disruption of such energy-generating commodity flows and assess the alternatives. With the capability of estimating economic impact, CTA researchers will be able to provide more comprehensive assessments on impacts due to transportation service interruption events. The Department of Transportation (DOT) and the Department of Homeland Security (DHS) will be interested in having such a capability.

Results and Accomplishments

The national freight demand model for each industry sector consists of two models: a freight generation model and a freight attraction model. Preliminary results indicated promising freight generation and freight attraction models. The results from this study will provide more accurate forecasts of future national freight demands. Analysts at local transportation agencies can use the results to further disaggregate published state-level commodity flow statistics to a higher resolution, which is critical for local transportation planning.

Most importantly, this study bridged a long-standing gap between freight flow statistics and the econometrics of industries. This capability enables transportation analysts to study freight flows within the United States and link their impacts directly to the state of the economy. With additional network modeling efforts, these freight demand models can be enhanced to allow assessment of regional economic impacts associated with temporary loss of transportation services on the transportation network.

Preliminary results of this project have been shown to a U.S. DOT program manager. The potential sponsor indicated that this system could help DOT's efforts in freight management and operations. A paper describing the methodology and the preliminary findings was accepted for presentation at the 2007 Annual Transportation Research Board (TRB) Meeting. The TRB meeting is a major peer-reviewed transportation conference held in Washington, D.C., each January in which members of federal agencies, including the DOT and DHS/TSA, and state/local policy-making officials generally participate.

S05-058: Non-Contact Ultrasonic Treatment of Metals in a Magnetic Field

John Wilgen, Roger Kisner, Roger Jaramillo, Gerard Ludtka, and Gail Mackiewicz-Ludtka

Project Description

Ultrasonic processing of materials in both the melt and solid phase is highly beneficial to the physical properties of metallic alloys. Commercially available ultrasonic processing systems require direct contact with the melt, resulting in undesirable chemical interactions when the acoustic probe/horn is inserted directly into the molten material. In addition, the localized nature of the horn probe results in a non-uniform distribution of acoustical energy within the melt crucible. The ability to couple acoustic energy efficiently via a non-contacting method would overcome a huge technological barrier to the more widespread use of ultrasonic processing.

We have developed a non-contact ultrasonic treatment method via induction heating in a high magnetic field. The exceptionally high energy efficiency of the resulting electromagnetic acoustical transducer (EMAT) is due to the unusually high magnetic fields (9–30 Tesla range), which reduces the drive current needed to achieve high acoustic pressure. This high-field EMAT provides an efficient non-contact method for coupling high-intensity ultrasonic energy directly to the sample surface. Furthermore, the applied ultrasonic excitation can be uniformly distributed over most of the sample's surface. This non-contacting ultrasonic treatment can be applied to metal alloy processing in either the solid and melt phase. The method can be coupled with thermal processing of materials, or used to advantage in circumstances where only high-intensity ultrasonic treatment is beneficial. The objective of this project was to demonstrate the superiority of the high-field ultrasonic processing method for producing enhanced material properties in metallic alloys.

Mission Relevance

The development of high-efficiency EMAT technology is important to a broad range of industries that cast metallic products. The use of this new EMAT technology in conjunction with the application of high magnetic fields has potential for addressing the needs of various industries within DOE's Energy Efficiency and Renewable Energy, Industrial Technologies Program (ITP). This concept permits more efficient continuous casting approaches for steel, aluminum, and other materials. The DOE Office of Freedom Car and Vehicle Technology (OFCVT) High Strength Weight Reduction Program has identified alternative processing technologies as a thrust area. Utilization of lightweight materials can be facilitated by the ability to process materials more energy efficiently, develop appropriate microstructures and properties, and reduce costs that accompany such processing. The OFCVT Heavy Vehicle Propulsion Program has significant interest in simultaneously applying thermal and mechanical energy without mechanical contact and considers this a potential growth area for a significant new R&D thrust.

Results and Accomplishments

A high-field EMAT has been used for non-contact ultrasonic processing of aluminum samples during solidification, which provides a successful demonstration of the concept. The magnetic field for the EMAT was supplied by a 20-Tesla resistive magnet located at the National High Magnetic Field Laboratory, and the drive current was provided by an induction coil. This combination resulted in an EMAT that delivered 0.5 MPa (5 atmospheres) of acoustic drive to the surface of the sample while coupling less than 100 W of incidental induction heating. In the initial experiment, aluminum samples of A356 alloy were heated to the liquid state and allowed to solidify at a controlled cooling rate while subjected to non-contact ultrasonic stimulation (at 165 kHz) provided by an induction coil located within the bore of the magnet.

Aluminum samples processed ultrasonically with the high-magnetic-field EMAT were compared with samples processed without EMAT excitation (no field) but with the same thermal treatment. Based on visual appearance, samples processed with EMAT stimulation showed notably improved surface conditions as compared with samples solidified without EMAT stimulation. Optical micrographs reveal obvious differences in microstructure. Micrographs for a no-EMAT sample reveal an obvious variation in microstructure, suggesting segregation of the silicon, which is manifest in different amounts of primary alpha (~pure aluminum) versus eutectic (alpha plus silicon-rich phase). By comparison, similar micrographs for a high-field EMAT processed sample showed no variations in microstructure uniformity.

Publication

Wilgen, J. B., et al. "Non-Contact Ultrasonic Treatment of Metals in a Magnetic Field." TMS 2007 Annual Meeting (The Minerals, Metals & Materials Society), February 25–March 1, 2007, Orlando, FL.

S05-061: Participation in the National Institute of Standards and Technology Iris Challenge Evaluation: Algorithms for Improving Iris Recognition

Kenneth W. Tobin, Jeffery R. Price, and Timothy F. Gee

Project Description

The Image Science and Machine Vision (ISMV) Group performs research in areas of image analysis and pattern recognition. Through this research opportunity we have participated in the National Institute of Standards and Technology (NIST) Iris Challenge Evaluation (ICE). ICE is the first large-scale, open, independent technology evaluation effort for iris recognition. The primary goal of ICE is to promote the development and advancement of iris recognition technology and assess the state-of-the-art capability. In this project, we investigated, implemented, and tested novel approaches for improving iris recognition that addresses shortcomings in the current technology relating to degraded image quality. Experimental evaluation has been performed on large image datasets provided through the ICE program that show improved segmentation performance of iris features and that provide new understanding and results related to the detrimental effects of iris dilation and ill-posed iris orientation relative to the imaging device. Our long-term goal is to strengthen ORNL's position to support our national security R&D agenda in areas of image-based biometrics.

Mission Relevance

This work is relevant to all programs where iris recognition for biometrics-based identification and verification is of interest. This includes opportunities with the DOE Advanced Technology Program (ATP), which has specific calls related to biometrics. The Office of Defense Nuclear Nonproliferation (a part of DOE NNSA) has a mission to "detect, prevent, and reverse the proliferation of weapons of mass destruction" where biometrics may play a key role in securing access to nuclear facilities. Furthermore, NIST is collaborating with other federal agencies including the FBI, National Institute of Justice (NIJ), Technical Support Working Group (TSWG), and Department of Homeland Security (DHS), which are interested in evaluating the accuracy of the technology today and in discovering improvements for future implementations.

Results and Accomplishments

At the beginning of this project, we became a participating member of the NIST ICE program, which provided us with 3000 iris images to facilitate our research. Iris recognition requires an accurate segmentation of the iris region (i.e., the circular region between the pupil and the sclera) prior to feature extraction and classification. Our goal was to improve the performance of iris recognition methods by developing a better understanding of those attributes image collection and iris pose that degrade system performance. Towards this end we have made progress in three primary areas.

1. Iris segmentation: By improving upon the baseline algorithm for iris segmentation, we achieved a recognition improvement of 5.75% from 92.75% to 98.5%.
2. Pupil dilation: Current algorithms for accommodating pupil dilation assume a first-order, linear deformation. We have shown through our own data collection with an infrared camera that this model is inaccurate. We have conducted preliminary experiments to characterize this deformation by analyzing how the iris pattern deforms under different degrees of dilation.
3. Cornea refraction: Current algorithms do not account for refraction caused by the optical properties of the human eye. We constructed a physiologically correct model of the human eye to examine the effects of refraction using ray-tracing simulations. We verified these results experimentally and are incorporating them into recognition algorithms.

S06-007: Preliminary Investigation of Medical Image Registration Using Deformable Models

James S. Goddard and Timothy F. Gee

Project Description

This project investigated the feasibility of using deformable-model-alignment methods to address a specific image alignment problem faced by medical research community. Researchers at the National Institutes of Health (NIH) are presently recording two-dimensional real-time infrared and visible optical images during exploratory surgery on both humans and animals. These images record, for example, kidneys, livers, and other specific regions in the body for later thermal analysis of physiological changes. A major problem for the analysis is that movement occurs during the surgery due to respiration, blood flow, or mechanical motion from the surgical procedure. These effects cause unacceptable alignment through the image sequence, making local temperature measurements impossible. Correcting alignment is difficult in that the motion is not global over the image but generally local in nature. Also, evaporative cooling adds random noise to the imagery, making the task more difficult. The soft organs and tissues are not rigid bodies but have deformable surfaces. In addition, the organs themselves are three-dimensional volumes with three-dimensional motion. While medical image registration has been well researched, the application of deformable registration to two-dimensional time image sequences with non-rigid three-dimensional structures has not been extensively studied. This research was focused on the development and analysis of deformable model methods to this image registration problem.

Mission Relevance

This work benefits the DOE science mission. Dr. Alexander Gorbach of the Bioengineering and Physical Science organization at NIH has described this alignment problem as a key research area that needs to be solved for their kidney and brain research and is of great interest to the medical community in general. We have had discussions with Dr. Gorbach about his needs and have learned a great deal about what he wants performed on the various sets of infrared video sequences of pig kidneys that he has provided for this study. From his additional description of the problem, we have determined that our experience in computer vision, video analysis, and digital signal processing is a good fit to answer his needs. He desires to geometrically register the organ within the image sequence, reduce noise and spurious local heat changes caused by evaporation, and use spectral analysis to derive physiological information about the animal. Dr. Gorbach has discussed how we might move forward from this project to an NIH proposal and what we might hope to accomplish.

Results and Accomplishments

Tasks that have been investigated during this project include (1) literature review of medical image registration; (2) noise removal; (3) segmentation methods; (4) registration methods for non-linear alignment; and (5) processing of local-area thermal signals. We have performed detailed analysis on two sets of infrared video sequences of a pig kidney recorded during surgery. Three methods of image registration have been examined and tested. The first uses elastic fitting with vector spline regularization. The second uses Lucas-Kanade point tracking with a third-order polynomial fit. The third uses organ segmentation and moment-based measurement. The moment-based method gives better alignment than the vector spline and Lucas-Kanade methods, although improved segmentation methods are needed. Because of the achieved registration across the video sequence, we have been able to perform the initial measurements and analysis of physiological signals that are of interest to Dr. Gorbach. We now measure the average intensity of a small rectangular region on the kidney across all frames in the video, providing a time signal of local kidney temperature.

Publication

Goddard Jr, J. S., et al. "Segmentation-Based Registration of Organs in Intraoperative Video Sequences." 2nd International Symposium on Visual Computing, November 6–8, 2006, Lake Tahoe, NV.

S06-008: In Situ Three-Dimensional Thermal Mapping Using Colliding-Pulse Two-Photon-Induced Luminescence

S. W. Allison, T. J. McIntyre, R. W. Shaw, and K. A. Meyer

Project Description

A spatially resolved, luminescence thermometry approach that is capable of producing in situ 3D thermal maps of operating systems is the goal of this effort. The approach is to inject pulsed laser light into opposite ends of a rare-earth-doped optical fiber. The laser wavelengths are chosen such that there is characteristic fluorescence that occurs only where the beams overlap. By controlling the relative timing of the two pulses, their overlap within the fiber will be adjustable. Because the fluorescence properties indicate temperature, a means is provided for sampling temperature along the fiber. This approach requires very short pulse lasers in order for the physical extent of the pulses to be short. This project used lasers of 150-fs duration. It will eliminate the need for tens or even hundreds of thermocouples by utilizing optical fiber as an elongated distributed temperature sensor. The technique can potentially be used to generate thermometric maps from below ambient to over 1500°C, depending upon the luminescent material selected. Not only is it a new form of thermometry, it is a new spectroscopic technique for rare earth and other activated luminescing materials.

Mission Relevance

ORNL is a multiprogram DOE laboratory, and this research is relevant to several programs within the specified mission. It is most relevant to part of DOE's strategic plan that relates to Energy Resources and the Offices of Energy Efficiency, Renewable Energy, Fossil Energy, Nuclear Energy and Science and Technology that serve this plan. Temperature measurements to be enabled by this technology have ubiquitous application from fuel cells to engines, industrial processes to nuclear reactors, building monitoring to HVAC controls, literally anywhere in which multiple temperature measurements are of interest.

Results and Accomplishments

The project successfully accomplished the demonstration of two-photon-induced fluorescence within rare-earth-doped optical fiber using femtosecond laser light sources. To attain the goal, a means for rapidly and locally heating the fiber along an approximate 1-cm length was achieved with excellent temperature control. Also, a mirror traversal system was set up and demonstrated for adjusting the flight path of one of the colliding lasers with sub-millimeter resolution and, most importantly, without affecting laser-to-fiber alignment. Temperature-dependent spectra were obtained for lengths ranging from 20 to 100 cm of erbium-doped fiber. The method allowed for detection of a temperature hot spot in a small region along the fiber. A key finding is the establishment of the parameters necessary for performing two-photon fluorescence spectroscopy in erbium fiber using femtosecond pulses. To our knowledge, this work is perhaps the first involving two-color femtosecond spectroscopy and erbium fiber. An unexpected, curious, and possibly useful result was the appearance of deep blue emission with injection of 1125-nm light. The overall results of the project indicate potential for spatially resolved temperature measurement. The first applications may be to high-temperature oven environments as are used for microwave processing of material and thermal mapping in steel manufacturing.

Publication

Allison, S. W., et al. 2006. "In-Flight Armature Diagnostics." Electromagnetic Launcher Symposium, May 22–25, 2006, Berlin, Germany.

S06-011: Hybrid Spread-Spectrum Sensor Telemetry, Tracking, and Information System

S. F. Smith, M. N. Ericson, and K. N. Fischer

Project Description

This research addresses the significant gap between commercially available radio-frequency (RF) communications systems and those needed to satisfy the demanding requirements associated with harsh environments. Currently, several spread-spectrum wireless signal-transmission protocols are available in the commercial market, including the dominant direct-sequence (DS) "WiFi" formats, a lower-power, low-speed, control-oriented protocol known as ZigBee, and the low-cost, frequency-hopping Bluetooth standard. Although adequate for most consumer applications, none are sufficiently robust to operate with high reliability in harsh military, research, and industrial sensor-telemetry and personnel/asset-tracking environments. The presence of large amounts of multipath, noise, and interference in those latter venues, plus the concurrent need for data security, location tracking, and support for operating potentially hundreds to thousands of devices in close proximity, clearly requires next-generation transmission methods.

In this project, we developed a novel signaling technique (one U.S. patent issued and two more pending) to address all the above deficiencies in a highly adaptable, software-programmable manner, coined hybrid spread-spectrum (HSS). The basic advantages of our new modulation form, as demonstrated in this project, can be summarized as follows: (1) it synergistically combines DS spread-spectrum and frequency/time hopping in a flexible multidimensional, orthogonal signaling scheme; (2) it is capable of excellent signal security (highly programmable); (3) it is an adaptive, robust protocol for high-reliability applications; (4) it can be operated in burst mode for very low power drain; (5) it has superior resistance to multipath and jamming; (6) it is easily deployed with modern chip technology; and (7) it is fully compliant with existing regulations for license-free RF operating bands.

Mission Relevance

This work is relevant to the DOE Office of Science (SC) offices of Electricity Delivery and Energy Reliability (OE), Energy Efficiency and Renewable Energy (EERE), Environmental Management (EM), Nuclear Energy (NE). Our advanced HSS signal transmission techniques will have wide application within the following DOE programs and federal agencies: DOE-SC (research systems); DOE-EERE/NE (industrial data links); Department of Defense (robust, secure tactical and sensor communications and tracking); DOE-EM and the Environmental Protection Agency (environmental monitoring and R&D); DOE-OE (low-cost, ubiquitous sensors and communications), National Aeronautics and Space Administration (spacecraft telemetry); DOE National Nuclear Security Administration (secure production-facility data links); the Defense Advanced Projects Agency (advanced communication technologies and sensor networking); National Institutes of Health (biomedical sensors and patient tracking); Department of Homeland Security (sensing arrays and telemetry). In addition, industries such as Boeing (airframe monitoring) and Navigational Sciences, a licensed CRADA partner (tracking of shipping containers, other applications), will benefit.

Results and Accomplishments

We demonstrated via software modeling of its signal-propagation characteristics that the HSS waveform family, with parameters optimized for specific applications, can operate with much higher reliability than the common commercial protocols (WiFi, ZigBee, and Bluetooth) in simulated typical, multipath-prone, indoor RF environments, as well as in rough outdoor terrain. Bit-error rates (BERs) were computed for both indoor and outdoor environments, represented by typical delay-spread and signal-reflection characteristics, with conditions of no, partial, and full-band jamming, which correspond to the full range of realistic reception conditions. In each case, the aggregate error rates experienced with HSS were close to those of the theoretical Gaussian noise-only case, indicating that HSS can effectively eliminate the normal degradations (data errors) due to multipath and interference. The simulations also confirmed HSS errors to be significantly lower than all of the commercial formats. In a representative partial-band jamming situation at a BER of 10^{-5}, WiFi was second best to HSS (some 11 dB worse), ZigBee was 20 dB worse, and Bluetooth was nearly 30 dB inferior. These results are fully consistent with the lesser spread-spectrum processing gains of the WiFi and ZigBee formats (11 dB and 6 dB, respectively, compared with >30 dB for HSS) and the well-known vulnerability of hopping systems like Bluetooth to partial-band interference. The enhanced reliability of HSS also requires fewer data retransmissions and thus better system power efficiency. The use of HSS techniques was also demonstrated in the project for improved multiple-access properties in general radionavigation systems. We also developed additional security-related features of HSS signaling that should be of prime interest to our national security–related sponsors.

S06-019: Novel High-Resolution Micromechanical Gyroscope

Panos G. Datskos, Slobodan Rajic, and Nickolay V. Lavrik

Project Description

This project focuses on measurement of inertial forces. Our approach for sensing angular acceleration uses a novel concept based on microelectromechanical systems (MEMS) devices. It utilizes the Coriolis force on an oscillating MEMS object when subjected to changes in rotation and has the potential to far exceed the present limitation for noise equivalent rotation of $NE\Omega < 10^{-4}$ deg/h using much simpler structures that can be made into large arrays. During this work, we will apply finite-element analysis and fundamental theoretical models to a series of mechanical structures with two degrees of freedom and various geometries. We will fabricate MEMS gyroscope structures and conduct experimental studies of the gyroscope responses as a function of its rotational movements. Our experiments will rely on the use of an optical detection technique that we have developed to measure resonance frequencies, amplitudes of oscillation, and deformations of MEMS transducers.

Mission Relevance

The proposed project is relevant to DOE national security missions in both science and nuclear security. The proposed work will advance the science of measurement of small forces and will impact many areas of science and sensors where measurement of small forces is required. The proposed work also has relevance to the mission of other federal agencies. In particular the DoD will benefit from advances made during this research as it applies to DoD navigation needs. Furthermore, the results of our studies will provide an enabling component to compass that does not rely on the earth's magnetic field but takes advantage of the earth's rotation. Our research is also relevant to the mission of Department of Homeland Security, in situations in which there is a need to obtain coordinates and navigation when GPS capability is either denied or malfunctioning.

Results and Accomplishments

During FY 2006, the project's first year, we made significant progress in the following four areas: (1) We designed new geometries and topologies for the MEMS gyroscope structures that are compatible with existing microfabrication techniques without significantly reducing the expected performance characteristics. In order to achieve a high figure of merit (i.e., low noise-equivalent-Ω, $NE\Omega_z$), the device must have several parameters optimized. For example in order to minimize $NE\Omega_z$, the resonator must have a low resonance frequency for the sensing element but high resonance frequency and driving amplitude for the driving resonator. (2) Using finite-element analysis, we successfully modeled the designed MEMS gyroscope structures using materials compatible with microfabrication techniques. This allowed us to properly select materials and geometries that are possible to microfabricate while maintaining values for important parameters such as high resonance frequency (in the range of kHz), high Q-factor in the order of 100,000, and reduced mechanical noise. (3) We gained new theoretical understanding of the effect of small rotations on MEMS devices, especially at room temperature. The magnitude of the forces studied in this work is of the order of 10^{-16} N. This is a relatively small force, and the effect of kT has to be taken into account at temperatures above cryogenic. We used models that describe the resonator and take into account the noise due to kT motion. (4)

We used bulk micromachining techniques to fabricate prototype MEMS devices that can operate as micromechanical gyroscopes. In FY 2007, we will test these devices and, using our models, refine the geometry and design for the fabrication of future devices. This work will greatly impact the science of and sensor development for measurement of small forces and will enable the realization of MEMS gyroscopes that have figures of merit comparable to those of more expensive and larger gyroscopes.

S06-024: Demonstration of Intra-Reactor Diagnostics for Catalytic Fuel Reformers

Jae-Soon Choi, William P. Partridge, L. Curt Maxey, Johney B. Green, and Galen B. Fisher

Project Description

Compact fuel reformers, which convert a broad array of hydrocarbons into hydrogen, can enable various advanced power generation technologies such as fuel cell–based auxiliary power units and hydrogen-assisted advanced engine operation. While monolith-based reformer designs have shown potential for small-scale reforming, significant technological improvements are needed for commercial implementation. It is particularly critical to further our understanding of the underlying process details to rationally and efficiently design and operate the system. However, highly non-isothermal and gradient-rich reformer operation has been very difficult to analyze via temporally and spatially integrated conventional reactor-outlet measurements. On the contrary, if localized intra-reformer information is available, it will benefit significantly various aspects of current R&D effort in the field: modeling, operating strategy development, and catalyst design. In this project, we propose to apply for the first time intra-reactor diagnostics to fuel reformers to obtain intra-reactor species and temperature distributions. SpaciMS (Spatially Resolved Capillary Inlet Mass Spectrometry) and fiber-coupled thermometry, which employ minimally invasive sampling probes, will be used to measure species and temperature distributions, respectively. The overall project goal is to demonstrate the ability of the diagnostics to measure useful information under a realistic fuel-reforming environment. The proposed research tasks include (1) preparation of probe, probe translation system, and reformer reactor; (2) assessment of intra-SpaciMS probe reactants/products condensation and undesired reactions; (3) evaluation of the thermal and chemical stability of probes; and (4) intra-reformer species and temperature measurements during steady- and transient-state catalytic methane partial oxidation.

Mission Relevance

Compact fuel reformer is viewed as a critical technology for realizing national energy efficiency and environmental goals. This project, designed to help to understand the complex reformer chemistry and to build applied systems, directly supports the mission of various DOE programs. For example, fuel reforming research is an integral part of Fossil Energy SECA (Solid State Energy Conversion Alliance) program. Moreover, Energy Efficiency and Renewable Energy Offices of FreedomCAR and Vehicle Technologies and Hydrogen, Fuel Cells and Infrastructure Technologies can benefit from the proposed intra-reactor diagnostics in their R&D activities related to distributed hydrogen generation. The U.S. Department of Defense funds multiple research programs to develop advanced military power generation technologies based on fuel cells. These advanced technologies require on-site or on-board hydrogen production via compact fuel reformers. Specifically, the fuel cell technology programs coordinated by U.S. Army Communications Electronics Research, Development and Engineering Center can benefit significantly from this research.

Results and Accomplishments

We have completed the FY 2006 portion of the project milestones: instrumentation development, evaluation of intra-SpaciMS-probe reactions, and species and temperature measurement during steady-state methane partial oxidation. First, we developed a method to produce a robust thermometry fiber-tip coating and a probe-translation system to achieve fine spatial resolution. In addition, we developed in-house fuel-reforming reactor capabilities. Regarding intra-SpaciMS-probe reaction of the sampled gas, we found that methanation, steam reforming, and methane combustion did not occur significantly up to 1000˚C. It means that our SpaciMS measurements were not biased by undesired intra-capillary reactions under the practically relevant methane-reforming conditions. The tested probes have also shown remarkable stability. Finally, we conducted steady-state methane partial oxidation at different space velocities, oxygen-to-carbon ratios, and thermal regimes and measured local species and temperature profiles inside the reformer. These first-of-a-kind measurements provided rich data, giving new insights into the underlying process mechanisms. The reaction was found mainly sequential in nature: rich combustion followed by steam reforming and water-gas shift reaction. The local equilibrium calculation, based on the measured temperature profiles, indicated clearly where the global process reached the equilibrium. This information has proven very useful for model refinement, as demonstrated in our collaboration with an industry reformer leader whose model validation had been done previously with reactor outlet speciation only.

S06-027: Optical Monitoring of Delivery Methods for Therapeutic Agents to Neural Tissues

B. M. Evans III, B. R. D'Urso, S. W. Allison, G. D. Griffin, and T. E. McKnight

Project Description

Portions of the brain may be either damaged or otherwise incapacitated due to stroke, tumor, or illness such as Parkinson's disease. A potential therapeutic advance for treating such conditions is the delivery of multipotent neural cells into damaged regions of the brain, but attempts to do so to date have met with only limited success. In fact, it has been shown that the majority of implanted cells do not survive 24 hours past the implantation procedure, and only 5–10% of implanted cells survive a few weeks past the initial grafting procedure. It is unknown whether these cells survive the implantation process, or if they die subsequent to implanting procedures. Other research has shown that delivering precise quantities of cells to the implantation site is extremely important and that poor outcomes may result from either low or high cell densities. This research involves the investigation of fiber-optic and electrophysiology-based techniques for monitoring the delivery of cell-based therapeutics to the site of neural disease in order to determine the viability of the tissues as they are delivered. This research is part of a collaborative effort with researchers at the Virginia Commonwealth University School of Medicine and the University of Virginia and is part of a multi-institution effort to develop technology for harvesting small amounts healthy tissue from individuals affected by neural disease, growing healthy neural cells based on harvested tissues, and subsequently implanting these tissues in areas of the central nervous system that are affected by disease.

Mission Relevance

The goal of characterizing therapeutic materials delivered to neural systems simultaneously with the delivery of those materials is relevant to DOE's Science mission. We are specifically addressing Science Strategic Goal General Goal 5, World-Class Scientific Research Capacity, and Program Goal 05.21.00.00, Harness the Power of Our Living World. These goals are similar to the medical applications and measurement sciences goals of the Office of Biological and Environmental Research. DOE has specific initiatives regarding interfacing with the neural environment in this office. The ability to monitor and categorize flows of materials is also of benefit to DOE's Nuclear Security mission.

Results and Accomplishments

During FY 2006, several tasks critical to the project were accomplished. Tagging the tissue of interest with green fluorescent protein (GFP) is one method of giving these tissues a characteristic optical signal. The optical properties of rat gliomal cells transfected with GFP were characterized using confocal microscope facilities at ORNL. We determined that the optimum excitation wavelength was 488 nm and that the maximum emission wavelength of these cells was 511 nm. We also determined that untagged cells in a stressed condition exhibited weak autofluorescence at 570 nm. An optical flow cell was fabricated incorporating a syringe pump and optical fiber excitation and collection fibers. This setup was used to experimentally determine the optimum collection angles for fluorescent and scattered light. A prototype optical catheter tip has been designed and is currently being fabricated based on these results. The detection of GFP transfected cells has been demonstrated with this device. Further experiments have been initiated to determine the effectiveness of this setup using cells marked with vital stains.

S06-075: High-Resolution WoodCAT Data Collection and Analysis

Justin S. Baba and Janakiramanan Ramachandran

Project Description

The development of alternative energy sources, particularly renewable sources such as biomass, is a key initiative for the United States to reduce its dependence on foreign sources of fuel. The nation's vast wood resources are being investigated as a biomass source for cost-effective bioethanol production. Currently, standard wood phenotyping tools are sample-destructive tests that are typically time intensive; therefore, a method that is rapid and nondestructive would be novel and advantageous. To meet this challenge, we sought to demonstrate the utility of a wide-field-of-view (FOV), high-resolution microCT scanner, namely, a WoodCAT scanner, for the noninvasive phenotyping of the bioenergy potential of candidate wood species. Our specific aims were to (1) acquire high-resolution (12-µm) and low-resolution (50-µm) X-ray CT images of a candidate wood core sample, (2) reconstruct the data at different resolutions (i.e., pixel binning factors), and (3) analyze the image data using various commercially available software tools for comparison.

Mission Relevance

This work is relevant to programs at DOE that perform R&D in wood-related biomass technologies. Furthermore, the wood pulp and paper industry has expressed considerable interest in the licensing and commercialization of a fully developed WoodCAT scanner system for wood quality assessments. As such, other beneficiaries of this project will be the Departments of Agriculture and Commerce through the increased use of wood as a bioenergy crop and through the impact of commercialization and utilization in the wood, pulp, and paper industries.

Results and Accomplishments

We have been successful in meeting our stated objectives. (1) We were able to acquire an ultra-high-resolution (8-µm) microCT scan at the Siemens' preclinical product facility in Knoxville, Tennessee, and a low-resolution MicroCAT II scan (50 µm) at ORNL. (2) The MicroCAT II scanned data was reconstructed at various pixel binning factors that corresponded to 108- and 216-µm image resolution, while the Siemens' scanned data was reconstructed at 8-µm image resolution. (3) The data was analyzed using amira® and winDENDRO® software tools to count the annular rings in the wood core sample. We determined that data reconstruction with a 4×4 pixel binning factor, which corresponds to 216-µm image resolution, is unsuitable for viewing and therefore counting of annular rings; a higher-resolution reconstruction, 108 µm or better, is needed. The 8-µm resolution data enabled viewing of individual wood cells and fibers but was marginal for the quantification of cellular parameters: length, width, and wall thickness. Nonetheless, we were able to demonstrate that a suitable ultrahigh-resolution data set can enable us to do both wood cellular parameter quantification, at better than 8-µm image resolution, and annular ring determination along with an investigation of the corresponding relative wood density variations, at 108-µm image or better resolution, using the same scanned data set.

S04-041: Chemical Vapor Deposition–Based Combinatorial Chemistry for New Hydrogen Storage Materials

T. M. Besmann, N. S. Kulkarni, J. J. Henry, R. J. Kasica, H. Wang, and R. B. Dinwiddie

Project Description

This project was initiated to explore the feasibility of chemical vapor deposition (CVD) for combinatorial studies in magnesium-aluminum (Mg-Al) systems for the purpose of hydrogen storage. In the past, conventional metal–organic chemical vapor deposition (MOCVD)–based approaches for magnesium deposition have been unsuccessful. The problems associated with MOCVD of magnesium were overcome with the successful design, construction, and implementation of a novel combinatorial plasma-enhanced metal-organic chemical vapor deposition (PE-MOCVD) system. A special feature of the system enables continuously varying alloy compositions (e.g., Mg-Al) in the deposited thick films. Finally, the observation of hydrogen absorption using thermal imaging was demonstrated.

Mission Relevance

One of the major objectives of the DOE Hydrogen Fuel Cell Initiative is to develop suitable hydrogen storage materials that meet the desired gravimetric storage and release requirements for fuel-cell-powered vehicles. Achievement of this objective will be aided by high throughput experiments for discovering novel hydrogen storage compositions. This project is a step in this direction.

Results and Accomplishments

Two significant accomplishments were achieved in FY 2006. The first was the codeposition of magnesium and aluminum compounds. The goal of the project was to demonstrate codeposition of two materials of interest in hydrogen storage that form hydrogen storage alloys, and thus produce a compositionally graded film. This was accomplished with magnesium and aluminum metal–organic precursors introduced through separate nozzles above a substrate. Subsequent electron probe microanalysis revealed the presence of both magnesium and aluminum in a coating, with compositional variation across the surface. Some carbon was also detected, which is an issue that will need to be addressed in future work. The second accomplishment was the rapid thermal imaging of hydrogen absorption in a metal. Samples of magnesium were placed in a high-pressure chamber containing a ZnSe window. Alternating evacuating and pressurizing the chamber to 10 bar and heating to 350°C caused the magnesium to absorb/desorb hydrogen. A rapid thermal imaging camera was successfully used to observe changes in surface emissivity, which indicated absorption/desorption.

S04-053: Fundamental Growth Mechanisms of Metal Nanoparticle-Carbon Nanotube Nanocomposite Materials

G. Malcolm Stocks, Jianxin Zhong, and David B. Geohegan

Project Description

Metal nanoparticle–carbon nanotube composites are new emerging nanomaterials with a variety of potential technological applications. Currently, fabrication of these nanocomposite materials proceeds via trial and error due to the lack of fundamental understanding of their growth mechanisms. A unique structural feature of carbon nanotubes is their surfaces of enormous curvatures. Consequently, it is expected that the mechanisms governing nanoparticle growth on such surfaces are different from those of traditional materials growth on flat surfaces. In this project, we used theoretical and experimental techniques to investigate the general principles governing the formation, structure, and stability of metal nanoparticles on surfaces of carbon nanotubes. In particular, we use theory (continuum theory, classical and first-principles molecular dynamics) and experimentation (growth of metallic nanoparticle on single-walled nanotubes) to uncover the fundamental growth mechanisms of nanoparticles on curved surfaces.

Mission Relevance

This work is directly relevant to DOE's research portfolio in basic science. In particular, it benefits DOE initiatives in materials science, nano-science, and hydrogen and fuel cell technologies. At ORNL this work is particularly relevant to some of the research directions within the Center for Nanomaterials Sciences (CNMS).

Results and Accomplishments

We made significant progress in understanding the mechanisms of growth of metal nanoparticles on carbon nanotubes. Using continuum elasticity theory, we have developed a novel concept, *bending-stress-induced self-organization*, for predicting the shape of metal nanoparticles grown on highly curved surfaces. In work published in *Appl. Phys. Lett.* **87**, 133105 (2005), we show that growth of a metal nanoparticle on surfaces of carbon nanotubes is three-dimensional and is described by a power law $L = aH^{0.5}$, where L is the length of the nanoparticle and H is its height. To understand the growth process at the atomistic level, we used simulated thermal annealing and molecular dynamics (MD) simulations and found that Au forms crystalline nanoparticles on single-wall carbon nanotubes (SWCNTs), in agreement with the prediction of the continuum theory and experimental observations. The simulation also showed that small nanoparticles of Au are mobile at room temperature on SWCNTs and that they form stable large nanoparticles through diffusion and coalescence. We further extended our study to systems beyond the metal nanoparticles and carbon nanotubes such as Si-nanoparticles and carbon nanohorns. In our paper being published in *J. Appl. Phys.* (2006), we show that as the size of a Si-nanoparticle changes, the nanoparticle undergoes structural transitions from a tent-like structure to a cage-like structure and further to a spherical compact structure.

On the experimental side, we produced SWCNTs using a pulsed-laser ablation technique and deposited Pt, Au, Pd, and Ag metal nanoparticle on the SWCNTs in an e-beam evaporation chamber. Our high-resolution transmission electron microscopic (TEM) and Z-contrast scanning transmission electron microscopic (STEM) images clearly show that uniformly distributed nanometer-sized particles form on the side walls of the SWCNTs. We have also studied the influence of post-deposition annealing on the nanoparticle size distribution and found that the mean size of nanoparticles increases with annealing temperature and the size distribution becomes greatly broadened. A power-law relationship $L = aH^b$ has been observed with $b = 0.40 \pm 0.10$ for Pt and $b = 0.316 \pm 0.024$ for Au. This power-law behavior is in agreement with the prediction given by the continuum theory.

Publications

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S05-022: Ionic Liquids as Novel Lubricants

Jun Qu, John J. Truhan, Sheng Dai, Huimin Luo, and Peter J. Blau

Project Description

This project initiated the development of a new class of ionic liquid–based lubricants with better friction and wear characteristics than conventional hydrocarbon oils to reduce parasitic energy losses and increase the reliability of moving parts in machinery, such as internal combustion engines. A group of ionic liquids with unique molecular structures have been invented at ORNL and have demonstrated very promising physical and lubricating properties. Results have suggested great potential benefits of using ionic liquid–based lubricants, such as (1) improving energy efficiency by friction reduction and allowing higher combustion temperatures; (2) extending service life by wear reduction; (3) expanding the usage of lubricants to higher temperatures with higher thermal stability; (4) reducing emissions due to ultra-low vapor pressure and less engine deposits; (5) reducing the need for expensive lubricant additives due to better intrinsic properties of ionic liquids, for example, boundary film formability and solvent nature; (6) safer transportation and storage because of non-flammability; (7) feasible to blend with oils and water to synthesize hybrid lubricants; and (8) higher flexibility in tailoring lubricating properties by molecular structure manipulation for specific applications. This proof-of-concept research of synthesis, characterization, and evolution of this new class of lubricants provides an initial scientific basis for further research and development.

Mission Relevance

Friction and wear are estimated to cost 6% of the U.S. gross national product, or around $700 billion annually. In the transportation sector, 10~15% of the energy generated in automobile engines is lost to friction, as indicated by past DOE-funded studies. A new class of high-performance, environmentally friendly lubricants developed and investigated in this study could lead to huge energy savings and a reduction of air emissions. The excellent lubricating properties, along with negligible volatility and high thermal stability, make ionic liquids also highly attractive for aerospace and military applications.

Results and Accomplishments

In this study, a variety of ionic liquids (ILs) with two cation structures, imidazolium and ammonium, and several anions, including Cl^-, Br^-, PF_6^-, Tf_2N^-, $BETI^-$, were synthesized by neutralization and metathesis reactions. Many ILs possess higher thermal stabilities than conventional hydrocarbon oils. Their onset decomposition temperatures (T_{onset}) exceed 350°C, compared with ~250°C for conventional hydrocarbon oils. Friction and wear studies have demonstrated promising lubricating properties of ionic liquids as neat lubricants or lubricant additives, particularly for use with difficult-to-lubricate metals like aluminum. The ORNL-invented ammonium ILs with Tf_2N^- anion outperformed both previously reported imidazolium ILs and baseline oils. About 30% friction reduction and 50% wear reduction have been achieved for steel-aluminum contacts lubricated by the ORNL ILs compared with a fully formulated engine oil. The inherent polarity of ILs is proposed to be responsible for the friction and wear reductions by forming a protective surface boundary film as a product of tribochemical reactions, which have been confirmed by surface chemical analyses using X-ray photoelectron spectroscopy (XPS). Other advantages of ILs include high thermal stability, negligible volatility, non-flammability, and better intrinsic properties that allow ILs-based lubricants to use fewer expensive lubricant additives. If successfully developed, this new class of lubricants will have a broad variety of applications for automobile, aerospace, and machinery. A U.S. patent was filed on 9/19/2006 (application number: 11533098) to cover the unique group of ammonium ILs invented at ORNL as lubricants or lubricant additives.

Publication

Qu, J., et al. 2006. "Ionic Liquids with Ammonium Cations as Lubricants or Additives." *Tribol. Lett.* **22**, 207.

S05-025: Large-Area, Flexible, Heteroepitaxial Diamond Films on Low-Cost Substrates for Wide-Ranging Electronic Applications

Lee Heatherly, Leslie Wilson, Robert W. Shaw, and Amit Goyal

Project Description

The superlative properties of diamond make it an attractive candidate for high-performance electronic devices. Diamond has an extremely high dielectric constant, high thermal conductance, high carrier mobility, and a negative electron affinity. These properties make it an ideal material for the manufacture of high-temperature semiconductors, ultra-fast semiconductors, high-voltage semiconductors, and cold cathode electron emitters for flat panel displays and field emission vacuum diodes. For most of these applications, the diamond must be in the form of near-single or single crystal geometry. This project deals with a procedure that can possibly provide large-area single-crystal diamond thin films suitable for many of the applications mentioned above. The procedure involves (1) the development of a suitable textured substrate that includes a thin iridium film as the top surface, (2) the dense nucleation of oriented diamond seed crystals on the iridium, (3) the growth of an epitaxial diamond film from the seed crystals, and (4) the characterization of the resulting diamond film as well as each step of the process.

Mission Relevance

This work is relevant to several possible federal as well as private funding sources. The Office of Electrical Transmission and Distribution program is expected to get funding for an initiative on high-power electronics, and diamond films are of great interest. The Defense Advanced Research Projects Agency (DARPA) will be extremely interested in diamond-based devices. We have spoken with Art Clemons, ORNL DARPA Program Manager, about this proposal. He is of the opinion that if we can demonstrate what is proposed, he is optimistic about possible funding from DARPA. The National Reconnaissance Office is funding work on the development of solar cells using polycrystalline diamond films for space applications, and this work should be very relevant to this effort. NASA will be very interested in these films for photovoltaic applications in space. As for private sources, the semiconductor industry in general will be very interested in a technology that promises mass production of multi-chip modules and faster devices.

Results and Accomplishments

During FY 2006, several of the stated goals were accomplished.

1. A suitable buffer stack was developed for the Ni-W RABiTS that allowed iridium and diamond to be epitaxially deposited. The buffers were necessary to prevent nickel from diffusing into the iridium and for maintaining the epitaxy of the iridium and diamond.
2. Iridium was successfully deposited epitaxially on the YSZ/Y_2O_3/Ni-W substrate by electron beam evaporation.
3. A diamond nucleation process was developed for increasing the diamond nucleation density on the iridium surface. This employed a DC-biased approach in a hot filament chemical vapor deposition (CVD) system.
4. Many CVD diamond films have been deposited using both hot filament and microwave excitation of the gases. These films have been characterized via scanning electron and transmission electron microscopy, Raman spectroscopy, X-ray diffraction, and other techniques.

The results obtained to date are very encouraging, and it appears that the stated goals of the proposal are achievable.

S05-032: Orientational Imaging in Biological Systems by Electromechanical Scanning Probe Microscopy: Galvani Experiment on the Nanoscale

Sergei V. Kalinin and Thomas Thundat

Project Description

The mechanical properties and physiological behavior of calcified and connective tissues are ultimately related to the relative ordering and orientation of a relatively small number of biopolymers, such as collagen. Connective tissues also determine growth and remodeling mechanisms and can serve as indicators of diseases or successful therapies. However, currently no experimental techniques are capable of accessing the orientation and local mechanical and electromechanical properties of collagen and other biopolymers on the nanometer and ultimately molecular scale. Piezoelectricity (i.e., linear coupling between electric field and mechanical deformation) is a ubiquitous feature of all biopolymers due to the simultaneous presence of polar bonding and optical activity. The piezoelectricity described by the third-rank tensor is extremely orientation dependent. In this project, we explored the applicability of electromechanical scanning probe microscopy to (a) image the ultrastructure of biomaterials by detecting the piezoelectric collagen in the matrix of non-piezoelectric hydroxyapatite and (b) determine local molecular orientation of collagen molecules through the detection of local electromechanical response vector.

Mission Relevance

The impact of this proposal on DOE programs is twofold. In general, the conversion between mechanical and electrical energy in biological and inorganic systems is the fundamental basis for multiple methods of energy generation, including energy harvesting, transformation in complex molecules, etc., and is of fundamental interest to Office of Basic Science. At the same time, functional behavior in biological and biomimetic systems is a topic of interest to many bio-related programs supported by the Office of Energy Efficiency and Renewable Energy. The evolution of ultrastructure in calcified and connective tissues during growth and remodeling processes and during deceases such as osteoporosis or cavity formation is a grand challenge for NIH institutes such as the National Institute of Dental and Craniofacial Research (NIDCR), the National Institute of Biomedical Imaging and Bioengineering (NIBIB), and the National Institute of Arthritis and Musculoskeletal and Skin Diseases (NIAMS). By developing a simple and easy-to-implement method to image the structure of these materials on the sub-10 nanometer level, this proposal provides a key imaging tool for ex situ studies of these phenomena. Extending beyond the piezoelectricity of biomolecules, more complex forms of electromechanical coupling are ubiquitous in biosystems, with examples ranging from flexoelectricity of molecular membranes to energy storage in mitochondria to activity in cardiomyocites. The capability to probe these processes on the nanoscale is the key to further advancements in biology.

Results and Accomplishments

Electromechanical imaging of calcified and connective tissues by piezoresponse force microscopy (PFM) has been successfully demonstrated at a resolution below 10 nanometers in a number of systems including tooth dentin and enamel, dog femur cartilage, and artificial collagen films. The comparison with atomic force acoustic microscopy, which is sensitive to local mechanical properties, has verified that PFM is virtually free of topographic cross-talk, verifying prior theoretical results. The structure of the enamel in the vicinity of dentin-enamel interface has revealed the presence of collagen fibrils, evidencing the incomplete mineralization of enamel matrix. Furthermore, the observed difference in electromechnical response between peritubular (PTD) and intertubular dentin resolved the different nature of tissue-forming proteins, supporting the hypothesis that PTD is a non-collagenous tissue and a product of the secretion of specialized proteins that facilitate the mineralization of the tubule wall. Based on the strong orientation dependence of piezoresponse signal, an approach for molecular orientation imaging has been suggested. The capability for collecting vector electromechanical data has been established and mathematical theory relating electromechanical response vector to Euler angles defining molecular or crystallographic orientation has been derived.

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S05-035: Development of an Intermediate-Temperature Solid Oxide Fuel Cell

T. R. Armstrong, A. E. Payzant, and S. Speakman

Project Description

The major issues hindering the development and implementation of the current class of high-temperature solid oxide fuel cells (SOFCs), operating above 650°C, are seals, stable metallic interconnects (i.e., in humid fuel and air), start-up time (currently tens of hours), and mechanical robustness. A SOFC that operates at temperatures less than 550°C offers several advantages over traditional high-temperature fuel cells, including the use of metallic brazes to seal the stack, iron-based alloys for the interconnect, and metallic cathodes. There is the potential in such a device to significantly reduce start-up time and improve thermal management in fuel cell systems. Recently ORNL has demonstrated that a new class of materials, specifically based on $A_2B_2O_x$ structure, are proton conductors at temperatures below 550 °C. This new material has the potential to act as a separation membrane and a SOFC. However, a number of technical and scientific challenges remain that this project sought to resolve. Several characteristics of the proton transport membrane are not well understood. For example, the electrolyte must be heated to ~500°C in humidified H_2 before appreciable hydrogen flux can be measured; however, after the electrolyte is "activated" at 500°C, H_2 conduction persists as the membrane is cooled to temperatures as low as 200°C and possibly even lower. Additionally, after activation the H_2 flux actually increases as the temperature is decreased. The mechanism by which protons migrate through the membrane is not known, nor is the limit of hydrogen uptake. Furthermore, the activity of dissociation of the fuel at surface sites is not understood, nor is its impact on the overall flux—surface dissociation is often the rate-limiting step in proton conduction. While all are important scientific questions to address, successfully leveraging funds to further develop this system rely exclusively on the construction and demonstration of a functional fuel cell. Consequently, this project sought to demonstrate proof of principle that this new class of materials could be used for fuel cell applications.

Mission Relevance

This work is relevant to the Solid State Energy Conversion Alliance (SECA) subprogram within the DOE Fossil Energy Program and to the Hydrogen Production and Delivery subprogram within DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program. If successful it is anticipated that this project could lead to new efforts for hydrogen separation, electrolysis, and fuel cells, which all support the President's Advanced Energy and Hydrogen Fuel Initiatives. The proof-of-principle experiments were designed to provide enough information to broadly impact power initiatives within DOD focusing on developing rapid start fuel cells for auxiliary power units and mobile power.

Results and Accomplishments

This project was carried out in four steps following a logical progression from (1) the development of thin electrolyte membranes; (2) the evaluation of suitable catalytic materials for the anode and cathode; (3) the demonstration of fuel cells based on the materials developed, and (4) post-demonstration analysis of the fuel cell materials to evaluate long-term stability issues. More than 20 fuel cells were fabricated during the course of this project. We demonstrated early that thin (<200 mm) cells could be easily fabricated; however, their mechanical integrity was poor. Consequently, two or more layers were laminated to produce a stable fuel cell for test. Simple noble metal electrodes consisting of either Pd, Au-Pd, or Pt were applied for both the anode and cathode prior to testing in humidified hydrogen (fuel) and air (oxidant) between 500 and 800°C. We were able to test several samples which gave open circuit voltages (OCV) greater than 0.7 V, which is indicative of a mixed-conducting electrolyte. These tests produced very low levels of power at 500°C, indicating promise for fuel cell applications. OCVs of 1 indicate ionic conduction and OCVs less than 1 suggest mixed conduction. This work found that the test samples were very susceptible to damage in our test fuel cell system. As a result there many issues remain unresolved and will require additional work in the future.

S05-036: Lead-Free Electromechanical Transducer Materials

David J. Singh and Takeshi Egami

Project Description

Piezoelectric materials are ubiquitous in transducers for applications ranging from shipboard sonar to medical ultrasound. The best materials are based on lead, and in fact the mechanism that leads to piezoelectric response in ferroelectric perovskites such as $Pb(Zr,Ti)O_3$ (PZT—the most common material) relies on the specific chemistry of lead. We had formulated a concept for producing ferroelectricity and piezoelectricity in this class of materials without lead. The goals of this project were (1) do proof-of-principle studies related to our frustration model and more generally to refine our understanding of these materials in chemical terms and (2) establish a materials-by-design activity at Oak Ridge National Laboratory centered initially around this topic. The scientific activity funded by the seed grant consisted of first-principles calculations to understand lattice instabilities in perovskites and neutron scattering studies of lead-free niobate materials in the family $(K,Na,Li)(Nb,Ta,Sb)O_3$.

Mission Relevance

Advanced materials are central to modern technology. DOE funds a wide variety of materials programs with a view to tailoring and discovering enabling materials for technology. The materials design aspect of this effort has relevance across DOE and other agencies. The specific target of this effort (piezoelectric and ferroelectric perovskites) is of particular relevance to the DOE Office of Transportation, the DOE Office of Basic Energy Sciences, the Office of Naval Research, and the National Science Foundation.

Results and Accomplishments

We used a combination of first-principles calculations and neutron-pair distribution function measurements to understand lattice distortions in perovskites in the presence of size disorder on the so-called “A-site” of the perovskite lattice. The results are related to the piezoelectric behavior of lead-free compositions discovered previously by researchers at Toyota Central Research and Development Laboratory and DENSO Corporation. Specifically, we did first-principles calculations for various supercells to model a variety of hypothetical lead-free compositions and demonstrated that ferroelectric behavior arises quite generally when there is substantial "A-site" size disorder in low-tolerance-factor perovskites. This is enabling for the design of many new ferroelectric materials. In addition, we carried out pulsed-neutron atomic pair-density function analysis on powder samples of lead-free ferroelectrics with compositions $(K_{0.47}Na_{0.47}Li_{0.04})NbO_3$, $(K_{0.48}Na_{0.48}Li_{0.04})Nb_{0.9}Ta_{0.1}O_3$, $(K_{0.485}Na_{0.485}Li_{0.03})Nb_{0.8}Ta_{0.2}O_3$, and $(K_{0.44}Na_{0.52}Li_{0.04})Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$. These compositions are very close to the morphotropic boundary between the orthorhombic and tetragonal phases. The lattice structure of $K_{0.5}Na_{0.5}NbO_3$ is orthorhombic, but the substitution of Li for K/Na and Ta for Nb drives the system to the tetragonal structure, and near the morphotropic boundary between the two phases, high piezoelectric response arises. Our analysis of the pair distribution function implies that the local structure remains orthorhombic even in the tetragonal phase. Thus the role of Li and Ta must be to break up the correlation of the local orthorhombic distortion into nano-domains, creating the tetragonal symmetry in average, similar to the behavior of lead-containing relaxor piezoelectrics such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ alloyed with $PbTiO_3$. This clarifies the nature of the local ferroelectric polarization and the role of the Li and Ta substitutions.

Publications

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S05-038: Sensing Arrays Based on Non-Nernstian Sensing Elements

Fred Montgomery, Dave West, Bruce Warmack, Mark Buckner, and Tim Armstrong

Project Description

Array-based sensing approaches can overcome difficulties associated with selectivity. The array approach relies on a sufficient variety of responses both to the specific analyte of interest and potential interferents, as opposed to strict selectivity for the analyte of interest in the presence of the interferents. In this project we proposed to develop arrays of "non-Nernstian" sensing elements that could detect ammonia (NH_3) in combustion exhausts. This is a practical sensing challenge as NH_3 is used as a reagent in selective catalytic reduction (SCR) treatment of combustion exhausts, and the presence of NH_3 in the treated exhaust is indicative of malfunction(s) in the SCR system. Since combustion exhausts are complex mixtures, containing interferents such as carbon monoxide (CO), oxides of nitrogen (NO_x), and hydrocarbons, along with varying amounts of oxygen, water vapor, and carbon dioxide, an array approach is appropriate for attempting to detect NH_3. We selected "non-Nernstian" elements to comprise the array since these types of sensing elements can be operated at high temperature (600–700^{o}C), and the signal they produce is a readily measurable DC voltage. To validate the concept, a number of individual sensing elements were fabricated and sequentially tested in simulated diesel engine exhaust. Pattern-recognition algorithms were developed and applied to data from selected sensors in order to design an array capable of measuring NH_3 in combustion exhaust.

Mission Relevance

This work is relevant to the Heavy Vehicles Propulsion Materials subprogram within the DOE FreedomCAR and Vehicle Technologies Program. Environmental stewardship is driving reductions in permissible NO_x emissions from diesel engines to levels that will require on-board remediation. The SCR technique is one of the most promising candidates for this purpose, and NH_3 sensors will be essential to monitor the function of the SCR system on the vehicle. Since the proof-of-principle experimentation was successful, we are hopeful that funding to further develop the sensor can be obtained from the FreedomCAR and Vehicle Technologies Program.

Results and Accomplishments

The project was carried out in three steps: (1) design and assembly of equipment (fixturing, etc.) for testing the sensing elements, (2) fabricating the sensing elements and testing them in simulated diesel exhaust, and (3) training and validating a machine-learning model. Eighteen test elements were fabricated and tested, and from these, the six most promising candidates were selected. Several of the elements gave very similar responses to NH_3 and the potential interferents CO, NO_x, and propylene (C_3H_6, a representative hydrocarbon), and inclusion of more than one similarly responding sensing element in the array would be redundant. Using the responses of the six selected elements as training inputs to a machine learning model (kernel regression) revealed the most of the predictive information for NH_3 concentration was contained in the output from just three sensing elements. These three elements were deployed in a simulated array, "trained" with the experimentally obtained data, and then "tested" in various ways using experimental data. The trained array demonstrated quantitative NH_3 concentration determination over the range 10–100 ppm in backgrounds containing the potential interferents (CO, NO_x, C_3H_6) in isolation or in combination. We thus consider this project successfully concluded.

S05-041: Out-Of-Autoclave Stabilization/Carbonization of Pitch-Based Carbon-Carbon Composites and Other Pitch Materials

James Klett, Chris Janke, and Cliff Eberle

Project Description

One of the most time-consuming and expensive steps in carbon-carbon processing is the high pressure carbonization step, or HIPIC. When pitch, a thermoplastic, is heated, it first melts and then off-gasses as it converts to carbon. The off-gassing tends to force the liquid pitch from the preform, resulting in bloating and/or foaming. Exceptionally high pressures and high temperatures (~2000°C) as well as very slow heating rates are used during carbonization to minimize pitch bloating/foaming and thermal stresses. Unfortunately, autoclaves with these temperature and pressure capabilities are very capital intensive as well as expensive to operate. Clearly, HIPIC is the bottleneck and the major cost driver in carbon-carbon production. To bypass the HIPIC bottleneck, oxidative stabilization (cross-linking) has been used to render a pitch or mesophase infusible (unmeltable) for carbonization and is used extensively with carbon fiber production.[1, 2, 3] Unfortunately, this technique can only be used on very thin composites (less than ~1/8 in. thick) because of the limited oxygen diffusion through the pitch matrix. ORNL has discovered a proprietary, non-oxidative, atmospheric pressure technique using a proprietary mesophase pitch for stabilizing and carbonizing the pitch matrix in carbon-carbon composites. This replaces the multiple, time-consuming, high-pressure impregnation and carbonization cycles of traditional processing with a similar number of short stabilization and carbonization cycles at atmospheric pressure. The objective of this project was to demonstrate this on thicker composites and to start to understand the fundamental mechanisms behind the stabilization method, so as to be able to optimize the process later.

Mission Relevance

This work is relevant to the Office of Transportation Technologies as well as the Space Programs Office. Recent work with the Space Programs has highlighted a need for more rapid lower cost pitch-based carbon-carbon composites for supporting the deep space radioisotope thermal generators. If successful, we expect that this project will initiate a new effort from both the Defense Advanced Research Project Agency (DARPA) and commercial companies such as ATK-Thiokol. While this project has its focus on providing a fundamental understanding, we fully anticipate that it will grow into a much broader program that will impact diverse technologies under development at the Department of Defense (DARPA, Air Force, Army) and the National Aeronautics and Space Administration. We have already been contacted by several of these agencies to discuss opportunities.

Results and Accomplishments

Initial work on this novel technique involved solvent impregnation of the composites to apply the mesophase pitch into the preforms. Injection molding was attempted but failed due to lack of pitch pellets, rather than the powder supplied. Therefore, several woven 3-D PAN-based carbon fiber performs 0.4 in. thick by 5 in. in diameter were impregnated in an isostatic press at 300ºC and at pressures less than 100 psi with the proprietary mesophase pitch, to simulate the RTM process. The parts were then carbonized to 1000ºC and graphitized to 2800ºC in less than 1 week and the density measured. This was repeated up to three times, and then the parts were cut into flexural test specimens and thermal conductivity test specimens and the properties measured. Samples were also evaluated under scanning electron microscopic (SEM) and optical image analysis to characterize the quality of the mesophase pitch-based graphite matrix.

The results of this work demonstrated the fabrication of carbon-carbon in less than 3 weeks with only three cycles. However, the density of the carbon composites produced in this work was less than typical (1.3 g/cm^3 compared to 1.9 g/cm^3 for the HIPIC process in a 3-D preform). The strength and modulus of the new process were less than half of that exhibited with similar composites made from the HIPIC process. While our initial processing did not yield the same impregnation efficiency, it is anticipated that with additional research, this cycle efficiency will improve by optimization of the mesophase pitch composition.

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S05-044: Understand and Optimize Thermal Creep Resistance in Nb–1%Zr for High-Temperature Applications

Steven J. Zinkle, Tai-Gang Nieh, Timothy E. McGreevy, and David T. Hoelzer

Project Description

The objective of this project was to investigate the key physical mechanisms controlling thermal creep deformation behavior of Nb–1% Zr, an alloy being considered for space power applications. Fully recrystallized samples of Nb–1%Zr with different textures were prepared by varying the cold work and annealing conditions. The texture was quantified using scanning electron microscopy, orientation image microscopy, and X-ray diffraction techniques. Tensile tests were subsequently conducted at 750°C and 1100°C over a wide range of strain rates. To provide further identification of the deformation mechanisms, strain rate change tests were performed to evaluate the stress exponents. The texture in the recrystallized Nb–1%Zr was found to significantly affect the flow stress of Nb–1%Zr at both 750 and 1100°C. A confirmatory thermal creep rate test performed at 1080°C for 2680 h demonstrated that Nb–1%Zr with texture designed to achieve high strength exhibited substantially lower thermal creep deformation than reported literature values.

Mission Relevance

This work is relevant to space reactor power programs of DOE, DoD, and NASA. Niobium alloys such as Nb–1%Zr are candidate structural materials for space power systems due to their good strength up to high temperatures, and good fabricability. However, large variations in the measured creep behavior of nominally identical Nb–1%Zr specimens have been reported. This variability in high-temperature strength significantly reduces the allowable design strength for this material and makes it an unattractive candidate for NASA space reactor applications. The objective of this project was to investigate the role of crystallographic texture on the elevated-temperature mechanical properties of Nb–1%Zr. If the texture effect can be understood and quantified, it would greatly increase the attractiveness of this alloy system for space reactor structures and would reduce the technical risk for the overall space reactor program.

Results and Accomplishments

Commercial Nb–1%Zr (4 mm sheet) was vacuum annealed at 1250°C for 2 h, cold-rolled to 80% reduction-in-thickness, and then vacuum annealed at 1300 to 1550°C for 2 h. The recrystallized microstructure was examined using backscattered scanning electron microscopy, and texture of the sheet was analyzed using X-ray diffraction and orientation image microscopy. At the lower annealing temperatures, the recrystallized grains preferentially aligned with the {111} habit planes normal parallel to the normal direction of the sheet and the <110> crystal directions parallel to the rolling direction. Annealing at 1500°C for 2 h resulted in a rotation of the grains about the {111} planes lying in the rolled plane from <110> to <121> alignment with rolling direction (i.e., a 30° change in grain orientation).

Tensile specimens from the 1500°C annealing condition were machined at 0° and 30° angles to the rolling direction in order to obtain different textures relative to the tensile axis. Tensile tests were performed in vacuum at 750 and 1100°C at strain rates 3.3×10^{-6} s^{-1} to 3.3×10^{-3} s^{-1}. The

750°C tensile tests did not exhibit a large strain rate dependence, whereas the tensile tests at 1100°C exhibited increasing strength with increasing strain rate. The 750°C tensile deformation appears to be controlled by dislocation glide, whereas the 1100°C deformation is controlled by dislocation power law or diffusional creep. For tensile tests conducted at both 750 and 1100°C at increasing strain rates, the flow stress of the 0°-oriented sample was about 20% higher than that of the 30°-oriented sample, indicating the material is stronger in the rolling direction. The measured stress exponent at 1100°C was a relatively high value of 14.8, suggesting power-law breakdown behavior. A thermal creep test with an applied stress of 17.2 MPa at 1080ºC on a 0°-oriented sample resulted in 0.25% deformation after 2681 h (2.6×10^{-10} s^{-1} creep rate). This is one-order-of-magnitude-less deformation rate than the 1% plastic extension after 1000 h reported in the literature for nominally identical Nb–1%Zr, which suggests texture has a significant effect on the high-temperature mechanical properties over a broad range of strain rates.

Publication

Nieh, T., et al. 2006. "Effect of Texture on the High Temperature Mechanical Properties of Nb-1% Zr Alloy." *Scr. Materialia*. **55**, 719.

S05-048: Thermoelectric Properties of Uranium Dioxide

Chad E. Duty, M. Jonathan Haire, Jim Kiggans, Hsin Wang, and Wallace Porter

Project Description

Uranium dioxide is a strong candidate for providing a materials breakthrough in thermoelectrics. The Seebeck coefficient for UO_2 is ~600 µV/K at room temperature, which is more than double that of the best thermoelectric materials today (~270 µV/K for doped BiTe alloys). The relative worth of thermoelectric materials is typically judged by a dimensionless thermoelectric figure of merit ($ZT = \sigma_e S^2 T / \kappa$), where σ_e is electrical conductivity, S is the Seebeck coefficient, T is temperature, and κ is thermal conductivity. A significant amount of effort over the past 50 years has been directed at developing a material with a high figure of merit, but the best documented results to date have barely achieved a value above 2. Recent experimental results suggest that uranium dioxide may exceed these values at elevated temperatures. Research by Thomas Meek and Jonathan Haire has shown that the electrical conductivity of doped UO_2 is four orders of magnitude higher than intrinsic, undoped UO_2 at room temperature. If this dramatic increase holds true at elevated temperatures and other properties hold relatively constant, UO_2 could produce a figure of merit of ~1.3 at 450°C and ~4.2 at 800°C. The goal of the current research is to validate this potential by fabricating UO_2 samples and measuring the thermoelectric figure of merit at room temperature and 450°C.

Mission Relevance

Thermoelectric materials are useful in various applications because they are highly reliable, silent, vibration free, small, and lightweight. A marginal increase in the figure of merit would make thermoelectric devices competitive with standard vapor-compression cooling systems, while a dramatic increase would lead to their widespread use in military, space, and commercial products. Thermoelectric devices can also be used in direct energy conversion.

The U.S. Department of Defense has set a figure of merit goal of 4 for thermoelectric materials. If UO_2 could demonstrate the potential to exceed or even approach this value, several DOD agencies, including Defense Advanced Research Projects Agency (DARPA), would be interested in further research for applications in DOD systems. In particular, Art Clemens (DOD Programs at ORNL) has been in contact with Dr. Edward Van Reuth of the Tactical Technology Office (TTO) at DARPA. The Navy is also exploring the use of thermoelectric materials for power conversion and generation on submarines.

Results and Accomplishments

Several doped UO_2 samples were manufactured by pressing and sintering UO_2 powder with small amounts of aluminum oxide. The density of these samples was much lower than expected (75–85% theoretical density). Additional samples were made using a different sintering agent and dopant material (TiO_2) to achieve densities of 87–90%. A few natural and titania-doped samples were selected for thermoelectric measurements. Thermal diffusivity and heat capacity were measured at room temperature and 450°C. The resulting thermal conductivity values were calculated to be between 3.6 and 4.5 W/mK. The electrical conductivity and Seebeck coefficient measurements were conducted in air, and thus limited to temperatures below 200°C to protect against oxidation. The electrical conductivity of the doped sample was 9 orders of magnitude lower than expected (likely due to the high surface roughness of the sample). Likewise, the surface roughness caused an unstable Seebeck coefficient reading of about 2000 µV/K. The resulting thermoelectric figure of merit for the doped sample at 450°C was estimated to be 1.6×10^{-6}. This unexpectedly low value is due to problems encountered during sample fabrication, the lack of detailed material characterization, and the surface roughness of the samples. A more comprehensive study that permits characterization and optimization of sample properties will be required to realize the thermoelectric potential of UO_2.

S05-051: Scalable Surface-Enhanced Raman Spectroscopy for Single-Molecule Detection and Characterization

Zhenyu Zhang, Gyula Eres, Baohua Gu, Robert N. Compton, Efthimios Kaxiras, and Wei Wang

Project Description

In this project, we propose an integrated theoretical and experimental effort aimed at establishing the validity of one central idea: development of scalable surface-enhanced Raman spectroscopy (SSERS) as a predictive analytical technique with single-molecule detection sensitivity. The scalability is to be achieved by spatially aligning two arrays of metal nanoparticles or nanoshells self-assembled or fabricated on lithographically patterned substrates. A nanoneck distance separates each nanoparticle pair within the nanoparticle arrays, defining a local surface-enhanced Raman spectroscopy (SERS) “hot spot.” Collectively, the hot spots merge to define a “hot zone,” rendering the device ultrahigh sensitivity for single molecule detection. The predictive power is to be achieved via the state-of-the-art multiscale modeling, hybridizing first principles approaches and classical electromagnetic descriptions within the generalized Mie theory. We will primarily explore the existence of collective phenomena in SERS caused by the multi-nanoparticle nature of the aligned geometry, and the feasibility of extracting angular information from the SERS signals. Together, the proposed research is to lay the foundation for making scalable SERS a powerful technique with ultrahigh sensitivity for single-molecule detection and characterization of chemical and biological agents. Such a device will have immense potential for application in a broad range of fields from chemical, biological, and biomedical research and trace element detection to homeland security applications.

Mission Relevance

This work is directly relevant to DOE's research portfolio in basic science. It is particularly relevant to DOE initiatives in materials science, nanoscience, and single-molecule imaging. At ORNL this work is particularly relevant to some of the research directions within the Center for Nanophase Materials Sciences.

Results and Accomplishments

During FY 2006, we accomplished the following. (a) We showed within the framework of the generalized Mie theory that large local field electromagnetic enhancement suitable for single-molecule SERS may occur due to collective phenomena. In particular, we studied one-dimensional nanoshell dimer arrays. Under optimal conditions, the local electromagnetic enhancement at the nanoneck region of a nanoshell dimer in the array can be 10 times higher than that due to an isolated nanoshell dimer. (b) We proposed a new chemical contribution to SERS, caused by the dynamic polarizability of the metal substrate as it is modulated by the diffusive scattering of the electrons within the substrate by the adsorbed molecules. The modulated polarization of the substrate coupled with the incident light will contribute to the Raman scattering enhancement. (c) We studied SERS using Au nanoparticle aggregates and ordered Au nanopillar arrays. We synthesized Au colloidal nanoparticles with a controlled size in a range from 5 to 100 nm and studied the relationship between colloidal aggregation and SERS. With controlled aggregation of Au colloidal particles, we observed a large enhancement of Raman signal. Furthermore, we developed a method to fabricate highly ordered Au nanopillar arrays using anodized aluminum oxide as a template. The ordered nanopillar arrays give reproducible SERS signals with thionine as a test molecule.

Publication

Ruan, C., et al. "Single-Molecule Detection of Thionine on Aggregated Gold Nanoparticles by Surface Enhanced Raman Scattering." *J. Raman Spectrosc.* Submitted.

S06-006: Characterizing Graphite Foam for Use in Electromagnetic and Acoustic Shielding

James Klett, Rick Lowden, and Greg Hanson

Project Description

The ability to prevent the emission of acoustic and electromagnetic signals from buildings and rooms is an important requirement for many national and homeland security missions. The purpose of this project was to characterize the electromagnetic and acoustic signature-management capabilities of the graphite foam developed at ORNL to determine whether it could be a cost-effective alternative to conventional technologies. To test the acoustic characteristics, a box 0.9 m on each side was constructed and lined with 2.5-cm.-thick graphite foam. An acoustic sound generator and microphones were placed in the box to measure the actual sound generated and the acoustic absorption of the incident wave on the surface of the interior wall. In addition, a microphone was placed outside of the box 1 m from the source. From these microphones, the sound absorption and transmission attenuation were measured. For the electromagnetic tests, a small box 0.3 m on each side made from 2.5-cm-thick graphite foam was made with a radio frequency (RF) antennae inside the box. The frequency was varied from 7–18 GHz, and the transmission loss through the box was measured with a network analyzer.

Mission Relevance

This work is benefiting both the DOE national security mission and the Department of Homeland Security. Furthermore, as a result of this project we have determined that the ORNL graphite foam may be a suitable, cost-effective liner for secure conference rooms in embassies and other government installations. We have been contacted by several agencies to discuss applications of this technology for acoustic, electromagnetic, and thermal signature management.

Results and Accomplishments

Following the procedures described above, we determined the acoustic and electromagnetic signature management capabilities of the foam. Our measurements of the acoustic characteristics showed a 15-db attenuation of incident acoustic energy and a 55-db transmission attenuation. The electromagnetic attenuation was measured to be more than 90 db in the frequency from 7–18 GHz. Several fabrication methods were used to test joining of the foams, such as butt joints, tongue and groove, and lap joints. Only the butt joints were found to have a decrease in the performance. However, the level of shielding never dropped below 60 db. These tests were successful and, as a result, permission was granted and funding obtained to construct a secure conference room in Building 5300 using the graphite foam.

S06-016: Quasi-Electrostatic Carbon Orientation Processing for Lithium Ion Battery Anodes and Other Applications

Jane Howe, Andrew Kercher, Mina Yoon, John Wilgen, and Nancy Dudney

Project Description

The proposed quasi-electrostatic carbon orientation (QCO) process will exploit electric fields to facilitate ordering of graphene layers during carbonization of "hard" and "soft" carbon precursors, with the objective of producing aligned nanostructured carbons. The technique has the potential to produce highly aligned, monolithic carbon plates and ribbons at much lower temperatures than those required for conventional graphitization of carbon. The carbons will be tested as anode materials for lithium ion batteries. Enhanced ordering of discrete graphitic domains in the carbon could lead to better diffusion of lithium ions through the carbon structure, resulting in higher power densities than are currently possible. Hard carbons possessing more aligned structure on a nanoscale should exhibit energy densities higher than theoretical prediction for conventional anode carbons but with a much lower degree of first-cycle irreversibility (characteristic of conventional hard carbons). In short, QCO processing could add a new means of structural manipulation on the nanoscale.

Mission Relevance

The QCO process, if proven, will benefit a number of programs and agencies. The DOE Office of Energy Efficiency and Renewable Energy would be interested in QCO for developing lightweight automotive materials and graphite electrodes for metals processing. The Department of Defense would be interested in applying the technology to lithium ion batteries for portable power applications and to low-cost, high-performance carbon fibers and heat spreaders.

Results and Accomplishments

During FY 2006, we made significant progress in both simulation and experimentation. We performed a computational study of the proposed system's response to electric field and temperature. Based on our preliminary mathematical modeling, a frequency of 600 kHz to 10 MHz is required to align the carbon at temperatures above 200°C. We constructed a QCO rig with a tunable frequency and field strength that can be heated up to 800°C. The rig has an electric field range of 0.1–10 kV/cm, which was chosen using data from the literature on electret processing of waxes. Room-temperature testing demonstrated that the rig was capable of achieving a resonance frequency of ~750 kHz at ~1.7 kV/cm. In our first experiments, which were undertaken using mesophase pitch, the key processing temperature was experimentally identified to be 230°C.

Our simulation work to date used a nanometer-sized carbon fragment as the starting model to mimic a mesophase pitch carbon precursor. The total energy calculations on nanometer-sized carbon fragments are based on density functional theory (DFT) as implemented in the VASP (Vienna Ab-initio Simulation Package) code. For nanoscaled graphite, the calculation predicted that it is very difficult to align the material in the desired direction without destroying its atomic arrangement. The material is extremely sensitive to the environment because the dangling bond states determine the overall properties of the material. Therefore, the structure can be easily destroyed even under small electric field, at about 0.1 kV/cm.

Experimentally, our initial tests used a field around 1.5 kV/cm. The discrepancy between the theoretical predication and the experimental field strength is obvious. We believe that the very low field predicted by the simulation was from using a structural model that is not representative of reality. In the simulation, the nanoscale carbon fragment model is surrounded by a vacuum without incorporating any C-H or C-O bonds as part of the structure. Moreover, the model is completely free of any impingement from the surrounding molecules. During FY 2007, we will modify our simulation using a new structural model and methodology.

S06-048: Microstructure and Defects in Energetic Materials and Radioactive Alloys

Gene E. Ice, Eliot D. Specht, Frederick J. Walker, Roger E. Stoller, John D. Budai, and Bennett C. Larson

Project Description

The objective of this project is to combine X-ray microbeam and diffuse scattering techniques to demonstrate a fundamentally new direction for the study of micron-sized samples. Materials properties depend sensitively on the kind and distribution of defects. Understanding defects in radiation-damaged materials and in energetic materials is particularly important to understand their behaviors, but the sensitive diffuse X-ray scattering characterization methods used for these materials have been challenged because of safety concerns regarding the handling of sufficient quantities for diffuse measurements. The availability of intense X-ray microbeam sources, efficient X-ray area detectors, and new technical approaches now makes it possible to measure these materials with samples ~5–7 orders of magnitude smaller than those for standard measurements. The small sample sizes will make it feasible to safely study damage mechanisms in irradiated materials at vastly lower activity levels than previously possible and to study defect structures in energetic materials samples with sizes below the shock-wave detonation limit.

Mission Relevance

This work will impact programs within the Department of Energy (DOE) and Department of Defense (DoD) that focus on materials development as applied to energetic materials and fusion and fission energy production. Existing computational efforts in both fields will particularly benefit from characterization using this tool because the measurements can be directly compared to important parameters relevant to the properties of energetic materials and neutron-irradiated materials. We expect X-ray microprobe methods will become an indispensable tool in the development of complex materials important to national security and next-generation nuclear energy. The techniques also have wide applications to combinatorial studies of materials to understand processing and/or compositional impacts on defects.

Results and Accomplishments

In FY 2006, the first year of this project, preparations were made for the first measurements. Since sample cooling is critical for measurements of defects in radioactive alloys, we designed a refrigeration system, acquired a Joule-Thompson cooler, and built a sample holder compatible with both this cooler and the Advanced Photon Source (APS) X-ray microbeam diffraction equipment. We also developed a plan in coordination with the University of Michigan Ion Beam Laboratory to use this cooling system to irradiate, transfer, and analyze samples while they are continuously cooled. This system will be of general use; it can be used to cool any type of sample for microdiffraction analysis. We also determined that data collection techniques for energetic materials can most readily be developed by using a surrogate (nonexplosive) material that is structurally similar and develops the same kind of defects. Conventional diffraction from this material, a mixture of barium fluoride and pentaerythritol, showed diffraction features similar to those of truly energetic materials. In addition, we made measurements to estimate the minimum grain size required to study diffuse scattering. These measurements studied the weak tails of the focused beam to understand the beam intensity distribution around the peak.

S06-061: Novel, Low-Cost, High-Mn-Containing Austenitic Stainless Steels and Alloys for High-Temperature Structural Applications

Philip J. Maziasz, Yukinori Yamamoto, Michael L. Santella, and Michael P. Brady

Project Description

The purpose of this project is to design and evaluate new alloy compositions of high-Mn and Al-modified austenitic stainless steels, which have both good creep resistance and good oxidation/corrosion resistance at high-temperatures. High-temperature strength and creep-resistance is based on the unique design of a stable Fe-Cr-Mn-Ni matrix, using state-of-the-art computational thermodynamics tools to determine phase stability over a range of complex alloy compositions. Alloy design results will be validated by casting trial heats of the chosen alloy compositions. The next step will be to add high-temperature strength to stable parent-phase alloys that exhibit good oxidation resistance by introducing either stable dispersions of Fe_2Nb or Mn_2Nb (or both) intermetallic Laves phases, or nano-NbC carbides, or mixtures of both intermetallics and nano-carbides. Creep testing will be used to further screen these alloys for high-temperature strength and for oxidation resistance. High-temperature oxidation and corrosion (water-vapor, sulfidation, carburization) resistance is based on additions of enough aluminum to form adherent, protective, and stable Al_2O_3 surface oxide scales. The development of stable, fully austenitic stainless steel alloys that form stable nano-precipitate dispersions and protective alumina scales, and which still have the superior formability/manufacturability and weldability of commercial Fe-Cr-Ni austenitic stainless steels, is the ultimate goal of this project.

Mission Relevance

Successful results from this project are directly related to fossil energy and other energy production programs, which are trying to achieve the difficult goals of higher-efficiency and cleaner energy production. This project will provide unique very high performance, low-cost Fe-

Cr-Mn-Al-Ni austenitic stainless steel that easily substitutes for conventional Fe-Cr-Ni austenitic stainless steels, which do not have enough performance and are becoming more costly (Ni-prices). Good high-temperature creep strength and oxidation resistance based on alumina scales may also replace Ni-based superalloys, which perform well but cost too much. These materials should also be directly applicable to efforts to extract oil from oil-shale and tar-sands, which require the most cost-effective, high-performance, heat-resistant, and corrosion-resistant stainless steel. These new stainless steels are directly or indirectly relevant to all other DOE projects needing high-temperature alloys (Gen IV Nuclear, Transportation) and may be attractive to Basic Energy Science if they demonstrate new, practical nanotechnology with good commercialization potential. These new low-cost, high-performance high-temperature austenitic stainless steels may well have applicability to defense programs (Department of Defense, Defense Advanced Research Projects Agency), distributed energy for military applications (microturbines, fuel cells), and national security or transportation applications requiring more heat-resistant and failure-resistance containers for transporting hazardous or dangerous materials (chemicals, nuclear waste, liquid natural gas, etc).

Results and Accomplishments

We began this project with computational thermodynamic calculations to identify the regions of the alloy-phase diagram that were 100% austenite [desired parent phase with face-center-cubic (fcc) crystal structure], with no delta-ferrite or other undesirable phases. We identified a wide area of Fe-Cr-Ni-Mn-Al compositions, selected several alloy compositions that varied only Cr, Mn and Ni, cast and processed small heats into wrought plate, and tested for microstructure, hardness, and oxidation behavior during an aging/screening test of 168 h at 800°C. Most of the alloys were 100% austenite parent phase, with no ferromagnetic behavior because they contained no delta-ferrite prior to aging. Several of the higher Cr-Mn alloys showed an increase in hardness after aging, due to precipitation of carbides and other phases during aging, but only two of those showed good oxidation resistance, and only one showed the desired protective alumina-scale formation for oxidation resistance. This project successfully identified several good base-alloy compositions that will be further alloyed and tested for high-temperature strength and creep resistance in FY 2007.

S06-063: Laser-Interference Direct Structuring of Zirconia for Dental Materials

Claus Daniel, Narendra B. Dahotre, Beth L. Armstrong, Peter J. Blau, and Jun Qu

Project Description

Adhesion of dental composite materials to the tooth surface (i.e., dentin and enamel) is a major concern in terms of dental component lifetime. Traditional fillings fail after 6 to 10 years due to a gradual degradation in surface adhesion. To improve the lifetime of dental components, we envision a laser treatment that uses interferometry to produce periodic, microscopic surface structures that could be applied to either the tooth surface or the dental composite or both, depending on the type of filling. The novelty of using a laser to treat teeth is the possibility of both chemically and physically nanostructuring these surfaces. Our expectation is that nanostructuring can lead to improvement in dental composites and adhesion to the tooth.

Within this context, the specific aim of this project is to demonstrate our laser interference technique by engineering and restructuring zirconia surfaces on the micro- to nano-scale as an example for dental and other implant materials. In our technique, a primary laser beam is divided into two or more beams that are then guided by an optical system to interfere with each other at the sample surface. The standing optical wave describes a periodic intensity pattern. If our hypothesis is correct, the patterned microstructures should show improved mechanical, tribological, and biointerface properties.

Mission Relevance

The U.S. population needs implant materials with longer lifetimes than materials in current use (6–10 years for dental fillings and about 15 years for orthodontic implants). Optimizing the biointerface represents the most important factor to achieving this goal. As such, this project will benefit the National Institute of Dental and Craniofacial Research (NIDCR) within the National Institutes of Health (NIH). Furthermore, the understanding of the phase changes, mechanical changes, and heat transportation will benefit the DOE Office of Science, Basic Energy Sciences Program (BES). Once the possibilities and limitations are understood, this technique can provide unique periodic microstructures and diffusion profiles that are not achievable using other techniques. Conceivably, the microstructured surfaces could also show improved tribological properties for automotive, space, and industrial applications. Therefore, this project may also benefit the DOE Office of Energy Efficiency and Renewable Energy.

Results and Accomplishments

During FY 2006, we made significant progress in four areas.

1. Yttria-stabilized zirconia pellets were prepared using both tape casting/lamination and pressing techniques.
2. With the use of a high-power Q-switched Nd:YAG laser with non-linear optics, we could determine the appropriate wavelength for optimized absorption and thermalization of the light switching between four harmonics from near infrared over visible down to ultraviolet. The most promising results so far were obtained at 355 nm. Absorption measurements to attain a better understanding are ongoing.
3. The near-surface microstructure could be significantly changed without any measurable ablation of the material. The initial grain size of about 1 to 2 µm could be scaled down to 10 to 20 nm within a surface layer of about 0.5 µm. Crystallographic texture and phases are changed and will be further analyzed.
4. The interference setup could be successfully installed and periodic micro-structural changes with micrometer spacing could be achieved on spot sizes with a diameter of 5.9 mm.

The successful sample preparation and these initial laser treatments show the possibility of changing the material on the micro- to nano-scale with macroscopic significance. The defect density and microstructure could be changed on the microscale, which will lead to a macroscopic property change in terms of mechanical and tribological properties and biointerface behavior. The structured zirconia will be tested in tribological and cell differentiation tests.

Nuclear Science and Technology Division

S05-001: Detecting Concealed Nuclear Materials with Photofission

Sara Pozzi, John Mihalczo, and Enrico Padovani

Project Description

The detection of shielded highly enriched uranium (HEU) is one of the most urgent concerns that nuclear nonproliferation and homeland security offices are facing. To address this need, recent efforts have been aimed at developing new measurement techniques for the rapid identification of fissile materials that could be concealed in shielded containers. A number of techniques that are currently being proposed rely on the use of photon sources to induce fission in the nuclear material, and on the detection of the subsequent gamma rays and neutrons from fission. The design and analysis of such measurements are based, in turn, on the use of Monte Carlo codes to simulate the interaction of neutrons and photons with the nuclear material, the shielding, and the radiation detectors. However, currently available Monte Carlo codes lack the ability to simulate the emission of correlated particles from photofission. The product of this research project provided a tool to address and solve this deficiency. The proposed methodology was based on the use of two existing and well-benchmarked codes, MCNP-X and MCNP-PoliMi, which were appropriately modified to allow the user to simulate active measurements based on the use of a photon source.

Mission Relevance

The work of this project is relevant to the goals of the Domestic Nuclear Detection Office (DNDO) of the Department of Homeland Security. As a result of this project, we are continuing this work through funding within a DNDO project led by Idaho National Laboratory (INL) to perform simulations and measurement analysis with the Monte Carlo tools developed within this LDRD project. This work is also relevant to the scope and goals of the NA-22 agency in the Department of Energy's National Nuclear Security Administration (NNSA), in particular to the subprogram "Modeling and Algorithms," which is aimed at developing new models and algorithms for the identification and characterization of fissile material.

Results and Accomplishments

In the course of this project, ORNL and Polytechnic of Milan, Italy, developed Monte Carlo tools that have unique capabilities in the fields of photonuclear interrogation of nuclear (and non-nuclear) materials. These tools are unique because they are able to (1) correctly simulate the neutron and photon field generated by photon interrogation of bulk materials, (2) track the neutrons and photons within the fissile and cargo materials, and (3) simulate the response of organic scintillators to neutrons and gamma rays emitted by the assembly, which typically consists of fissile and moderating/attenuating materials. The Monte Carlo codes that were developed as a result of this project have been validated recently by DNDO. In this framework, the simulation results were compared with experimental data and good agreement was found. The Monte Carlo codes have been requested by several other institutions, including research institutions in Russia. Future work includes modifications to the latest version of MCNP-X, and release of the code through ORNL's Radiation Safety Information Computational Center.

Publications

Pozzi, S. A., et al. "Monte Carlo Modeling of Photon Interrogation Methods for Characterization of Special Nuclear Material." PHYSOR, September 10–14, 2006, Vancouver, Canada.

Pozzi, S. A., et al. "Monte Carlo Modeling of Delayed Neutrons from Photofission." *Nucl. Sci. Eng.* Submitted.

Pozzi, S. A., et al. "Nuclear Materials Identification by Photon Interrogation." *Mathematics & Computations*, September 12–15, 2005, Avignon, France.

S06-039: A Novel Radio-Luminescent Glass Designed for Safe User Applications

C. W. Alexander, R. W. Smithwick, L. A. Lewis, and L. A. Boatner

Project Description

The goal is to develop a new approach for producing radio-luminescent materials in which the radioactive activator is physically incorporated in the bulk of a glass phosphor. The incorporation of the activator will be achieved by in situ irradiation of ^{6}Li (lithium) to produce a ^{3}H ion (tritium) upon exposure to a high neutron flux. Incorporation of the tritium will facilitate a 360-degree luminescence activation region within the glass phosphor. Such a configuration is expected to greatly increase the luminescent output and create a radiologically safe material that may be applied to both bulk and nano-sized materials. The final product will be (1) self-powered by the incorporated tritium, (2) highly luminescent, (3) unique in its emission wavelength, (4) durable, (5) environmentally rugged and safe to personnel and equipment, and (6) amenable to fabrication in a variety of shapes and sizes. The concept is applicable to both silicate and phosphate-based glasses.

Mission Relevance

The new materials developed in this effort will provide a unique approach to evaluating potential applications in support of radiologically safe products, such as radio-luminescent (i.e., self-powered) lightweight marking and signaling media, egress-marking additives, paint, and other applications. Interest in such radio-luminescent materials is extremely high within the Department of Defense, Department of Justice, the Department of Homeland Security, and other agencies for the purpose of monitoring individuals, high-value assets, radioactive material, and military personnel.

Results and Accomplishments

A series of lithium silicate glasses doped with Nd (neodymium) was prepared with varying neodymium activator concentrations that covered a compositional range extending from a fraction of a percent of Nd to several percent. These samples were subsequently characterized in a series of optical experiments with the goal of identifying the Nd concentration that yielded the optimum luminescence output. Optical absorption and other optical measurements were performed in the wavelength region extending from 180 to 3000 nm, and the Nd^{3+} f-f transitions from the $^4I_{9/2}$ level to the Nd excited states were identified. The spectral data were used to plot the absorption coefficient (in cm^{-1}) as a function of the Nd concentration present in the glass melt. Direct observations of the IR luminescence output were also made for the series of samples using an image intensifier equipped with a narrow-pass IR filter. These observations clearly identified those glass samples that contained a narrow range of Nd concentrations that yielded the most intense IR output when excited by broad wavelength visible light. These observations have restricted the Nd concentration to a range that will now be examined in detail using an integrating sphere system in order to obtain quantitative light yield results and, thereby, further refine the value for the Nd concentration that results in the optimum performance in terms of light output of the doped lithium silicate glass. Several hundred grams of lithium carbonate containing isotopically enriched ^6Li (~95% ^6Li) were obtained, and this material is currently being chemically purified by Nucsafe, Inc., using ion-exchange methods. Upon receipt of the purified ^6Li, lithium silicate glass specimens will be cast that incorporate the optimum Nd activator concentration determined as outlined above. These specimens will then be employed in the second phase of the investigations designed to yield a new type of radio-luminescent glass.

S06-045: Exploring Layered Materials with Neutron and Photon Spectroscopy to Determine the Depth and Water Content in Subsurface Layers of Planets

Hatice Akkurt, James Paul Holloway, and Sara Pozzi

Project Description

The objective of this project is to investigate the feasibility of using neutron detection and photon spectroscopy methods to determine the composition and thickness of layered materials. Since the heterogeneous layering problem is very difficult to solve in a general sense, initially, the specific focus of this project will be to develop a method for identifying regions with water and determining the depth and concentration of it in subsurface layers. The primary application of the method will be water detection, and hence life detection, in lunar and planetary exploration. The project will be conducted in two phases. First, an algorithm will be developed to determine only the depth and water content in subsurface layers. For this task, many simplifying assumptions will be made to reduce the number of unknowns. Then, this algorithm will be improved to solve the more complicated problem of determining the composition of the top layer in addition to the water content and depth of the bottom layer. Hence one of the severe limiting assumptions will be eliminated. For this project, we will carry out a significant number of Monte Carlo simulations for forward calculations and develop an algorithm to invert the problem to determine the unknowns. If our efforts are successful, a reliable, robust, practical algorithm will be developed and several proof-of-principle measurements will be performed to validate the method.

Mission Relevance

The immediate application of this project is lunar and planetary characterization; hence, the main agency that will benefit from this project is the National Aeronautics and Space Administration (NASA). The detection and characterization of water-rich regions on planets has been of great interest to NASA. Because of the President's exploration initiative that will return astronauts to the Moon, it is recently of great interest for NASA to determine the presence of water/ice in the permanently shadowed regions near the poles. This has important implications for support of extended human presence on the Moon and Mars. For this project, it is assumed that the unknown material is water; however, the approach can be extended or implemented to find any other materials of interest. After a proof-of-principle approach is developed and validated with measurements, follow-on proposals will be prepared to eliminate the limiting assumption and generalize the approach. The ultimate goal is to perform environmental surveying, either remotely or in the field on Earth, its moon, and on other planets. This will be particularly useful for environmental monitoring—looking for subsurface contaminant layers or looking for subsurface minerals. Therefore, if our efforts are successful, we expect that other organizations will be interested in this technology, including the Department of Homeland Security (DHS) and industry.

Results and Accomplishments

For this initial year, our efforts focused primarily on the first phase of the project—the development of an algorithm to determine the depth of water depth and its concentration. For this purpose, a significant number of Monte Carlo computations, using the MCNP code, were performed for varying water depth and fractions to determine the response and sensitivity. The photopeak areas for a wide range of selected gamma lines were computed. Furthermore, the neutron detector response was computed to investigate whether the additional information from these detectors will provide any useful information. From these forward calculations, ways of inverting the problem for the development of an algorithm that could solve for depth and water fraction have been investigated. Although the solution can be found using this preliminary algorithm, two main issues need to be addressed next year: (1) the uniqueness of the solution and (2) the practicality of the algorithm, due to the number of transport computations required in each step. Next year, this approach will be further investigated and revised to overcome these issues. Further, sensitivity to density has also been investigated. It has been found that neutron detector response can be useful to update density information at each iteration. Moreover, it is expected that the computations and findings in this phase of the project will help with the next phase as well.

S06-052: Carbonate Thermochemical Cycle for the Production of Hydrogen

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Project Description

This project explores the feasibility of a novel thermochemical cycle that uses the formation of stable uranium compounds to produce bulk quantities of hydrogen. Uranium is one of only a few metals that are capable of more than one valence state under easily attainable conditions. Changes in the uranium oxidation state can drive the decomposition of water into hydrogen and oxygen. Sodium carbonate is added to facilitate and control the transitions in uranium oxidation states. This thermochemical cycle has several advantages over competing processes because the chemical mechanisms proposed have (1) no more than two hydrogen-producing steps to minimize equipment requirements, (2) no inventory of volatile hazardous chemicals, and (3) operating temperatures that are compatible with common materials of construction. This proposed work will (a) corroborate the postulated mechanisms, (b) analyze the process efficiency, and (c) establish the technical and environmental viability of the process.

Mission Relevance

This project will directly support the Presidential Initiative on hydrogen economy. Replacing fossil fuels will require massive quantities of hydrogen to supply fuel for cars and other industrial purposes. The United States Department of Energy (DOE) Hydrogen Program will benefit the most from the success of this project. It is generally accepted that thermochemical cycles are the most efficient methods to produce hydrogen at large scale. Because this uranium carbonate cycle releases no carbon dioxide (CO_2), this thermochemical process can use heat provided by nuclear reactors, making it an environmentally acceptable bulk-hydrogen source. Therefore, DOE's Nuclear Research Programs will also benefit from the development of this process. The Department of Defense also benefits from the success of this project because of its critical need for hydrogen to feed fuel cells and serve as an alternative fuel for battlefield vehicles.

Results and Accomplishments

Several experiments were performed during FY 2006 that demonstrated the production of hydrogen using uranium oxides as the starting material. In addition, thermodynamic calculations were made based on possible reaction equations for various uranium oxides to assess which oxides can produce the most hydrogen.

Our experimental plan consists of the following three approaches for the production of hydrogen:

1. Use of U_3O_8 as one of the starting materials. We originally postulated that starting with U_3O_8 would result in a cyclic two-step thermochemical process. Hydrogen production was observed in consecutive reaction sets using the same material.
2. Use of UO_2 as one of the starting materials. Hydrogen production was observed in consecutive reaction sets using the same material. The production of hydrogen was greater with this material than with U_3O_8.

3. Use of an aqueous-phase process to ensure the production of uranyl tricarbonate, a compound that is difficult to produce by dry reactions. This aqueous-phase production of uranyl tricarbonate is a highly pH-dependent reaction. Uranyl tricarbonate could assist with the liberation of oxygen during the back reaction and complete the cycle.

Results from these experimental activities suggest that the approach we need to pursue is to first produce hydrogen by converting UO_2 into UO_3, then transform the UO_3 into uranyl tricarbonate, and finally convert the tricarbonate into UO_2 to complete the cycle. We will concentrate on determining the viability of these steps for the remainder of this project.

S04-038: Coupled-Cluster Theory with Effective Three-Body Forces

T. Papenbrock, D. J. Dean, G. Hagen, D. Bernholdt, and R. J. Harrison

Project Description

Three-nucleon forces are a fact of life for nuclei. Such forces also emerge in quantum chemistry and solid-state physics due to renormalization group procedures. They are an important ingredient in ab initio nuclear structure calculations, and their role has only been understood in light nuclei. Coupled-cluster theory is capable of an ab initio description of medium-mass nuclei. This makes it necessary to implement three-body forces within this approach. It is the aim of this project to derive the underlying equations, to implement the numerical solution of these equations through a Fortran-90 program, and to perform proof-of-principle calculations in light nuclei.

Mission Relevance

The investigation of the three-nucleon force is an important part of contemporary microscopic nuclear structure physics. Its understanding could lead to a better and more precise description of nuclear structure and nuclear reactions, with potential applications in nuclear energy and national security. As a result of this project, our work in coupled-cluster theory will continue as part of a much larger effort of microscopic modeling in nuclear theory through a grant from the SciDAC-2 (Scientific Discovery through Advanced Computing) UNEDF (Universal Nuclear Energy Density Functional) program. This grant is sponsored by DOE's Office for Nuclear Physics, Office for Advanced Scientific Computing Research, and by the National Nuclear Security Agency.

Results and Accomplishments

There are several accomplishments. First, we have derived the coupled-cluster equations in the presence of three-body forces. These equations are employed in nuclear structure calculations but might also be useful in quantum chemistry or solid-state physics once degrees of freedom are integrated out or "downfolded." Second, we wrote a Fortran-90 program that numerically solves these equations. Third, we performed proof-of-principle calculations for helium isotopes. Our results show that the main contribution of the three-nucleon force stems from its expectation value in the employed Slater determinant. This is an important result as it facilitates the involved computations, and it might result in a considerable reduction in the number of three-nucleon matrix elements. This paves the way for explorations into heavier nuclei and for applications in weakly bound nuclei.

S05-013: Excited-State Quantum-Classical Molecular Dynamics

Predrag S. Krstic, Robert J. Harrison, and Bobby Sumpter

Project Description

Computer simulations of the dynamics of molecular systems often encounter serious limitations, both phenomenological and quantitative in nature, due to the inability to treat transition dynamics and evolution beyond the ground Born-Oppenheimer electronic surface. Since these problems are present whether one considers a reactive or above-thermal collision, a photon-induced process in a molecule or a nano-device, or charge transfer in an active site of a protein, there is a tremendous interest in chemistry, nano-science, molecular photonics, molecular biology, and various applications of particle-cluster interactions (fusion energy research, semiconductor industry), for better understanding and characterization of molecular dynamics with excited electronic states. Leadership-scale computational power, nonadiabatic collision physics, and computational chemistry expertise at ORNL can enable a robust response to this challenge. These key issues for many applications of the molecular dynamics are currently poorly understood, and existing methods and codes are limited to particular applications and are not general purpose. To address these deficiencies, we proposed the development of a theoretical, algorithmic, and computational framework describing the corresponding excited-state, many-body dynamics by applying multiphysics described by the quantum-classical Liouville equation and multiresolution techniques for solving the quantum part of the problem. The aim of this project was to prototype these ideas in a suite of computer codes for excited-state, quantum-classical molecular dynamics.

Mission Relevance

This research strengthened ORNL's scientific computing by providing unique capabilities for simulating the most difficult and challenging problems of nano-, chemistry-, and energy-related sciences. The proposed research provides a foundation for further development of excited-state molecular dynamics, consistently described by the quantum-classical Liouville approach and the Multi-Configuration Time-Dependent Hartree-Fock (MCTDHF) method, with potential for opening a new long-term program at ORNL that would enhance the theoretical studies of dynamically perturbed large systems to a significantly higher quality. This work is directly relevant to the DOE Basic Energy Science, Chemical Sciences program and to the missions of the Defense Advanced Research Projects Agency (DARPA), the Air Force Office of Security Forces (AFOSF), the Office of Naval Research (ONR), nano-sensors, high strength–weight smart materials, reactive chemical dynamics; the National Institutes of Health (NIH), scientific computation for the advancement of the biomedical field; the National Aeronautical and Space Administration (NASA), astrophysical atomic physics; and the DOE Office of Fusion Energy Sciences (OFES), complex atomic interactions at the edge plasma.

Results and Accomplishments

We made substantial progress in several areas central to developing a unique ability for the quantitative simulation of few electron systems. The central technical challenge was time evolution of a wave function in multiresolution form, and we explored several standard propagators, including Arnoldi, Lanczos, and other forms, with the most successful being a third-order Runge-Kutta, total variation diminishing. However, this is an explicit method with all of the limitations thereof, and hence we developed a novel separated representation for efficient inversion of the Crank-Nicholson and corresponding higher-order Pade approximants. These methods were implemented in a prototype version of MADNESS and applied to evolution of several 1- and 2-electron systems in Hatree-Fock (HF) and multi-configuration HF wave functions. We are preparing two new publications resulting from this research.

S05-030: Development of Readout Electronics for the ALICE Electromagnetic Calorimeter

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M. Bobrek, C. L. Britton, W. L. Bryan, K. N. Castleberry, and M. S. Emery

Project Description

The study of nuclear matter under extreme conditions of temperature and density via high-energy heavy-ion collisions has made remarkable progress over the last 20 years at accelerators in the United States and abroad. The physics goals focus on determining the properties of the quark-gluon medium that is created in these collisions and on learning more about the fundamental building blocks of matter in our universe and how they interact, as described by the theory of Quantum Chromodynamics (QCD). Within this context, the goal of this project was to develop a system design for readout of the proposed Electro-Magnetic Calorimeter (EMCal) in the ALICE ("A Large Ion Collider Experiment") experiment at the Large Hadron Collider (LHC). The proposed ALICE EMCal detector will measure the energy of individual particles produced in nucleus-nucleus collisions, such as Pb+Pb at the LHC. The EMCal is designed to have a sufficient resolution for jet reconstruction even in the high-multiplicity environment (several tens of thousands of elementary particles) of a head-on nucleus-nucleus collision. Jet reconstruction is a necessary requirement to characterize the produced state of matter, consisting of quarks and gluons, in these collisions. In this project, we addressed issues of signal shaping, noise, and data acquisition interfacing requirements and performed a beam test with the first EMCal prototype modules at Fermilab (FNAL) in November 2005.

Mission Relevance

This work is relevant to the mission of DOE's Office of Nuclear Physics (ONP), which seeks to understand the fundamental forces and particles of nature as manifested in nuclear matter. Investigating the properties of hot nuclear matter is one of the five main scientific questions in the most recent Nuclear Science Advisory Committee (NSAC) Long Range Plan (2002). The NSAC subcommittee on Heavy-Ion Nuclear Physics further recommended in 2004 that participation at the LHC should become a new component of the U.S. Heavy-Ion Program. Thirdly, ONP approved a LHC detector upgrade for heavy-ion physics as a Major Items of Equipment project (CD0), for which this project is directly relevant. In fact, the CD0 approval came shortly after our beam test at FNAL, and the positive results directly informed this decision.

Results and Accomplishments

With help from the LHC and ALICE host laboratory in Geneva, Switzerland (CERN), we first assembled a test setup with a working data acquisition and readout system here in the United States. This involved locating and adapting many different pieces of both custom hardware and software. We also made a preliminary study of the EMCal electronics design to determine which modifications of the PHOS electronics were needed. We then arranged and lead a first beam test with EMCal prototype modules at FNAL in November 2005. We were able to show first preliminary results from the beam tests, regarding noise, resolution, and efficiency, more or less on-line at FNAL, and presented them at a DOE review shortly afterwards. Since then, a collaboration of U.S. institutions interested in the physics of the ALICE EMCal has been formed, presented a technical proposal to CERN, and gone through a DOE CD-1 review.
The ORNL HERANs group for has been given primary responsibility for the readout of the ALICE EMCal, with Terry Awes of ORNL serving as electronics subsystem supervisor and David Silvermyr as responsible for online computing. ORNL is currently one of only five DOE-supported U.S. institutions approved by the DOE and the ALICE collaboration to join the ALICE project.

S05-057: Development of a Revolutionary Solar Neutrino Detector

Jeff Blackmon, Yuri Efremenko, Alfredo Galindo-Uribarri, Charlie Rasco, and Qinglin Zeng

Project Description

The study of neutrinos emitted from the sun has provided crucial insights into the properties of the sun and of neutrinos themselves. However, neutrinos that result from hydrogen fusion in the sun's core and provide the only accurate probe of current energy production have remained largely beyond detection. To address this deficiency, we have developed revolutionary new detector concepts that capitalize on breakthroughs in organic scintillator technology to enable precision measurements of the energy spectrum of neutrinos emitted from hydrogen fusion in the sun's core. We investigated novel segmentation and triggering techniques to improve efficiency and sensitivity over previously proposed instruments, performed realistic simulations to characterize the response of the detectors to neutrino-induced reactions and major background sources, developed and tested algorithms for distinguishing neutrino signals from background, and quantified and compared the performance of our designs. By establishing the capabilities of these novel detector concepts through extensive simulation, we have laid the groundwork for construction and testing of a ton-scale prototype detector and eventual deployment of a full-scale (greater than 100 tons) instrument in a deep underground laboratory.

Mission Relevance

This work will allow the current rate of energy production by nuclear fusion in the sun's core to be accurately determined for the first time and will enable a better understanding of the properties of the neutrino, directly addressing part of the mission of DOE's Division of Nuclear Physics (NP) under the Office of Science. "Determining the fundamental properties of neutrinos and fundamental symmetries by using neutrinos from the sun and nuclear reactors" is a stated specific long-term goal of the NP Division. A recent study sponsored by four divisions of the American Physical Society recommended “development of a spectroscopic solar neutrino experiment capable of measuring the energy spectrum of neutrinos from the primary pp fusion process in the sun” as one of the three highest priorities in neutrino science. This work also directly impacts the National Science Foundation’s Directorate of Mathematical and Physical Sciences, which aims to develop a deep underground science and engineering laboratory, a top recommendation of the Nuclear Science Advisory Committee’s 2002 Long Range Plan for Nuclear Science. This project will position ORNL to take a leadership role in developing, deploying, and operating a solar neutrino detector aimed at these important scientific objectives.

Results and Accomplishments

Realistic Monte-Carlo models were developed using the GEANT4 toolkit for three different solar neutrino detector architectures. Detector response was simulated for neutrino and background events. Algorithms were developed to discriminate the detector response induced by neutrino events from the response due to background sources. We found the primary factor affecting efficiency and background suppression to be the degree of segmentation. The most important source of background was shown to be 2 random beta decays in time coincidence; however, reconstruction algorithms were developed that suppressed this background to a fraction of the neutrino event rate. We included realistic optics and studied the effect of optical imperfections on the detector response in a parameterized way. Small degrees of optical imperfections (up to 10%) were found to diffuse the collected light over a much broader number of channels but to affect total light collection only modestly. We established that the discrimination of neutrino events from background events is not significantly affected by optical imperfections. Our results demonstrate that achieving single-photoelectron sensitivity will enable a simpler and more robust detector design though complicating the triggering scheme. However, we also demonstrated that energy resolution plays an important role but is sensitive to the particular assumptions of the model and is more uncertain. A better understanding of energy resolution and design of the front-end trigger are topics requiring further R&D.

S06-020: Big Bang Cosmology and Online Simulation Suite

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Project Description

One of the fastest growing and most widely popularized (e.g., the Nobel Prize in 2006) research field in physics is cosmology—the study of the birth, structure, evolution, and fate of our universe. One powerful approach in cosmology is to calculate the amount of light elements (e.g., hydrogen, helium, lithium) synthesized in the early universe and, through comparison with observations, put limits on such crucial parameters as the total amount of “normal” matter in the universe. However, while there are thousands of cosmologists who need this information, only a few have the specialized codes to follow this approach. We have created a working prototype of the world’s first suite of online interactive computer codes that enables researchers around the world to run these important calculations. Our codes enable users to customize the calculations and share their results with colleagues. We will also improve the input to existing Big Bang codes by assessing the latest information on thermonuclear reactions that form light elements in the Big Bang and run our suite of codes to put new constraints on the matter density of the universe.

Mission Relevance

Our overall goal is to launch a program in cosmology research at ORNL. This program would involve numerous aspects including improving the nuclear physics input to Big Bang calculations, enabling calculations of non-standard Big Bang models, investigating the role of exotic particles in the early universe, and maintenance and future development of our software suite. In the DOE Office of Science, the Office of High Energy Physics supports research into the origin, properties, and interactions of elementary particles and other basic constituents of matter, while the Office of Nuclear Physics supports research into the nature of matter and energy including astrophysics and the early universe. Both offices have expressed interest in our research program. National Aeronautics and Space Administration (NASA) sponsors research into cosmology and the early universe, and their Applied Information Systems Research Program sponsors the development of software systems that support NASA science goals. Finally, the National Science Foundation (NSF) Division of Astronomical Sciences also sponsors research in cosmology and the early universe through their Astronomy and Astrophysics Research grants. Both NASA and NSF have stated that our research is appropriate for funding through their programs.

Results and Accomplishments

In FY 2006, we developed the first version of our “bigbangonline” software suite. Users of this system, now freely available at bigbangonline.org, can specify the latest set of input nuclear physics and cosmological parameters to set up their custom early universe simulation, and the latest primordial abundance observations to determine the constraints on cosmology parameters. The suite features excellent visualization tools to completely customize publication quality plots and enables sharing of simulation results between users. The online codes are currently being debugged and the features extended and improved with the advice of collaborators. We are striving to complete a well-featured suite as soon as possible so that the reviewers of our follow-on proposals can try it out for themselves during the review process. Additionally, we have done an extensive literature search on the input nuclear physics information to the code in preparation for future assessments and have also assembled the bigbangonline.org web site to serve as a gateway to the codes and a repository of information on Big Bang and early universe studies.

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