Energy Frontier Research Centers

Technical Summaries

August 2016; Revised 1/31/2017
science.energy.gov/bes/efrc

U.S. DEPARTMENT OF ENERGY | Office of Science

INTRODUCTION

Since its inception in 2009, the U. S. Department of Energy's Energy Frontier Research Center (EFRC) program has become an important research modality in the Department's portfolio, enabling high impact research that addresses key scientific challenges for energy technologies. Funded by the Office of Science's Basic Energy Sciences program, the EFRCs are located across the United States and are led by universities, national laboratories, and private research institutions. These multi-investigator, multi-disciplinary centers bring together world-class teams of researchers, often from multiple institutions, to tackle the toughest scientific challenges preventing advances in energy technologies. The EFRCs' fundamental scientific advances are having a significant impact that is being translated to industry.

In 2009 five-year awards were made to 46 EFRCs, including 16 that were fully funded by the American Recovery and Reinvestment Act (ARRA). An open recompetition of the program in 2014 resulted in four-year awards to 32 centers, 22 of which are renewals of existing EFRCs and 10 of which are new EFRCs. In 2016, DOE added four new centers to accelerate the scientific breakthroughs needed to support the Department's environmental management and nuclear cleanup mission, bringing the total number of active EFRCs to 36. The technical research summaries in this document describe the planned work of these 36 EFRCs and list all the partner institutions and associated senior investigators. The index at the end of the document includes keywords, grand challenges, and references to BES reports that the leadership of each EFRC has identified as relevant to their centers.

TABLE OF CONTENTS

Ordered first by Institution and then by Director

Center for Electrochemical Energy Science (CEES)
Paul Fenter, Argonne National Laboratory 1

NorthEast Center for Chemical Energy Storage (NECCES)
M. Stanley Whittingham, Binghamton University 3

Center for Emergent Superconductivity (CES)
Peter Johnson, Brookhaven National Laboratory 5

Light-Material Interactions in Energy Conversion (LMI)
Ralph Nuzzo, California Institute of Technology 7

Energy Frontier Research in Extreme Environments (Efree)
Russell Hemley, Carnegie Institution of Washington 9

Center for Actinide Science & Technology (CAST)
Thomas Albrecht-Schmitt, Florida State University 11

Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy (UNCAGE-ME)
Krista Walton, Georgia Institute of Technology 13

Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC)
Cynthia Friend, Harvard University 15

Center for Nanoscale Controls on Geologic CO2 (NCGC)
Donald DePaolo, Lawrence Berkeley National Laboratory 17

Center for Advanced Solar Photophysics (CASP)
Victor Klimov, Los Alamos National Laboratory 19

Center for Excitonics (CE)
Marc Baldo, Massachusetts Institute of Technology 21

Solid-State Solar-Thermal Energy Conversion Center (S3TEC)
Gang Chen, Massachusetts Institute of Technology 23

Center for Biological Electron Transfer and Catalysis (BETCy)
John Peters, Montana State University 25

Center for Next Generation of Materials by Design: Incorporating Metastability (CNGMD)
William Tumas, National Renewable Energy Laboratory 27

Center for Bio-Inspired Energy Science (CBES)
Samuel Stupp, Northwestern University 29

Argonne-Northwestern Solar Energy Research Center (ANSER)
Michael Wasielewski, Northwestern University 31

Fluid Interface Reactions, Structures and Transport Center (FIRST)
David Wesolowski, Oak Ridge National Laboratory 33

Energy Dissipation to Defect Evolution (EDDE)
Yanwen Zhang, Oak Ridge National Laboratory 35

Center for Performance and Design of Nuclear Waste Forms and Containers (WastePD)
Gerald Frankel, Ohio State University 37

Center for Molecular Electrocatalysis (CME)
R. Morris Bullock, Pacific Northwest National Laboratory 39

Interfacial Dynamics in Radioactive Environments and Materials (IDREAM)
Sue Clark, Pacific Northwest National Laboratory 41

Center for Lignocellulose Structure and Formation (CLSF)
Daniel Cosgrove, Pennsylvania State University 43

Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio)
Maureen McCann, Purdue University 45

Center for Mesoscale Transport Properties (m2M)
Esther Takeuchi, Stony Brook University 47

Center for the Computational Design of Functional Layered Materials (CCDM)
John Perdew, Temple University 49

Center for Gas Separations Relevant to Clean Energy Technologies (CGS)
Jeffrey Long, University of California, Berkeley 51

Spins and Heat in Nanoscale Electronic Systems (SHINES)
Jing Shi, University of California, Riverside 53

Catalysis Center for Energy Innovation (CCEI)
Dionisios Vlachos, University of Delaware 55

Center for Geologic Storage of CO2 (GSCO2)
Scott Frailey, University of Illinois at Urbana-Champaign 57

Nanostructures for Electrical Energy Storage (NEES)
Gary Rubloff, University of Maryland 59

Inorganometallic Catalyst Design Center (ICDC)
Laura Gagliardi, University of Minnesota 61

Center for Solar Fuels (UNC)
Thomas Meyer, University of North Carolina 63

Materials Science of Actinides (MSA)
Peter Burns, University of Notre Dame 65

Center for Hierarchical Waste Form Materials (CHWM)
Hans-Conrad zur Loye, University of South Carolina 67

Center for Frontiers of Subsurface Energy Security (CFSES)
Larry Lake, University of Texas at Austin 69

Photosynthetic Antenna Research Center (PARC)
Robert Blankenship, Washington University in St. Louis 71

GRAND CHALLENGES INDEX 73

BES REPORTS INDEX 74

TOPICAL INDEX 75

EXPERIMENTAL AND THEORETICAL METHODS INDEX 77

Center for Electrochemical Energy Science (CEES)
EFRC Director: Paul Fenter
Lead Institution: Argonne National Laboratory
Start Date: August 2009

Mission*: to develop a fundamental understanding and robust control of the reactivity of electrified oxide interfaces, films and materials relevant to lithium-ion batteries.*

Energy storage is a strategic technology that enables the large-scale use and distribution of electrical energy as well as mobile technologies such as electric vehicles and portable electronic devices. Lithium-ion batteries (LIBs) are attractive because they offer inherently high energy densities through the conversion of electrical and chemical energy through electrochemical reactions. However, LIBs place severe demands on the performance of the active materials. These reactions rely on the reversible lithium insertion in the battery electrodes and associated redox reactions. Challenges include the need to control deleterious side reactions such as electrolyte decomposition at the electrode-electrolyte interface (e.g., solid-electrolyte interphase "SEI" formation), dissolution of the active materials, and the need to restructure the electrode framework materials at high lithium capacities.

The *Center for Electrochemical Energy Science* (CEES) explores the electrochemical reactivity of oxide materials that represent the positive electrode (e.g., cathode) in many lithium ion battery (LIB) systems. To this end, CEES seeks to *observe* and *understand* the reactivity of electrified oxide interfaces, films and materials, and to *control* these complex lithiation processes through the use of novel structures, architectures and chemistries. Such an understanding will define new conceptual approaches to prevent side-reactions, minimize over-potentials, and enable substantial improvements in energy density of the battery. In this way, the research program is designed to explore the fundamental limits of LIB technologies and to enable disruptive advances in energy storage systems.

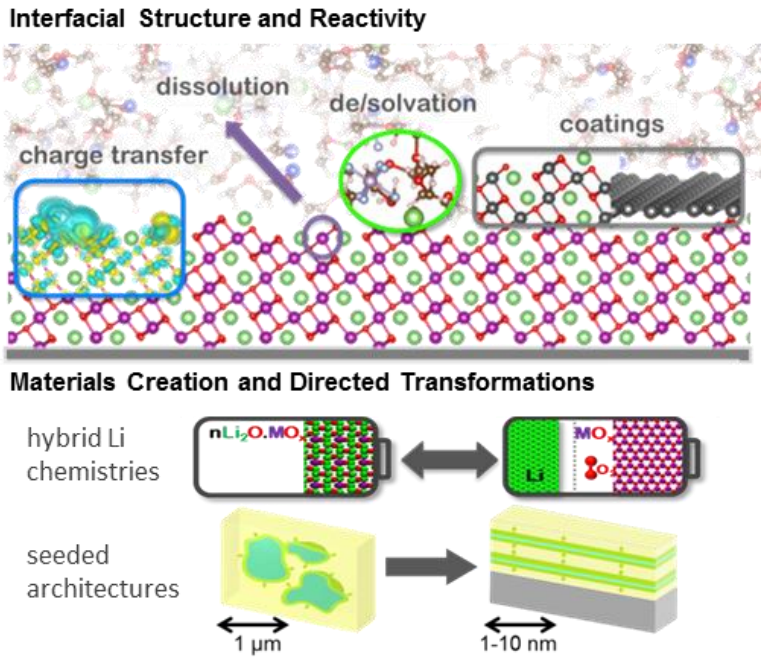


Figure: (Top) Schematic of interfacial structures and coatings to control secondary reactions at insertion electrodes interfaces. (Bottom) Directing chemical reactivity through the use of advanced architectures for conversion reactions and novel chemistries associated with hybrid Li^+/Li-O reactions.

To this end, CEES addresses two broad issues: (indicated schematically in the **Figure**).

- **Interfacial Structure and Reactivity**: *Can we control reactions at the oxide-electrolyte interface by leveraging a robust molecular-scale understanding of its structure and reactivity?* The transport of ions across the electrode/electrolyte interface leads to over-potentials, and side reactions (e.g., cathode dissolution at elevated potentials) associated with interface-specific reactions. These interfacial aspects of electrochemistry introduce substantial challenges, but

simultaneously offer many avenues for controlling and guiding reactivity through interfacial modification.

- **Directed Transformations:** *Can we discover new approaches that can be used to direct the character and nature of electrochemical reactions within electrode materials?* Here, we seek to influence the pathway of an electrochemically-driven reaction within an electrode. There are two focus areas of research. In one subtask, we seek to use dimensionality to control conversion chemistries in the lithation of nano-structured electrodes. In a second subtask, we seek to explore the use of dual functioning electrode/electrocatalyst materials to enable reversible lithium and oxygen extraction from a lithium-transition metal-oxide crystal structure while allowing partial redox of the transition-metal and oxygen ions.

These guiding questions will be addressed using the unique and proven multi-pronged approach that CEES has established and used since 2009. To this end, CEES will probe the intrinsic reactivity of well-defined model oxide systems, with molecular-scale sensitivity and resolution, to reveal the inherent complexity of electrochemical systems (including the relevant active materials, electrolyte, etc.). The use of precisely defined materials, structures and interfaces (for example, structurally and compositionally defined epitaxial thin films) will enable direct observations of the relevant reactions without the complications of inactive materials and complex electrode morphologies inherent to conventional systems. This understanding, leveraged with the development of novel materials, architectures and chemistries, will be used to observe and direct electrochemical reactivity in these systems. These approaches, enabled by our deep cross-cutting capabilities of materials synthesis, characterization, and theory will lead to new approaches to control electrochemical reactions under the extreme conditions found in lithium-ion battery systems.

Center for Electrochemical Energy Science (CEES)	
Argonne National Laboratory	Paul Fenter (Director), Michael Thackeray (Deputy Director), Khalil Amine, Maria Chan, Larry Curtiss, Jeffrey Elam, Timothy Fister, Christopher Johnson
Northwestern University	Mark Hersam (Institutional Lead) , Scott Barnett, Michael Bedzyk, Vinayak Dravid, Tobin Marks, Christopher Wolverton
University of Illinois at Urbana-Champaign	Andrew Gewirth (Institutional Lead) , Ralph Nuzzo, Nancy Sottos, Scott White
Purdue University	Jeffrey Greeley

Contact: Paul Fenter, Director, Fenter@anl.gov
(630)-252-7053, http://www.cees.anl.gov

Northeast Center for Chemical Energy Storage (NECCES)
EFRC Director: M. Stanley Whittingham
Lead Institution: Binghamton University
Start Date: August 2009

Mission Statement*: To develop an understanding of how key electrode reactions occur in cathode materials for Li based batteries, and how they can be controlled to improve electrochemical performance, from the atomistic level to the macroscopic level through the life-time of the operating battery.*

The design of the next generation of rechargeable batteries requires both the development of new chemistries and the fundamental understanding of the physical and chemical processes that occur in these complex systems. Although some significant advances have been made to prepare and utilize new materials, efforts towards the understanding of mechanisms have waned. This will eventually choke efforts to efficiently develop new materials if this issue is not addressed now. Batteries are inherently complex and dynamic systems, their electrochemistry, phase transformations, and transport processes often varying throughout their lifetime. Although often viewed as simple to use by the customer, their successful operation relies heavily on a series of complex mechanisms, involving thermodynamic instability in many parts of the charge-discharge cycle and the formation of metastable phases. The requirements for long-term stability are extremely stringent and necessitate control of the chemistry at a wide variety of temporal and structural length scales. This in turn necessitates the development and use of new characterization tools to monitor these processes. The overall goal is to understand the transformations (and their rates) that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery. The four-year scientific research goals are:

1. Attain reversible multi-electron transfer in a cathode material using lithium, using the model compound ε -$VOPO_4$.
2. Close the gap between the theoretical and practical energy density for intercalation compounds, using the model compound $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$.
3. Understand performance limiting transport in positive electrode structures from the local through the meso to the macroscale.

These research goals will be achieved by dividing our research effort into three closely connected and integrated thrusts; the theory effort is integrated into thrusts 1 and 2.

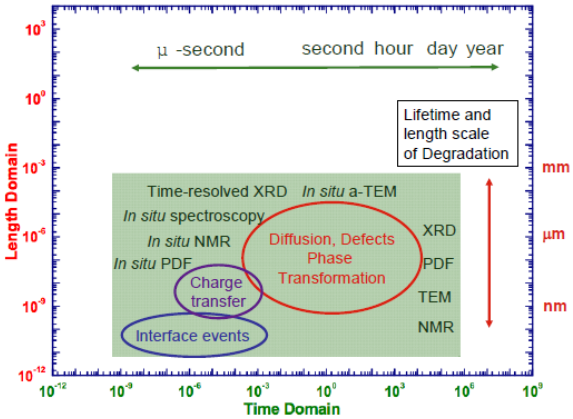
Thrust 1: Intercalation Materials Chemistry. This thrust will identify the key parameters that are required to optimize intercalation reactions in the active material in the electrodes. We will determine:

(i) The structural parameters required for rapid ionic (Li^+) motion (and thus high rate), particularly at close to full lithium removal.
(ii) The minimal electronic (and ionic conductivity), required to completely extract Li from materials for different crystal structures and particle sizes.
(iii) How to control (minimize) structural changes so as to enable redox processes involving more than one electron
(iv) The key structural parameters required to enable battery chemistries involving ions other than Li^+.

Thrust 2. Electrode Transport - Establishing the Local-Meso-Macro Scale Continuum. This thrust will establish a comprehensive understanding of the ionic and electronic transport in model electrode materials and establish a direct link to electrochemical performance through the correlation of physical phenomena in the increasingly complex hierarchy of a model battery electrode. We will determine:

(i) Definitive links of local ionic and electronic transport to correlated physical phenomena occurring across and within phase transformations.
(ii) The complex ionic and electronic pathways at the meso to microscale to develop a working theory of composite electrode design.

Thrust 3: Cross-Cutting Diagnostics: Developing the characterization and diagnostic tools to investigate battery function. This thrust will involve the development of novel *in-* and *ex-situ* experimental approaches aimed at probing electrical energy storage (EES) materials at three levels: atom, single crystal/particle, and across the electrode heterostructure. An emphasis is placed on *in-situ* methods that use multiple experimental tools simultaneously or that combine imaging with spectroscopy. *In-situ* spectroscopy is crucial as the materials are exceptionally dynamic over all levels of material structure during the operation of a battery and can be highly sensitive to ambient contamination if *ex-situ* techniques are employed. Metastable phases, including key reaction intermediates can relax to form different phases if probed by ex-situ techniques. For the three levels discussed above, several major developments are proposed:



(i) *Atomic level structure:* operando XAS, diffraction, PDF, SAXS, and NMR, annular dark/bright field STEM imaging of both heavy and light elements.
(ii) *Single crystal/particle level imaging:* Strain mapping with CXDI, high energy resolution STEM-EELS; and Nano-scale mapping at the nm-level (at the Debye length) across interfaces – including oxidation state mapping, in situ TEM, high energy resolution STEM-EELS.
(iii) *Imaging of reactions across the electrodes heterostructure:* Imaging the whole electrode intact ideally under operando conditions, through development of high resolution PDF/SAXS tomography and compatible operando electrochemical cells; structural insights with NMR experiments of studies of transport connected with MRI, PFG and SIMS studies of structure and tortuosity.

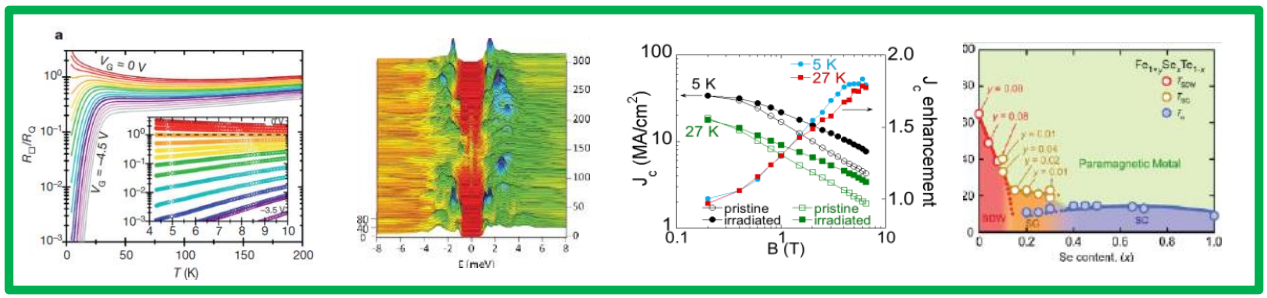
Northeast Center for Chemical Energy Storage (NECCES)	
Binghamton University	M.S. Whittingham (Director, Thrust 1 leader), L. Piper, G. Zhou, N. Chernova
Rutgers University	G. Amatucci (Assoc. Director, Thrust 2 leader), F. Cosandey, P. Batson, N. Pereira
University of Cambridge	C.P. Grey
Massachusetts Institute of Technology	Y-M. Chiang
Argonne National Laboratory	K. Chapman (Thrust 3 leader), P. Chupas
University of Michigan	K. Thornton
University of California, San Diego	Y.S. Meng, P. Ong
University of California, Santa Barbara	A. Van der Ven
University of Illinois, Chicago	J. Cabana
University of California, Berkeley	G. Ceder

Contact: M. Stanley Whittingham, Director, stanwhit@binghamton.edu
607.777.4623, http://necces.binghamton.edu

Center for Emergent Superconductivity (CES)
EFRC Director: Peter D. Johnson
Lead Institution: Brookhaven National Laboratory
Start Date: August 2009

Mission Statement*: To discover new high-temperature superconductors and improve the performance of known superconductors by understanding the fundamental physics of superconductivity.*

As U.S. electrical energy consumption continues to grow, the nation's electrical power transmission grid faces fundamental structural challenges of capacity, reliability and efficiency if it is to meet the needs of the 21st century. Electricity demand will grow by 50% in the US and by 100% globally by 2030, with nearly all of that growth in cities and suburbs where the overhead power lines and underground cables are already saturated. Power delivery and control solutions based on superconductors could solve these crises by using their demonstrated higher current carrying capacities over conventional cables, self-healing fault current limiting capabilities, and substantial increases in efficiency. However, there remain many fundamental materials and physics challenges which must be addressed in order for superconductivity to have a broad impact on the electrical grid.



From left to right: Superconductor-insulator transition in cuprate thin films driven by field-effect technology; STM measured superconducting gaps in the vortex core region in an FeTeSe superconductor; Magnetic field dependence of the critical current density J_c demonstrating the critical current enhancement due to ion-irradiation of commercial YBCO coated conductors; Phase diagram of the iron-based superconductor FeTeSe.Phase diagram for the iron based superconductor $FeTe_{1-x}Se_x$ as a function of the doping level x.

The objective of the *Center for Emergent Superconductivity* (CES) is to explore fundamental research issues with the objective to overcome key barriers leading to the viable application of high temperature/high current superconductivity. This will be achieved by enabling the design of superconducting materials with optimal physical and critical properties for deployment of a 21st century superconducting power grid. Thus, the most profound challenge of CES is to understand the fundamental mechanisms of high-temperature and high-current superconductivity sufficiently so as to direct discovery of new or improved families of materials with higher critical temperatures and currents. Considerable progress has already been made in this area with the demonstration that ion irradiation may be used to enhance the critical current carrying capabilities of commercial superconducting cable.

The central mission for the CES is the development of a broadly defined *Materials Genome Initiative* that encompasses three highly coordinated fundamental research directions specifically designed to work symbiotically towards the greater goal of the fundamental understanding high-temperature superconductivity. These are: a) the development of techniques to create new classes of superconducting

materials by design; b) a fundamental understanding of the mechanism of high-temperature superconductivity in existing materials, including the cuprates and Fe-based superconductors; and c) a fundamental understanding of the current carrying limiting properties of existing high-temperature superconductors that will lead to applications performance enhancement by design. We expect the unification of these priority research directions will prove transformative in our fundamental understanding and provide the basis for predictive design of new families of high-temperature superconductors.

Center for Emergent Superconductivity (CES)	
Brookhaven National Laboratory	Peter D. Johnson (Director) J. C. Séamus Davis, John M. Tranquada, Cedomir Petrovic, Ivan Bozovic, Genda Gu, Qiang Li, Mark Dean, Jon Rameau
Argonne National Laboratory	Mike Norman, Wai Kwok, Alexei Koshelev, Duck-Young Chung, Dean Miller, Ulrich Welp, Mercouri Kanatzidis
Florida State University	Laura Greene
University of Illinois, Urbana-Champaign	David Ceperley, Peter Abbamonte, Jim Eckstein, Philip W. Phillips, Daniel Shoemaker, Jian-Min Zuo
Rutgers University	Gabi Kotliar
Los Alamos National Laboratory	Leonardo Civale

Contact: Peter D. Johnson, Director, pdj@bnl.gov
631-344-3705, http://www.bnl.gov/energy/ces/

Light-Material Interactions in Energy Conversion (LMI)
EFRC Director: Ralph Nuzzo
Lead Institution: California Institute of Technology
Start Date: August 2009

Mission Statement: *To tailor the morphology, complex dielectric structure, and electronic properties of matter so as to sculpt the flow of sunlight and heat, enabling light conversion to electrical energy with unprecedented efficiency.*

The Light-Material Interactions in Energy Conversion Energy Frontier Research Center (LMI-EFRC) is a national resource for fundamental optical principles and photonic design used for solar energy conversion. This Center is a foundational partnership between scientific world leaders in optical properties of matter, internationally recognized experts in photovoltaic energy conversion, and innovators in the design and fabrication of novel electronic and photonic materials. The Center features a team of researchers spanning Caltech, Harvard, Lawrence Berkeley National Laboratory, Stanford, and University of Illinois at Urbana-Champaign. In its renewal phase, the LMI-EFRC is comprehensively addressing new opportunities for very high efficiency solar energy conversion, making scientific discoveries that enable the efficient utilization of the entire visible and infrared solar resource.

Objectives for 2014-2018

The overarching objective of the LMI is to develop fundamental principles and new photonic materials and structures that can yield advances in ultrahigh solar conversion efficiency. Specifically, we aim to:

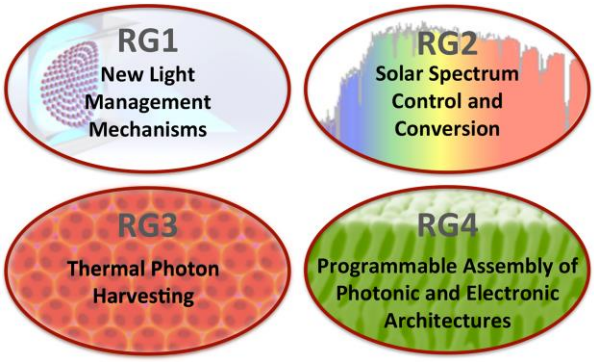
- Identify new mechanisms, materials, and enabling structures for the control and exploitation of light-material interactions along with predictive mathematical methods for their inverse design.
- Design photonic principles and fully integrated structures delivering unprecedented capabilities for control and conversion of the solar spectrum to greatly enhance photovoltaic efficiency.
- Establish fundamental principles for the utilization and control of thermal photonics with a holistic view of both the emitter and absorber, and discover new structures and materials that enable efficient and useful forms of energy conversion.
- Develop advanced materials and fabrication methods for the programmable assembly of electronic and photonic architectures in arbitrary form factors that enable more efficient electron transport, photon capture, optical power flow and dispersion in devices that harness passive and actively controlled light-matter interactions.

Selected Accomplishments to Date

- Discovered new principles of photon emission to maximize photovoltaic conversion efficiencies, providing the foundations of current world record single, dual, and quadruple-junction solar cells.
- Designed photonic crystals with record performance, demonstrating the first optoelectronically active 3D photonic crystal LED and selective thermal emitters with unprecedented stability.
- Advanced quantum dot materials and new principles of photonic design enabling luminescent solar concentrators with record concentration ratios and levels of performance.
- Developed assembly schemes and interface materials for quadruple junction, four terminal solar cells with efficiencies of 44% at concentrations of 1000 suns.
- Developed light-driven material synthesis processes that enable energy conversion materials to develop their own complex architectures in response to illumination conditions.
- Established mathematical methods that enable the design and optimization of photonic structures for light-trapping, spectrum-splitting, and control of near-field thermal emission.
- Identified light-matter interaction principles and synthesis methods impacting the companies Alta Devices, Caelux, Semprius, MC10, and Electroninks Inc, all co-founded by LMI investigators.

Center Research Team and Scientific Organization

The Center is organized scientifically into four research groups (RGs) that address scientific themes related to light-matter interactions, with each team spanning multiple institutional partners and designed to address our four-year scientific objectives.



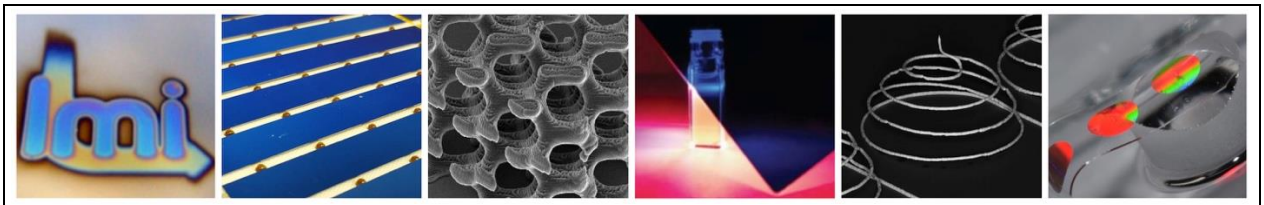
Research groups of the LMI-EFRC.

RG1 New Light Management Mechanisms: Exploring new mechanisms and metaphotonic structures for controlling and usefully mediating light-material interactions along with predictive mathematical methods for their inverse design. RG1 is a theoretically motivated effort to develop building block components and optical mechanisms connecting to RG2, RG3, and RG4.

RG2 Solar Spectrum Control and Conversion: Designing photonic principles and fully integrated structures delivering unprecedented capabilities for control and conversion of the solar spectrum to greatly enhance photovoltaic efficiency.

RG3 Thermal Photon Harvesting: Establishing fundamental principles for the utilization and control of thermal photonics, and discovering new structures and materials that enable efficient and useful forms of energy conversion.

RG4 Programmable Assembly of Photonic and Electronic Architectures: Developing powerful new methods for programmable assembly of photonic, electronic, and optoelectronic architectures that yield both materials and device specific elements of enhanced performance.


Representative LMI research efforts, from left: refractive index design via porous Si etching; concentrating photovoltaics capturing diffuse and direct irradiance; gyroid photonic crystal fabricated by two-photon lithography; photonic mirror and quantum dot design for luminescent solar concentrators; printed conductive Ag microstructures; conformal metafilm of Si nanoposts.

Light-Material Interactions in Energy Conversion (LMI)	
California Institute of Technology	Ralph Nuzzo (Director), Harry Atwater, Andrei Faraon, Nate Lewis, Austin Minnich
Harvard University	Jennifer Lewis
Lawrence Berkeley National Laboratory	Paul Alivisatos, Eli Yablonovitch, Xiang Zhang
Stanford University	Mark Brongersma, Jennifer Dionne, Shanhui Fan
University of Illinois, Urbana-Champaign	Paul Braun, Ralph Nuzzo, John Rogers

Contact: Carrie Hofmann, LMI-EFRC Assistant Director, carrie.hofmann@caltech.edu
(626) 395-1945, http://lmi.caltech.edu

Energy Frontier Research in Extreme Environments (EFree)
EFRC Director: Russell J. Hemley
Lead Institution: Carnegie Institution of Washington
Start Date: August 2009

Mission: *To accelerate the discovery and synthesis of energy materials using extreme conditions.*

The majority of our energy challenges are, at their core, due to intrinsic limitations of available materials with the required properties. By creating new materials with superlative properties including exceptional strength-to-weight ratios, resistance to corrosion, enhanced energy storage capacities, improved catalytic function and superior conversion and transport mechanisms, revolutionary energy savings can be achieved. Materials play a key role in all aspects of energy storage, conversion and utilization, and new materials are needed to improve performance in broad aspects of energy systems from solar, batteries, and fuels to new structural materials. In particular, entirely new strategies are required to access paradigm-shifting, transformative materials.

While traditionally most materials are created at or near ambient pressure, exploiting extreme environments, notably high pressures and temperatures, has tremendous potential for manipulating matter to synthesize next-generation materials with transformative impacts on energy. Moreover, materials in these extreme environments often exhibit optimal properties for energy applications. For example, extreme environments are capable of producing materials with unprecedented mechanical, thermal, and electronic properties.

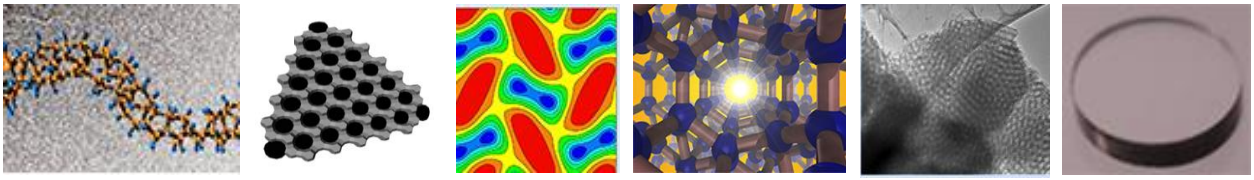


Figure 1. *Left to right: Structure of a one-dimensional carbon nanothread. The final step in the synthesis of zeolite-templated carbon. Electron density map of crystalline dense Li showing an inverse relationship to that of hydrogen. Structure of Si_{24}, showing the open framework structure. TEM image of highly crystalline mesoporous stishovite synthesized using high-pressure nanocasting. Single-crystal diamond window grown by CVD techniques***.**

EFree addresses specific knowledge gaps in the discovery of these paradigm-shifting, transformative energy materials. (Fig. 1). Novel materials to be discovered are broadly applicable to all classes of frontier energy research. The Center targets three focus areas, dictated by classes of energy materials and applications: advanced structural materials, novel energy conversion materials, and revolutionary energy transport materials. Our mission is to study materials under extreme conditions to deepen our understanding of materials behavior, enabling new materials to be discovered and, ultimately produced by design for practical use at ambient conditions.

To achieve this goal, EFree personnel work to synthesize fundamentally new materials and to exploit these for energy science through a focus on understanding kinetically stabilized routes to ambient pressure. We focus on studying, manipulating and ultimately controlling materials in regimes outside their fields of thermodynamic stability. In this, we employ new methodological approaches that allow access to new regions of phase space by treating recoverable high-pressure compounds as precursors for subsequent ambient-pressure manipulation. We also exploit pressure to mediate kinetically controlled synthesis of

new materials in the solid state. Here, alternative reaction pathways are 'engineered' by using pressure to control the structure of precursors. In many systems, these pathways need not lead to thermodynamically stable reaction products, but to other new materials that can be stabilized by exploiting the kinetic limits of reaction rates. Finally, we also use chemical pressure and epitaxial growth to enhance the ambient-pressure stability of materials that exhibit exceptional high-pressure energy transport properties. By design, these approaches are highly synergistic and are exploited to forge effective collaboration across the Center using both experiment and theory (Fig. 2).

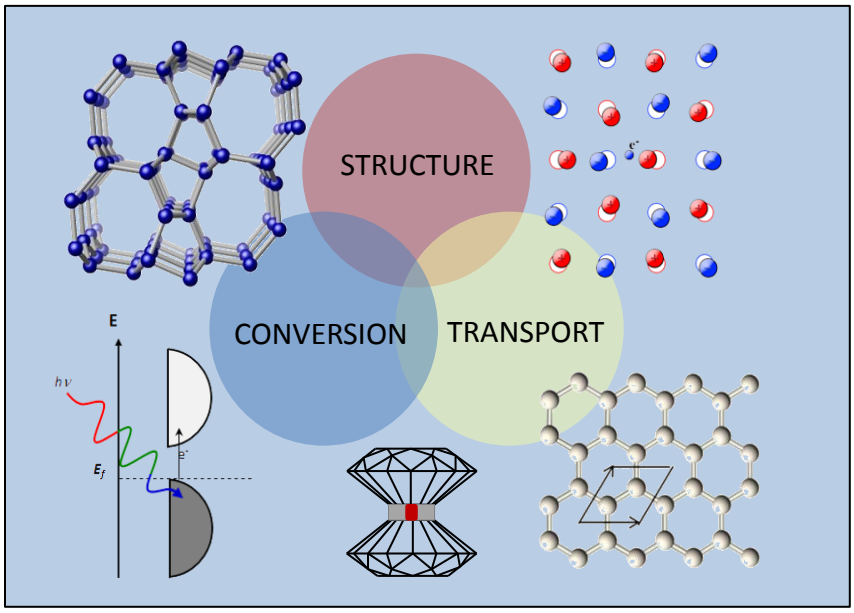


Figure 1. *EFree uses of extreme conditions for synthesis and stabilization of advanced structural, energy conversion, and transport materials.*

EFree thus employs integrated experimental and theoretical studies directed toward discovery, synthesis, and recovery of materials with exceptional properties using extreme conditions, especially high pressures and temperatures. The Center's overarching goal is in-depth understanding of kinetic stabilization mechanisms needed for the creation of revolutionary materials for robust real-world energy applications.

Energy Frontier Research in Extreme Environments (EFree)	
Carnegie Institution of Washington	Russell Hemley (Director), Timothy Strobel (Associate Director), Stephen Gramsch (Managing Director), Maria Baldini, Reinhard Boehler
California Institute of Technology	Brent Fultz
Colorado School of Mines	P. Craig Taylor, Laksmi Krishna
Cornell University	Roald Hoffmann, Neal Ashcroft
Lehigh University	Kai Landskron
Pennsylvania State University	John Badding, Vincent Crespi, Nasim Alem
University of Tennessee	Konstantin Lokshin
George Washington University	Tianshu Li, Russell Hemley

Contact: Russell J. Hemley, Director, rhemley@ciw.edu
301-793-1752, http://efree.carnegiescience.edu

Center for Actinide Science & Technology (CAST)
EFRC Director: Thomas Albrecht-Schmitt
Lead Institution: Florida State University
Start Date: August 2016

Mission Statement*: To unite materials chemists, separations scientists, condensed-matter physicists, and theoreticians into a cohesive research unit with the common goal of solving long-standing problems associated with the nuclear legacy of the Cold War.*

Cultivating new technologies that solve the vast challenges associated with nuclear waste from the Cold War will require an advanced science-based understanding and predictive capabilities for controlling *f*-element (actinide and lanthanide) molecules and materials in solution and solid state that utilizes the most advanced spectroscopic tools available. The Center for Actinide Science & Technology (CAST) brings together groups of scientists with *f*-element expertise from Florida State University, the National High Magnetic Field Laboratory, Florida International University, Los Alamos National Laboratory, Lawrence Berkeley National Laboratory, Purdue University, and the University of Pennsylvania to facilitate synergistic cross-fertilization between chemists, physicists, materials scientists, and theoreticians. Our focus is on developing our unique expertise in synthesis, spectroscopy, and theory to develop first-principals, predictive electronic structure approaches to achieve the design, synthesis, and characterization of both low-temperature and high-temperature waste forms as well as new molecular systems that gain unprecedented control of chemical selectivity during processing. We will develop new synthetic methodologies, providing a detailed understanding of electronic structure from both experimental and computational perspectives, and addressing new separations schemes treating tank waste. A key impact of this research will be to develop practical, resilient, and experimentally-verified computational tools for describing complex chemistry, physics, and materials science both in the solid state and in solution. These advancements in experiment and theory will provide a revolutionary understanding of actinide materials under normal and extreme conditions, and in turn lead to wide-ranging applications in the nuclear sciences. This will advance our predictive capabilities in *f*-element science with implications across the periodic table.

Synthesis of Solid State, Complexes, and Molecular Materials. The actinide extended structure and molecular materials systems that are the focus of CAST will utilize the unique synthetic capabilities at FSU, LANL, and LBNL. A host of critical physical property measurements on these materials will take place at the NHMFL making use of both the unique facilities that will allow us to probe properties under a variety of extreme magnetic field, temperature, pressure, etc. conditions. Similarly, the synthesis of specialized actinide complexes and molecular materials will take place at FSU, LANL, LBNL/UC-Berkeley, and partner laboratories. The preparative efforts will include the design, synthesis, and optimization of new and existing ligands containing light atoms (B, C, N, O containing conjugated ligands) for the development and evaluation of transuranic separations. The ligand design and complexation studies with lanthanide, thorium, and uranium will take place at the University of Pennsylvania and Purdue University.

Electronic Structure. There are no broadly available, reliable predictive electronic structure approaches for the strongly correlated materials, both solid and molecular, that are the focus of CAST. We are expanding our approaches to employ high-accuracy electronic structure methods for the reliable predictions of the properties of actinide compounds. Results from the calculations will be validated through synergistic collaborations with experiment. Hard X-ray XES and RXES also will be used to determine precise *f*-occupancies. Complementary to the aforementioned occupied state probe will be unoccupied state measurements conducted using ligand K-edge XAS and non-resonant inelastic X-ray scattering, for which LANL has unique expertise.

Solution Chemistry. The solution chemistry effort will focus on revolutionizing the predictive capability for actinide complexation/exchange reactions with specific focus on developing new actinide separation strategies. Interplay between the theoretical and experimental efforts will center on quantifying *f*-element-ligand interactions and fine-tuning these interactions to maximize selectivity. The combined CAST X-ray spectroscopic expertise (XAFS, XES, RIXS, ligand K-edge XAS) will be utilized to probe the electronic structure and speciation of *f*-element species dynamics relevant to separations processes in solution with actinide-light atom bonds, and used to benchmark the theoretical and simulation efforts. Adding to the X-ray approaches, will be the unique capabilities of the CAST team in solution thermodynamics (including calorimetry), kinetics, and advanced optical spectroscopies will be focused onto the same systems.

Center for Actinide Science & Technology (CAST)	
Florida State University/NHMFL	Thomas Albrecht-Schmitt (Director), Susan Latturner, Kenneth Knappenberger, Kenneth Hanson, Eugene DePrince, Stan Tozer, David Hobart (Director of Operations)
Florida International University	Ines Triay (Deputy Director), Christopher Dares, Konstantinos Kavallieratos
National High Magnetic Field Laboratory	David Graf, Ryan Baumbach
Lawrence Berkeley National Laboratory	John Gibson
Purdue University	Susanne Bart
Los Alamos National Laboratory	Stosh Kozimor, Andrew Gaunt, Enrique Batista, Ping Yang
University of Pennsylvania	Eric Schelter

Contact: Thomas Albrecht-Schmitt, Director, albrecht-schmitt@chem.fsu.edu
850.841.9525, http://cast.chem.fsu.edu/

Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME)
EFRC Director: Krista S. Walton
Lead Institution: Georgia Institute of Technology
Start Date: August 2014

Mission Statement*: To develop a deep knowledge base in the characterization, prediction, and control of acid-gas interactions with a broad class of materials to accelerate materials discovery for large-scale energy applications.*

Acid gases are ubiquitous in multiple large-scale energy applications. For example, SO_x and NO_x are critical components of energy-related gas mixtures. Modern flue gas management involves catalysts that convert these species to less harmful products, as well as membrane and sorbents that can be degraded by these gases. As illustrated in Figure 1, degradation and deactivation effects of acid exposure can reduce access to active metal sites, block pores, reduce overall porosity, and destroy favorable textural properties. These degradation effects are often decisive factors in the practical use of materials such as sorbents for carbon capture, acid gas conversion, and natural gas purification. There are two major challenges in solving these problems: the mechanism of acid gas interactions with complex materials is poorly understood, and the ability to predict or prolong the lifetimes of functional materials is severely limited.

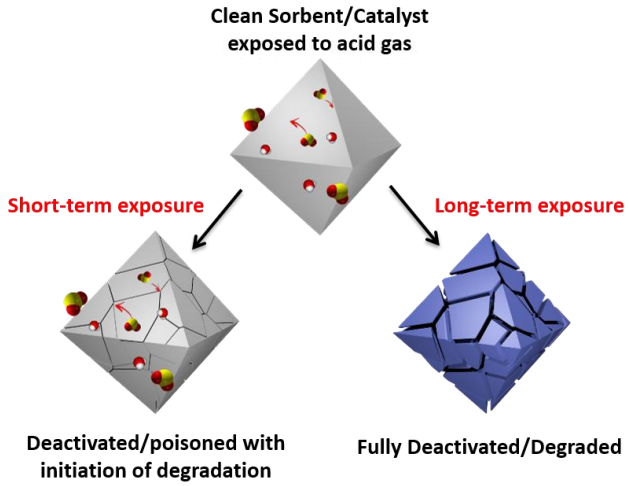


Figure 1: Changes induced in sorbents/catalysts upon short- and long-term exposure to acid gases. Materials are typically treated as passive in these environments, but can change dramatically upon exposure to SO_x, NO_x, and H_2S.

Objectives

UNCAGE-ME seeks to provide a fundamental understanding of acid gas interactions with solid materials through integrated studies of the interaction of key acid gases (CO_2, NO_2, NO, SO_2, H_2S) with a broad range of materials. We combine the application of *in situ* molecular spectroscopic studies of both the surface functionalities and bulk structures of materials relevant to catalysis and separations under relevant environmental conditions with complimentary multiscale computational and theoretical modeling of acid gas interactions with solid matter. Insights gained by the multi-investigator, multidisciplinary teams will allow us to achieve the following long-term, 4-Year Goals set forth for the Center:

1. Develop a deep knowledge base characterizing acid gas interactions applicable to a broad class of materials.
2. Develop fundamental knowledge allowing practical predictions of materials interacting with complex gas environments on long time scales.
3. Advance fundamental understanding of the characterization and control of defects in porous sorbents.
4. Accelerate materials discovery for large-scale energy applications by establishing broadly applicable strategies to extend material stability and lifetime in the presence of acid gases.

Center Research Team and Scientific Organization

The Center conducts research in three major thrust areas:

Thrust I - Model Metal Oxides: The interaction of small amounts of acid gases with sorbents/catalysts can dramatically affect their surface chemistry, useful lifetime and ease of regenerability. The overarching goal of Thrust I is to gain a molecular level understanding of the surface chemistry of acid gas interaction with model sorbents (oxides) and catalysts (supported metals and oxides) and their structural evolution. This will provide structure-performance relationships for the rational design of more efficient sorbents for acid gas removal and more stable catalysts for CO_2 utilization.

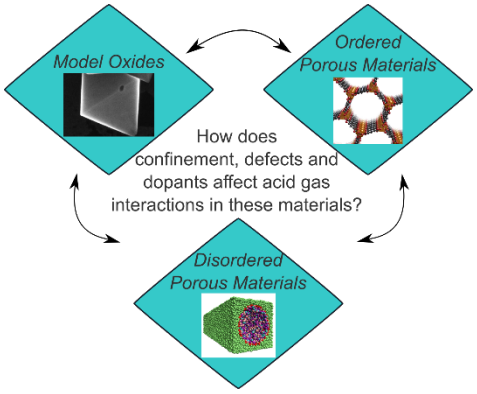


Figure 2: Overview of three research thrust areas.

Thrust II - Ordered Porous Materials: The stability of crystalline, high surface area adsorbents such as metal-organic frameworks (MOFs) towards acid gases is a major obstacle in their development as successful materials for energy-related applications. The main goal of this Thrust is to determine the structural features that control this (in)stability. The main hypothesis is that acid gas stability of such materials, and their potential degradation upon exposure to acid gases, are driven by local defects or centers susceptible to acid attack distributed throughout the material. If this is the case, characterization and control of the local defects/reactive centers is vital to enhancing material performance.

Thrust III - Disordered Porous Materials: Our efforts using crystallographically ordered porous materials in **Thrust II** will be complemented by **Thrust III**, which will center on disordered porous materials including templated or carbide-derived carbons and supported amines. Both classes of materials have significant heterogeneity with regard to structure in the final form used in acid gas separations and catalysis, yet both are made from more well-defined precursors or supports, which gives a basis for understanding the complex structures of these materials. **Thrust III** aims to create a body of knowledge that ultimately relates the support structure and amines/heteroatoms/defects to its interaction, stability and/or degradation characteristics in the presence of NO_x, SO_x, CO_2, and H_2O.

Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME)	
Georgia Institute of Technology	Krista Walton, Christopher Jones, David Sholl, Sankar Nair, Michael Filler, Phillip First, Ryan Lively, Thomas Orlando
Oak Ridge National Laboratory	Sheng Dai, Gernot Rother, Tjerk Straatsma, Bobby Sumpter, Zili Wu
University of Alabama	David Dixon
University of Florida	Sergey Vasenkov
Lehigh University	Jonas Baltrusaitis, Israel Wachs
Pennsylvania State University	Susan Sinnott
Washington University St. Louis	Sophia Hayes
University of Wisconsin	JR Schmidt

Contact: Krista Walton, UNCAGE-ME Director, walton@efrc.gatech.edu
404-894-5254, http://efrc.gatech.edu

Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC)
EFRC Director: Cynthia Friend
Lead Institution: Harvard University
Start Date: August 2014

Mission Statement: *To drive and conduct transformative research in mesoscale science for sustainable catalysis, with full integration of multi-scale experimental, theoretical and computational approaches.*

IMASC is seeking fundamental understanding for the purpose of developing novel mesoporous catalysts (non-zeolite) for sustainable processes that drive the conversion and production of platform chemicals. Understanding reaction kinetics, building innovative catalyst architectures and improving reaction selectivity under catalytic conditions is leading to new opportunities to decrease fuel consumption through creation of more efficient processes. IMASC is advancing the scientific grand challenge question "how do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?" through integrated efforts at Harvard University, Tufts University, Lawrence Berkeley and Lawrence Livermore National Laboratories, and the Fritz Haber Institute in Germany.

IMASC Strategic and Research Objectives:

IMASC **Strategic Objectives**:

- To develop principles for designing efficient catalytic processes based on fundamental understanding from experiment and theory
- To apply, test and refine these principles on mesoporous materials under working catalytic conditions.

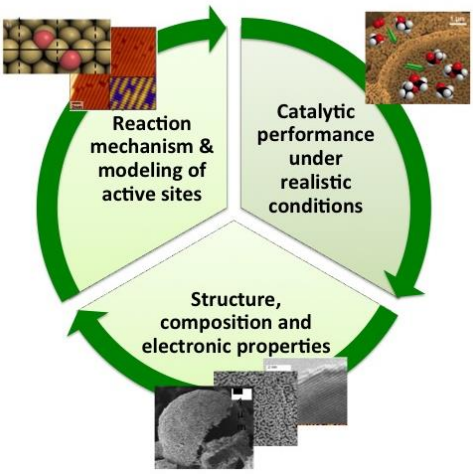


Fig. 1: A schematic representation of IMASC's approach to develop mesoscale architectures for sustainable catalysis

IMASC research is strategically organized into three Focus Areas (Fig. 1) capitalizing on a judiciously chosen combination of technical skill sets that are designed to address the following ***research objectives*** necessary to achieve our strategic objectives, mission and vision:

1. Delineate reaction mechanisms of selective oxidation, hydrogenation and dehydrogenation reactions in order to establish paradigms for predicting selectivity and activity.
2. Understand the function of dilute alloy surfaces and develop models for predicting materials compositions to optimize activity and selectivity.
3. Advance the methodology for studies under reaction conditions—vapor and liquid phase—in order to relate catalytic function to surface composition, structure and electronic properties.
4. Identify the design elements in building mesoscale catalyst architectures and establish principles for their controlled synthesis.
5. Parameterize structure-activity-selectivity relationships to develop models for rapidly selecting catalyst materials and reaction conditions for specific reactions.

IMASC Research Team and Research Focus Areas:

The IMASC team includes chemists, physicists, chemical engineers, and materials scientists who are performing research organized into three research Focus Areas: (1) Reaction Mechanisms and Modeling of Active Sites; (2) Understanding Performance under Catalytic Conditions; and, (3) Structure, Composition and Electronic Properties (cross-cutting theme).

Focus Area 1 (FA1): ***Reaction Mechanisms and Modeling of Active Sites.*** The mechanisms of selective catalytic hydrogenation and oxidation are being investigated on the molecular scale on well-defined single crystal surfaces and on complex mesoporous materials under highly controlled conditions (Figure 1). Studies are leading to a comprehensive model of reaction mechanisms, including elementary chemical steps and the nature of active sites. Investigations underway include a range of (host) materials, including Cu, Ag, and Au combined with active metals (e.g., Pd, Ni and Pt). Designed meso- and nanoporous materials are synthesized as catalysts. FA1 is focusing on relating reaction selectivity to materials composition and structure as we continue to build up a sophisticated general model for these classes of reactions. Atomistic theory is providing insight into the interplay of electronic and geometric structure in determining bonding and reactivity of molecular intermediates. This research is beginning to inform catalyst design through close coupling with research in the other Focus Areas.

Focus Area 2 (FA2): Understanding Performance under Catalytic Conditions. The efficacy of specific mesoporous architectures for catalytic activity and selectivity under realistic reaction conditions is being established through reactor studies. The unique capability of temporal analysis of products (TAP) experiments to quantitatively determine rate constants is combined with studies in flow reactors for vapor phase processes *in situ* (1 atm. pressure). This research is closely coupled with the research in FA1 to refine the working hypotheses about what materials properties and reaction conditions yield better performance (Fig. 1). Close coupling with FA 3 is used to model the effect of mesoporous geometry to the local surface concentrations of reactants and products through multi-scale simulations.

Focus Area 3 (FA3): Understanding Structure, Composition and Electronic Properties under catalytic conditions. This cross-cutting research theme is enabling development and use of advanced theoretical and experimental tools for understanding the effects of surface composition, structure and electronic properties on the catalytic reactivity of the model and mesostructured materials and the scale-up from the atomic scale to the mesoscale architectures. Powerful microscopies and x-ray probes are combined to understand the working reactive surfaces. Multiscale theory is providing a fundamental understanding of both the materials synthesis and the evolution of the mesoscale materials under reactive conditions.

Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC)	
Harvard University	Cynthia Friend (Director), Efthimios Kaxiras (Deputy Director), Challa Kumar (Managing Director), David C. Bell, Robert Madix
Tufts University	Maria Flytzani-Stephanopoulos, E. Charlie H. Sykes
Lawrence Berkeley National Laboratory	Miquel Salmeron
Lawrence Livermore National Laboratory	Juergen Biener

Contact: Cynthia Friend, Director, friend@fas.harvard.edu
617-495-4052, http://efrc.harvard.edu

Center for Nanoscale Controls on Geologic CO_2 (NCGC)
EFRC Director: Donald J. DePaolo
Lead Institution: Lawrence Berkeley National Laboratory
Start Date: August 2009

Mission Statement*: To enhance the performance and predictability of subsurface storage systems by understanding the molecular and nanoscale origins of CO_2 trapping processes, and developing computational tools to translate to larger-scale systems.*

The vision for the Center is to understand, predict, and enhance the performance of underground CO_2 storage systems. Specific goals are to produce (1) a next-generation understanding of the nanoscale-to-mesoscale chemical-mechanical behavior of shale - a critical material for a low-carbon energy future, (2) quantitative models for the efficiency of reservoir capillary trapping and its effect on solution and mineral trapping, (3) methods to predict mineralogical trapping, and (4) theory, experimental data, and computational tools to allow nanoscale effects to be translated to mesoscale and continuum scale model equations and parameters.

The NCGC consists of a team of highly qualified investigators with expertise in, and access to, the most advanced analytical and computing facilities available for furthering fundamental knowledge of the geochemical aspects of geologic carbon storage, in particular the chemistry of mineral-fluid interfaces and fluid-fluid interfaces that control the physics of fluid flow and chemical reactions. Experimental investigations will transition from simplified analogue materials to more realistic geologic materials. Newly developed characterization and experimental approaches will be integrated with mesoscale chemical-mechanical-hydrologic modeling and simulation to achieve a transformational predictive capability for stratigraphic- and reservoir CO_2 trapping efficiency and reliability.

Scientific gaps that the Center will address are:

1. The origin and evolution of wetting properties of complex, reactive fluids in contact with common minerals encountered in carbon storage
2. Reactivity between fluids and minerals in nanoporous to macroporous rocks
3. Long term-evolution of capillary-trapped CO_2
4. The response of fractured shale to intrusion of CO_2-containing mixed fluids
5. Theory and computational tools that allow the large scale and long-timescale evolution of fluid-rock systems to be simulated such that they reflect the nanoscale and mesoscale properties of geological materials at far-from equilibrium conditions.

The research of the NCGC is divided into three Thrust Areas that address (1) the sealing effectiveness of fractured shales, (2) reservoir processes that control secondary trapping (capillary, dissolution and mineral trapping) and (3) developing the computational tools and insight necessary to model mesoscale couplings and material properties and dynamics. Systems of study will include well-characterized natural rock and mineral samples, and synthetic materials fabricated by established methods and methods to be developed. A key aspect of our approach is to bring multiple characterization methods, and diverse complementary expertise, to bear on the same experiments, and to integrate modeling and simulation with experiments. The Center will leverage the characterization and computational facilities at LBNL (Advanced Light Source, Molecular Foundry, National Energy Research Scientific Computing Center), ORNL (Spallation Neutron Source, High Flux Isotope Reactor, Center for Nanomaterials Science) and other synchrotron facilities (Advanced Photon Source at Argonne Laboratory, Stanford Synchrotron Radiation Laboratory, and the National Synchrotron Light Source at Brookhaven Lab).

Stratigraphic Trapping by Fractured Shale: Thrust Area 1 aims to provide an understanding of the resilience of seals to CO_2 leakage, i.e.: "Is flow of brine-CO_2 mixtures along fractures a self-enhancing or a self-limiting phenomenon?" The answer to this question is challenging, because brine-CO_2 flow through fractures induces processes that promote fracture opening (mineral dissolution) but, also, processes that promote fracture closing or clogging (mineral precipitation, dissolution of asperities, alterations of fracture mechanics, generation of colloids). These processes are challenging to examine, because they involve couplings between different phenomena (surface chemistry, rock mechanics, multiphase flow, molecular diffusion) at multiple scales (nanometers to millimeters).

Reservoir Trapping Processes: Thrust Area 2 aims to provide a better understanding of the fundamental scientific questions that constrain the most uncertain components of reservoir trapping; the role of residual and mineral trapping, their corresponding rates & efficiencies, and their long term evolution in heterogeneous subsurface systems.

Modeling Approaches for the Mesoscale Challenge: Thrust Area 3 aims to build on the progress made in NCGC to address the mesoscale challenge from the DOE BES Basic Research Needs *report From Quanta to the Continuum: Opportunities for Mesoscale Science.* This Thrust is organized into three broader topics on 1) Mesoscale Reaction Rates: Upscaling Reaction Rates from Molecular to Pore Scale, 2) Mesoscale Fractures: Modeling Fracture Networks, and 3) Mesoscale Reactive Transport: Theoretical and Computational Approaches for Upscaling to the Mesoscale.

Center for Nanoscale Controls on Geologic CO_2 (NCGC)	
Lawrence Berkeley National Laboratory	Don DePaolo (Director), Carl Steefel (Deputy Director, Theme Lead), Jonathan Ajo-Franklin (Theme Lead), Benjamin Gilbert, Tim Kneafsey, Peter Schuck, Tetsu Tokunaga, David Trebotich, Jiamin Wan
Oak Ridge National Laboratory	Andrew Stack, Gernot Rother, Larry Anovitz
Ohio State University	David Cole
Princeton University	Ian Bourg (Theme Lead)
Purdue University	Laura Pyrak-Nolte
Stanford University	Sally Benson, Hamdi Tchelepi
Washington University, St. Louis	Young-Shin Jun

Contact: Donald J. DePaolo, Director, DJDePaolo@lbl.gov
510-486-7560, http://esd1.lbl.gov/research/facilities/ncgc/

Center for Advanced Solar Photophysics (CASP)
EFRC Director: Victor I. Klimov
Lead Institution: Los Alamos National Laboratory
Start Date: August 2009

Mission Statement*: To exploit fundamental interactions between nanomaterials and light with the goal of producing disruptive advances in the efficiency of solar energy conversion.*

Solar light is a tremendous resource of clean energy. Widespread use of solar energy will require technologies that offer a dramatic increase in photoconversion efficiency *simultaneously* with reduced cost, which will require disruptive advances relying on new physical principles and novel materials. Quantum-confined semiconductor nanocrystals (NCs) are fascinating structures offering tremendous promise in the area of solar energy conversion into either electricity or chemical fuels. The development of NC-based approaches lies at the intersection of chemistry, physics, materials science and engineering. The Center for Advanced Solar Photophysics (CASP) unites world-class experts spanning these disciplines toward the purpose of harnessing the unique properties of quantum-confined semiconductor materials to facilitate the realization of the next generation of low-cost, high-efficiency solar photoconversion systems.

As an established leader in the design, synthesis and exploitation of novel nanomaterials that exhibit advanced, solar-relevant physical phenomena, CASP continually strives to achieve new levels of efficiency in NC-based photovoltaic (PV) devices. In addition, we are vigorously investigating a broad range of approaches toward applying the unique properties of nanomaterials to boost the efficiencies of existing or emerging PVs above present limits. This multifaceted research program is captured in four main Themes (Fig. 1), each of which strives to address a specific, essential question:

- *How can we enhance the efficiency of carrier multiplication in engineered nanomaterials?* The observation of carrier multiplication (the generation of multiple excitons by a single absorbed photon) in NC-based PVs is a singular example of advanced nanoscale physics being brought to bear on real solar cells. While the efficiencies of this phenomenon in NCs are enhanced relative to those in bulk semiconductors, they are still not high enough to considerably impact power conversion efficiency limits. In the **Carrier Multiplication by Design Theme**, we investigate how structure-based control over carrier cooling, and carrier-photon and carrier-carrier interactions can drive CM efficiency to the theoretical limit.
- *How can we use nanomaterials to harness the full solar spectrum more efficiently?* The ultimate conversion efficiency of standard PV devices is limited by two main channels of energy loss: the inability to capture lower-energy, sub-band-gap photons, and the dissipation of the excess energy of above-band-gap photons as heat. In the **Advanced Photon Management Theme**, we employ NCs to make better use of such photons through up- or down-conversion schemes (collectively called "spectral reshaping") as well as to augment sunlight harvesting with inexpensive luminescent solar concentrators.
- *How can we manipulate inter-particle coupling to control charge and energy transport in mesoscopic assemblies?* Our understanding of the unique physical phenomena that arise in nanoscale materials has rapidly advanced, but to be relevant, these phenomena must be active in macroscopic devices. In the **Functional Mesoscopic Assemblies Theme**, we develop approaches for integrating engineered NCs into mesoscopic assemblies that retain original functionalities and augment them with efficient carrier transport and other emergent phenomena associated with controlled inter-particle coupling.

- *How can unique nanoscale phenomena be exploited in advanced photoconversion devices?* Currently, optimizing the performance of solar cells based on NCs relies on tuning their properties to meet the needs of a conventional PV architecture. To overcome the limitations of this traditional concept, in the **Advanced Device Architectures Theme**, we will explore new photoconversion schemes tailored for a specific nanostructure and optimized *via* convergent evolution of both the material and the device architecture.

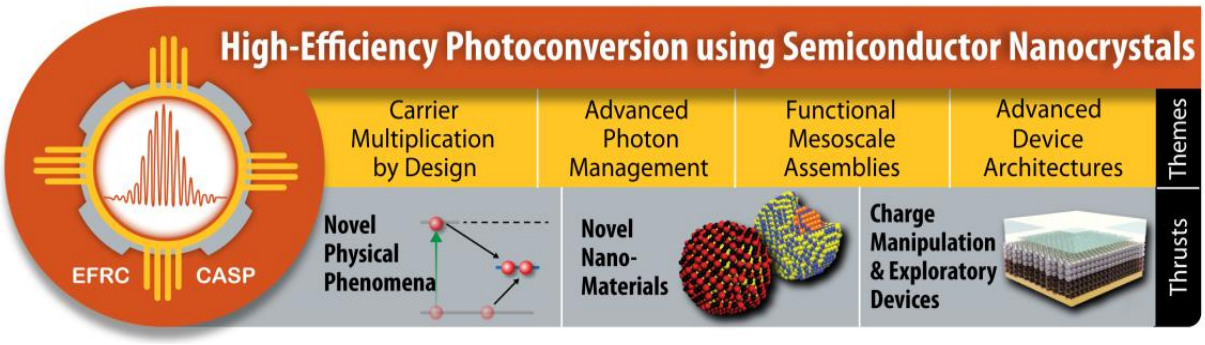


Figure 1. Research themes address essential questions using the capabilities housed within CASP's three Thrusts.

To tackle these research Themes we utilize world-class capabilities and expertise organized within a Thrust structure that supports a comprehensive approach to all relevant aspects of each problem. The **Novel Physical Phenomena (NPP) Thrust** combines capabilities in optical and scanning-probe spectroscopies emphasizing state-of-the-art femtosecond and single-NC techniques with theory, modeling and simulation that encompass effective-mass, tight-binding, quantum chemistry, and atomistic techniques. The **Novel NanoMaterials (NNM) Thrust** provides advanced capabilities for implementing materials-by-design concepts in the synthesis of engineered NCs and multifunctional nanocomposites using colloidal and plasma-based techniques. Finally, the **Charge Manipulation and Exploratory Devices (CMD) Thrust** houses unique capabilities for probing transport in mesoscopic QD arrays, as well as for fabrication and characterization of NC-based devices with architectures that exploit novel nanoscale physics.

Center for Advanced Solar Photophysics (CASP)	
Los Alamos National Laboratory	Victor Klimov (Director), Jeff Pietryga, István Robel, Kirill Velizhanin
National Renewable Energy Laboratory	Matt Beard (Associate Director), Justin Johnson, Joey Luther, Art Nozik
University of California, Irvine	Matt Law
University of Minnesota	Uwe Kortshagen
George Mason University	Alexander Efros, Andrew Shabaev
University of Pennsylvania	Cherie Kagan
University of Chicago	Giulia Galli

Contact: Victor I. Klimov, Director, klimov@lanl.gov
(505) 665-8284, http://casp.lanl.gov, http://www.centerforadvancedsolarphotophysics.org

Center for Excitonics (CE)
EFRC Director: Marc Baldo
Lead Institution: Massachusetts Institute of Technology
Start Date: August 2009

Mission Statement*: To supersede traditional electronics with devices that use excitonics to mediate the flow of energy.*

Exciton - *a quasiparticle excitation consisting of a bound electron and hole that mediates the absorption and emission of light, especially in disordered and low-dimensional materials.*

In this Center, we seek to supersede traditional electronics with devices that use excitons to mediate the flow of energy. Mastering the properties of excitons offers the ability to guide energy at the nanoscale, and transform it with a flexibility that is impossible in conventional systems. Our objectives are to increase the efficiency of solar photovoltaic cells, and to develop new materials and structures for high brightness solid state lighting.

We pursue these goals with three teams.

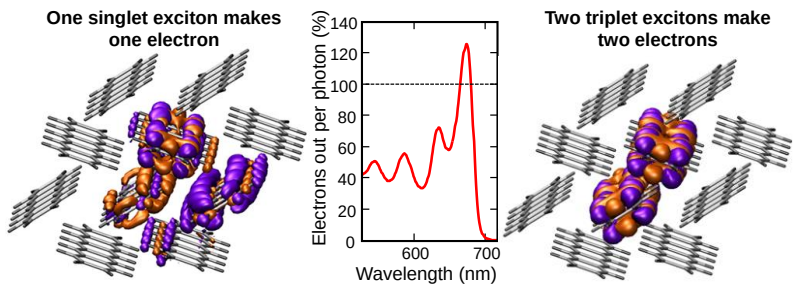
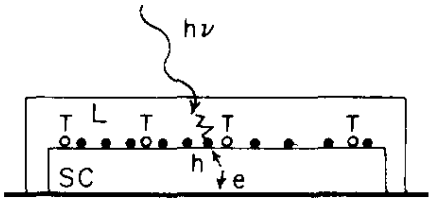


Figure 1. Unlike electrons, excitons can be split. In the Center for Excitonics, we have used singlet exciton fission in pentacene to generate at least 1.26 electrons per photon.

Team 1: Multiexciton Physics & Applications
(*Baldo*, *Bawendi*, *Bulović, Dauler, Willard, van Voorhis*)

Singlet exciton fission is one focus of our fundamental studies of exciton splitting in different materials. In conventional nanocrystalline semiconductors, *Bawendi* and *Dauler* have performed extensive single molecule spectroscopy showing that excitation of secondary electrons must out-compete rapid thermalization losses. But in molecules *Baldo* and *Van Voorhis* demonstrated that these losses are spin disallowed, meaning that exciton fission can be almost perfectly efficient. Our present efforts concentrate on the interface between molecular excitons and inorganic materials, including colloidal nanocrystals. In particular, we seek to couple molecular triplet excitons to silicon. The aim is to sensitize silicon solar cells, doubling the photocurrent from high-energy solar photons ($\lambda < 550$ nm), and ultimately boosting power conversion efficiencies to 30% or more.



Second, any exciton fission in the organic coating could provide two e–h pairs per absorbed photon.

Figure 2. Dexter's 1979 proposal for sensitization of a semiconductor (SC) by an organic layer (L) capable of singlet exciton fission.

Team 2: Excitonic Antennas and Quantum Transport
(Aspuru-Guzik, Bathe, Black, Dincă, Nelson, Schlau-Cohen)

This team is led by *Alán Aspuru-Guzik* and is inspired by photosynthesis. Whereas Team 1 examines localized excitons, this team studies delocalized excited states in molecular assemblies known as excitonic

antennas. Light harvesting structures in photosynthesis collect and transport solar radiation in the form of excitons with near unity efficiency using a wide variety of design principles that tailor operation for each organism's environment. Indeed, photosynthesis exploits excitons and exhibits much larger levels of long range disorder than conventional solar cells. Its tolerance of disorder allows photosynthetic 'circuits' to be assembled at low energy cost, and consequently, the energy payback time of a leaf is as short as several days - ~100× lower than conventional solar cells.

Our efforts to understand natural excitonic antennas and fabricate synthetic analogs are broken into four aims:

(i) **Theory** – How do excitonic antennas operate?
(ii) **Spectroscopy** – How can we observe excitonic transport in antennas?
(iii) **Synthesis** – Can we build artificial antennas?
(iv) **Quantum transport** – How can we protect excitons against disorder?

Team 3: Two dimensional Excitonic Crystals
(Jarillo-Herrero, Tisdale, Englund, Kong, Levitov, Li, Nelson, Stach)

This team is led by *Pablo Jarillo-Herrero* and *Will Tisdale*. Crystalline, and just a few atoms thick, the 2D transition metal dichalcogenides (TMD) exhibit the best electronic properties of any known semiconductor while still remaining excitonic at room temperature. This combination of properties is especially attractive for energy applications, especially solid state lighting, where bound excitons enhance luminescence relative to free carrier materials, the outstanding charge transport properties reduce Ohmic losses, and the 2D sheets can be readily integrated with other electronic materials. Scientifically, the material properties of the 2D TMDs are also appealing. They exhibit unique phenomena such as an exceptional dependence on strain, and strong luminescence from trions – formed when an exciton binds with one additional electron or hole and becomes singly charged.

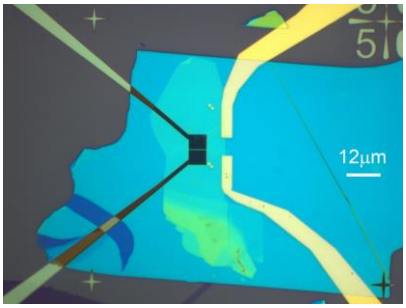


Figure 3. A $MoTe_2$-based LED and solar cell, built by *Jarillo-Herrero*.

Our efforts in this team are divided into four aims:

(i) **2D LEDs and Photovoltaics** – both as scientific platforms and potential applications
(ii) **Energy transfer** – coupling 2D materials to 0D excitonic materials
(iii) **Synthesis** – novel fabrication for improved crystal quality and novel functionality
(iv) **Exciton polaritons** – for long range energy transfer and potentially coherent control

Center for Excitonics (CE)	
Massachusetts Institute of Technology	Marc Baldo, Mark Bathe, Moungi Bawendi, Vladimir Bulovic, Mircea Dinca, Dirk Englund, Pablo Jarillo-Herrero, Jing Kong, Leonid Levitov, Ju Li, Keith Nelson, Gabriella Schlau-Cohen, Will Tisdale, Troy Van Voorhis, Adam Willard
MIT Lincoln Laboratory	Eric Dauler
Harvard University	Alan Aspuru-Guzik
Brookhaven National Laboratory	Charles Black, Eric Stach

Contact: Marc Baldo, baldo@mit.edu
617-452-5132, http://www.rle.mit.edu/excitonics/

Solid-State Solar-Thermal Energy Conversion Center (S^3TEC)
EFRC Director: Gang Chen
Lead Institution: Massachusetts Institute of Technology
Start Date: August 2009

Mission Statement*: To advance fundamental science and to develop materials for harnessing heat from the Sun and terrestrial sources and converting this heat into electricity via solid-state thermoelectric, thermophotovoltaic, and thermogalvanic technologies.*

The DOE EFRC center entitled "Solid-State Solar-Thermal Energy Conversion Center (S^3TEC Center)" is formed by the Massachusetts Institute of Technology, in partnership with Boston College, Duke University, the University of Houston, the University of Missouri, the Northwestern University, Brookhaven National Laboratory, and Oak Ridge National Laboratory. The S^3TEC Center was founded in 2009 with the vision to create an intellectual base for advancing the fundamental science of energy-carrier coupling and transport for thermal-to-electrical energy conversion, originally based on thermoelectric (TE) and thermophotovoltaic (TPV) technologies. The Center was renewed in 2014 with the expanded scope that now includes thermogalvanics (TG) and spin transport studies in addition to exploration of new phenomena in photon, phonon and electron transport, topological properties, and energy conversion mechanisms.

These heat-to-electricity energy conversion technologies represent a drastic departure from conventional thermal-mechanical energy conversion engines. They are solid-state and do not involve intermediate mechanical energy conversion. They are attractive for their compactness, scalability, and environmental friendliness, but currently are not efficient enough to compete against conventional energy conversion technologies. Since its inception, the fundamental knowledge gained at the S^3TEC Center has been successfully used to design new materials and to demonstrate proof-of-principle prototypes to achieve leaps in efficiency of these technologies, with an emphasis on approaches that have the potential to be low-cost. The S^3TEC Center's focus on fundamental studies of the transport of electrons, phonons, and photons, and the interactions among these carriers has led to improvements in material performance and promising technology demonstrations, including achieving 7.4% and 6.8% efficiencies of solar TE and solar TPV generators, respectively, which are significantly higher than prior state-of-the-art.

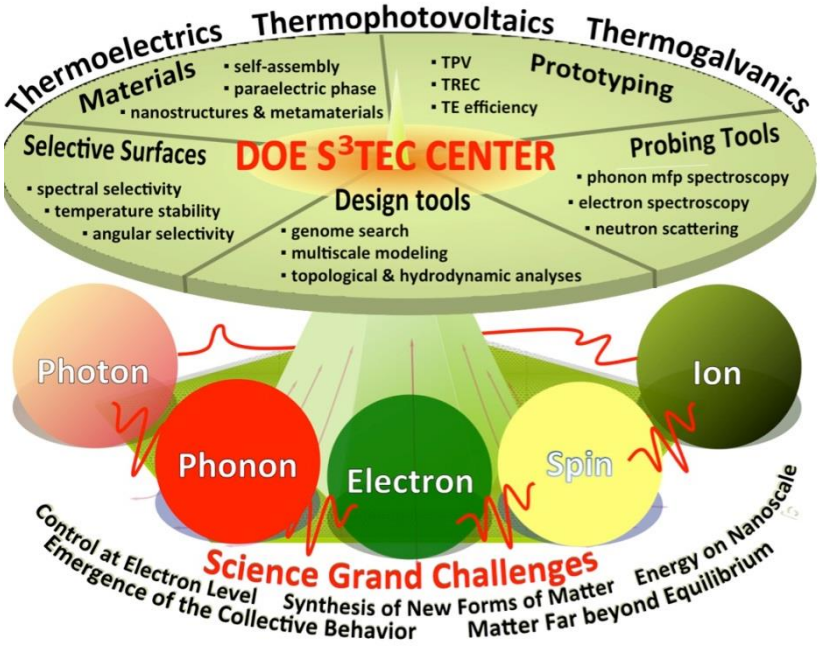


Figure 1. Vision of S^3TEC Center. The Center focuses on electron and spin, ion, phonon, and photon transport and interactions underpinning direct heat-to-electricity energy conversion based on thermoelectric, thermogalvanic, and thermophotovoltaic technologies. Addressing grand challenges yields new materials and methods for simulation and characterization.

The renewed S^3TEC Center not only builds on the progress made but also significantly expands its research horizons: harnessed energy sources include not only solar but also terrestrial heat; in addition to TE and TPV, thermogalvanics joined the list of pursued technologies through our proposed study on thermally regenerative electrochemical cycles (TREC); the fundamental energy carriers studied include not only electrons, phonons, and photons, but also ions and spin; the emphasis on computational material design and mesoscale simulation to guide material synthesis is increased; topological properties of electronic and photonic materials are explored for energy harvesting and conversion applications. Figure 1 illustrates the vision behind the S^3TEC center and the scope of research it encompasses.

TE, TREC, and TPV technologies have high potential for a transformative growth in our efforts to harness an almost endless energy supply from the sun and terrestrial heat sources. However, successful development of these technologies can be achieved only through fundamental breakthroughs in materials design and understanding of transport processes. While we know to a certain degree how to control photons, we know much less about how to control electrons and ions in this context, and very little about how to control phonons. Many fundamental questions and challenges lie ahead, and to address them, the S^3TEC Center strives to take our fundamental understanding to the logical next step: to designing materials and processes that can be scaled up, so that research can be applied to meet the energy challenges of our nation and the world.

The Center aims to address the DOE's grand challenges, connecting nanoscale materials to gigawatts electricity, by advancing the basic science underpinning direct energy conversion technologies, through discovering materials that meet the needs of applications in terms of performance, cost, and reliability. By studying TE, TG, and TPV technologies in one Center, great synergy is generated in basic science, technology, and applications. The Center advances and employs photon, neutron, and electron beams and first-principles simulation tools to enable the probing and understanding of the transport processes of the carriers and the prediction of their properties relevant for energy conversion.

This understanding will aid in the design and synthesis of materials to validate the theory and construct proof-of-principle prototypes demonstrating the potential to achieve high heat-to-electricity conversion efficiency. The S^3TEC Center builds on its established management structure, which continues to encourage and strengthen synergistic collaborations, nurture future leaders in energy technology, and engage the public through outreach activities.

Solid State Solar Thermal Energy Conversion Center (S^3TEC)	
Massachusetts Institute of Technology	Gang Chen (Director), Evelyn N. Wang (Associate Director), Mildred Dresselhaus, Marin Soljacic, Keith Nelson, Yang Shao-Horn, Caroline Ross, Nicolas Hadjiconstantinou, Alexie Kolpak, Liang Fu (Seed Fund)
University of Houston	Zhifeng F. Ren
Duke University	Olivier Delaire
University of Missouri	David J. Singh
Northwestern University	Jeffrey Snyder
Boston College	David Broido
Brookhaven National Laboratory	Yimei M. Zhu

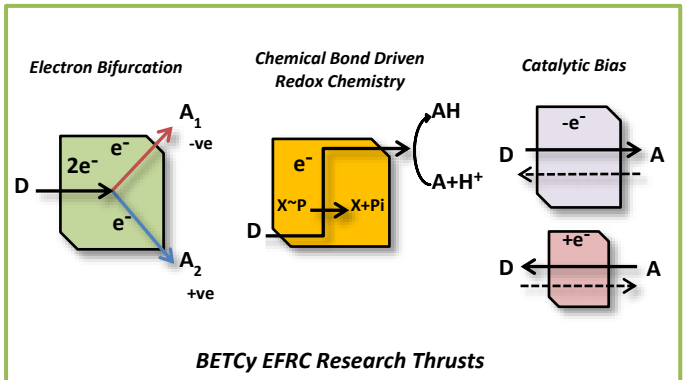
Contact: Prof. Gang Chen, Director, gchen2@mit.edu
617-253-3523, http://s3tec.mit.edu/

Center for Biological Electron Transfer and Catalysis (*BETCy*)
EFRC Director: John Peters
Lead Institution: Montana State University
Start Date: August 2014

Mission Statement*: To investigate electron bifurcation, electron-ion coupling, and redox catalysis in model enzymes to provide a detailed understanding of mechanisms of electron transfer reactions involved in the efficient conversion of electrochemical potential into chemical bond energy.*

The focus of the Biological Electron Transfer and Catalysis (*BETCy*) EFRC research is elucidating mechanisms of conversion of electrochemical potential into chemical bond energy and is organized into three integrated Thrusts.

- **Thrust 1** focuses on the mechanism of coupling exergonic and endergonic electron transfer reactions by electron bifurcation.
- **Thrust 2** investigates coupling chemical bond energy and electrochemical potential in electron transfer to achieve very low potential reductions.
- **Thrust 3** focuses on elucidating atomic level determinants of enzymatic redox properties and their relationship to catalytic bias.



BETCy EFRC Research Thrusts

We are developing a collective knowledge of metalloenzymes as models for redox reactions by applying physical science and computational tools to characterize biochemical reactions catalyzed by multi-subunit enzymes harboring arrays of iron-sulfur clusters and flavin cofactors. Understanding these mechanisms is central to overcoming the thermodynamic barriers that currently limit production of reduced products and fuels.

Biological systems have elegant strategies for converting electrochemical potential energy into chemical bond energy (e.g., C-H, H-H, and N-H) stored in reduced compounds that can serve as advanced biofuels. One significant limitation for the production of highly reduced compounds is that their production in natural and industrial processes relies on low oxidation-reduction potential chemicals as feedstocks. However, unique biochemical strategies exist to generate pools of reducing equivalents that can serve as a source of electrons for chemical bond formation from low oxidation-reduction potential feedstocks.

We are focusing on a newly discovered biochemical mechanism termed “electron bifurcation”, which upgrades electrochemical potential by effectively coupling endergonic and exergonic reactions in an overall thermodynamically favorable process. The underlying mechanistic details governing electron bifurcation are, however, still poorly understood and a more in-depth understanding of this phenomenon could lead to “game changing” and transformational advances in strategies to direct electron flow. These studies provide a blueprint for bio-inspired, multi-electron catalytic processes that can ultimately utilize electrons of varying reduction potentials to drive chemical reactions. We are also working to elucidate how biology uses a combination of chemical bond energy and electrochemical potential to accomplish

very difficult reduction of low potential reactions (e.g., CO_2 and N_2 reduction) using electron donors of modest reduction potentials.

The goal of the BETCy EFRC is to provide a fundamental understanding of mechanisms to overcome key thermodynamic barriers that limit the production of reduced products where energy is stored in the form of C-H, H-H, and N-H bonds. The three interrelated research Thrusts of the BETCy EFRC emphasize: mechanisms of electron bifurcation in driving low potential oxidation-reduction reactions. The research of the BETCy EFRC builds on recent seminal discoveries in biology and provides the basis for attacking key knowledge gaps and expanding the knowledge base that is essential for realizing the true potential of bioenergy and bio-inspired catalysis as prominent components of the global energy production portfolio. We have assembled a strong team of investigators with complementary research interests and technical skills to accomplish the proposed interdisciplinary tasks. The work is having a profound scientific impact on understanding and predicting matter and energy at the atomic level and in generating a blueprint for efficient control of electron flow into energy products and chemicals.

The work is directly in line with and addresses three of the five Basic Energy Sciences Advisory Committee (BESAC) Grand Challenges including: *1. Control of material processes at the level of electrons, 2. Design and perfect atom and energy efficient synthesis of revolutionary new forms of matter with tailored properties, 3. Characterize and control matter away, far away, from equilibrium* (which is the essence of electron bifurcation reactions). In addition, the proposed BETCy EFRC goals embrace the Basic Research Needs (BRNs) outlined in the BES Workshop Report on *Catalysis for Energy*, and makes strong connections with the *Hydrogen Economy* and *Solar Energy Utilization* BRNs.

The research plan of the *BETCy* EFRC is designed to exploit unique biochemical mechanisms that have yet to be explored substantively in the context of bioenergy, but that have the potential for innovative advancement. The successful outcome of this research will be a collection of fundamental principles that serve as a blueprint to enable the tailored re-design of biological systems and enzymes to control matter and energy at the level of electrons and molecules to provide the foundations to create new energy technologies.

Center for Biological Electron Transfer and Catalysis (BETCy)	
Montana State University	John W. Peters (Director), Brian Bothner, Eric Boyd, Ross Carlson
University of Georgia	Michael W.W. Adams (Associate Director of Research)
National Renewable Energy Laboratory	PinChing Maness (Associate Director of Project Management), Paul King
University of Washington	Caroline Harwood
Arizona State University	Anne Jones
Utah State University	Lance Seefeldt
University of Kentucky	Anne-Frances Miller
Duke University	David Beratan

Contact: John Peters, Director, john.peters@chemistry.montana.edu
(406) 994-7212, http://eu.montana.edu/betcy-efrc/

Center for Next Generation of Materials by Design (CNGMD): Incorporating Metastability
EFRC Director: William Tumas
Lead Institution: National Renewable Energy Laboratory
Start Date: August 2014

Mission Statement*: To dramatically transform the discovery of functional energy materials through multiple-property search, incorporation of metastable materials into predictive design, and the development of theory to guide materials synthesis.*

To realize the ***Next Generation of Materials by Design***, we will couple first-principles theory with state-of-the-art high throughput and directed synthesis and characterization including novel *in-situ* methods to understand and predict structure, properties, and phenomena at the molecular, nano, and meso scales. This EFRC is specifically designed to address several critical scientific gaps that must be overcome before computational materials design becomes a robust tool delivering new functional materials — namely 1) ***multiple-property design***, 2) ***accuracy and relevance***, 3) ***metastability***, and 4) ***synthesizability***. This approach will expand and accelerate the discovery of accessible materials for energy applications.

The Center for Next Generation of Materials by Design (CNGMD) EFRC aims to discover and synthesize novel functional materials including non-equilibrium structures in a predictive manner. Accordingly, the five goals of the CNGMD EFRC are:

- ***Goal 1: Design and discover new energy-relevant materials*** *with targeted functionalities by integrating theory, high-throughput computation, synthesis, and characterization.* This integrated approach to accelerating materials design incorporates both multi-property design and the inclusion of metastable materials.
- ***Goal 2: Develop foundational tools*** *for theory, synthesis, and characterization to enable the next generation of Materials by Design*, including theoretical methods for rapidly predicting atomic and electronic structure, novel *in-situ* characterization, and high-throughput synthesis and characterization techniques.
- ***Goal 3: Incorporate metastable materials*** *into Materials by Design and establish an understanding of metastability including composition, structure and formation energies for polymorphs, semiconductor alloys and defects.* We will specifically investigate four broad classes of metastability relevant to inorganic semiconductors for optoelectronic applications: polymorphism, semiconductor alloys, defects, and thermochemically metastable compounds (Fig. 1)**.**
- ***Goal 4: Develop theory-driven synthesis approaches to guide synthesis*** *of new materials, including metastable systems, by coupling theory and state-of-the-art in-situ characterization to probe materials growth pathways.* We seek to understand the thermodynamics of intermediate states (e.g., nucleation) as well as transient and local conditions (e.g., high chemical potentials of species established by decomposition of reactive precursors) to explain how the materials in Goal 3 can be achieved.
- ***Goal 5: Promote and disseminate*** *the Next Generation of Materials by Design to the broader materials science community*. This includes making our methodology and data accessible as well as organizing conference symposia and workshops.

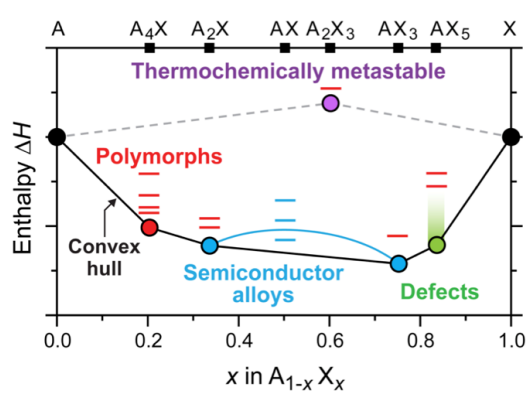


Fig. 1: Four classes of metastability being addressed by CNGMD.

Our materials focus is on semiconductors for solar energy conversion, solid-state lighting, power electronics and related technologies—all areas that need transformative materials. Our current work includes six research projects (P1-P6) as well as outreach activities and foundational tool development.

- **P1: Pnictide Search** integrates theory and experiment to discover new semiconducting nitrides, a relatively unexplored class of materials, most of which are inherently metastable. SnN, a new metastable binary nitride, has been realized.
- **P2: Polymorphs and Synthesizability** takes a multipronged approach combining theory and experiment to predict, synthesize and explore synthetic pathways to specific polymorphs. Initial focus is on Mn, V and Ti oxides as exemplary polymorphic materials. We have developed *Polymorph Sampler*, a new first-principles approach to predict polymorph stabilities and distributions.
- **P3: Chalcogenide Alloys** uses first principles calculations to predict alloy phase diagrams for realizing new functionality. New features have been found to emerge in heterostructural alloys compared to conventional isostructural alloys. This has been demonstrated in the SnCaS and MnZnO systems (Fig. 2).
- **P4: Defect Phase Diagrams** integrates theory and experiment to explore the nature and energetics of complex defects in creating functional materials. The effective electronic doping of wide-gap Ga_2O_3 has been achieved.
- **P5: Perovskite-Inspired Materials Search** identified defect tolerance and long carrier lifetime as the key features of the hybrid organic-inorganic halide perovskite photovoltaic absorbers. Based on the resultant design principles, nine new classes of potential materials have been identified and five new materials with desired properties have been demonstrated.
- **P6: Piezoelectric Materials Search**, a new project started in 2016, is developing Pb-free piezoelectric materials, including theoretically predicted but previously unsynthesized metastable materials. Two such materials have been realized.

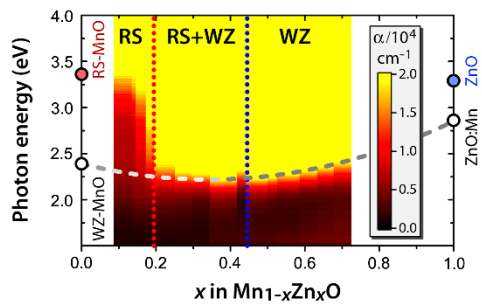


Fig. 2: Measured absorption coefficient α (contour plot) and calculated band gaps (dashed line) for Mn-Zn-O alloys.

Center for Next Generation of Materials by Design (CNGMD)	
National Renewable Energy Laboratory	William Tumas (Director) David Ginley (Chief Experimentalist) John Perkins (Program Integrator) Stephan Lany, Andriy Zakutayev
Lawrence Berkeley National Laboratory	Gerbrand Ceder (Chief Theorist), Kristin Perrson
Massachusetts Institute of Technology	Alexie Kolpak, Tonio Buonassisi
SLAC National Accelerator Laboratory	Michael Toney
Harvard University	Daniel Nocera, Roy Gordon
Oregon State University	Janet Tate
Colorado School of Mines	Vladan Stevanovic, Brian Gorman

Contact: William Tumas, EFRC Director, bill.tumas@nrel.gov
303-384-7955, www.cgnmd-efrc.org

Center for Bio-Inspired Energy Science (CBES)
EFRC Director: Samuel I. Stupp
Lead Institution: Northwestern University
Start Date: August 2009

Mission Statement*: To discover and develop bio-inspired systems that reveal new connections between energy and matter.*

The goal of the Center for Bio-inspired Energy Science (CBES) is to develop artificial materials and systems that take inspiration from biology to optimize the way we use energy and interconvert between different energy forms, for example converting chemical energy into mechanical energy the way muscles do in living organisms. Our team members have innovated in the areas of self-assembly, the interface of biology and materials science, as well as in theory and simulation. CBES research addresses the following two DOE grand challenges: "how do we characterize and control matter away-especially very far away-from equilibrium?" and "how can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?" Our work also addresses the DOE's basic research need for "new science for a secure and sustainable energy future." CBES is scientifically organized into three main thrusts with many inter-thrust connections, which will increase and strengthen throughout the existence of the Center. We facilitate strong inter-connectivity among all three groups, yielding outstanding scientific synergy for discovery and ideas.

In **Thrust 1** we focus on artificial materials that show functions that emulate the fundamental properties of cells, extracellular matrices, and tissues in the context of energy use and transduction. Our team has identified three primary bio-inspired research areas: artificial muscles, artificial organelles, and stimulus-driven adaptive materials. The work on **artificial muscles** is focused on systems that can interconvert between chemical and mechanical energy forms (as muscles do). The challenge of discovering the right strategies to transduce stored chemical energy into mechanical motion in materials requires not only synthetic innovation in soft matter but also the use of computational models to find structures in which small energy inputs result in large deformations and forces. In this work, we take advantage of the great computational and theoretical capabilities of the team and also of the enormous recent progress made in DNA nanotechnology to help us discover muscle-like structures in polymer-nucleic acid hybrid materials. Inspired by biological organelles that utilize feedback mechanisms to mediate chemical reactions, we develop **artificial organelles** that have the capacity to mediate efficiently synthetic reactions as cells do and in ways that chemical laboratories and chemical factories cannot at present. For this purpose, we conduct experiments with precisely positioned micro-particles mediating related chemical events with the goal to discover emergent principles for self-regulating reactions. Another interesting characteristic of biological matter is the ability to dynamically change shape in response to the environment. This characteristic is possibly most prominent in the changes undergone by cells during differentiation, proliferation, and migration, using energy inputs to achieve these functions. In the context of bio-inspiration we have defined this problem as the challenge of developing **adaptive materials** that respond to stimuli such as light and mechanical forces to mutate their structures and properties.

In **Thrust 2** we explore the bottom-up conversion of energy to motion in artificial nanometer to micrometer scale colloids that behave collectively far from equilibrium. Miniaturizing machines down to the nanoscale raises both fundamental questions and novel opportunities to perform tasks that mimic or improve upon biological machines. Unlike most synthetic machines, which rely on centralized engines, biological organisms convert energy into motion in a highly *distributed* fashion: macroscopic forces emerge from the coordinated actions of many chemically powered, molecular scale actuators (motor

proteins). Distributed energy conversion in biology offers several advantages that motivate the pursuit of much simplified *non-biological* colloidal machines, in which energy is harnessed at colloidal scales to produce emergent behaviors at the mesoscale and perform useful functions at the macroscale. Our work aims to significantly extend these capabilities to create **colloidal motors** capable of increasingly complex locomotive forms, to control motor activity remotely through external stimuli, to improve the efficiency of colloidal motors by many orders of magnitude, and to engineer switchable interactions among colloidal motors to guide their collective behaviors. By combining computer simulation, continuum modeling, and a suite of experimental systems spanning scales from nano- to macroscopic, the team aims to discover how the distributed activity of **ensembles of colloidal motors** produce emergent collective behaviors. Once again, cellular behavior inspires our design. Cells undergo dramatic changes in size and shape; they crawl or swim through diverse environments; they capture and transport external cargo; they grow, proliferate, and differentiate; they self-organize to form tissues and organs. Each of these remarkable capabilities relies on the coordinated action of many individual actuators distributed throughout the cell. With this inspiration, the CBES projects aim to create colloidal machines that mimic – in rudimentary form – the mechanical functions of living cells. These non-biological, **artificial cells** are composed of many colloidal motors within a flexible membrane through which chemical fuel is delivered. Through the collective motions of the confined motors, we envision microscale artificial cells capable of *controllable deformations*, *switchable mechanical properties*, and *autonomous locomotion*. Hierarchical assemblies of these "cells" produce macroscopic, non-equilibrium materials that harness distributed energy conversion and actuation to perform useful functions.

Another critical axis of energy management in biology is connected with modes of charge transport that are not known in artificial matter, such as long-range electron transfer in photosynthesis through media of low conductivity or the selective ionic fluxes across cell membranes that can convert chemical to electrical energy. Therefore in **Thrust 3** we focus sharply on bio-inspired energy and charge transport modes. We are particularly interested in solar energy conversion systems comprising low-dielectric active materials, in which the major obstacle to efficient energy conversion is a low yield of charge collection due to random, rather than directional, motion of electrons. We address this challenge by exploring, computationally and experimentally, the non-equilibrium phenomenon of **quantum ratcheting**. We are also investigating how to control selectivity and directionality of non-equilibrium ion fluxes by theoretically and experimentally designing nanoscale **bio-inspired ion pumps**.

Center for Bio-inspired Energy Science (CBES)	
Northwestern University	Samuel Stupp (Director), Chad Mirkin, Monica Olvera de la Cruz, Mark Ratner, George Schatz, Igal Szleifer, Emily Weiss
University of Pittsburgh	Anna Balazs
Pennsylvania State University	Kyle Bishop
New York University	Paul Chaikin
University of Michigan–Ann Arbor	Sharon Glotzer
Harvard University	George Whitesides

Contact: Samuel I. Stupp, Director, s-stupp@northwestern.edu
(847) 491-3002, http://cbes.northwestern.edu/

Argonne-Northwestern Solar Energy Research (ANSER) Center
EFRC Director: Michael R. Wasielewski
Lead Institution: Northwestern University
Start Date: August 2009

Mission Statement*: To revolutionize our understanding of molecules, materials, and methods necessary to create dramatically more efficient technologies for solar fuels and electricity production.*

The ANSER Center is fulfilling this mission by developing a fundamental understanding of solar energy conversion dynamics, by designing and synthesizing new nanoscale architectures with extraordinary functionality, and by linking basic solar energy conversion phenomena across time and space to create emergent energy conversion systems operating with exceptional performance. The ANSER Center addresses a common set of fundamental questions that must be answered to successfully utilize sunlight as a renewable energy source for fuels and electricity. By attacking the common questions intrinsic to solar fuels and electricity in the same research center, the ANSER Center provides opportunities for cross-cutting solutions not possible by addressing only fuels or electricity alone:

- How can multi-scale predictive theory and computational modeling lead to the design and discovery of novel organic, inorganic, and hybrid systems?
- How do molecular and materials structure and order determine the efficiency of light capture, charge separation, and long-range charge transport?
- What are the fundamental multi-scale temporal and spatial requirements for efficient charge transport across interfaces to deliver multiple redox equivalents to catalysts and electrodes?
- How can molecular and materials properties be tailored to exploit hierarchical assembly for solar fuels and electricity systems scalable from the nanoscale to the mesoscale?

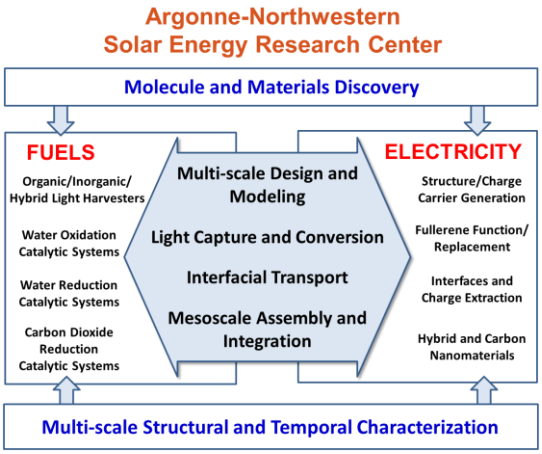


Fig. 1. The ANSER Center integrated research program is built on the strengths of molecule and materials discovery and multi-scale structural and temporal characterization.

ANSER Center strengths include molecule and materials discovery and high-resolution spatial and temporal analytical techniques and tools. Specialized X-ray facilities, such as the Advanced Photon Source at Argonne National Laboratory, provide atomic-scale structural information using state-of-the-art *in situ* X-ray absorption and scattering techniques. Ultrafast time-resolved absorption, emission, and vibrational spectroscopy along with time-resolved electron paramagnetic resonance (EPR) spectroscopy and appropriate computational simulation and modeling at ANSER Center laboratories provide detailed information on mechanisms and dynamics.

Subtask 1: Molecules, Materials, and Systems for Solar Fuels. Our greatest challenge is efficient fuel production at acceptable rates and driving forces. The ANSER Center is employing a hierarchical approach to understanding catalyst and photocatalyst function; thus, requiring a level of integration that cannot be achieved by any single research group. ANSER Center catalyst discovery is strongly hypothesis-driven, nicely complementing but not duplicating the approach of our collaborator, the DOE Joint Center for Artificial Photosynthesis (JCAP) Energy Innovation Hub. The ANSER Center emphasizes catalysts ranging

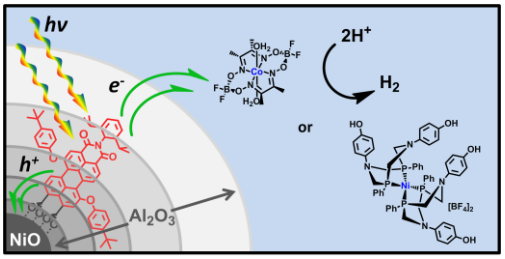


Fig. 2. Photocatalytic proton reduction by molecular catalysts in solution via electron transfer from a purpose-synthesized organic chromophore bound to a semiconductor surface.

from molecules, to clusters, to nanoparticles, to bulk materials that: a) are derived from plentiful elements, b) have promising compositions that are thermodynamically inaccessible as bulk (macroscopic) materials, and c) may enable access to new mechanistic pathways, thereby moving beyond perceived fundamental or practical limits on catalyst performance, including catalyst kinetics and overpotentials. Solar fuels research is exploring and exploiting new ideas about: a) organic/inorganic/hybrid light harvesters, b) water oxidation catalysis, c) water reduction catalysis (e.g. Figure 2), and d) carbon dioxide reduction catalysis.

Subtask 2: Molecules, Materials, and Systems for Solar Electricity. Photovoltaic cells fabricated from relatively simple, non-toxic, earth-abundant, mechanically flexible, and low-cost materials offer the prospect of efficient large-scale solar electricity production. Efficiencies have advanced dramatically in the past five years, driven by an ever-increasing, but by no means complete, understanding of the relevant chemistry, materials science, physics, and performance limits. A closely integrated, highly productive interplay of synthesis, characterization at multiple time and length scales, and theoretical analysis and prediction, led to a number of ANSER Center "firsts" in materials design, mechanistic understanding, and performance metrics. Following the same collaborative strategies, ANSER Center solar electricity research continues to explore and exploit new ideas about: a) perovskite-based hybrid solar cells (e.g. Figure 3), b) active layer polymer/small molecule structure-exciton dynamics, c) fullerene acceptor uniqueness and designed replacements, d) new interfacial materials and phenomena, and e) unconventional carbon nanomaterial and metal-organic active layers. ANSER Center research is testing ideas driven by theory to understand at a fundamental level how photovoltaic cell performance is affected by nanoscale/mesoscale architectural-electronic structure relationships in soft-matter and in hybrid soft-matter/hard-matter solar cells, photon capture, exciton creation and decay, exciton dissociation/quenching, and charge transport, electrode microstructure, doping, and surface chemistry. Understanding these phenomena feeds back directly to developing light capture and charge delivery strategies to power solar fuels catalysts as well.

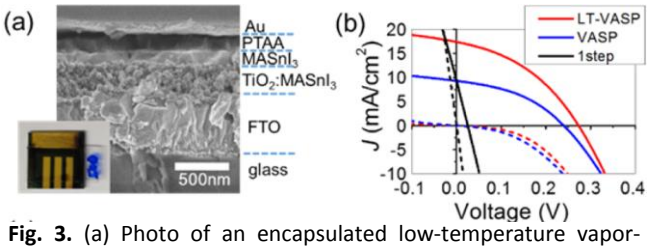


Fig. 3. (a) Photo of an encapsulated low-temperature vapor-assisted solution processed device and a cross-sectional scanning electron micrograph of a functional device and (b) current-voltage characteristics of lead-free perovskite devices.

Argonne-Northwestern Solar Energy Research (ANSER) Center	
Northwestern University	Michael Wasielewski (Director), Michael Bedzyk, Robert Chang, Mark Hersam, Joseph Hupp, Mercouri Kanatzidis, Tobin Marks, Mark Ratner, George Schatz, Samuel Stupp, Emily Weiss
Argonne National Laboratory	Lin Chen, Alex Martinson, Michael Pellin (Deputy Director), David Tiede
Yale University	Victor Batista, Gary Brudvig, Robert Crabtree, James Mayer
University of Chicago	Luping Yu
University of Illinois	Sharon Hammes-Schiffer

Contact: Michael R. Wasielewski, Director, m-wasielewski@northwestern.edu
(847) 467-1423, http://www.AnserCenter.org

Fluid Interface Reactions, Structures and Transport (FIRST)
EFRC Director: David J. Wesolowski
Lead Institution: Oak Ridge National Laboratory
Start Date: August 2009

Mission Statement*: To develop fundamental understanding and validated, predictive models of the unique nanoscale environment at fluid-solid interfaces that will enable transformative advances in electrical energy storage and electrocatalysis.*

Fluid-Solid Interfaces (FSIs) share a common characteristic – the juxtaposition of dense fluids (*e.g.* aqueous, polar organic, ionic liquid), with charged and reactive surfaces (*e.g.* electrodes, catalyst substrates). Transport of ions and molecular reactants through the fluid (typically nanoconfined) to the surface (typically nanotextured) results in charge storage in the so-called electrical double layer (EDL) and/or surface reactions that result in pseudocapacitance or electrocatalytic conversions. The unique structural and dynamic properties of the FSI emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes and substrates. The finite size, shape, directional bonding, charge distribution and polarizability of solvents and solutes are convoluted with their ability to reorient, 'un-mix', and react with one another and the substrate. The truncated surface exposes under-coordinated atoms, defects, dopants and active sites that drive interactions with the fluid by bond relaxation, charge redistribution, sorption and intercalation. The FIRST Center addresses fundamental gaps in our current understanding of FSIs to answer these questions of high importance to future energy technologies:

- *How does the interfacial region differ in structure, dynamics and reactivity from the bulk properties of the juxtaposed fluid and solid phases?*
- *How do altered interfacial fluid properties couple with complex substrate nanogeometries and functionalities to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?*
- *Can we achieve a quantitative, atomic-nanoscale understanding of FSI phenomena that will enable informed selection and design of fluid and solid components, chemistries and interfacial geometries to attain desired FSI functionality?*

Our goal is to unleash the ever-increasing power of computer simulations to illuminate the atomistic origins of FSI phenomena and guide the creation of new systems for energy storage and chemical conversion. However, because of current limitations in computational approaches, modeling efforts must be integrated

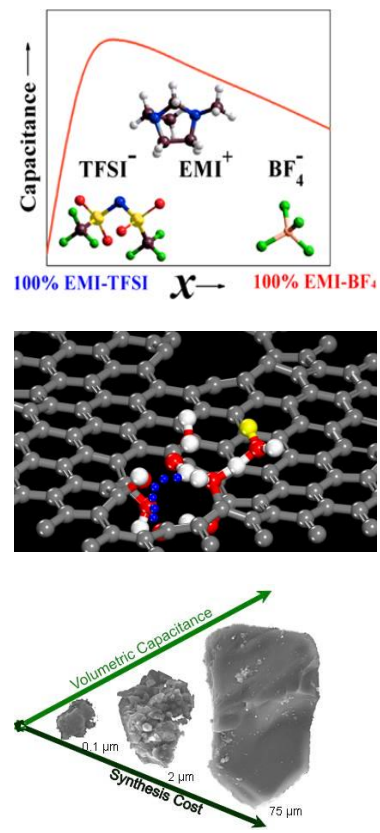


Figure 1 **Top**: Classical Density Functional Theory (CDFT)-predicted capacitance maximum for a mixed ionic liquid electrolyte (Lian, et al., *ACS Energy Lett.* **2016**, *1*, 21). **Middle**: Selective H^+ transport through OH-terminated defect in single layer graphene predicted using *ab initio* DFT and reactive classical MD simulations, and validated exerpimentally (Achtyl, et al., *Nature Comm.* **2015**, *6*, 6539); **Bottom**: Supercapacitor electrodes made from large particles of nanoporous carbide-derived carbon (CDC) enigmatically demonstrate better capacitance and rate handling than electrodes with small particles of the same material (Dyatkin, et al. *J. Power Sources* **2016** , *306*, 32).

with atomic/nanoscale and macroscopic experimental studies of real FSIs. We synthesize and probe very simple interfaces, such as single graphene sheets, atomically-flat single crystal surfaces, etc., in contact with simple electrolyte solutions, to validate computational models of such interfaces, and in turn to use these models to better interpret the experimental results. We then use insights and inferences from these models, applied to more complex interfaces such as slit pores, nanoscale surface curvature, multimodal porosity distributions, surface defects and functional groups, etc. to predict their interfacial structures and transport properties, which can then be tested in real functional interfaces such as supercapacitor electrodes and catalytic substrates.

A range of multiscale models will be needed in order to fully understand and predict the properties of complex interfaces. A FIRST goal is to determine how simple our interfacial models can be, and still capture the essential behavior of the interfaces of interest, such as our classical density functional theory models applied to supercapacitors (**Fig. 1**, top). Such coarser-grained models are generally far less computationally-intensive than first-principles approaches, enabling us to simulate larger systems over longer time scales than can be addressed using even the currently-available petaflop computers. Another foundational aspect of the FIRST Center is our ability to synthesize and characterize novel substrates (including various forms of carbon and transition metal carbonitrides) and electrolytes (including room temperature ionic liquids) with highly controlled properties and unique functionality (**Fig. 1**, middle). In order to probe the atomic/nanoscale properties of interfacial systems, we apply a sophisticated array of neutron and X-ray scattering methodologies (**Fig. 2)**, and we have developed entirely new analytical approaches, such as electrochemical strain microscopy (*e.g.* Come, et al., *Nano Energy* **2015**, *17*, 27).

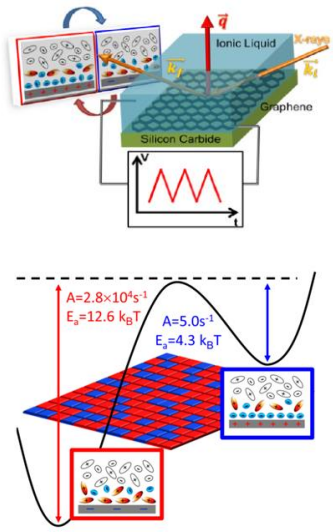


Figure 2. Top: schematic of Electrochemical X-ray reflectometry (XRR) cell developed at the Advanced Photon Source, Argonne National Lab.
Bottom: XRR reveals that ionic liquids at charged graphene surface exhibit coexisting cation- and anion-terminated patchy phases. (Uysal, et al., *J. Phys. Condens. Matt.* **2015**, *27*, 032101).

Fluid Interface Reactions, Structures and Transport (FIRST)	
Oak Ridge National Laboratory	David Wesolowski (Director), Sheng Dai (Thrust Leader), Nina Balke, Nancy Dudney, Paul Kent, Alexander Kolesnikov, Daniel Lutterman, Shannon Mahurin, Eugene Mamontov, David Mullins, Michael Naguib, Gernot Rother, Robert Sacci, Raymond Unocic, Huiyuan Zhu
Argonne National Laboratory	Paul Fenter
Drexel University	Yury Gogotsi (Cross-Cut Coordinator)
Penn State University	Adri van Duin
University of California, Davis	Alexandra Navrotsky
University of California, Riverside	De-en Jiang, Jianzhong Wu
University of Delaware	Joel Rosenthal
University of Minnesota	Matthew Neurock
Vanderbilt University	Peter Cummings (Thrust Leader)

Contact: David J. Wesolowski, Director, wesolowskid@ornl.gov
865-574-6903, http://web.ornl.gov/sci/first/

Energy Dissipation to Defect Evolution (EDDE)
EFRC Director: Yanwen Zhang
Lead Institution: Oak Ridge National Laboratory
Start Date: August 2014

Mission Statement*: To develop a fundamental understanding of energy dissipation mechanisms in tunable concentrated solid-solution alloys, and ultimately control defect evolution at the early stage in a radiation environment; and to yield new design principles and accelerate science-based material discovery of radiation–tolerant structural alloys for energy applications.*

Approaches for improving the performance of structural materials have been intensively investigated for many decades due to their importance in many applications. Solid solution strengthening, traditionally by alloying minor elements into pure metals, is one of the most widely used methods to achieve specific desirable properties, including radiation tolerance. While it has long been recognized that specific compositions in binary and some ternary alloys have enhanced radiation resistance, it remains unclear how the atomic structure and chemistry affect defect formation and damage evolution. This project directly addresses this knowledge gap in order to enable future-generation energy technologies.

The evolution of radiation–induced defect concentration in alloys can be described by three simplified competing processes (Fig. 1): defect production from collision cascades (1st term), vacancy–interstitial recombination within the diffusion volume during the cascade events (2nd term), and extended defect cluster formation from the accumulation of the cascade damage and absorption of point defects by nano-scale features (sinks) such as additional phases, interfaces, grain boundaries, and precipitates (3rd term). The first two terms are short-time processes up to a few picoseconds, while the 3rd term includes the processes over a much longer time scale. Localized atomic displacements from direct knock-on processes have long been considered to dominate the formation of defects. The work here examines the hypothesis that electronic excitations, heat flow, and the interaction between these may be critical, and that a fundamental understanding of roles of electrons, phonons, and magnons in energy dissipation is necessary for the developing new materials.

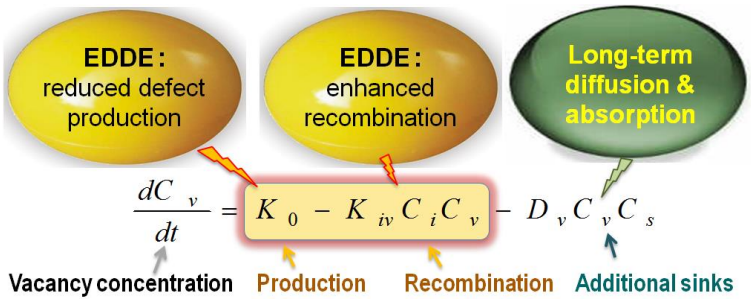


Fig. 1 Simplified terms showing competing processes controlling radiation–induced vacancy concentration. K_0 is the defect production rate; K_{iv} the recombination rate coefficient; and C_i, C_v, D_v and C_s the interstitial and vacancy concentration, the vacancy–sink coefficient, and the sink density; respectively. Similar equations hold for interstitials and other defects.

A new class of materials shows great promise, and may be synthesized with atomic-level control: Single–Phase Concentrated Solid Solution Alloys (SP–CSAs) containing two to five or more multiple principal elements. Two distinctive intrinsic properties are expected: (1) disordered local chemical environments that significantly enhance electron scattering that affects energy dissipation processes, and (2) unique site-to-site lattice distortions that lead to atomic level compressive or tensile stress and complex energy landscapes, which affect defect migration and impart exceptional mechanical properties. To realize the potential of these transformative alloys, we must understand the roles of all constituents in their

structural stability and their effects on energy dissipation mechanisms at the level of electrons and atoms. While most current research efforts seek to increase sink density (i.e., 3rd term), we focus on the reduction of damage accumulation by acting on the early stages of radiation effects (i.e., 1st and 2nd terms). In the EDDE Center, we progressively advance alloy complexity from elemental Ni to quinternary SP–CSAs (Fig. 2). The ***overarching goal*** of the EDDE EFRC is to develop a fundamental understanding of how the energy of radiation is dissipated, and ultimately to control defect dynamics and microstructural evolution in structural alloys. Specifically, we seek to understand and quantify the mechanisms of energy dissipation through electronic, vibrational, and magnetic excitation, and how these mechanisms are influenced by alloy complexity.

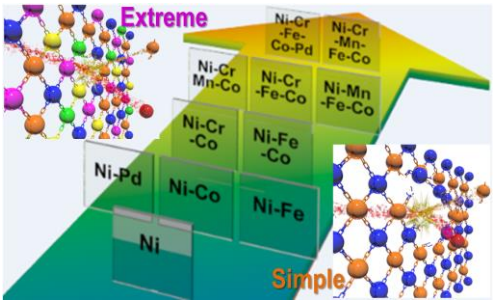


Fig. 2 Increasing complexity in *fcc* single–phase concentrated solid solution alloys.

Two thrusts are designed to test our ***hypothesis*** that modifying alloy complexity will enable us to control defect dynamics at the early stage of radiation damage, which will ultimately allow enhanced radiation tolerance at the later stage under extreme radiation conditions. In Thrust 1, *Energy Dissipation,* we will determine how input energy is partitioned and ultimately dissipated among the electrons and atoms and how these processes are modified by the compositional disorder. In Thrust 2, *Defect Evolution,* we will determine how energy partitioning and energy exchange between the atomic and electronic systems influence the formation, nature and time evolution of defects in irradiated materials, and how compositional complexity alters defect processes. We will also take advantage of recent theoretical and computational developments, many of which were made by members of our Center, to explore for the first time a comprehensive electronic and atomic description of an irradiated material very far from equilibrium. The combination of state-of-the-art experiments and multi-scale computational approaches will offer the possibility to develop critical knowledge needed for controlling and engineering the properties and performance of a material at the ultimate scale – that of atoms and electrons.

The EDDE Center engages a diverse mix of principal investigators and key personnel with complementary experience and skills. Most participants contribute to both Thrusts, thus maximizing synergies and coordination. Strong university involvement enhances educational outreach. Success of the EDDE Center will yield new design principles for radiation-tolerant structural alloys for applications in nuclear energy, and new defect engineering paradigms for much broader science and technology.

Energy Dissipation to Defect Evolution (EDDE)	
Oak Ridge National Laboratory	Yanwen Zhang (Director), Hongbin Bei, Yury N. Osetskiy, German D. Samolyuk, G. Malcolm Stocks, Fuxiang Zhang
Lawrence Livermore National Laboratory	Alfredo A. Correa
Virginia Tech	Magdalena Caro
University of Michigan	Lumin Wang
University of Tennessee	William J. Weber
University of Wisconsin-Madison	Ian M. Robertson
University of Wyoming	Dilpuneet (DP) S. Aidhy

Contact: Yanwen Zhang, Director, Zhangy1@ornl.gov
865-574-8518, http://edde.ornl.gov/

Center for Performance and Design of Nuclear Waste Forms and Containers (WastePD)
EFRC Director: Gerald Frankel
Lead Institution: The Ohio State University
Start Date: August 2016

Mission Statement*: To understand the fundamental mechanisms of waste form performance and apply that understanding to design new waste forms with improved performance.*

WastePD will develop innovative approaches and solutions through the synergistic interactions of individuals who are experts in the degradation behavior, modeling, and design of glasses, ceramics and metal alloys. WastePD is the first center ever created to address the degradation of this diverse group of materials in a comprehensive and coordinated manner. The science goals are grouped into three common topics: corrosion mechanisms via advanced characterization, environmental impacts, and materials design. The fundamental understanding of the degradation mechanisms of the waste forms and containers will allow DOE to develop new materials with improved properties, to prevent environmental contamination and to explore totally new disposal concepts. The waste forms of interest are tank waste transformed into glass, ceramic materials containing radionuclides, and metal canisters that protect the various waste forms.

The synergistic activities between the materials classes in the areas of experimental techniques, computational methodologies, and design approaches are a key component of WastePD. These synergistic activities will stimulate the achievement of new discoveries and reveal physical insights that would otherwise have been overlooked or not recognized. Sharing the understanding of the degradation mechanisms of glasses, ceramics, and metal alloys will lead to identification of commonalities and new materials design rules.

Glass Projects

DOE's Office of Environmental Management (EM) currently manages high-level wastes stored in underground tanks that have already begun to leak. This waste will be immobilized as borosilicate glass before disposal. Accurate prediction of the performance of a disposal facility therefore requires understanding and control of waste glass corrosion over geologic time-scales. This remains a major challenge because of the very slow reactions that occur between two unstructured media that are far from equilibrium (glass and gel). Additionally, a series of coupled processes occurring at the nexus between water being the solvent and water being a solute are responsible for the overall rate of glass water reactions. It is only possible to understand and control glass corrosion through closely coupled theory, simulation, and experimentation. Improved understanding of the composition/structure effects on these processes would allow for rational design of glass waste forms with predictable long-term performance. The research will be conducted in three projects as shown in Figure 1. The three glass projects are R*ate-Limiting Mechanism of Glass Corrosion*; *Composition and Environmental Effects on Glass Corrosion Rate*; and *Rational Glass Design*.

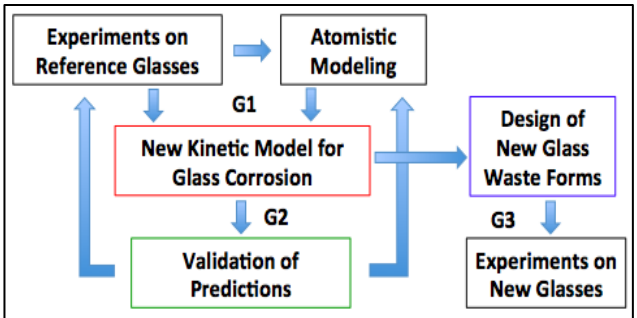


Fig. 1. Flow of glass projects.

Ceramics Projects

Not all of the DOE-EM wastes can be managed by bulk waste processing technology, as highly volatile components e.g., ^{129}I and $^{135}CsCl$ cannot be effectively incorporated into a borosilicate glass waste form. Single phase crystalline ceramics or multiphase assemblages have been investigated as alternative waste forms to borosilicate glass for high level waste (HLW), excess plutonium from dismantled nuclear weapons, and minor actinides separated during fuel reprocessing. The ceramics team targets fundamental understanding of radionuclide incorporation, confinement and transport behavior in bulk crystalline ceramics and across solid-solid and solid-liquid interfaces that can be closely linked with the ceramic waste form degradation and stability under near field conditions. The approach taken in this research is summarized in Figure 2. The two ceramics projects are: *Integrated Computation and Experimental Approach in Designing Waste Forms* and *Tailoring Performance and Degradation Mechanisms of Crystalline Waste Forms*.

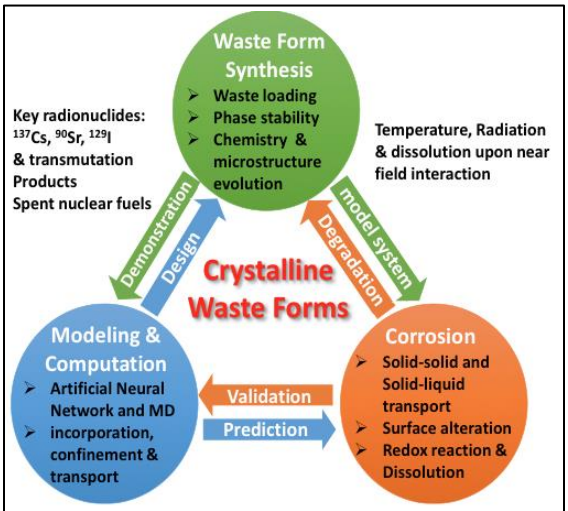


Fig. 2. Integrated approach for waste form design, evaluation and mechanistic understanding of crystalline ceramics

Metals Projects

Corrosion resistant alloys (CRAs) are used as materials of construction for canisters containing nuclear waste and have been proposed as waste forms for certain HLWs (e.g., pyrochemical metal wastes and isolated ^{99}Tc). CRAs are Fe- or Ni-based alloys that achieve their superior corrosion properties through the development of a thin protective surface oxide film, called a passive film. Unfortunately, CRAs are susceptible to rapid attack in the form of localized corrosion such as pitting, crevice corrosion, and stress corrosion cracking under conditions where the passive film breaks down locally. Improved CRAs could alter the nature and performance of any storage or disposal facility. The metals projects will study CRAs and use Integrated Computational Materials Engineering (ICME) to develop new and improved CRAs. This has never before been attempted. The two Metals projects are *Tailored Alloying in Corrosion Resistant Alloys (CRAs) and Development of New CRAs* and *Atmospheric Pitting and Cracking of Stainless Steels*.

Center for Performance and Design of Nuclear Waste Forms and Containers (WastePD)	
Ohio State University	Gerald Frankel (director), Jenifer Locke, Christopher Taylor, Wolfgang Windl
Pacific Northwest National Laboratory	Joseph Ryan, John Vienna
Rensselaer Polytechnic Institute	Jie Lian
Pennsylvania State University	Seong Kim
University of Virginia	John Scully
Center Energie Atomique, France	Stéphane Gin
Questek Innovations	Gregory Olson
Louisiana State University	Jianwei Wang
University of North Texas	Jincheng Du

Contact: Gerald Frankel, WastePD Director, frankel.10@osu.edu
(614) 688-4128, https://efrc.engineering.osu.edu

Center for Molecular Electrocatalysis (CME)
EFRC Director: Morris Bullock
Lead Institution: Pacific Northwest National Laboratory (PNNL)
Start Date: August 2009

Mission Statement*: To understand and design molecular electrocatalysts for conversions between electrical energy and chemical energy.*

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a critical role in future energy storage and energy delivery systems. Electrocatalytic processes involving multi-proton and multi-electron redox reactions are pervasive in energy science, and are critical for sustainable, carbon-neutral energy. The Center for Molecular Electrocatalysis addresses fundamental challenges in understanding how molecular electrocatalysts function, and uses this knowledge to rationally design new classes of molecular electrocatalysts for important energy storage and utilization reactions. Closely coupled experimental and theoretical studies include catalyst design and synthesis, mechanistic investigations, electrochemical and spectroscopic characterization, determination and control of thermochemical parameters for metal complexes, and evaluation of catalytic activity.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad (1)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad (2)$$

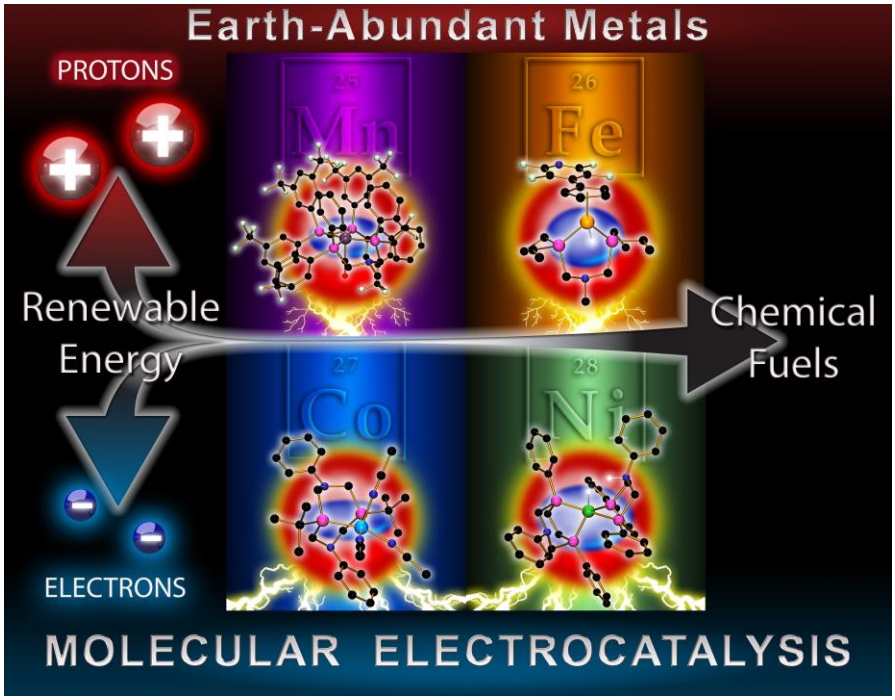
$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3 \qquad (3)$$

Electrocatalytic reactions studied range from two-proton, two-electron processes to six-proton, six-electron reactions. A unique approach in this Center is a focus on the delivery of protons to (or from) the active site of molecular catalysts.

The prevalence in energy science of reactions that require controlled movement of protons and electrons suggests an immense scope for the methods to precisely control the delivery and removal of protons.

The reduction of protons derived from water to form hydrogen is shown in eq. 1 (forward direction). The reverse process, the oxidation of H_2, is the reaction used in hydrogen fuel cells to convert the chemical energy in the H-H bond to electricity. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is critical for fuel cells, providing the reductive half-reaction to balance the oxidative half-reaction of H_2. The reduction of nitrogen to ammonia stores energy in N-H bonds, and use of NH_3 in fuel cells converts the chemical energy of the N-H bonds to electrical energy by oxidation of NH_3.

Molecular catalysts offer a remarkable degree of structural control – and therefore the precise probing of relationships between catalyst structure and activity – that are much more difficult for heterogeneous catalysts and enzymes. *We seek to further develop this knowledge of structure-activity relationships.* The two-, four-, and six-*electron* redox processes in eqs. 1-3 for H_2, O_2, and N_2, are also two-, four-, and six-*proton* processes. Facile and controlled movement of both electrons *and* protons from solution to substrates bound at the active metal site is essential for these electrocatalytic reactions. Proton transfers must be very carefully controlled to obtain optimal rates and efficiency of molecular electrocatalysts. The generality of proton transfer processes in most fuel generation and utilization reactions makes understanding these processes at a fundamental level of enormous importance.



Proton relays are functional groups that play a crucial role in the delivery of protons to (or from) the active site of catalysts. They have been shown to play an important role in hydrogenase enzymes, the oxygen-evolving complex, and other biological systems.

Primary goals of the Center for Molecular Electrocatalysis are to:

- Develop an understanding of the fundamental principles that form the basis for designing catalysts with unprecedented activity and efficiency, with a focus on relaying H^+ and e^-.
- Improve catalyst design by predicting and controlling thermodynamic and kinetic features of catalysts, including their first, second, and outer coordination spheres.
- Understand and control mesoscale solvent organization to improve proton delivery.
- Implement and evaluate the impact of coupling proton and electron transfers as a design principle for electrocatalysis, including the use of concerted electron-proton transfer and chemical mediators.
- Advance the computational methodology needed to design new catalysts, toward accelerated discovery by modern computational approaches

Center for Molecular Electrocatalysis (CME)	
Pacific Northwest National Laboratory	Morris Bullock (Director), Aaron Appel (Deputy Director), Simone Raugei, Michael Mock, Molly O'Hagan, Eric Wiedner
Yale University	James Mayer
University of Illinois	Sharon Hammes-Schiffer
University of Wisconsin-Madison	Shannon Stahl

Contact: Morris Bullock, Director, morris.bullock@pnnl.gov
509-372-6589, http://efrc.pnnl.gov

Interfacial Dynamics in Radioactive Environments and Materials (IDREAM)
EFRC Director: Sue Clark
Lead Institution: Pacific Northwest National Laboratory
Start Date: August 2016

Mission Statement*: To master molecular to mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (γ,β) radiation.*

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental science to support innovations in processing high-level radioactive wastes (HLW). IDREAM facilitates the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular to mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (γ,β) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task. IDREAM activities focus on aluminum (oxy)hydroxides, as they are a key principal component of bulk waste materials to which a variety of other metal ions and radionuclides partition.

Through novel and highly integrated experimental, computational, and theoretical approaches, we propose to develop the ability to predict and control the critical physicochemical phenomena currently preventing the application of more efficient and cost-effective tank waste removal and processing strategies. Our work will span from the molecular scale (e.g., speciation and dynamics of key solution species), to interfacial dynamics (e.g., dissolution and precipitation rates and mechanisms), to particle scale (e.g., particle interactions), and will involve realistic conditions of extreme alkalinity, low water activity, and ionizing radiation. IDREAM will provide a scientific foundation for emergent phenomena in high-level radioactive waste (HLW) processing, such as dissolution rates, aging phenomena, and slurry behavior including adhesion, friction, gelation, and rheology.

IDREAM is structured around four highly interactive Research Goals dealing specifically with chemically complex, low water activity environments and highly concentrated, alkaline aqueous solutions:

1) Understanding molecular speciation of metals and their chemical reactivity in the fluid phase
2) Understanding chemical dynamics at (oxy)hydroxide interfaces during nucleation, growth, and dissolution
3) Quantifying the role of surface chemistry in these extreme environments on (oxy)hydroxide particle interactions, aggregation, and coarsening
4) Quantifying the unique effects of ionizing radiation in these systems across spatial and temporal scales.

IDREAM has a central theme of aluminum chemistry because it is an important component of the bulk solids to which other metal ions and radionuclides are partitioned, and because of its commanding role in the future of HLW processing. This focus provides an integrating theme across the four Research Goals. The integrated disciplinary perspective of IDREAM will accelerate the transformative understanding of complex interfacial phenomena that are driven far from equilibrium. We will exploit a broad range of characterization tools and computational resources within our collaborating institutions and at DOE user facilities.

For Research Goal 1 we are focus on molecular speciation, and we strive to understand solvent dynamics, chemical reactivity, solute organization, and pre-nucleation species in highly alkaline systems of concentrated electrolytes. Research Goal 2 involves extending fluid phase dynamics to nucleation, particle growth, and interfacial reactivity in highly alkaline systems of concentrated electrolytes. Particle interactions and quantifying the chemical and physical phenomena leading to hierarchical microstructures of aggregates and other response dynamics that couple across scales to create emergent properties of heterogeneous systems are the focus for Research Goal 3. Research Goal 4 is focused on the influence of radiation in the systems studied in Research Goals 1-3. Here, we are quantifying the role of γ and β radiation in driving interfacial reactivity far from equilibrium.

By better understanding chemical interactions across scales of time and space, we can explain poorly understood macroscale phenomena, such as waste stream rheology, slurry agglomeration, and control of precipitation. This will provide the foundation for improving mixing systems, preventing pipe clogging and membrane fouling, and enable design of new, robust waste treatment systems. The knowledge gained in IDREAM will be broadly applicable to other complex heterogeneous processing problems related to materials and energy production. We will draw from experiences in the well-established industrialized Bayer process for production of aluminum. The impact of IDREAM also extends to many other complex heterogeneous interfacial problems, such as predicting subsurface colloid transport, designing coal slurry processing, and developing suspension-based biomass processing.

Interfacial Dynamics in Radioactive Environments and Materials (IDREAM)	
Pacific Northwest National Laboratory	Sue Clark (Director), Carolyn Pearce, Kevin Rosso, Jaehun Chun, Greg Kimmel, Greg Schenter, Sebastien Kerisit, Jim De Yoreo, Nigel Browning
Washington State University	Aurora Clark, (Deputy Director), Andy Felmy
University of Washington	Xiaosong Li
Oak Ridge National Laboratory	David Wesolowski, Andrew Stack, Katherine Page
Georgia Institute of Technology	Thomas Orlando
Notre Dame Radiation Laboratory	Jay Laverne

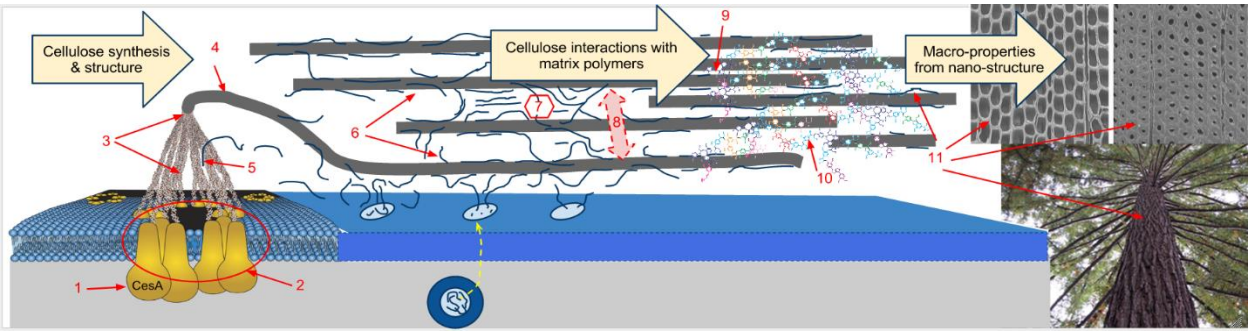
Contact: Sue Clark, IDREAM Director, sue.clark@pnnl.gov
509-372-6180

Center for Lignocellulose Structure and Formation (CLSF)
EFRC Director: Daniel J. Cosgrove
Lead Institution: Pennsylvania State University
Start Date: August 2009

Mission Statement*: To develop a nano- to meso-scale understanding of plant cell walls, the main structural material in plants, and the mechanisms of their assembly, forming the foundation for significant advances in sustainable energy and novel biomaterials.*

Cellulosic biomass (lignocellulose) holds great promise as a large-scale, renewable and sustainable source of liquid biofuels for transportation, if we could overcome technical obstacles stemming from its complex, hierarchical structure. Despite its huge economic importance, many aspects of lignocellulose structure and formation remain shrouded in mystery. For instance, little is known of the details of how the cellulose-synthesizing nano-machine at the cell surface links simple sugar molecules into long strands and extrudes them at the cell surface in such a way that they make a strong, insoluble and highly inert crystalline fibril. Likewise, the processes by which simple polymers are transformed into a strong and recalcitrant biomaterial are not well understood.

CLSF goals are to develop a detailed nano- to meso-scale understanding of plant cell wall structure and its mechanism of assembly, from the molecular mysteries of how glucose is assembled by cellulose synthase complexes to form cellulose microfibrils to the orderly, hierarchical interaction of cellulose with other components to form cell walls with diverse properties. The diagram below sketches some of the key points for lignocellulose formation, starting with cellulose synthesis by cellulose synthases (CESA) organized into a protein complex embedded in the plasma membrane (left, points 1-2), followed by cellulose crystallization and interactions with hemicelluloses to form a cohesive wall (points 3-8) and then changes that accompany lignin polymerization within the wall (points 9-11).



New understanding of these processes will form the scientific foundation for designing rational, science-based pretreatments to deconstruct cell walls and for using genetic techniques to coax plants into making modified walls for significant advances in sustainable energy and novel materials. It will also yield insights into biomimetic ways to transform simple molecules into complex polymeric materials with diverse physical and chemical properties.

CLSF research is organized around two themes concerned with the process of cellulose synthesis and the rules of assembly of cell wall components to make a cell wall with specific physical properties.

CLSF Theme 1 probes the mechanism of cellulose microfibril (CMF) formation. Specific objectives include: (1.1) Determination of the structure and in-vitro activity of plant cellulose synthase (CESA) by biochemical means, X-ray crystallography and electron microscopy, as well as by computational modeling of the dynamics of glucan synthesis by a CESA protein. (1.2) Assessing the roles of parts of the CESA protein for cellulose synthesis by genetic modification and analysis of CESA activity and cell wall phenotypes. (1.3) Analysis of the contributions of CESA isoform to the activity of the Cellulose Synthesizing Complex (CSC) and properties of the microfibril and macrofibril through microscopic and genetic experiments. (1.4) In-depth characterization of the plant CSC by isolating an active CSC, modeling CMF formation in silico, and identifying proteins that interact with CSCs that synthesize cellulose in secondary cell walls. (1.5) Reconstitution of a functional CSC from purified plant components by assembling the essential components of the plant CSC.

CLSF Theme 2 investigates the nano- and meso-scale structure and assembly of cell walls and the basis for their important physical and biological properties. Research objectives include: (2.1-2.2) Analysis of mesoscale wall architecture and dynamics by Atomic Force Microscopy (AFM), small-angle neutron scattering, and solid-state Nuclear Magnetic Resonance (ssNMR) in combination with enzymatic and genetic modifications of the wall. (2.3) Testing of the current model of the grass cell wall using enzymatic, biomechanical and physical approaches. (2.4) Testing how matrix polymer delivery relates to cellulose biosynthesis and order using click-labeling of matrix polysaccharides combined with analysis by AFM and transmission electron microscopy. (2.5) Analysis of the mobility of water, polysaccharides and proteins by neutron scattering and ssNMR to assess influence of wall components and wall charge on wall dynamics. (2.6-2.7) Incorporation of new as well as existing data into computational models of primary and secondary cell wall architecture and material properties. (2.8) Analysis of the physical effects of lignin polymerization in cell wall explants and analogs, including mobility of water and polysaccharides. (2.9) Development and use of sum frequency generation (SFG) spectroscopy (a) to analyze meso-scale organization of cellulose in single cell walls and (b) to refine the interpretation of SFG spectra.

Center for Lignocellulose Structure and Formation (CLSF)	
Penn State University	Daniel J. Cosgrove (Director), Charles Anderson, Ying Gu, Seong Han Kim, Manish Kumar, Janna Maranas, Karl Mueller, B. Tracy Nixon, Ming Tien
North Carolina State University	Candace Haigler, Yaroslava Yingling
Massachusetts Institute of Technology	Mei Hong
Oak Ridge National Laboratory	Hugh O'Neill
Stony Brook University	Chang-Jun Liu
University of Rhode Island	Alison Roberts
University of Texas El Paso	James D. Kubicki
University of Virginia	Jochen Zimmer

Contact: Daniel J. Cosgrove, Director, dcosgrove@psu.edu
(814) 863-3892, www.lignocellulose.org

Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio)
EFRC Director: Maureen McCann
Lead Institution: Purdue University
Start Date: August 2009

Mission Statement*: To master the ability to reconfigure all partially reduced carbon from plant cell walls into desired molecules.*

New capabilities to predict, design and control the chemistries of carbon could enable the transition from fossil-based to sustainable transportation fuels. Lignocellulosic biomass, a renewable and carbon-neutral resource, has the potential to displace an estimated annual equivalent of three billion barrels of oil in the U.S. alone. However, biomass has only one-third the energy density of crude oil and lacks petroleum's versatility as a feedstock for fuels and chemicals. These limitations keep biomass conversion below the efficiency level needed for strategic impact while the scientific challenge of routing carbon from one molecular context to another remains unmet.

The polysaccharides and lignins of the plant cell wall form a complex, cross-linked polymeric structure of substantial physical and chemical resilience that impedes access of catalysts to targeted chemical bonds. Its complexity results in heterogeneous product streams after catalytic or pyrolytic processing. Cross-links among plant cell wall biopolymers generate nanoscale architectures and distinct mesoscale domains that have dramatically different properties than those observed in mixtures of biopolymers. C3Bio research demonstrated that the disparity between theoretical and actual yields of liquid hydrocarbons and high-value chemicals is a consequence of this structural complexity. C3Bio now develops critical systems-level understanding of how biomass structural complexity at molecular, nanoscale, and mesoscale levels impacts the yields and selectivities of desired reaction products from catalytic and pyrolytic transformations. We will establish the fundamental science required to modulate cell wall complexity and catalytically transform intact biomass in order to gain unprecedented control of effective routing of carbon: we will specify both the structures within, and the reaction products from, lignocellulosic biomass.

Goal 1: Develop Catalytic and Pyrolytic Processes Specifically Designed for the Structural Complexity of Biomass. We investigate the kinetics and mechanisms of catalytic and pyrolytic pathways to advance applicability and selectivity in intact biomass conversion and use native and synthetic biopolymers and biomass genetic variants to define modified substrate performance in conversion pathways. Goal 1 impacts include lignin evolving from a material used primarily as biorefinery process fuel to a material with utility and value equal to that of biorefinery carbohydrates. We will gain ability to deliver intermediate products from biomass polysaccharides in high yields and with carbon atom conservation for upgrading to drop-in liquid fuels. Pyrolysis will become a feasible technology to make simplified bio-oils for HDO catalysis.

Goal 2: Redesign the Structure of Biomass for Carbon- and Energy-efficient Catalytic and Pyrolytic Transformations*.* C3Bio data on biomass performance in catalytic conversion provide new targets for the genetic engineering of tailored biomass, push the state-of-the-art of meso-scale and multi-scale modeling, and allow for greater predictability and understanding of properties of molecular architectures. At the mesoscale, we modulate localized carbon density, cell-cell adhesion, and target modifications to specific cell types. Multi-scale modeling will accelerate identification of the most chemically labile and stable linkages. Goal 2 impacts are new understanding to use trait stacking to increase the intrinsic carbon density of the biomass and also brittleness at the time of comminution to produce optimized biomass. A

codesign approach will maximize yield and selectivity of reaction products by modifying the substrates *in planta* and creating novel catalyst delivery systems.

Goal 3: Deliver Innovative Pathways for Targeted Product Portfolios from Tailored Biomass. Post-catalytic residues provide modified substrates and architectures for subsequent transformations. We apply our imaging and analytical toolkits to identify the control points and deliver legacy scientific understandings of how chemical reaction kinetics and biomass properties at the nano-scale (porosity, surface chemistry) and meso-scale (particle size and geometry) affect product formation rates and product profiles. We aim to enable advanced catalyst, reactor, and biomass design beyond "no carbon left behind" to achieve unprecedented control over the routing of carbon from biomass into fuels and chemicals – "a place for every carbon and every carbon in its place".

Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio)	
Purdue University	Maureen McCann (Director), Nathan Mosier (Associate Director), Rakesh Agrawal, Nicholas Carpita, Clint Chapple, Nicholas Delgass, Hilkka Kenttamaa, Rick Meilan, Fabio Ribeiro
National Renewable Energy Laboratory	Gregg Beckham, Michael Crowley, Bryon Donohoe, Michael Himmel, Melvin Tucker
University of California, Santa Barbara	Mahdi Abu-Omar (Associate Director)
University of Tennessee	Joseph Bozell
Northeastern University	Lee Makowski

Contact: Maureen McCann, Director, mmccann@purdue.edu
765-496-9640, http://www.purdue.edu/discoverypark/c3bio/

Center for Mesoscale Transport Properties (m2m)
EFRC Director: Esther Takeuchi
Lead Institution: Stony Brook University
Start Date: August 2014

Mission Statement*: To understand and provide control of transport properties in complex battery systems with respect to multiple length scales, from molecular to mesoscale (m2m); to minimize heat and maximize work of electrical energy storage devices.*

At its essence, energy is the sum of heat and work: $\Delta E = q + w$. As such, the ultimate goal for any energy storage system is to maximize useful work (w) and minimize the generation of waste heat (q). During the operation of an energy storage system, ions and electrons are transported over multiple size domains where the sum of these processes leads to complex physics. Resistance evolves over time due to phase changes in the solids and changes in the composition and structure of the interfaces. These complicating factors must be considered to derive the full panoply of information needed for rational design and predictive modeling of materials useful in energy storage systems. While inefficiency can be approached at the macro level, emphasizing bulk parameters and bulk methods cannot fully interrogate or address the inherent heterogeneity of ion and electron flux contributing to the local resistance within an electrode and at the interfaces. In order to develop the capability to predict and ultimately control energy storage systems, these inefficiencies must be understood not just as a bulk property (heat), but rather as localized resistance at the molecular to mesoscale (*m2m*) levels.

The goal of the *m2m* EFRC is to enable deliberate design of materials and components to achieve higher performing, longer life, and safer energy storage systems through acquisition of new fundamental knowledge about ion and electron transport and electron transfer properties of energy relevant materials, over multiple length scales, across interfaces and over time. The expected research outcomes are that the Center will provide the conceptual approaches to predict materials properties, processing outcomes, and functional characteristics which determine conduction and electron transfer properties, including the complexities of interfaces and time. The information gained will enable design of materials and systems to bridge the gap between theoretical energy content and functional energy delivery.

The Center will frame the key scientific investigations along three Scientific Inquiry Areas (SIA) that pose the following questions:

1) What are the *fundamental limits* of ion and electron transport and electron transfer over multiple length scales?

This question will be addressed by investigating transport and transfer phenomena for redox active moieties with several configurations. The roles of structure, crystallite size and particle size will be considered.

2) How do the phenomena change across *multiple domains* including interfaces? Which systems level interactions are synergistic, independent, or antagonistic?

The influence of physical properties, surface functionalization, and process on the transfer and transport properties and the function of composite electrodes will be explored.

3) How do the transport phenomena evolve *over time* in systems not at equilibrium?

The effect of extended cycling on energy related solids will be studied to determine the effect of time.

The ***m2m*** Center will achieve the goals via:

1) integration of researchers in materials, characterization, theory and electrochemical systems interrogation.
2) use and development of microscopic and nanoscopic science based tools to provide characterization insights, highlighted in Figure 1.
3) synthetically tunable model redox active materials and electrolytes which will be shared among center members to facilitate interaction and data interpretation.
4) frequent communication and assessment.

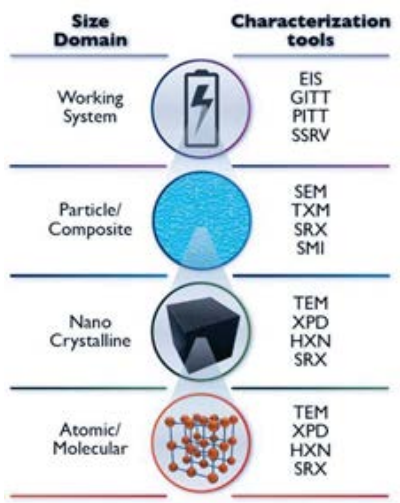


Figure 1. Characterization tools across multiple size domains

The Center will access and utilize five notable facilities: the Advanced Energy Research and Technology Center (AERTC) and CEWIT at Stony Brook University, and the Interdisciplinary Science Building (ISB) including a 1200 sq ft dry room, National Synchrotron Light Source II (NSLS-II), and Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory. AERTC will be the home base of the Center, providing access to a suite of new analytical instrumentation. CEWIT (Center of Excellence for Wireless Information Technology) will act as the data storage site for the Center.

Center for Mesoscale Transport Properties (*m2m*)	
Stony Brook University	Esther Takeuchi (Director), Amy Marschilok (Center Operations Officer), Kenneth Takeuchi, Stanislaus Wong, Maria Fernandez-Serra
Brookhaven National Laboratory	Hong Gan, Mark Hybertsen, Ping Liu, Eric Stach, Feng Wang, Jun Wang, Yimei Zhu
Georgia Institute of Technology	Elsa Reichmanis
University of North Carolina	Joseph DeSimone, Chris Luft
University of California, Berkeley	Nitash Balsara
Oak Ridge National Laboratory	Nancy Dudney
Columbia University	Alan West
Rensselaer Polytechnic Institute	Robert Hull
University of Texas at Austin	Guihua Yu

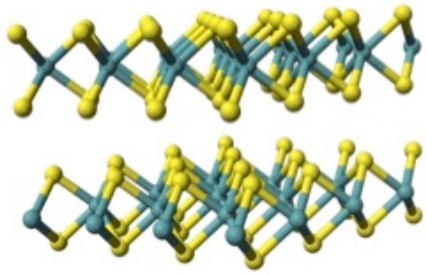
Contact: Esther Takeuchi, Director, esther.takeuchi@stonybrook.edu
631-216-7414, http://www.stonybrook.edu/m2m/

Center for the Computational Design of Functional Layered Materials (CCDM)
EFRC Director: John P. Perdew
Lead Institution: Temple University
Start Date: August 2014

***Mission Statement**: To develop, apply and validate methods to calculate the electronic structure of layered and two-dimensional materials that have the potential for clean energy technologies.*

***Research Plan**:* While these electronic structure methods can be useful for the design of many new materials, we focus on layered materials. We aim to predict how their properties are affected by composition, structure, interfaces, defects, and strain, and to design such materials to catalyze the evolution of hydrogen, a clean fuel, by solar-driven splitting of water. Validation and motivation are by experimental synthesis and characterization.

Background: New or modified materials with desired functionalities play an essential role in the development of clean-energy technologies, such as solar cells, batteries, and catalysts to generate hydrogen fuel by water-splitting. Because there are so many possible materials, it is impossible to grow and test them all in the laboratory. Computational design of materials with desired properties, based on first-principles theory and modeling, is a practical alternative. (The figure shows the structure of MX_2 layered materials).



Layered materials are typically composed of planar sheets, with strong bonds between the atoms within a layer and weak bonds between the layers. A collection of many layers is a three-dimensional (3D) material, while one or a few layers make a 2D material. Variation of properties with dimensionality is an appealing feature of these materials. The 2D materials can be grown on a substrate, or exfoliated from the 3D materials. Extraneous atoms can bind at the surface, or take up residence between the layers. The surfaces of many materials are contaminated by contact with air. The layered materials interact only weakly with the molecules in air, but can be modified by controlled exposure to free atoms.

Some layered materials have no fundamental energy gap. Graphene (unsupported 2D carbon) is a celebrated example. But interest for applications has shifted to “beyond-graphene” 2D semiconductors, such as boron nitride (BN) or molybdenum disulfide (MoS_2), and to heterostructures made by stacking different 2D crystals. Other transition-metal dichalcogenides (TMD’s MX_2, as pictured above), such as WS_2, WSe_2, and $MoSe_2$, are also of interest, as are layered oxides.

Layered 2D and 3D materials display many potentially useful properties. The direct energy gap in 2D MoS_2, which can be tuned by material modification, opens up the possibility of flexible optoelectronic or photovoltaic applications. Photo-excited electrons and holes can be spontaneously separated in a 2D heterostructure. A single layer of the 1T polytype of MoS_2 can catalyze the photo-induced splitting of water. Small ions can intercalate between the layers of a material, as in a lithium battery.

CCDM is organized into three thrusts and two cross-cutting fora:

- **Thrust 1. Theory.** *Density functional and correlated-wavefunction methods development*. A strong component of fundamental methods development and testing is a unique contribution of our Center.
- **Thrust 2. Computation and Modeling.** A. *First-principles computation and design of layered materials*. B. *Multi-scale modeling with first-principles input for extended defects in layered materials*.
- **Thrust 3. Synthesis and Characterization.** A. *Growth and characterization of layered materials*. B. *Catalysis and water splitting in layered materials*.
- **Cross-cutting Forum A.** *Properties of layered and 2D materials.*
- **Cross-cutting Forum B.** *Applications of layered and 2D materials.*

Some major achievements of the first two years: Accurate but efficient density functionals including van der Waals interaction have been developed and extensively tested. Also higher-level methods for strong correlation, including robust coupled-cluster and particle-particle random phase approximation.

Bending a 2D material has been computationally predicted to have major effects on electronic structure and thus on the electrical conductivity and catalytic properties. Some 2D materials have been predicted to be topological insulators. Multi-scale and continuum models have been developed to describe extended defects, growth and phase transformations.

Chemical vapor deposition techniques have been developed to grow uniform MoS_2 films or highly-ordered islands. A charge-density wave has been observed in few-layer $TiSe_2$ by TEM. The composition and crystallinity of MoS_2 can be engineered for catalytic performance. Joint computational/experimental studies have shown that intercalation of Cu atoms and Ni ions can transform the inexpensive layered material birnessite from an inefficient water oxidation catalyst into a very active one. A new catalyst for the oxidation step of water-splitting, $CoTe_2$, has been prepared.

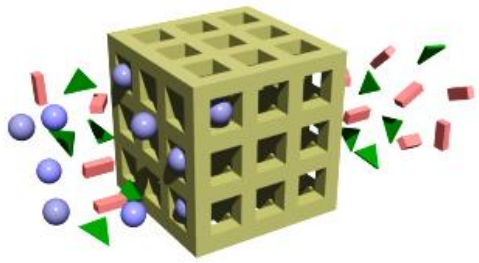
Center for the Computational Design of Functional Layered Materials (CCDM)	
Temple University	John P. Perdew (Director), Michael L. Klein, Xiaoxing Xi, Eric Borguet, Maria Iavarone, Daniel R. Strongin, Michael J. Zdilla, Xifan Wu, Adrienn Ruzsinszky. Qimin Yan
Rice University	Gustavo E. Scuseria
Duke University	Weitao Yang
Northeastern University	Arun Bansil
University of Pennsylvania	David J. Srolovitz
Princeton University	Mikko Haataja
Drexel University	Goran Karapetrov
North Carolina State University	Linyou Cao
Brookhaven National Laboratory	Yimei Zhu
University of Texas, El Paso	Jianwei Sun

Contact: John P. Perdew, Director, perdew@temple.edu
(215) 204-1407, http://efrc.cst.temple.edu

Center for Gas Separations Relevant to Clean Energy Technologies (CGS)
EFRC Director: Jeffrey R. Long
Lead Institution: University of California, Berkeley
Start Date: August 2009

Mission Statement*: To develop new materials and membranes that enable energy-efficient separation of gas mixtures, as required in the clean use of fossil fuels and in reducing emissions from industry. Particular emphasis is placed on separations that reduce CO_2 emissions from power plants and energy-intensive gas separations in industry and agriculture.*

Separation processes are estimated to be responsible for 10-15% of our total energy consumption. Given the expected increase in global population and the possibility of large-scale carbon capture and sequestration, this percentage is anticipated to increase significantly. Reducing the total energy costs of separations would be a major contribution towards lowering our overall energy useage. The aim of the Center for Gas Separations (CGS) is to develop new strategies and materials that enable energy-efficient gas separations, based on molecule-specific chemical interactions, together with a fundamental understanding of the properties and performance of the materials.



The challenge is to remove the fundamental scientific barriers that currently prohibit the efficient separation of gases essential to the development of clean energy technologies. In gas separations these challenges are significant. The differences between the relevant gas molecules are small and therefore we need to use the type of molecular control that is offered by nanoscience and synthetic chemistry to tailor materials that have exactly the right adsorption and diffusion selectivity to enable an economic separation process.

The center brings together personnel with expertise in the following areas of emphasis:

- *Materials Synthesis*: The synthesis of new gas-permeable materials with control over the molecular functionalities to preferentially adsorb gas molecules is essential. Our focus here will be on: (i) generating novel metal-organic frameworks exhibiting molecule-specific chemical interactions and (ii) new membrane constructs incorporating these materials.
- *Materials Characterization*: Detailed atomic-level structural characterization of the new materials will be necessary both before and after exposure to gas samples in order to probe hypotheses on interaction mechanisms. In addition, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding will be needed to demonstrate efficacy and test computational models.
- *Computational Separations*: A strong computational component to the research will be essential for understanding the chemical interactions at a molecular level, as well as for guiding the synthetic efforts toward materials exhibiting high specificity and tunable interaction energies.

We aim to develop fundamental new means of synthesizing materials with tailored molecular interactions, while generating new options for energy-related gas separations, including the separation of CO_2 from power plant flue streams, the separation of CO_2 from natural gas deposits, the separation of oxygen from air, and the separation of various industrially relevant hydrocarbon mixtures.

Center for Gas Separations Relevant to Clean Energy Technologies (CGS)	
University of California, Berkeley	Jeffrey Long (Director), Jeffrey Neaton, Jeffrey Reimer, Berend Smit (Deputy Director), Ting Xu, Omar Yaghi
Lawrence Berkeley National Laboratory	Brett Helms, Jeffrey Kortright, Maciej Haranczyk, David Prendergast, Simon Teat, Steve Whitelam
Texas A&M	Hong-Cai Zhou
University of Minnesota	Laura Gagliardi, Michael Tsapatsis
National Energy Technology Laboratory	David Hopkinson
National Institute of Standards and Technology	Craig Brown
École Polytechnique Fédérale de Lausanne	Wendy Queen

Contact: Hiroyasu Furukawa, Managing Director, furukawa@berkeley.edu
510-643-3832, http://www.cchem.berkeley.edu/co2efrc/

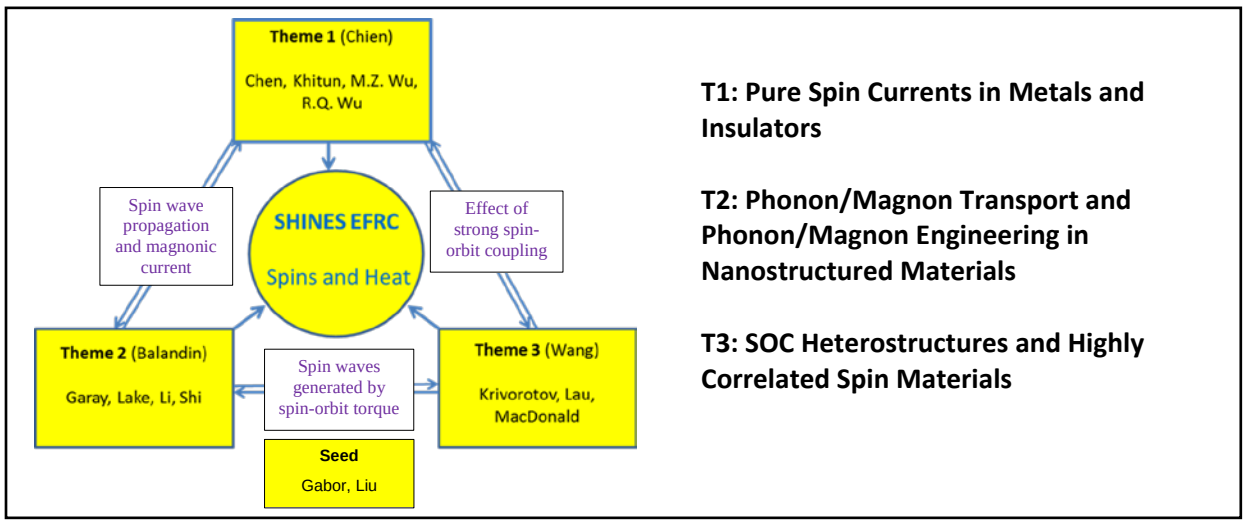
Spins and Heat in Nanoscale Electronic Systems (SHINES)
EFRC Director: Jing Shi
Lead Institution: University of California, Riverside
Start Date: August 2014

Mission Statement*: To explore the interplay of spin, charge, and heat and to control the transport of spin and energy for achieving significantly higher energy efficiencies in nanoscale electronic devices.*

The four-year objectives for the SHINES center include (1) better understanding of and significant improvement in pure spin current effects in nanoscale electronic devices, including magnonic switching, spin-torque oscillations, spin-orbit torques, and spin Seebeck effect through novel materials and heterostructures; (2) engineering of acoustic phonon and magnon transport in nano-structured materials via controlling their dispersions and interactions; and (3) exploration of spin-orbit coupling for low energy effects and spin superconducting condensate for dissipationless spin and energy transport.

The SHINES center is organized in the following three interactive themes:

Theme 1 (T1): Pure spin currents in metals and insulators
This theme involves five members: Chien, Chen, Khitun, M.Z. Wu and R.Q. Wu and 5 cross-team members: Lake (T2), Li (T2), Shi (T2), Wang (T3), and Krivorotov (T3). The theme is led by Chien. The main focus is on more efficient generation and detection of pure spin currents in metals and insulators and more efficient spin current-driven magnetization dynamics in both magnetic metal and insulator devices. The specific tasks include: high-precision determination of the spin Hall angle and spin diffusion length in strong spin-orbit coupling metals, especially ferromagnetic metals; search for large spin Hall angle and long spin diffusion length for high-efficiency energy conversion from heat; improved understanding of the spin Hall



angle and anomalous Hall effect in ferromagnetic metals and alloys; demonstration of spin torque oscillators (STO) in magnetic insulator devices based on the spin Seebeck effect; investigation of the Gilbert damping mechanism in doped and undoped magnetic insulator films; demonstration of magnonic switching in magnetic insulator-based thin film devices with point contact geometry; experimental investigation and micromagnetic simulations of magnonic switching dynamics; and measurements of propagating spin wave dynamics in magnetic insulator films and two-dimensional magnonic crystals.

Theme 2 (T2): Phonon/magnon transport and phonon/magnon engineering in nanostructured materials

This theme involves 5 members: Balandin, Garay, Lake, Li, and Shi, and 4 cross-theme members: M.Z. Wu (T1), Khitun (T1), Wang (T3), and MacDonald (T3). The theme is led by Balandin. The main focus of this theme is on the control of phonon/magnon properties to manipulate heat transport in nanostructured materials. The specific tasks include: demonstration of the acoustic phonon engineering effects on phonon dispersion and thermal transport (e.g. thermal conductivity) in nanostructured materials through material and structural property optimizations; demonstration of acoustic phonon spectrum modifications in spatially confined hetero- and nano-structures; fabrication and demonstration of two-dimensional magnonic crystals with band gaps via material and structural tuning; spectroscopic measurements of propagating chiral spin wave edge modes; determination of phonon/magnon temperature distributions in doped and undoped magnetic insulator films subjected to temperature gradient via Brillouin light scattering; investigation of physical mechanism of the spin Seebeck effect in magnetic insulators; demonstration of magnon/phonon Hall effect (i.e. anomalous Righi-Leduc effect) in magnetic insulator crystals; and experimental and theoretical investigations of the physical origin of the effect.

Theme 3 (T3): Spin-orbit coupling heterostructures and highly correlated spin materials

This theme involves 4 members: Wang, Krivorotov, Lau, and MacDonald, and 3 cross-theme members: Chien (T1), Lake (T2), and Balandin (T2). The theme is led by Wang. The specific tasks include: demonstration and investigation of efficient spin-orbit torques in topological insulator/magnetic insulator heterostructures; theoretical and simulation studies of the effects of the spin-orbit torque on magnetization switching; demonstration and optimization of frequency-doubling high-efficiency spin torque oscillator nanodevices; better understanding of magnetization dynamics with micromagnetic simulations; measurements of spin-orbit coupling effects on electrical transport properties (e.g. weak localization and anti-localization) in transition metal dichalcogenide (TMD) nano-devices; measurements of temperature dependence of electron-phonon coupling in suspended TMD devices; theory and demonstration of spin superconductivity associated with the magnetic condensate in magnetic insulator nano-devices; and investigation of the stability and physical properties of the magnetic condensate.

Spins and Heat in Nanoscale Electronic Systems (SHINES)	
University of California, Riverside	Jing Shi (Director), Alexander Balandin (Associate Director), Nathaniel Gabor, Alexander Khitun, Roger Lake, Jianlin Liu
University of California, Irvine	Ilya Krivorotov, Ruqian Wu
University of California, Los Angeles	Kang L. Wang
University of California, San Diego	Javier E. Garay
Johns Hopkins University	Chia-Ling Chien
Colorado State University	Mingzhong Wu
Ohio State University	Chun-Ning (Jeanie) Lau
University of Texas at Austin	Elaine (Xiaoqin) Li, Allan MacDonald
Arizona State University	Tingyong Chen

Contact: Jing Shi, Director, jing.shi@ucr.edu
(951) 827-1059, http://efrcshines.ucr.edu/

Catalysis Center for Energy Innovation (CCEI)
EFRC Director: Dionisios G. Vlachos
Lead Institution: University of Delaware
Start Date: August 2009

Mission Statement*: To develop innovative, transformational heterogeneous catalytic technologies for economically converting lignocellulosic (non-food-based) biomass into bioproducts and fuels.*

The Catalysis Center for Energy Innovation (CCEI) focuses on developing innovative, science-based heterogeneous catalytic technologies for transformation of lignocellulosic (non-food-based) biomass materials into fuels and bioproducts. Biomass offers a unique opportunity for a sustainable society with unprecedented impact on the US economy, energy security and independence. For this vision to be realized, we must overcome major scientific hurdles that are present due to the inherent complexity of biomass materials and associated processes.

The overall objectives of CCEI are to develop the enabling technologies for biomass conversion that lead to viable, economic operation of future biorefineries and to educate the workforce needed to further develop and implement these new technologies.

Since biomass feedstocks vary considerably by source and the number of candidate reactions is huge, the CCEI mainly focuses on developing a fundamental science base for controlling the scission and formation of C-H, O-H, C-C and C-O bonds by choosing a select number of reactions from a representative group of processes. Reactions typically take place in a complex, multiscale environment that renders the rational design of these processes and catalysts challenging. Our overarching goal is to develop methods and concepts that overcome this challenge and form the foundations of modern biorefineries. The cornerstone of the CCEI lies in advancing catalysis and its integration into processes that deliver innovative technologies for the conversion of building blocks of cellulose and hemi-cellulose, i.e., of sugars (produced from the hydrolysis of biomass). We have assembled an interdisciplinary team of principal investigators that brings together the necessary expertise and synergism to tackle these complex problems. We exploit various complementary catalytic technological platforms that are anticipated to play key roles in future biorefineries for energy, fuels, and chemical production. Examples include the production of renewable aromatics, of functionalized aliphatics, and other target bioproducts along with the production of fuels in the diesel and jet range. A unique trait of CCEI is the ability to carry out fundamental science in very complex problems, to introduce new inexpensive catalysts, and to integrate these catalysts into processes.

We have organized the following three crosscutting enablers as the backbone of the center's research to address the inherent complexities of the environment in which reactions take place: (1) synthesis of novel hierarchical multiscale materials with proper functional groups, (2) multiscale modeling, and (3) in situ characterization of materials. These enablers are integrated within all research thrusts to quickly advance scientific breakthroughs. We develop multiscale models to understand the chemistry and to design new materials. We synthesize hierarchical multiscale materials that are hydrothermally stable, possess tunable porosity with bio-inspired functionality grafted active sites, and minimize resistance to molecular motion while allowing shape selectivity. Furthermore, we design cutting-edge characterization methods to probe reactions, often under in situ environment.

The CCEI outcomes include a fundamental understanding of the reaction mechanisms of representative biomass thermochemical transformations, a rational framework for multiscale hierarchical catalytic materials and process design, science-based innovative technologies for biomass utilization, education of students and postdocs, and effective outreach/dissemination pathways to other scientists, students, and the public.

Catalysis Center for Energy Innovation (CCEI)	
University of Delaware	Dionisios G. Vlachos (Director), Stavros Caratzoulas, Douglas J. Doren, Raul F. Lobo, Basudeb Saha, Stanley I. Sandler, Klaus H. Theopold, Donald A. Watson, Bingjun Xu
Brookhaven National Laboratory/Yeshiva University	Anatoly Frenkel
California Institute of Technology	Mark E. Davis
Columbia University/Brookhaven National Laboratory	Jingguang G. Chen
Georgia Institute of Technology	Christopher W. Jones
Lehigh University	Mark A. Snyder
Rutgers University	Marianthi G. Ierapetritou
University of Massachusetts Amherst	Wei Fan, Friederike C. Jentoft
University of Minnesota	Paul J. Dauenhauer, J. Ilja Siepmann, Michael Tsapatsis
University of Pennsylvania	Raymond J. Gorte, Christopher B. Murray

Contact: Dionisios (Dion) G. Vlachos, CCEI Director, vlachos@udel.edu
(302) 831-2830, www.efrc.udel.edu

Center for Geologic Storage of CO_2 (GSCO2)
EFRC Director: Scott M. Frailey
Lead Institution: University of Illinois at Urbana-Champaign
Start Date: August 2014

Mission Statement*: To generate new conceptual, mathematical, and numerical models applicable to geologic storage systems in specific and strategically identified research areas, based on uncertainty and limitations observed in field pilots and CO_2 injection demonstration projects, laboratory experiments, and the experience of researchers.*

The Center for Geologic Storage of CO_2 aims to improve fundamental understanding of one of the most important questions regarding the geologic storage of CO_2 and other fluids: ***What are the mechanisms of injection-induced microseismicity, and can we control and predict its occurrence?***

Five specific research questions have been designed to address this overarching question.

How can we unravel the links between induced microseismicity and the stress field?
The *central hypothesis* is that small, critically stressed fractures in the subsurface, distributed in clusters with variable orientation are triggered to slip as a response to small changes in the in-situ stress field, associated with minor changes in pore pressure. This research question includes aspects of processing, interpreting, and understanding the relation between microseismic waveform data and anisotropic changes of the in-situ rock conditions. Rock samples will be prepared in the laboratory to mimic a fracture zone at in-situ stress and pressure conditions. By injecting fluids at low pressures, the artificial fracture will be tested for slip. This research question will compare field-scale observations of induced seismicity with acoustic emission (AE) data from laboratory experiments by using waveform data from AEs and field-scale observations of microseismic events, to establish and describe links between microseismicity and the stress field. Numerical experiments will be conducted to assess pore pressure propagation at the continuum scale in order to simulate slip on critically stressed fractures with very small changes to pore pressure.

How do reservoir-scale geologic features relate to geomechanical and seismic properties of rocks?
The *central hypothesis* is that new research on geologic architecture, approaches relating geomechanical properties and seismic velocities to geologic facies, and on depositional-based approaches to simulating geologic facies will lead to significant advances in modeling three-dimensional (3D) spatial variation in geomechanical properties and seismic velocities. Reservoir geology will be related to geomechanical properties through studies and quantitative analysis of combined borehole data sets. The contribution of geologic factors, across scales, to the variance in geomechanical and petrophysical properties will be quantified. The results will be expanded to scenarios for 3D sedimentary architecture and structure. The 3D models for geomechanical properties and seismic velocities will be incorporated into geologic models and used in interpretive forward modeling of seismic velocities.

How can measurements of geomechanical properties at pore and core scales be improved?
The *central hypothesis* is that completion of coordinated but distinct laboratory-scale experiments focusing on characterization of thermo-hydro-mechanical properties of rock will provide improved measurement capability and will enable the linkage of important reservoir material behavior processes, specifically injection-induced microseismicity, across the pore and core scales. This research question includes new (e.g., X-ray computed tomography [CT] scanning, advanced ultrasonics) and conventional (e.g., AE, electrical resistivity) experimental measurement methods to study the effects of brine and CO_2 injection on the stress field, mechanical properties, and induced microseismic activity of rock samples. The influences of stress and saturation on the observed behavior will be separated by testing different

sample sets similarly. Intact samples will be tested to establish baseline behavior. Samples that contain pre-modified simulated defects will be tested under the same saturation to enhance stress fields and thus understand those influences.

How do pore fluid pressure fluctuations transmit in, and affect the state of, realistic porous and fractured media? The *central hypothesis* is that modeling coupled stress, strain, and multiphase flow processes that induce microseismicity must have pore-scale geologic heterogeneity represented. Geologic heterogeneity of flow paths within rock samples can lead to localized increase in pore pressure, leading to localized failure within the rock matrix or slippage of pre-existing fractures across scales, thus inducing microseismic events. Models of pore-scale heterogeneity will be developed based on high-resolution CT scans of rock core. Simulators that couple multiphase flow and geomechanical response will be used to investigate key mechanisms triggering microseismic events in various stochastic realizations of the rock. The models will be validated through comparison with pore- and core-scale experiments.

In the presence of specific geologic attributes/features, how do CO_2 and brine mixtures affect the geomechanical and seismic properties of rocks? The *central hypothesis* is that geochemical reactions promoted by CO_2 alter the stress field and reduce mineral strength along grain boundaries, thus promoting fracture propagation. These geochemically induced fracturing events are hypothesized to be the main cause of post-injection microseismic events when pore pressures are decreasing. This research is differentiated by spatial scale. Similar cores will be characterized, exposed to CO_2-saturated brine, and then evaluated for changes in mineralogy, rock mechanical properties, and fracturing. Nanoindentation, sliding friction, and scratch tests will be used to assess changes to mechanical properties of rocks exposed to CO_2-saturated brine. Cores will be subject to triaxial pressure cycling before and after exposure to CO_2-saturated brine. The effect of pressure cycling on mineralogical alteration, and the effect of mineralogical alteration on stress-strain during pressure cycling, will be evaluated using high-resolution pore-scale imaging, strain gauge measurements, and nano-to-micro-scale mineralogical analyses.

To test the hypothesis and validate models, a subsurface observatory, the Illinois Basin–Decatur Project, will be used within each of these research questions.

Center for Geologic Storage of CO_2 (GSCO2)	
University of Illinois at Urbana-Champaign	Scott Frailey (Director), Edward Mehnert (Associate Director), Ange-Therese Akono, Robert Bauer, James Best, Alexey Bezryadin, Jennifer Druhan, Ahmed Elbanna, Roman Makhnenko, Roland Okwen, John Popovics, Albert Valocchi, Steve Whittaker
University of Texas-Austin	Charles Werth
NORSAR	Volker Oye, Bettina Goertz-Allmann
Wright State University	Robert Ritzi, David Dominic, Naum Gershenzon
Schlumberger	Sergey Stanchits
University of Southern California	Muhammad Sahimi, Theodore Tsotsis, Kristian Jessen
SINTEF	Michael Jordan, Pierre Cerasi
University of Notre Dame	Kenneth Christensen
Texas Tech University	Dustin Sweet, Calvin Barnes, Paul Sylvester
NETL	Angela Goodman, Dustin Crandall

Contact: Scott M. Frailey, GSCO2 Director, SFrailey@illinois.edu
217-244-7412, http://www.gsco2.org/

Nanostructures for Electrical Energy Storage (NEES)
EFRC Director: Gary W. Rubloff
Lead Institution: University of Maryland
Start Date: August 2009

Mission Statement*: To reveal scientific insights and design principles that enable a next-generation electrical energy storage technology based on dense mesoscale architectures of multifunctional nanostructures.*

In its first phase (2009-2014) NEES focused on the design and electrochemistry of heterogeneous, multifunctional nanostructures as the building block for electrical energy storage (EES) configurations offering high power and stability during charge/discharge cycling. Using prototype materials relevant to Li ion batteries, NEES has employed both novel single-nanostructure platforms and "forests" of densely packed nanostructure arrays to fuel insights into nanostructure electrochemistry.

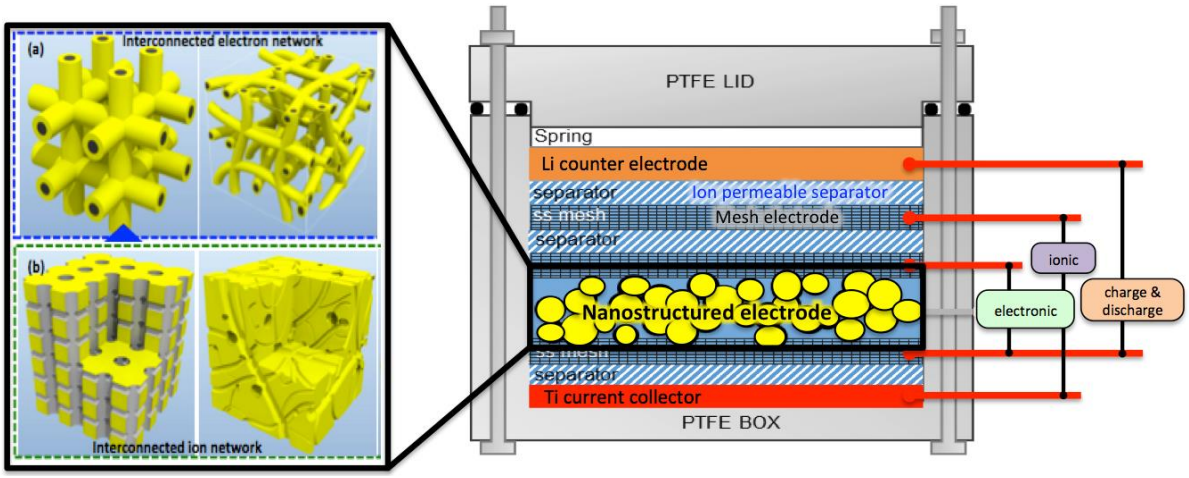


Figure 1. Mesoscale architectures of nanostructured electrodes, compared by *In-operando* ionic & electronic conductivity measurements as a function of charge state (degree of lithiation) and charge/discharge cycles.

In its second phase (2014-2018) NEES is concentrating on the arrangement of precision nanostructures into dense mesoscale architectures and the new scientific challenges that result. These investigations begin with achievable architectures (Fig. 1), which raise questions such as: What 3-D synthesis strategies translate the benefits of precision nanostructures to dense mesoscale assemblies? How does the EES behavior of regular/ordered architectures compare with that of pseudorandom counterparts? How well do metrics for the latter, such as porosity and tortuosity, forecast EES performance? The dense packing of nanostructures into mesoscale architectures raises new questions about ion and electron transport in confined nanogeometries, e.g.: Will electrolyte nanoenvironments contain and supply ions in sufficient concentration to fully utilize EES storage layers in the nanostructures? What design guidelines are needed to balance electron and ion transport (in current collectors and electrolyte respectively) to achieve high power? Will surface charge vary along nanostructures, and what role might it play in electrolyte ion transport phenomena (e.g. electrokinetics)? Comparisons between the diverse electrode architectures developed in NEES are being compared using a new configuration that enables separate determination of ion and electron transport kinetics and conductivity.

NEES also seeks to understand capacity degradation and failure in nanostructure-based EES - an ambitious effort to establish a science of nanostructure degradation, simultaneous with or in advance of a prototype

nanostructure-based EES technology. NEES is using advanced nano/micro scale platforms (Fig. 2) to identify degradation/failure in both early (<10's of cycles) and extended-term (~50-1000 cycles) charge/discharge cycling, from which follow-on experiments can address validation of proposed degradation. Test structures can be constructed and tested to validate proposed degradation mechanisms.

As an ambitious alternative for safe, high performance EES, NEES is working on solid electrolyte materials and synthesis of interdigitated 3-D structures for solid state nano/micro batteries (Fig. 3), closely coupled with multiphysics modeling. Synthesis techniques play a strong role here in enabling viable 3-D configurations. Solid electrolyte layers are particularly central to success, not only in solid state batteries but also to serve as ion-conducting passivation/protection layers for exploiting the high energy density of metal anodes in other battery systems.

These directions build on NEES expertise in the science of electrochemical interfaces, pioneering nanocharacterization methods, and a portfolio of modeling and simulation techniques from molecular to micro/macro scale. NEES research is addressing a variety of advanced battery chemistries as well as Li ion, involving metal anodes, multivalent ions, sulfur and oxygen cathodes, employing controlled materials and nanostructures to understand, assess and improve EES behavior.

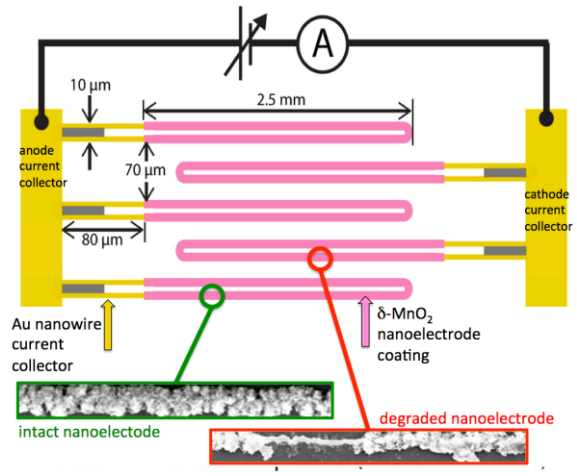


Figure 2. Long nanoelectrodes as testbeds for nanobattery degradation and failure mechanisms.

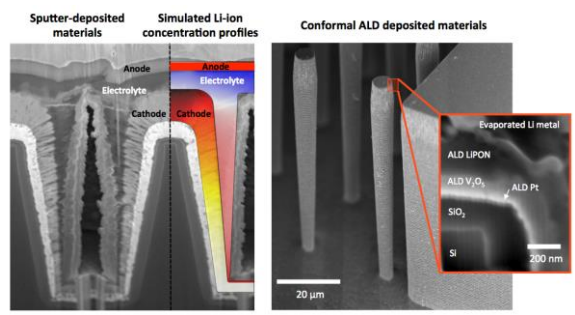


Figure 3. 3D solid-state batteries using different synthesis techniques, with multiphysics model of Li transport.

Nanostructures for Electrical Energy Storage (NEES)	
University of Maryland	Gary W. Rubloff (Director), Sang Bok Lee (Deputy Director), John Cumings, Chunsheng Wang, YuHuang Wang, Liangbing Hu, Janice Reutt-Robey, Bryan Eichhorn
Sandia National Laboratories	Kevin Leung, A. Alec Talin, Katherine Jungjohann, Farid El Gabaly
University of California, Irvine	Reginald Penner, Zuzanna Siwy, Phil Collins
Yale University	Mark Reed
University of Florida	Charles R. Martin
University of California, Los Angeles	Bruce Dunn
University of Utah	Henry White
Michigan State University	Yue Qi

Contact: Gary Rubloff, Director, rubloff@umd.edu
301-405-3011, www.efrc.umd.edu

Inorganometallic Catalyst Design Center (ICDC)
EFRC Director: Laura Gagliardi
Lead Institution: University of Minnesota
Start Date: August 2014

Mission Statement*: To guide the discovery of superior catalysts by integrating computational modeling with experiments in well-defined systems that are amenable to high-throughput search and discovery.*

The **vision** of the ICDC encompasses accelerating the development of supported cluster catalysts with the following characteristics:

- ***Uniform mesoscale structures*** that can be synthesized reproducibly, which are ideal for both full experimental structural characterization and computational modeling.
- ***Clusters*** that are well-defined and uniform in structure and composition, but isolated from each other on supports to minimize cluster-cluster interactions and agglomeration/sintering.
- ***Catalyst structures*** amenable to high-throughput experimental screening, very reliable quantum mechanical predictions on prototype exemplars, and computational high-throughput screening.

There are remarkably few experimental examples of well-defined supported subnanometer cluster catalysts due to the challenge of synthesis and limits of stability. The primary examples are supported metal clusters, for which a few highly selective and active catalysts have been described. Critical factors are cluster size, shape, composition, and positioning of atoms/ions of specific metals when the clusters comprise more than one type of metal atom/ion. ICDC studies how these various factors affect adsorption properties, stability, reaction rates and selectivity.

The potential number of candidate cluster catalysts is enormous, making it impractical to synthesize even a modest fraction of them, much less to characterize their structures, physical properties, and catalytic efficacy. Therefore, ICDC guides the selection of synthesis targets computationally. Furthermore, we develop and demonstrate synthesis strategies that are very broadly applicable.

An ultimate goal of the computations is high-speed (high-throughput) predictive characterization of putative cluster structures, stabilities, and catalytic competency to yield a database of potential catalysts that is unparalleled in size and chemical diversity. Powerful, newly developed quantum chemical methods have predictive accuracy for complex catalytic problems that were not amenable to reliable theoretical predictions as recently as ten years ago. Data mining for these hypothetical structures, together with strategic implementation of high-level theory for specific hypothetical and real examples and for novel synthetic strategies will accomplish the following **strategic objectives**:

- ***Provide sufficient information*** about how newly synthesized catalysts guide reactions through sequences of elementary steps, some of which pertain to more than one process.
- ***Develop*** new strategies and methods for computationally-guided discovery of useful catalysts.
- ***Design*** new methods for rapid synthesis of previously unexplored well-defined catalytic clusters, including those with compositions unattainable on the macroscopic scale, on supports that both isolate the clusters and offer easy access to reactants.
- ***Develop*** new approaches for the discovery and theoretical explanation of structure/function relationships in catalysts in the largely unexplored cluster size range < 200 atoms.

The specific scientific focus and challenge is the energy-efficient liquefaction of natural gas, either by catalytic conversion to alcohols or by catalytic conversion of C1, C2, and C3 species to C6 to C10 hydrocarbons. It requires the mastery of a set of generic reactions - the key being catalysis. Despite the very specific technical focus, we anticipate that much of what is learned about catalyst design and discovery will prove transferrable to other important problems in chemical catalysis. The ability to test

hypotheses *in silico*, followed by experimental validation, over an enormous and arbitrarily modifiable database of hypothetical catalysts is expected to lead to compelling, transferrable catalyst design rules and potentially lead to the discovery or design of new mechanisms and desirable new catalytic chemistry. Computational design, screening, and synthesis is complemented by high-throughput experimental screening enabled by the expertise and instrumentation developed by Center members at The Dow Chemical Company.

One key to achieving experimentally uniform clusters in this critical mesoscale size range is the use of highly uniform mesoporous metal-organic frameworks (MOFs) and surface-supported porphyrins as scaffolds and supports, or for cluster buildup activity, selectivity and lifetime. The key feature of the new materials is an array of "nodes" that have large and controllable separations, with only organic linkers between them (see **Fig. 1**.).

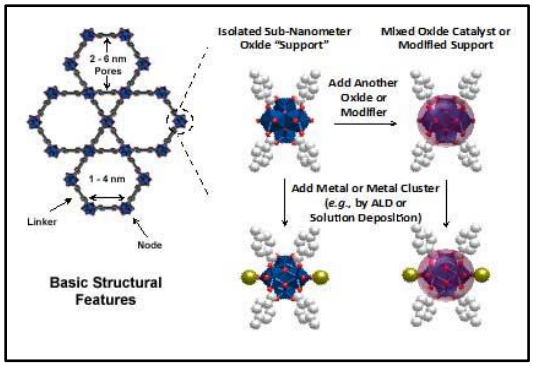


Figure 1. Schematic of the new class of materials

Research Strategies. ICDC is organized by **research themes**: a) Quantum Simulations and Computational Screening, b) Novel Material Synthesis, c) Material Characterization, and d) Catalysis. The early experimental work was driven by experience-based hypotheses, with the goal of moving toward computationally-driven design as the Center matures, always directed toward specific reactions of high interest to DOE. The research, therefore, has two sides that map to the four research themes:

1. Hypothesis-driven work to develop catalytic material structure/function relationships for target reactions, using synthesis, characterization, catalytic assessment, and modeling/computations to explain observations and suggest new materials.
2. Work to develop new experimental and theoretical methods and tools to explain observations and suggest new materials. Progress is achieved by investigating target reactions with available computational and experimental techniques. The results of the simulations help to achieve a fundamental understanding of the materials and their catalytic activities, inspire new experiments, and reveal more clearly where computational tools need improvement.

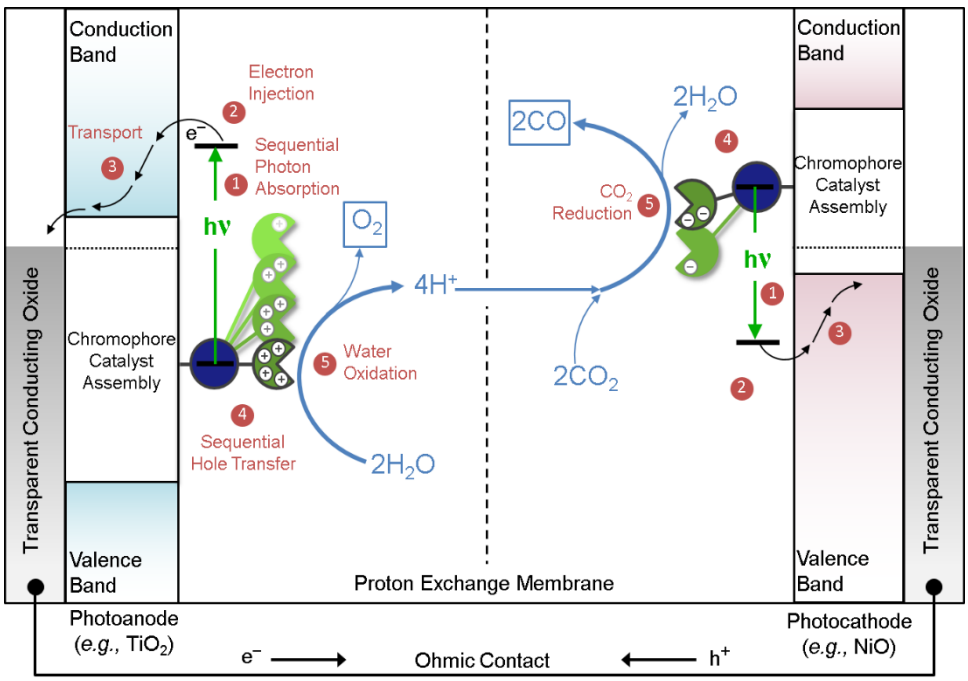
Inorganometallic Catalyst Design Center (ICDC)	
University of Minnesota	Laura Gagliardi (Director), Christopher Cramer (Executive Committee) Connie Lu, R. Lee Penn, Andreas Stein, Ian Tonks, Donald Truhlar
Northwestern University	Joseph Hupp (Deputy Director), Omar Farha (Executive Committee), Justin Notestein, Randy Snurr
University of California-Davis	Bruce Gates (Executive Committee)
Pacific Northwest National Laboratory	Johannes Lercher, Donald Camaioni
Argonne National Laboratory	Karena Chapman, Alex Martinson
Clemson University	Rachel Getman
Dow Chemical Company	Edward Calverly
NuMAT	Will Morris

Contact: Laura Galiardi, Director, gagliard@umn.edu
612-625-8299, http://www.chem.umn.edu/icdc/

Center for Solar Fuels (UNC EFRC)
EFRC Director: Thomas J. Meyer
Lead Institution: University of North Carolina at Chapel Hill
Start Date: August 2009

Mission Statement: *To conduct research on dye sensitized photoelectrosynthesis cells (DSPECs) for water splitting and tandem cells for the reduction of carbon dioxide to carbon-based solar fuels.*

The UNC EFRC Center for Solar Fuels is conducting research on solar energy conversion and storage based on solar fuels. Research in the Center extends from the basic science of fundamental processes and new materials to integrating components into surface-stabilized assemblies, and assemblies into device prototypes. A broad, multidisciplinary approach is used in a highly collaborative setting. EFRC research integrates capabilities and expertise in chemistry, physics, and materials science with a focus on the Dye Sensitized Photoelectrosynthesis Cell (DSPEC) for solar energy conversion by water oxidation to oxygen and reduction of carbon dioxide to carbon-based fuels.



TARGET METRICS

- Converting solar photons into redox equivalents in the attached chromophore-catalyst assembly with >90% efficiency (steps **1** and **2**).
- Building up multiple redox equivalents at catalyst sites for water oxidation or CO_2 reduction with efficiencies >95% on the timescale of the light source, seconds for ambient sunlight (steps **3** and **4**).
- Achieving catalytic rates of $>10^2$ s^{-1} (step **5**).
- Achieving overall device efficiencies of 15% with 10^7 cycles/year and a 95% retention in photoreactivity.

Dye-Sensitized Photoelectrosynthesis Cell (DSPEC) for CO_2 Reduction to CO

THE DYE SENSITIZED PHOTOELECTROSYNTHESIS CELL (DSPEC).

The dye sensitized photosynthesis cell provides a systematic approach to solar fuels by integrating molecular light absorption and catalysis with the high bandgap properties of nanoparticle films of semiconductor oxides. Research on DSPEC device prototypes in the UNC Center for Solar Fuels utilizes an integrated, modular approach. Parallel research efforts are pursued on catalysts for water oxidation and CO_2 reduction, light-harvesting chromophores and chromophore arrays, synthesis and characterization of chromophore-catalyst assemblies, nanoparticle oxide films, core/shell structures and stabilizing overlayers by atomic layer deposition (ALD), dynamics of interfacial electron transfer, photoanodes for water oxidation, photocathodes for CO_2 reduction, and assembly and evaluation of DSPEC device prototypes.

Current research builds on the results of continued catalyst development for CO_2 reduction and water oxidation, targeting catalysts that are stable through 100,000s of turnovers at rates that exceed 10 s^{-1}. Catalysts are being integrated with organic and metal complex chromophores that are designed to absorb light broadly in the visible spectrum giving excited states capable of undergoing electron or hole injection to oxide anodes or cathodes. Assembly structures are being explored that link multiple chromophores to a single catalyst in molecular and polymer scaffolds. The successful core/shell photoanode architecture is being extended to new materials and to new core/shell structures in order to maximize solar efficiencies, and to *p*-type oxides for photocathode and tandem cell applications with a special focus on CO_2 reduction. ALD, electropolymerization, and polymer overlayer strategies are being exploited to stabilize surface structures and control interfacial properties and dynamics. The results of steady-state and time-resolved photocurrent and transient absorption measurements are being used to evaluate interfacial electron transfer dynamics and how they dictate cell performance, and to identify and overcome deleterious pathways leading to assembly instability. Measurements on device prototypes are being extended to long-term performance and to zero-gap configurations appropriate for device applications.

Research in the Center for Solar Fuels is multidisciplinary and highly integrated. The challenges posed by the research are met by the team-based structure below. Based on past success and promise for the future, the Center is poised to have, what could be, a transformative impact on solar energy conversion and storage and a role to play in the world's energy future.

RESEARCH	TEAM	RESEARCH FOCUS
Synthesis and Catalysis	Catalysis	Catalyst development and mechanistic studies on solution and interfacial catalysts for water oxidation and CO_2 reduction. Evaluation of catalysts in assemblies and device prototypes for photoanode and photocathode applications.
	Assemblies	Design, synthesis, and characterization of molecular, oligomer and polymer chromophore-catalyst assemblies for applications in water oxidation and CO_2 reduction at *n*- and *p*-type semiconductors.
Interfaces and Devices	Interface Dynamics	Provide detailed understanding of surface mechanisms that guide design of molecular systems and materials to improve functional performance of DSPEC photoanodes and photocathodes.
	Photocathode	Design, synthesis and characterization of hole-transporting semiconductor nanomaterials, core/shell structures, and light-absorbing sensitizers for high-performance photocathode applications integrated with molecular catalysts for CO_2 reduction.
	Photoanode	Optimization of solar-driven water oxidation at dye-sensitized photoanodes.

Center for Solar Fuels (UNC)	
University of North Carolina at Chapel Hill	T.J. Meyer (Director), J.M. Papanikolas (Co-Deputy Director), G.J. Meyer (Co-Deputy Director), J.M. Atkin, M.S. Brookhart, J.F. Cahoon, J.L. Dempsey, Y. Kanai, R. Lopez, A.J.M. Miller, A.M. Moran, C.K. Schauer, J.L. Templeton, M.K. Brennaman, S.L. Marquard
Brookhaven National Laboratory	J.T. Muckerman
Georgia Institute of Technology	J.R. Reynolds
University of Texas at San Antonio	K.S. Schanze

Contact: Thomas J. Meyer , Director, UNC EFRC Center for Solar Fuels, tjmeyer@unc.edu
919-843-8313 www.efrc.unc.edu

Materials Science of Actinides (MSA)
EFRC Director: Peter C. Burns
Lead Institution: University of Notre Dame
Start Date: August 2009

Mission Statement*: To conduct collaborative, multidisciplinary, novel and transformative research on actinide materials emphasizing actinide ceramic, metallic, hybrid, and nanoscale materials; effectively integrate experimental and computational approaches; and solve research questions that are critical to the energy future of the nation.*

The Materials Science of Actinides Center unites researchers to conduct research in actinide materials science, with an emphasis on control at the nanoscale. Actinides are, in many ways, at the frontier of exploration of the periodic table, as their chemistry is complicated by the importance of the 5*f* electrons, relativistic effects of the electrons, their complex redox chemistry, and their radioactivity. Owing to this complexity and the relative difficulty of working with actinides, research in actinide chemistry and actinide-based materials has lagged far behind that of most other elements in the periodic table, both in theory and synthesis and design for special properties, such as radiation resistance of actinide-bearing materials.

In actinides, the delocalization/localization of 5*f* electrons presents the possibility of control of materials processes at the level of electrons. These properties emerge from the complex correlations of atomic (composition and short and long-range order) and electronic (f-electron) constituents. In this center, we heavily emphasize new synthesis approaches for actinide materials that are likely to lead to revolutionary new forms of matter with tailored properties. New materials that we emphasize are based upon the self-assembly of actinides into nanoscale materials with the potential to create new technologies. Radiation in actinide materials creates a system that is very far away from equilibrium, and a core focus of this center is to examine the behavior of actinide-based materials under extreme conditions of radiation, pressure and temperature.

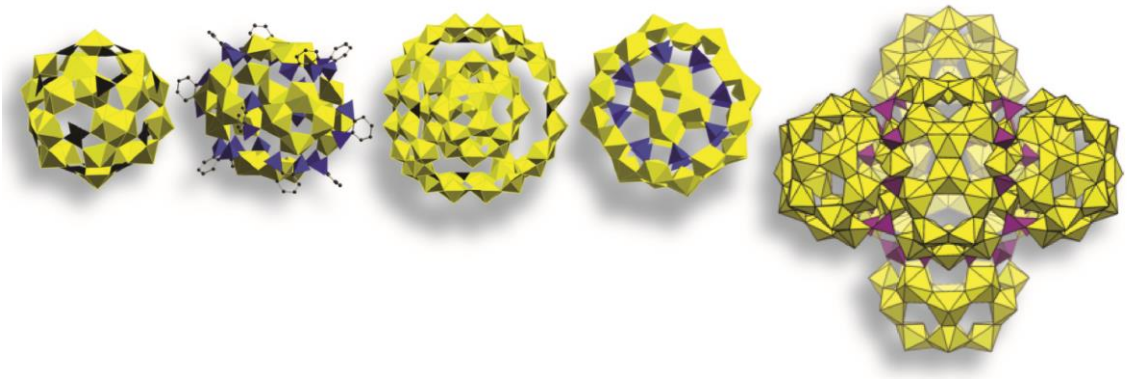


Figure 1. Examples of uranyl peroxide cage clusters containing uranyl polyhedra and, from left to right: phosphite, carboxyphosphonate, nitrate, molybdate, and phosphate (Qiu et al. *Chemical Reviews* **113**, 1097-1120 (2013)).

Three major Research Themes in actinide materials science are central to MSA's efforts. These themes are: (i) Nanoscale cage clusters, (ii) complex ceramic and metallic materials, and (iii) materials under extreme environments. Four cross-cutting themes are: (i) Novel synthesis methods for actinide materials across length scales, (ii) thermodynamics of actinide materials across length scales, (iii) integration of

computational analysis and experimental results for actinide materials, and (iv) relevance of research to the nuclear fuel cycle.

The **nanoscale cage clusters theme** focuses on the self-assembly and properties of a large family of nanoscale actinyl-based cage clusters discovered by this group (Fig. 1). We seek to develop a fundamental understanding of the science of nanoscale actinide materials. Emphasis is on the assembly mechanisms, solution behavior, aggregation, stability, bonding, and ion pairing of these clusters.

The **complex ceramic and metallic materials theme** extends rigorous experimental determination and computational simulation of thermodynamic parameters of important actinide materials including oxides, selected metals, intermetallics, nitrides, and carbides containing plutonium, neptunium, or uranium. Work includes measurement of heat capacity, thermal expansion, and elasticity of a variety of actinide materials to guide theory and to provide critical data for next-generation nuclear reactors.

The **materials under extreme environments theme** addresses the many phenomena in actinide solids that are radiation dose, temperature, and/or pressure dependent – such as, order-disorder transformations, other phase transitions, and chemical decomposition. The coupling effects of extreme temperature and pressure environments with strong radiation fields are emphasized.

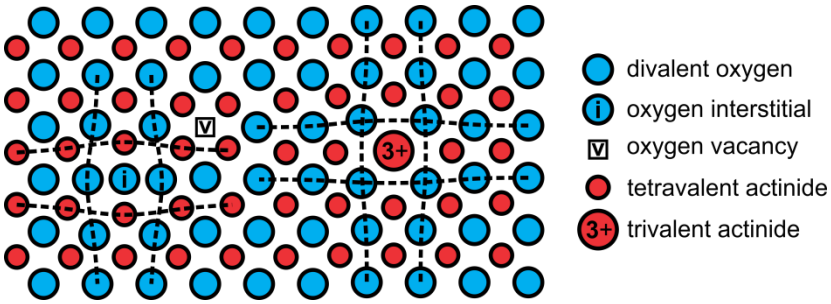


Figure 2. Cation reduction causes structural distortions in the actinide oxide lattice that are identical to that caused by Frenkel defects (Tracy et al. Nature Communications **15**, 507-512 (2016)).

Materials Science of Actinides (MSA)	
University of Notre Dame	Peter Burns (Director), Jeremy Fein, Amy Hixon, Edward Maginn
Stanford University	Rodney Ewing, Wendy Mao
University of California-Davis	Alexandra Navrotsky, Mark Asta, William Casey
George Washington University	Christopher Cahill
Oregon State University	May Nyman
Los Alamos National Laboratory	Albert Migliori
University of Minnesota	Laura Gagliardi
University of Tennessee	Maik Lang
University of Akron	Tianbo Liu

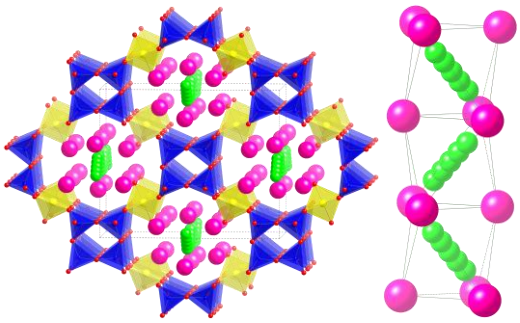
Contact: Peter C. Burns, Director, pburns@nd.edu
(574) 631-7852, http://msa-efrc.com

Center for Hierarchical Waste Form Materials (CHWM)
EFRC Director: Hans-Conrad zur Loye
Lead Institution: University of South Carolina
Start Date: August 2016

Mission Statement*: To combine experiment and modeling to develop the chemistry and structure motifs needed to create hierarchical materials that effectively immobilize nuclear waste in persistent architectures.*

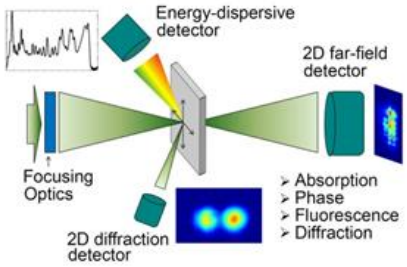
This EFRC is organized to develop the basic science necessary from which new, hierarchical waste forms can emerge. The center will combine experiment, characterization and modeling to develop and validate chemistry and structure motifs that can lead to materials that effectively immobilize nuclear waste elements. New hierarchical structures will be developed via a bottom–up synthetic approach supported by advances in characterization and modeling, where new chemical insights will provide critical understanding of fundamental mechanisms of complexation and speciation for these novel structures.

A simple and very practical working definition of a hierarchical structure is that of a structural motif contained within a larger structure or framework. Conceptually, the hierarchical structures will consist of porous structures, either repeating (crystallographically ordered) or non-repeating (disordered), whose cavities will be occupied by crystalline or non-crystalline fillers. Examples of porous structures include porous crystalline salt inclusion materials (SIMs), metal-organic frameworks (MOFs), porous silica (including Prussian-blue and silver salt functionalized versions), and surface functionalized nanoparticles assembled into hierarchical constructs. Examples of fillers include crystalline salt phases, simple molecular species, silver salt nanoparticles, Prussian-blue nanoparticles, and multi-metallic nanoparticles, all either freely located inside the pores or tethered/bonded to the pore walls. The synthesis of such hierarchical structures will be achieved by exploiting previously underutilized or unrealized chemistries.



The structure of $[Cs_3F][(UO_2)(Si_4O_{10})]$ (left), and the salt-inclusion (right).

The resultant structures will be characterized using a wide variety of techniques both existing and novel, including in-situ diffraction at synchrotron and neutron facilities. Sample characterization will take advantage of in-laboratory diffraction equipment at Alfred University, state of the art calorimetry measurement systems at Clemson University, thermal analyzers at the University of South Carolina (USC), and beam line facilities, including the National Synchrotron Light Source II (NSLS II) at Brookhaven National Laboratory (BNL) for X-ray tomography and in-situ small angle X-ray scattering (SAXS) measurements. In addition, access to Savannah River National Laboratory's (SRNL's) 773-A category 2 nuclear facility will enable us to create radioactive versions of hierarchical structures, in addition to the surrogate versions, so as to better understand the unique properties of forms containing elements such as technetium.



Simultaneous XRF and DPC studies available on the X-ray nanoscale resolution beamline at NSLS-II.

The stability/metastability of these hierarchical materials and their components will be modeled using multi-scale techniques to provide guidance with regard to their preparation and behavior. Atomistic modeling of alloy nanoparticles utilizing derived Charge Optimized Many Body (COMB) potentials, and simulating atomic-scale processes will cover the lowest scales. Thermochemical models, in part informed by the atomistic models, will be developed for complex phases/structures such as the salt inclusion phases that allow prediction of stability, vapor pressure, melting point, and melt viscosity, through extending approaches such as constrained equilibrium and additivity of sub-components. At the mesoscale, phase field methods will be generated for simulations of porous solids using atomistic datasets of surface energies, thermodynamic models, and configurational thermodynamics. The overarching results will involve the integration of simulation and data-enabled discovery that can lead to revolutionary forms of matter with tailored properties.

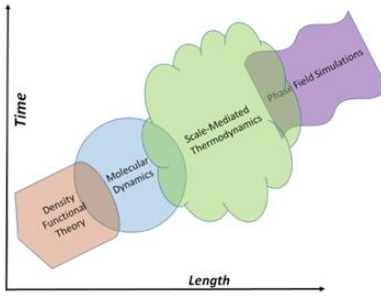


Illustration of bridging scales in modeling waste forms.

Center for Hierarchical Waste Form Materials (CHWM)	
University of South Carolina	Hans-Conrad zur Loye (Director), Theodore Besmann, Natalia Shustova, Hui Wang
Savannah River National Laboratory	Jake Amoroso, David DiPrete, Charles Crawford
Pacific Northwest Laboratory	Charles Henager, Shenyang Hu
Alfred University	Scott Misture
Clemson University	Kyle Brinkman
Brookhaven National Laboratory	Lynne Ecker, Simerjeet Gill
University of Florida	Simon Phillpot
Commissariat à l'Energie Atomique	Agnes Grandjean

Contact: Hans-Conrad zur Loye, Director, zurloye@mailbox.sc.edu
803-777-6916, http://chwm.sc.edu/

Center for Frontiers of Subsurface Energy Security (CFSES)
EFRC Director: Larry W. Lake
Lead Institution: The University of Texas Austin
Date Started: August 2009

Mission Statement*: To understand and control emergent behavior arising from coupled physics and chemistry in heterogeneous geomaterials, particularly during the years-to- decades time scales over which injection for geologic CO_2 storage will drive natural systems far-from-equilibrium.*

Geologic CO_2 storage (GCS) is key for mitigating greenhouse gas emissions, but to be effective GCS must overcome three primary technical challenges: sustaining large storage rates for decades, using underground space efficiently, and controlling undesired or unexpected behavior. To meet these challenges the *Center for Frontiers of Subsurface Energy Security* (CFSES) pursues scientific advances with the goal to (i) establish scientific understanding of far-from-equilibrium processes in heterogeneous geologic media, and (ii) develop novel materials and methods for controlling those processes. Specific examples of our **science goals** are:

- Understand *chemical-mechanical coupling* by identifying mechanisms and time/length scales for self-reinforcing fracture propagation and fluid leakage through those fractures.
- Combine experiments and computational chemistry to examine the *structural (mechanical) and chemical interactions* between wet supercritical CO_2 and clays. We also seek advanced models of noble gas and isotope partitioning between immiscible fluid phases.
- Understand and predict *modes* (compact viscous flow vs. capillary channels) *and fluxes* of reactive CO_2 migration through brine-saturated geomaterials with cm-to-m scale heterogeneity.
- Capitalize on the improved understanding of these processes to design, develop and apply *novel materials* that will alter fluid-assisted perturbations in heterogeneous geomaterials.

The **impact** of the proposed research will be a new scientific foundation for defining the physical constraints on challenges for GCS, and for identifying novel materials and strategies to overcome these constraints. The science will be valuable for broader policy considerations associated with greenhouse gas emissions, the risks in operating storage sites, and the appropriate mix of incentives and regulation for GCS operation.

Keywords: Geomechanics, geological CO_2 storage, relative permeability, primary drainage, hydraulic fracturing, phase-field fracture formulation, adaptive finite elements, porous media, caprock, fractures, multiphase flow, reservoir rock, noble gases, migration-fractionation, geochemical tracers, hydration energy, Bravo Dome, porous media, , micromechanics , chemo-mechanical coupling, saline aquifers, mineral trapping, lattice Boltzmann method, pore network modeling

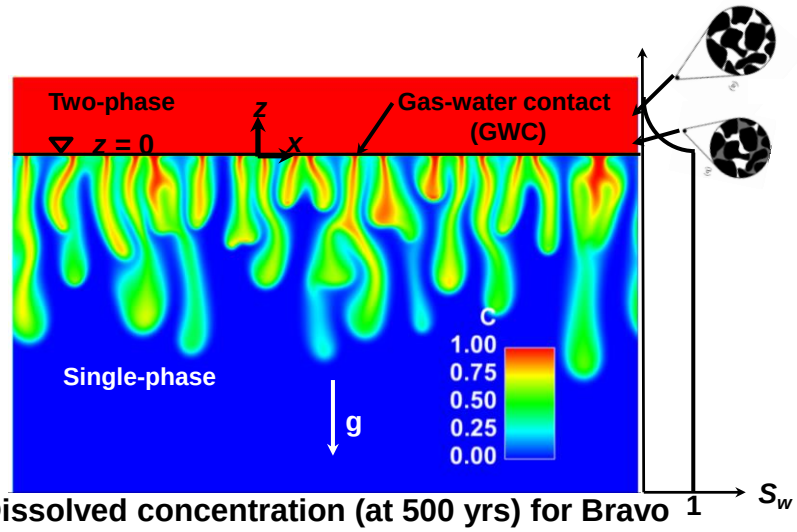
CFSES has already addressed science questions underlying two current concerns for GCS: storage security and risk assessment. Example projects include the following.

Science to Inform Storage Security

Far-from-equilibrium states during CO_2 displacement of brine: CFSES has developed an advanced model for buoyancy driven convective dissolution of CO_2 into brine. CO_2 is normally lighter than water and will hence float on top of it. However, mixtures of CO_2 and water are denser than either causing there to be

a local instability—heavy fluid over light—that forms instabilities (figure) that vastly increase the surface area between CO_2 and water; hence increasing the rate of dissolution.

Impact: Dissolution into water is one of the main mechanisms for storing CO_2. Modeling the fingers suggests the storage rate is 3 times faster than previous estimates.



Dissolved concentration (at 500 yrs) for Bravo Dome properties with 50 kPa entry pressure.

Science to inform GCS risk assessment

Far-from-equilibrium CO_2-mediated geochemistry and caprock integrity: Work within CFSES has quantified mineral dissolution and precipitation on the time scale of a field test (11 days) and long-term storage (1000 years). The work provides insight into the impact of geochemical reactions on injectivity, trapping of CO_2 and caprock integrity. The work can guide potential site selection based on the geochemistry of the site. **Impact:** Other CFSES projects are investigating the effects that chemical interactions will have on storage site mechanical properties. The results of this project will frame this work and provide calibration.

Emergent phenomena during CO_2 plume migration: signature of heterogeneous fluid/rock properties: Modeling of flow through permeable media is normally done in the viscous-dominated flow regime. However, buoyancy forces are likely to dominate viscous flow in the majority of the storage domain because of small fluid pressure gradients caused by the very long storage times. Modeling of this type of flow represents a paradigm shift in the way in which such modeling is normally done. Meso-scale heterogeneity that is typically under represented in conventional flow simulations will strongly influence flow paths, saturations, geochemical reactions, and long-term fate. **Impact:** This project experimentally investigates the combined effect of heterogeneity, viscous forces and buoyancy.

Center for Frontiers of Subsurface Energy Security (CFSES)	
The University of Texas at Austin	Larry W. Lake (Director), Hilary Olson (Assistant Director), Tip Meckel and Matthew Balhoff (Theme Leads), M. Bayani Cardenas, David DiCarlo, Nicolas Espinoza, Nick Hayman, Marc Hesse, Susan Hovorka, Keith Johnston, Masa Prodanovic, Mary F. Wheeler, Changbing Yang
Sandia National Laboratories	Grant Heffelfinger (Associate Director), Anastasia Ilgen (Assistant Director), Thomas Dewers and Mario Martinez (Theme Leads), Panina Newell, Hongkyu Yoon

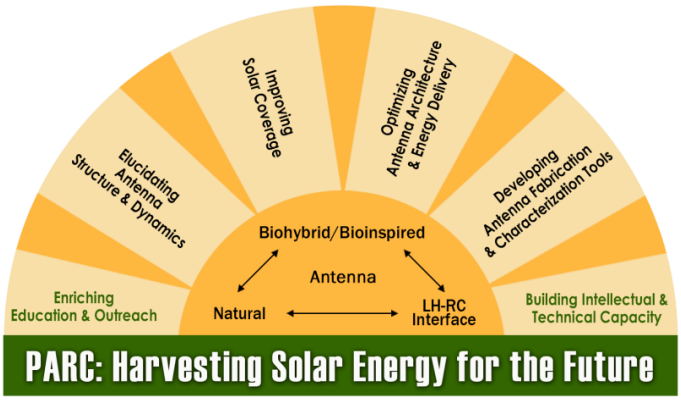
Contact: Larry W. Lake, Director, larry_lake@mail.utexas.edu
(512) 471-8233; http://www.utefrc.org/

Photosynthetic Antenna Research Center (PARC)
EFRC Director: Robert E. Blankenship
Lead Institution: Washington University in St. Louis
Start Date: August 2009

Mission Statement: *To understand the basic scientific principles that underpin the efficient functioning of natural photosynthetic antenna systems as a basis for design of biohybrid and bioinspired architectures for next-generation systems for solar-energy conversion.*

Scientific Themes. Through basic scientific research, PARC seeks to understand the principles of light harvesting and energy funneling as applied to three programmatic themes:

1. *Natural Antennas*: Structure and Efficiency
2. *Biohybrid and Bioinspired Antennas*: Design and Characterization
3. *Antenna-Reaction Center Interface*: Organization and Delivery



Unifying Research Activities. The three scientific themes are connected by the idea that enhancements of photosynthetic light harvesting and the design of the biohybid and bioinspired antenna will draw upon the lessons learned from natural systems. The thematic activities are joined by interrelated research threads, including to:

- Elucidate antenna structure and dynamics
- Improve solar coverage
- Optimize antenna architecture and energy delivery
- Develop antenna fabrication and characterization tools

Global Impact. All of the PARC activities have the broader goals to:

- Enrich education and outreach
- Build intellectual and technical capacity

Specific Objectives for Theme 1—Natural Antennas: Structure and Efficiency

PARC seeks to understand the structure and function of the wide variety of natural photosynthetic antenna systems, including their efficiency, mechanism of action, regulation, assembly and repair. Emphasis is placed on developing new antenna systems using techniques of molecular and synthetic biology that increase the efficiency and functionality of living photosynthetic organisms. The specific objectives are to:

- Determine structures of native and modified antenna systems and correlate with function
- Understand subcellular organization of antenna systems in different photosynthetic organisms
- Examine physiological consequences of modified/alternate antenna in diverse organisms
- Confer visionary new functional attributes into living photosynthetic organisms

The overall aim is to determine and manipulate the antenna architecture and composition to maximize photosynthetic efficiency and functionality in any such organism.

Specific Objectives for Theme 2—Biohybrid and Bioinspired Antennas: Design and Characterization
PARC will use first principles and readily accessible constituents to create mesoscale antennas with tailorable performance specifications with regards to spectral coverage, absorbance intensity, and efficiency of exciton delivery and transduction. The specific objectives are to:

- Develop self-assembled macromolecular arrays based on tunable synthetic pigments coupled to natural or designer polypeptide scaffolds
- Control mesoscale architecture of antennas in lipid bilayers or liposomes
- Nanopattern arrays of biohybrid/bioinspired antennas and reaction centers (RCs) on surfaces in various geometries, including nanoscale lines and dots

The overall aim is to design biohybrid and bioinspired architectures for energy collection and storage.

Specific Objectives for Theme 3—Antenna-Reaction Center Interface: Organization and Delivery
PARC seeks a fundamental understanding of antenna-RC interfaces in native, biohybrid, and bioinspired antennas optimized for total control over molecular (structural, energy, redox) characteristics for delivery of energy, electrons or redox equivalents to downstream processes such as catalysis, fuels production or photocurrent generation. The specific objectives are to:

- Understand and manipulate the interfacing and regulation of antenna and RC units in native photosynthetic systems
- Extend the functionality of biohybrid and bioinspired arrays to include sites of energy trapping and photochemistry at defined positions
- Fabricate multi-component assemblies or networks of electronically communicating antennas and RCs on surfaces to promote long-range, directional energy flow

The overall aim is to understand and control the coupling of antenna and RC functions in solar energy conversion systems.

Photosynthetic Antenna Research Center (PARC)	
Washington University in St. Louis	R.E. Blankenship (Director), D. Holten (Associate Director and Theme 3 Lead), H. Pakrasi (Theme 1 Lead), C. Kirmaier, M. Gross
Los Alamos National Laboratory	G. Montaño
North Carolina State University	J. Lindsey
Northwestern University	P. Loach and P. Parkes-Loach
Oak Ridge National Laboratory	D. Myles and V. Urban
Pennsylvania State University	D. Bryant
Princeton University	G. Scholes
Sandia National Laboratory	J. Timlin
University of California, Riverside	D. Bocian
University of Glasgow, UK	R. Cogdell
University of Illinois	K. Schulten
University of New Mexico	A. Shreve
University of Pennsylvania	P.L. Dutton and C. Moser
University of Sheffield, UK	N. Hunter (Theme 2 Lead)

Contact: Robert E. Blankenship, Director, blankenship@wustl.edu
314-935-7971; http://parc.wustl.edu/

GRAND CHALLENGES INDEX

The Basic Energy Sciences Advisory Committee (BESAC) Grand Challenges report, "Directing Matter and Energy: Five Challenges for Science and the Imagination", identifies the most important scientific questions and science-driven technical challenges facing Basic Energy Sciences (BES) and describes the importance of these challenges to advances in disciplinary science, to technology development, and to energy and other societal needs. Each EFRC addresses one or more of these grand challenges. For more information, see http://science.energy.gov/bes/efrc/research/grand-challenges/.

How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?.....7, 19, 21, 23, 29, 31, 43, 45, 55, 63, 71

How do remarkable properties of matter emerge from the complex correlations of atomic or electronic constituents and how can we control these properties?.....1, 5, 9, 11, 13, 17, 19, 23, 29, 31, 33, 37, 41, 45, 49, 55, 63, 65, 69

How do we characterize and control matter away—especially very far away—from equilibrium?.....1, 3, 5, 9, 11, 17, 19, 23, 25, 27, 29, 31, 35, 37, 41, 43, 47, 55, 57, 63, 65, 67, 69

How do we control materials processes at the level of electrons?.....3, 5, 7, 9, 11, 19, 21, 23, 25, 27, 31, 35, 37, 39, 43, 47, 49, 53, 59, 61, 63, 65

How do we design and perfect atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties?.....3, 5, 7, 9, 11, 13, 15, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 47, 49, 51, 55, 59, 61, 63, 65, 67, 71

BES REPORTS INDEX

BES-sponsored workshop reports engaged participants from universities, industry, and DOE laboratories to help identify research directions for a decades-to-century energy strategy. The 36 Energy Frontier Research Centers directly address the use-inspired energy challenges articulated in these reports. For more information, see http://science.energy.gov/bes/efrc/research/bes-reports/.

Advanced Nuclear Energy Systems.....11, 35, 41, 65
Carbon Capture: Beyond 2020.....13, 17, 51, 69
Catalysis for Energy.....9, 13, 15, 25, 29, 31, 33, 39, 45, 49, 55, 61, 63
Clean and Efficient Combustion of 21st Century Transportation Fuels.....31, 49, 51
Computational Materials Science and Chemistry: Accelerating Discovery and Innovation through Simulation-Based Engineering and Science.....3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 27, 29, 31, 33, 39, 41, 43, 49, 51, 55, 59, 61, 63, 65, 67, 69, 71
Electrical Energy Storage.....1, 3, 9, 33, 47, 49, 59
Environmental Management.....11, 37, 41, 65, 67, 69
From Quanta to Continuum: Mesoscale Science.....3, 5, 7, 9, 15, 17, 19, 21, 23, 27, 29, 31, 33, 39, 41, 43, 45, 47, 51, 55, 57, 59, 61, 63, 65, 69, 71
Geosciences: Facilitating 21st Century Energy Systems.....9, 17, 51, 57, 69
Hydrogen Economy.....9, 25, 27, 31, 39, 49, 51, 55, 63
Materials under Extreme Environments.....7, 9, 11, 23, 33, 35, 41, 49, 65
New Science for a Secure and Sustainable Energy Future.....7, 11, 15, 19, 23, 27, 29, 31, 33, 39, 43, 45, 53, 55, 57, 63, 69
Science for Energy Technology: Strengthening the Link between Basic Research and Industry.....7, 9, 11, 19, 23, 27, 29, 31, 33, 45, 47, 49, 51, 55, 57, 59, 61, 63, 65, 69
Solar Energy Utilization.....7, 9, 19, 21, 23, 25, 27, 29, 31, 39, 45, 49, 63, 71
Solid-State Lighting.....7, 21, 23, 27
Superconductivity.....5, 9, 11

TOPICAL INDEX

biofuels (including algae and biomass).....25, 43, 45, 55, 71
bio-inspired.....25, 29, 31, 39, 43, 55, 71
carbon capture.....13, 17, 51
carbon sequestration.....17, 43, 57, 69
catalysis
  heterogeneous.....9, 13, 15, 31, 33, 45, 49, 55, 59, 61, 63
  homogeneous.....29, 31, 39, 45, 55, 63
charge transport.....1, 3, 5, 7, 9, 19, 21, 23, 27, 29, 31, 33, 47, 59, 63
corrosion.....37, 59, 65
defects.....3, 7, 9, 11, 13, 19, 23, 27, 33, 35, 49, 57, 59, 63, 65
energy storage (including batteries and capacitors).....1, 3, 9, 11, 33, 39, 47, 49, 59
hydrogen and fuel cells.....9, 25, 27, 31, 39, 49, 51, 55, 63
interface
  gas/liquid.....17, 55, 57
  gas/solid.....9, 13, 17, 23, 37, 45, 49, 51, 55, 57, 59, 61
  liquid/solid.....1, 3, 17, 19, 23, 27, 31, 33, 37, 39, 41, 45, 47, 49, 55, 57, 59, 61, 63, 65, 71
  metal/oxide.....7, 11, 13, 15, 19, 23, 27, 31, 37, 41, 47, 53, 55, 59, 61, 63, 65
  metal/semiconductor.....7, 11, 19, 23, 27, 31, 47, 59, 63, 71
  organic/metal.....7, 23, 31, 45, 47, 59, 63
  organic/organic.....7, 17, 29, 31, 43, 45, 47, 51, 71
  organic/oxide.....3, 7, 13, 21, 23, 31, 47, 51, 59, 63, 65
  organic/semiconductor.....7, 21, 23, 27, 29, 31, 33, 47, 59, 63
  semiconductor/semiconductor.....7, 11, 19, 21, 23, 27, 31, 49, 63
  solid/solid.....1, 3, 7, 17, 19, 23, 27, 31, 45, 47, 55, 57, 59, 63, 65
materials
  actinide.....11, 37, 65, 67
  biological (DNA, protein).....25, 29, 43, 45, 71
  cellulose.....43, 45, 55, 59
  ceramic.....3, 5, 7, 9, 11, 37, 59, 65
  glass.....7, 9, 37, 67
  ionic liquid.....23, 29, 33, 59
  metal.....7, 11, 15, 23, 27, 31, 33, 35, 37, 47, 53, 55, 59, 61, 63, 65
  optoelectronic and metamaterial.....7, 9, 19, 21, 23, 27, 49, 63
  organic semiconductor.....21, 23, 27, 31, 63
  oxide.....1, 3, 5, 7, 9, 11, 13, 15, 19, 23, 27, 31, 33, 37, 47, 49, 53, 55, 59, 61, 63, 65, 67
  polymer.....7, 13, 21, 23, 29, 31, 43, 45, 47, 51, 59, 63, 65, 71
  porous.....3, 7, 9, 11, 13, 15, 23, 31, 33, 51, 55, 57, 59, 61, 63, 65, 67
  rare earth elements.....7, 11, 21, 23, 65, 67
  semiconductor.....7, 9, 11, 19, 21, 23, 27, 29, 31, 33, 49, 59, 63
  transparent conductor.....7, 19, 21, 23, 27, 31, 33, 63
  wide band-gap semiconductor.....7, 9, 11, 19, 21, 23, 27, 31, 63
materials and chemistry by design.....1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 27, 29, 31, 33, 35, 37, 39, 43, 45, 49, 51, 55, 59, 61, 63, 65, 67, 71
mechanical behavior.....7, 17, 23, 33, 43, 49, 51, 57, 59
membrane.....13, 31, 51, 59
mesostructured materials.....3, 7, 9, 15, 17, 19, 21, 23, 29, 31, 33, 43, 45, 47, 55, 57, 59, 63, 65, 71
nanostructured materials
  0D.....7, 19, 21, 23, 29, 33, 47, 59, 63, 65, 67
  1D.....7, 9, 19, 21, 23, 27, 29, 31, 33, 47, 59, 63, 65
  2D.....1, 3, 7, 13, 19, 21, 23, 27, 29, 31, 33, 47, 49, 53, 59, 63, 65
  3D.....3, 7, 13, 15, 19, 21, 23, 27, 29, 31, 33, 43, 45, 47, 51, 55, 59, 61, 63, 65, 71
  nanocomposites.....3, 7, 9, 19, 23, 31, 43, 45, 47, 53, 59, 63, 65
nuclear (including radiation effects).....11, 35, 37, 41, 65, 67
optics.....7, 19, 21, 23, 27, 31
phonons.....7, 9, 23, 27, 31, 35, 53
photosynthesis (natural and artificial).....21, 31, 39, 63, 71

separations.....11, 13, 33, 41, 45, 51, 55, 65
solar
fuels.....9, 25, 27, 31, 39, 63, 71
photovoltaic.....7, 9, 19, 21, 23, 27, 29, 31, 49, 63
thermal.....7, 23, 27
solid state lighting.....7, 21, 23, 27
spin dynamics.....5, 21, 23, 31, 35, 53
spintronics.....21, 23, 53
superconductivity.....5, 9, 11
synthesis
atomic layer deposition.....5, 19, 27, 31, 59, 63
novel materials.....1, 3, 5, 7, 9, 11, 13, 15, 19, 23, 27, 29, 31, 33, 35, 39, 43, 45, 49, 51, 55, 59, 61, 63, 65, 67, 71
scalable processing.....7, 11, 13, 19, 23, 31, 51, 55, 59, 65
self-assembly.....7, 11, 13, 19, 29, 31, 33, 43, 51, 55, 59, 63, 65, 67, 71
thermal conductivity.....7, 9, 23, 35, 53
thermoelectric.....9, 23, 27, 53

EXPERIMENTAL AND THEORETICAL METHODS INDEX

classical mechanics.....17, 19, 23, 25, 29, 31, 33, 39, 43, 51, 57, 61, 65
continuum modeling.....3, 7, 17, 29, 31, 33, 39, 43, 47, 55, 57, 59, 61, 69, 71
density functional theory (DFT).....1, 3, 5, 9, 11, 13, 15, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57, 59, 61, 63, 65, 67, 71
electron microscopy.....1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 23, 27, 29, 33, 35, 37, 43, 45, 47, 55, 57, 59, 61, 65, 71
extreme scale computing.....17, 57
finite element method.....7, 19, 31, 43, 57, 59, 63, 69
high-throughput screening methods.....3, 21, 27, 31, 49, 51, 55, 59, 61
laser diagnostics.....19, 23, 27, 31, 65
lithography.....7, 19, 21, 23, 29, 31, 59, 71
mesoscale modeling.....3, 5, 7, 15, 17, 19, 21, 23, 29, 31, 33, 43, 45, 47, 51, 55, 57, 59, 61, 67, 71
molecular dynamics (MD).....3, 9, 11, 13, 15, 19, 21, 23, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 49, 51, 55, 57, 59, 61, 63, 65, 67, 71
monte carlo (MC).....3, 5, 7, 9, 13, 19, 21, 23, 29, 31, 35, 37, 41, 43, 51, 53, 55, 57, 59, 61, 65, 67, 71
multiscale modeling.....3, 5, 7, 13, 15, 17, 19, 23, 27, 29, 31, 33, 35, 37, 41, 43, 45, 47, 49, 51, 55, 57, 59, 61, 67, 71
near-field scanning optical microscopy.....3, 7, 11, 23, 27, 31, 43, 71
neutron diffraction and scattering.....3, 9, 11, 13, 17, 23, 33, 35, 41, 43, 51, 59, 65, 67, 71
neutron spectroscopy.....3, 9, 11, 13, 23, 33, 41, 71
next generation optimization methods.....7, 9, 19, 27, 61
quantum mechanics.....5, 7, 9, 11, 13, 15, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 43, 45, 49, 51, 53, 55, 61, 63, 65, 71
scanning probe microscopy.....3, 5, 7, 9, 11, 13, 15, 19, 23, 27, 29, 31, 33, 37, 41, 43, 45, 47, 49, 55, 59, 61, 65, 71
surface science.....1, 11, 13, 15, 19, 23, 27, 29, 31, 33, 37, 41, 43, 47, 49, 55, 57, 59, 61, 63, 65, 69, 71
ultrafast physics.....5, 11, 19, 31, 35, 49, 63, 71
X-ray diffraction and scattering.....1, 3, 5, 9, 11, 13, 17, 19, 23, 25, 27, 29, 31, 33, 35, 39, 43, 45, 47, 51, 55, 57, 59, 61, 65, 67, 71
X-ray imaging.....1, 3, 9, 11, 31, 45, 47, 57, 59, 65
X-ray spectroscopy.....3, 9, 11, 15, 17, 23, 27, 31, 35, 43, 45, 47, 51, 55, 59, 61, 65, 67

FRONT COVER IMAGE

Electron density map of crystalline dense Li showing an inverse relationship to that of hydrogen.
Provided by the Energy Frontier Research in Extreme Environments (EFree) EFRC led by Russell Hemley at the Carnegie Institution of Washington (page 9).

CONTACT

Basic Energy Sciences
U.S. Department of Energy
SC-22/Germantown Building
1000 Independence Ave., SW
Washington, D.C. 20585
sc.bes@science.doe.gov
Phone: 301.903.3081
Fax: 301.903.6594
http://science.energy.gov/bes/efrc

DISCLAIMER

This report is a compilation of accounts of work sponsored by an agency of the United States Government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.