

Session A – Organic Photovoltaics - Grand Ballroom South**Parallel Scientific Session I - May 26, 2011
Grand Ballroom South**

10:15 - 10:35

T-A01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA

[CST] [Xiaoyang Zhu](#) and [Jennifer Lyon](#)*University of Texas at Austin*

A memorial tribute to Paul F. Barbara (1953-2010), world-renowned laser spectroscopist, Professor of Chemistry at the University of Texas at Austin, member of the National Academy of Sciences and founding Director of the DOE Energy Frontier Research Center on Understanding Charge Separation at Interfaces in Energy Materials (EFRC:CST). Here we celebrate Paul's "lifetime in the excited state," including his numerous scientific achievements, academic developments and, above all, his tireless enthusiasm for the pursuit of fundamental scientific knowledge.

10:35 - 11:15

T-A02 - CHARGE SEPARATION AND TRANSFER AT ORGANIC SEMICONDUCTOR INTERFACES: FROM SINGLE MOLECULES TO SINGLE CRYSTALS

[CST] [Xiaoyang Zhu](#), [Peter J. Rossky](#), Loren Kaake, Adam Willard, Michael Bedard-Hearn, and Raluca Gearba*University of Texas at Austin*

We highlight recent successes in our coordinated experimental and theoretical efforts to understand fundamental charge separation and transfer (CST) mechanisms at model organic photovoltaic (OPV) interfaces. Experimentally, we have developed a femtosecond electric field meter based on nonlinear optical spectroscopy to probe charge separation dynamics at organic donor/acceptor interfaces. In contrast to traditional approaches such as transient absorption where signals from interfacial CST processes are often overwhelmed from processes in the bulk donor or acceptor phase our technique is most sensitive to charge separation at the interface and thus allows us to probe key charge separation mechanisms e.g. the dependences of charge separation rates on relative molecular orientation at the interface or the amount of excess energy from optical excitation. We are applying our theoretical developments in a mixed quantum-classical nonadiabatic molecular dynamics simulation to directly simulate the coupled nuclear and excitonic dynamics of model OPV molecular systems allowing a priori observation of dynamical electronic events. Thus we can study the same processes as measured experimentally without imposing an assumed model for molecular-scale structure or active kinetic processes. Examples of results from simulation that visualize the nanoscale electronic excited state dynamics of oligomers of PPV and thiophene as well as their interfaces with C₆₀ will be described.

11:15 - 11:35

T-A03 - PLASTIC SOLAR CELLS: SELF-ASSEMBLY OF BULK HETEROJUNCTION NANO-MATERIALS BY SPONTANEOUS PHASE SEPARATION

[CEEM] [Alan Heeger](#)*University of California, Santa Barbara*

I will describe the discovery of ultrafast photoinduced electron transfer as the scientific foundation for the creation of a technology for low cost "plastic" solar cells. This initial charge separation occurs at a time scale two orders of magnitude faster than the first step in photo-synthesis in green plants. Charge collection at the electrodes is accomplished through self-assembly of bulk heterojunction (BHJ) nano-materials by spontaneous phase separation. I will focus on the details of the operating mechanism; the origin of the open circuit voltage (Voc), the role of morphology on the charge separation and charge collection at the electrodes, the need for charge selective buffer layers and the origin of the limitations on the fill factor (FF). I will focus on our recent studies of the competition between sweep-out and recombination and on studies of recombination mechanisms in BHJ solar cells.

11:35 - 11:55

T-A04 - UNDERSTANDING THE MORPHOLOGY OF ORGANIC PHOTOVOLTAICS

[PHaSE] [Thomas Russell](#)*University of Massachusetts Amherst*

PHaSE's technical focus is aimed at basic research underpinning the conversion of the sun's energy into electrical power, using organic polymer-based and related composite materials. The Center's research is pursued by highly interdisciplinary

research cross-over among three basic focus areas (Energy Research Groups): design and synthesis, assembly and morphology, photophysical evaluation and basic device design. Synthetic targets are conjugated homopolymers, block copolymers and segmented structures, and molecule/polymer/nanoparticle composites that can be varied to tune electron withdrawing and electron donating functionality. The design and fabrication of high efficiency photovoltaic devices requires precise control over the nanoscale morphology, molecular ordering, and interfacial properties of all of the components comprising the device. Photophysical details of charge and energy transport within nanostructured composite films, coupled with absorption and efficiency measurements, provide a typical set of "test solar cell" parameters. "Feedback" discussions among these areas speeds up the selection of the most promising strategies for pursuit.

11:55 - 12:15

T-A05 - HIGH EFFICIENCY ORGANIC PHOTOVOLTAIC CELLS: MICROSTRUCTURAL, ELECTRONIC STRUCTURAL, AND INTERFACIAL MATERIALS DESIGN

[ANSER] Tobin Marks¹, Lin Chen², Luping Yu³, Mark Ratner⁴, and Robert Chang⁴

¹Northwestern U.; ²Argonne National Lab.; ³U. of Chicago; ⁴Northwestern U.

Research in organic photovoltaic (OPV) cells has made impressive advances over the last three years with cell laboratory efficiencies now reaching 9%. The upper theoretical limit of power conversion efficiency for single-layer OPVs is ~23%. Organic cells offer the potential of low-cost, readily manufacturable, and durable solar power for a wide range of in-door and out-door applications. Further gains in efficiency and durability, to that competitive with high-performance inorganic photovoltaics, will require understanding breakthroughs in active, interfacial, and passive cell materials. This project involves an integrated basic research program by an experienced and highly collaborative interdisciplinary team of investigators with expertise in organic materials synthesis and characterization, interfacial science, quantum theory, and solar cell fabrication and characterization. This lecture describes recent experimental and theoretical results from this effort, focusing on the fascinating effects on OPV response characteristics of the active layer bandgap, carrier mobility, exciton dynamics, and how these in turn are affected by materials processing methodology as well as interfacial layers inserted between the active layer and cell electrodes. It will be seen that previously unrecognized nanostructural details such as how the organic layers contact the electrode can play a major role in enhancing cell power conversion efficiency to near 8% as well as enhancing cell durability.

**Parallel Scientific Session II – May 26, 2011
Grand Ballroom South**

1:45 - 2:05

T-A06 - THE INTERFACE SCIENCE OF PHOTOVOLTAIC SOLAR ENERGY CONVERSION: CHARGE TRANSFER AT INORGANIC-ORGANIC AND INORGANIC-INORGANIC INTERFACES MODULATED BY HOLE- AND ELECTRON-SELECTIVE INTERLAYERS

[CISSEM] Neal Armstrong¹, Erin Ratcliff¹, Brian Zacher¹, Gordon MacDonald¹, Laura Schirra¹, Oliver Monti¹, Xerxes Steirer¹, Dana Olson², Jens Meyer³, Antoine Kahn³, Hyeunseok Cheun⁴, and Bernard Kippelen⁴

¹University of Arizona; ²National Renewable Energy Laboratory; ³Princeton University; ⁴Georgia Institute of Technology

Emerging PV technologies require efficient charge formation and selective charge harvesting, competing with charge recombination processes that steal power from the PV platform. Interfaces between active layers and charge harvesting electrodes, and between active layers, electrodes and barrier films (which prevent ingress of ambient gases), determine the efficiency and lifetime of emerging PV technologies. We will provide here an overview of the science underlying selective harvesting of photo-generated charges, and the interfacial processes that lead to high efficiency and long device lifetimes. Emerging PV platforms based on highly dispersed organic/inorganic hybrid films require charge selective interlayers at each contact. For hole-collection these films can be surface-grafted, electrodeposited, or spin-cast conducting polymers, or p-type wide bandgap metal oxides. For electron collection n-type metal oxide films are typically used. This presentation will summarize the way in which surface composition controls the energetics of the interlayer, its charge harvesting selectivity, and its compatibility with PV active layers.

2:05 - 2:25

T-A07 - STRATEGIES TO CONTROL THE MORPHOLOGY OF ORGANIC PHOTOVOLTAICS

[PHaSE] Dhandapani Venkataraman

University of Massachusetts Amherst

Our aim to develop methods based on self-assembly to reliably assemble organic semiconductors into nanoscale structures relevant for photovoltaic cells and discover optimal structures for efficient organic photovoltaic cells. This talk will focus on strategies that are currently being pursued in PHaSE and their current status. Specifically, this talk will focus

on our molecular understanding of the formation of bulk heterojunction structures. It will also focus on the development and assembly of novel conjugated polymer architectures and structures into nanoscale structures based on our understanding.

2:25 - 2:45

T-A08 - MODIFYING THE WORK FUNCTION OF TRANSPARENT CONDUCTING OXIDES THROUGH INTERFACE CHEMISTRIES FOR INVERTED ARCHITECTURE ORGANIC-PHOTOVOLTAICS

[CISSEM] [Bernard Kippelen](#), Yinhua Zhou, Hyeunseok Cheun, William Potscavage Jr., Canek Fuentes-Hernandez, Seth Marder, Jens Meyer, and Antoine Kahn

Georgia Institute of Technology

In this talk, we will discuss the important role played by interfaces in the operation of organic photovoltaic devices. We will first show how the modification of the electronic properties of the transparent electrode can be used to change the geometry of the solar cell and build solar cells that do not require the use of low-work function, chemically reactive electrodes. Such inverted device architectures promise to have superior stability compared to conventional organic solar cells. Then, we will discuss the use of contact materials that do not use indium-tin-oxide or vacuum-deposited metal electrodes. In such solar cells both electrodes are comprised of conducting polymer films that are modified to become either hole or electron collecting electrodes. Finally, we will describe examples of organic solar cell architectures in which all layers are comprised of polymers that can be processed from solution. We believe that these strategies pave the way to very low-cost photovoltaic technologies with light-weight and flexible form factors, and a variety of new studies focused on the chemistry and electronic properties of these new materials with OPV active layers.

2:45 - 3:05

T-A09 - THE ROLE OF NANOSCALE ARCHITECTURE IN THE PERFORMANCE OF CONJUGATED POLYMER-BASED PHOTOVOLTAIC DEVICES

[MEEM] [Benjamin Schwartz](#), Sarah Tolbert, Yves Rubin, Daniel Neuhauser, Nikos Kopidakis, Alex Ayzner, Stephanie Doan, Chris Tassone, Bertrand Tremolet de Villers, Krastina Petrova, and Daniel Kilbride

University of California, Los Angeles

Although traditional polymer/fullerene solar cells make use of spin-coated blends of the two materials, producing a so-called bulk-heterojunction, we find that a sequential solution-deposition method, first spin-coating the polymer and then the fullerene, can produce reproducible, high-efficiency polymer-based solar cells. Part of the reason that the sequential deposition method works so well is that it leaves the polymer in a highly crystalline state, opening a long-range energy transfer mechanism that helps separate excitations on the polymer into charge carriers on the different organic components. In light of this new mechanism, we have reexamined the exciton diffusion length in polymeric materials like P3HT using both modified TiO₂ and fullerenes as quenchers, and found that when the polymer is highly crystalline, excitons can easily be quenched as distances of over ~30 nm. This is several times longer than the canonical numbers for the exciton diffusion length in the literature, and suggests several new routes for both developing new materials and optimizing device architecture to produce efficient, inexpensive, polymer-based solar cells.

3:05 - 3:45

T-A10 - MATERIALS AND DEVICES FOR ORGANIC PHOTOVOLTAIC DEVICES

[RPEMSC] [Colin Nuckolls](#), [Theanne Schiros](#), and [Ioannis Kymissis](#)

Columbia University

We are developing new organic semiconductor materials that are explicitly designed to give controlled nanoscale structure at the interface in heterostructure photovoltaic device configurations. One such concept is the development of a shape-complementary interface between curved donor (doubly concave contorted hexabenzocoronene) and acceptor (C₆₀) molecules. Devices based on this concept have achieved relatively high open circuit voltages within 10% of the theoretical limit. X-ray measurements indicate an extended "ball-and-socket" structure and fast charge transfer between molecular partners in intimate electronic contact at the donor-acceptor interface in bilayer device structures. The data suggests that the improved functional device performance results from an improved donor-acceptor interface that enhances exciton dissociation. A second concept involved development of materials that undergo a heat-induced self-assembly process to form pi-stacked, columnar superstructures that merge into a 3-D network of cables. The 3-D network functions as a scaffold for the molecular recognition and directed assembly of C₆₀, thereby forming a nanostructured p-n bulk heterojunction. When incorporated into a solar cell, this reticulated heterojunction provides a significant increase in the power conversion efficiency over the parent compound.

Parallel Scientific Session III – May 26, 2011
Grand Ballroom South

4:00 - 4:20

T-A11 - EXCITONIC ANTENNAS FOR SOLAR CELLS

[CE] Marc Baldo, Troy Van Voorhis, Jiye Lee, Priya Jadhav, Carmel Rotschild, and Phil Reuswig
MIT

The lowest cost solar cells manufactured to date employ a single material to absorb light. These cells are known as single junction solar cells, and their efficiency is limited by the bandgap energy of the solar cell material. The bandgap sets the lowest energy photon that can be absorbed, and it also determines the voltage that the solar cell can produce. Our EFRC proposed to push beyond the so called 'single junction' efficiency limit by converting the wavelengths of sunlight to match silicon's bandgap and wavelength cutoff at 1100nm. Ideally, all sunlight in the blue and green with wavelengths shorter than 550nm should be converted into two photons at 1100nm. Next, two photons with wavelengths in the region 1100nm to 2200nm can be combined into a single photon at 1100nm. If successful, this can increase the efficiency of a silicon solar cell to about 40%. To downshift and split photons we exploit singlet exciton fission. We will discuss our recent demonstration of efficient singlet fission and charge extraction from tetracene. To up-convert and combine photons we propose to convert sunlight into a coherent source and then use phase matched wavelength conversion. We will describe our recent progress towards incoherent pumping of a high quality factor resonator.

4:20 - 4:40

T-A12 - EXCITON MANAGEMENT IN ORGANIC PHOTOVOLTAICS

[CEN] Mark Thompson¹, Barry C. Thompson¹, Stephen Bradforth¹, Sean Roberts¹, Matthew Whited¹, Robert McAnally¹, Beate Burkhart¹, Stephen Forrest², and Jeramy Zimmerman²
¹University of Southern California; ² University of Michigan

We have explored the use of both polymeric and molecular materials for extending the active wavelengths for photovoltaic devices into the near infrared. I will discuss the use of these materials as donor materials in both lamellar and bulk heterojunction OPVs, illustrating how these materials can be used to enhance both the efficiency and Voc. The exciton is a critical part of each of these processes, and being able to control the location, lifetime and energy of the exciton is essential to achieving high efficiency. We have investigated methods for tuning exciton energies and controlling their migration paths, both intramolecularly and within a thin film. I will discuss our most recent work with porphyrinic materials for OPVs. This involves a careful materials design study that leads to both low energy absorption (into the nearIR) and the use of substituted porphyrins to efficiently harvest photons through the entire visible spectrum. Both long wavelength and broad absorption are achieved with high extinction ($> 10^5 \text{ cm}^{-1}$). Moreover, we have measured the intra- and intermolecular exciton dynamics for both singlet and triplet excitons in these materials.

4:40 - 5:20

T-A13 - DYE-SENSITIZED PHOTOELECTROSYNTHESIS CELLS: FROM SYNTHESIS TO ASSEMBLY

[UNC] Javier Concepcion, Rene Lopez, and Kenneth Hanson
UNC

The efficiencies of dye-sensitized solar cells (DSSCs) and dye-sensitized photoelectrosynthesis cells (DSPECs) are dictated by the interfacial structure, semiconductor, and intra-assembly dynamics. A UNC EFRC goal is to use a modular approach to DSPECs for water splitting and reduction of CO₂. In this approach, individual components for light absorption, intramolecular and interfacial electron and proton transfer, and catalysis are investigated and integrated in molecular assemblies on the surfaces of high band gap oxide semiconductors. Performance of the resulting device configurations is evaluated by transient laser, photocurrent, and product measurements. In this presentation we will summarize recent progress towards this goal including 1) synthesis and characterization of interfacial catalysts for water oxidation and CO₂ reduction, 2) development of vertically structured arrays of TiO₂, Nb₂O₅ and SrTiO₃ electrode materials fabricated by pulsed laser deposition, 3) strategies for assembly and stabilization of chromophores and catalysts on metal-oxide surfaces, and 4) quantitative evaluation of the resulting structures by laser spectroscopic and photocurrent measurements.

5:20 - 5:40

T-A14 - COMPUTATIONAL MOLECULAR ELECTROCATALYSIS: THE ROLE OF PROTON RELAYS IN H₂ OXIDATION AND EVOLUTION CATALYSTS[CME] Michel Dupuis¹, Simone Raugei¹, Roger Rousseau, Shentan Chen, M.H. Ho, R. Morris Bullock, Daniel L. DuBois, Jenny Y. Yang, Sharon Hammes-Schiffer², Alexander V. Soudakov², Samantha Horvath², and Laura E. Fernandez²
¹*Pacific Northwest National Laboratory*; ²*Pennsylvania State University*

The rational design of improved molecular electrocatalysts for small molecule activation (for example H₂, O₂, N₂, H₂O) requires a detailed molecular level understanding of the energetic and mechanistic factors controlling the movement of protons and electrons during the catalytic cycle. Ni(P₂N₂)₂²⁺ complexes are a family of mononuclear nickel complexes with cyclic diphosphine ligands that incorporate amine bases as a mimic of enzyme functionalities. The presence and positioning of the amine bases near the metal center is the critical structural feature for the activity[1-2] and the efficiency of these catalysts, as these bases facilitate the heterolytic cleavage or formation of the H-H bond while acting as proton relays in the management of the proton and electron movement during the catalytic cycle. We will highlight novel first-principles studies of the catalytic cycles of the Ni(P₂N₂)₂²⁺ catalysts. Complexes with N-H and Ni-H bonds ("Proton-hydride" species) are key intermediates. H₂ oxidation and evolution proceed via heterolytic bond cleavage or formation of the H-H bond. We will discuss what we have learned about these catalysts, the importance of the proton relays, their number, their active and inactive states, the role of solvent and water molecules in giving rise to fast turnover rates, and aspects of proton coupled electron transfers in the electrocatalytic steps. The concept of proton relays is being extended to O₂ and N₂ reduction reactions. REFERENCES: [1] DuBois D. L. and Bullock R. M., *Eur. J. Inorg. Chem.* 2011, 1017; [2] Yang, J. Y.; Chen, S.; Dougherty, W. G.; Kassel, W. S.; Bullock, R. M.; DuBois, D. L.; Raugei, S.; Rousseau, R.; Dupuis, M.; Rakowski DuBois, M. *Chem. Comm.* 2010, 46, 8618.

5:40 - 6:00

T-A15 - A TWO-JUNCTION ARTIFICIAL LEAF: OPTIMIZING ARTIFICIAL ANTENNAS AND REACTION CENTERS FOR SOLAR-DRIVEN WATER TO HYDROGEN REDOX PROCESSES

[BISfuel] Ana L. Moore, Thomas A. Moore, Devens Gust, Antaeres' Antoniuk-Pablant, Jesse Bergkamp, Gerdenis Kodis, Matthieu Koepf, Jackson Megiatto, Dalvin Mendez, Smitha Pillai, Benjamin Sherman, and Yuichi Terazono
Arizona State University

The objective of this research is to design an artificial leaf that combines selected features of photosynthesis with dye-sensitized photovoltaic technology to achieve solar-to-fuel efficiencies that surpass those of photosynthesis or single-junction PV-driven electrolysis of water. Features from photosynthesis include pigments and catalysts inspired by those used in water-oxidizing photosystem II (PSII) and in bacterial photosynthesis. The combination of these two pigment systems in an artificial construct will harvest approximately twice the photon flux of natural photosynthesis, thereby providing a much improved match of the solar spectrum to the chemical work of driving water oxidation and proton reduction. Features and principles taken from technology include the use of DSSC-type photoelectrodes sensitized by these pigments and assembled in a tandem, two-junction system architecture. Excited dyes on the photoanode will inject electrons into semiconductors such as SnO₂, leaving an oxidized high-potential sensitizer to drive the catalyst. The second photosystem will be sensitized by low-potential naphthalocyanines/phthalocyanines which are functional mimics of bacteriochlorophyll and absorb light in the near IR. These dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to drive the reduction of protons to hydrogen. A redox relay will connect the output of the photoanode to the input of the low-potential photoelectrode.

Parallel Scientific Session IV – May 27, 2011
Grand Ballroom South

8:00 - 8:20

T-A16 - SYNTHESIS OF ORGANIC AND HYBRID MATERIALS FOR PHOTOVOLTAICS

[PHasE] Todd Emrick
UMass-Amherst

This lecture will describe progress in the synthesis of novel conjugated polymers and nanocomposites with the ultimate objective of producing plastic solar cells with higher efficiency and at lower cost than can be done today. Two primary lines of research will be highlighted: 1) the synthesis of hybrid materials, in which semiconductor particles, such as quantum dots, are surface-functionalized with conjugated polymers, such as poly(phenylene vinylene) and poly(3-hexylthiophene), and 2) the fabrication of robust cross-linked assemblies and materials from functionalized polythiophene based diblock and triblock copolymers. Particularly noteworthy is the ability to stabilize crystalline forms of these

conjugated polymers through cross-linking chemistry performed in solution and/or in the solid state. In addition to key synthetic elements, the structural and photophysical characterization of these materials will be presented, including UV-Vis absorption, photoluminescence, and transmission electron microscopy data that provides insight into polymer assembly in the solid state.

8:20 - 8:40

T-A17 - NANOSCALE CHARACTERIZATION OF CHEMICALLY MODIFIED OXIDE SURFACES AND EARLY STUDIES OF THE DYNAMICS OF SMALL NUMBERS OF CHARGE CARRIERS IN NANOSCALE VOLUMES

[CISSEM] David Ginger¹, Bradley Macleod¹, Andreas Tillack¹, Matthew Gliboff¹, Kristina Knesting¹, Hong Li², Jean-Luc Bredas², Sergio Paniagua², Seth Marder², Matthew Schalnat³, Jeanne Pemberton³, and Mariola Macech³

¹University of Washington ; ²Georgia Institute of Technology; ³University of Arizona

This talk will summarize our use of new tools to characterize the chemical and physical properties of oxide/organic interfaces at nanometer length scales, and first results of a new approach to imaging the dynamics of small numbers of charge carriers in nanoscale volumes, in the active layers of organic solar cells (OPVs). Dipolar molecular modifiers are now widely used to tune the wettability of oxide surfaces, their effective work function, and rates of heterogeneous electron transfer. Orientation of these molecules, which controls the dipolar fields at the oxide surface and rates of charge harvesting/injection, is being probed in our center by a combination of surface vibrational spectroscopies, X-ray reflectivity, and angle-dependent near-edge x-ray absorption fine structure (NEXAFS) at DOE synchrotron physics facilities (e.g. SLAC). In parallel with these studies we have recently developed a time resolved scanning probe microscopy to image the dynamics of small numbers of charge carriers in nanoscale volumes which is extremely sensitive to nanoscale morphology and disorder in the OPV active layer. It was previously possible to image carrier dynamics on sub-millisecond time scales, using time-resolved electrostatic force microscopy (trEFM). Recent efforts have improved the time resolution of this technique by over two orders of magnitude - opening up wide range of new interfacial phenomena to characterization at the nanoscale.

8:40 - 9:00

T-A18 - SOLAR ABSORPTION EFFECTS WITH ORGANIC MACROMOLECULAR PHOTOVOLTAIC MATERIALS

[CSTEC] Theodore Goodson III

University of Michigan

The absorption of solar energy program of the University of Michigan's CSTEC-EFRC seeks to find a deeper understanding of how the solar absorption process can be enhanced in particular organic materials. The group has developed a strong collaboration involving synthesis, optical experiments, and theory with Silsesquioxanes as one of the main target materials. The goal is to increase the solar absorption in different part of the spectrum with organic materials thru intramolecular interactions in the cage-like compounds and with particular functional groups on the cage. The team has developed new structure-function relationships between the fabricated and theoretically designed structures which have driven the experiments. The team of Michigan scientists and engineers use a broad spectrum of tools to investigate these materials, including femtosecond absorption and energy transfer measurements, time-resolved Raman, and transient absorption dynamics. This is accompanied with detailed electronic structure and dynamics calculations from the equally strong group of theorist in the team. In this talk the major accomplishments of the absorption group will be reviewed.

9:00 - 9:20

T-A19 - FULLY PHASE-COHERENT MULTIDIMENSIONAL OPTICAL SPECTROSCOPY FOR MEASUREMENT OF EXCITON AND MULTIEXCITON DYNAMICS

[CE] Keith A Nelson

MIT

Direct measurements of exciton dynamics and transport are critical in order to reach a fundamental understanding and how exciton properties and interactions are mediated by factors that might be engineered, including chromophore electronic structure, multichromophore complexation and aggregation, and material morphology. We have developed a versatile method for conducting multidimensional coherent optical spectroscopy of excitons, multiexcitons, and exciton-polaritons in inorganic, organic, and hybrid systems. The measurements have revealed coherent multiexciton energetics and dynamics, correlations among multiple exciton-polaritons, and organic J-aggregate exciton correlation lengths and inhomogeneities. In a typical experiment, multiple optical fields in different beams interact with the sample in succession to generate exciton coherences, biexciton coherences, and perhaps triexciton and even higher-order coherences; a time period passes during which coherent exciton or multiexciton oscillations take place and additional optical fields reduce the multiexciton coherence to a single-exciton coherence that finally radiates the signal that is measured as a function of the

time period, revealing the coherent oscillations, the multiexciton energetics and dephasing, and the extent of high-order multiexciton correlation that is possible. The entire measurement is controlled through reconfigurable beam shaping and femtosecond pulse shaping, with no interferometers or moving parts.

9:20 - 9:40

T-A20 - MEG TO MORPHOLOGY: THEORY APPLIED TO PHOTOVOLTAIC CONCEPTS

[RPEMSC] [David Reichman](#), Ashraf Alam, and Mark Hybertsen

Columbia University; Purdue University and Brookhaven National Laboratories

Theoretical progress in the Columbia EFRC is outlined. Studies range from phase-field modeling of how heterojunction morphology impacts organic solar cell performance to the understanding and use of multiple exciton generation in both organic molecular systems as well as nanostructured materials. Our efforts both compliment ongoing experimental activity as well as pave the way toward new experiments and design concepts aimed at increasing the understanding and efficiency of the fundamental building blocks of novel photovoltaic devices.

Session B – Inorganic Photovoltaics - Grand Ballroom Central

Parallel Scientific Session I – May 26, 2011 Grand Ballroom

10:15 - 10:35 (Joint with Session A)

T-B01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA

[CST] [Xiaoyang Zhu](#) and [Jennifer Lyon](#)

University of Texas at Austin

A memorial tribute to Paul F. Barbara (1953-2010), world-renowned laser spectroscopist, Professor of Chemistry at the University of Texas at Austin, member of the National Academy of Sciences and founding Director of the DOE Energy Frontier Research Center on Understanding Charge Separation at Interfaces in Energy Materials (EFRC:CST). Here we celebrate Paul's "lifetime in the excited state," including his numerous scientific achievements, academic developments and, above all, his tireless enthusiasm for the pursuit of fundamental scientific knowledge.

1:45 - 2:05

T-B02 - EXCITONICS IN NANOCRYSTAL QUANTUM DOTS

[CE] [Moungi Bawendi](#)

MIT

This talk will focus on three topics: 1. the study of excitons and biexcitons at the level of single quantum dots in CdSe nanocrystals, 2. the observation of fluorescence from single quantum dots emitting in the near IR, beyond 1 micron, and 3. exciton diffusion in close packed films of quantum dots. As an example for the first topic, we will show that the quantum yield of biexcitons can be obtained using photon correlation spectroscopy of single quantum dots. As an example for the second topic, we will show that PbS nanocrystals with fluorescence beyond 1 micron can be observed at the single quantum dot level. As an example for the third topic, we will show how surface treatments can change the rate of exciton diffusion in closed packed films of quantum dots.

2:05 - 2:25

T-B03 - NANOSTRUCTURED COMPOUND SEMICONDUCTORS FOR SOLAR ENERGY CONVERSION: FROM INTERFACES TO INTERMEDIATE BAND ABSORPTION

[CSTEC] [Rachel Goldman](#), Roy Clarke, Steve Forrest, Harley Johnson, Peicheng Ku, Cagliyan Kurdak, Joanna Millunchick, Xiaoqing Pan, Jamie Phillips, Vanessa Sih, Katsuyo Thornton, and Citrad Uher

University of Michigan

Currently, the highest efficiency solar cells are based upon compound semiconductor thin films. Further efficiency increases will require decreases in intrinsic loss mechanisms. Specifically, thermalization and transparency losses are linked as the bandgap energy cannot be simultaneously increased and reduced. Therefore, we are exploring new compound semiconductor materials architectures with outstanding electronic transport properties that can also absorb a greater portion of the solar spectrum. Within the inorganic photovoltaics thrust of CSTEC, we examine interface structure, carrier transport, and absorption in nanostructured compound semiconductors, including site-controlled nanostructures,

type II bandoffset materials, and highly mismatched alloys. Our coupled experimental-computational approach has enabled several achievements including the discovery of bowing of the atomic layers within quantum dots (QDs), with a half-layer stacking shift that may provide electronic decoupling of the QDs from the substrate, the development of a phase-field crystal model to examine QD/cap interfaces, the development of a transmission electron microscopy method for real-time studies of photo-induced transformations of the structure and electrical properties, the achievement of luminescent site-controlled QDs, and new insights into the role of the wetting layer and QD size variations on the sub-bandgap external quantum efficiency of QD intermediate-band solar cells.

2:25 - 2:45

T-B04 - SIMULATIONS OF OPTICAL ABSORPTION IN NANOWIRE ARRAYS FOR PHOTOVOLTAIC APPLICATIONS

[CEN] Chenxi Lin, Ningfeng Huang, and Michelle L. Povinelli

University of Southern California

We use electromagnetic simulations to study the effects of nano- and microscale patterning on light absorption in thin films for photovoltaic applications. We focus on vertically oriented semiconductor nanowire arrays and identify design rules for increasing broadband absorption across the solar spectrum. We quantify broadband absorption by calculating the ultimate efficiency, an upper bound on efficiency that assumes perfect carrier collection. For crystalline silicon nanowires, we have shown that optimized periodic arrays can have higher ultimate efficiency than unpatterned thin films, even though they contain less absorptive material. Design of the arrays to allow excitation of guided resonance modes increases absorption. We have further used optimal design strategies to demonstrate aperiodic structures with >100% absorption increase relative to their periodic counterparts. We have also examined the effect of metallic caps on the nanowire tips; we find that silver, gold, and copper hemispherical caps all decrease the solar efficiency. We compare silicon nanowire arrays to nanowire arrays consisting of GaAs and other common III-V materials. For each nanowire height and material, we determine the nanowire size and spacing that maximizes ultimate efficiency. For direct band gap materials such as GaAs, the ultimate efficiency converges more quickly as a function of height to the perfect absorption limit than for crystalline silicon, which is an indirect band gap material.

2:45 - 3:05

T-B05 - NANOPHOTONICS FOR OPTIMAL SOLAR THERMOPHOTOVOLTAIC SYSTEMS

[S3TEC] Marin Soljacic

MIT

In solar thermophotovoltaic systems, solar energy heats up an object to large temperatures; the object emits thermal radiation that is subsequently converted into electricity, using a narrow-gap PV cell. Theoretical models suggest that nanophotonic techniques could be used to design systems with very attractive over-all solar-electricity conversion efficiencies. In particular, one could explore nanophotonic techniques to optimally tailor the flow of thermal radiation, as well as tailoring the properties of thermal emission itself. We present results of our theoretical modeling of optimal solar-TPV systems, as well as first experimental results on various nanophotonic components of such systems.

3:05 - 3:25

T-B06 - PHOTOPHYSICS OF SEMICONDUCTOR NANOSTRUCTURES IN RELATION TO PROBLEMS OF SOLAR ENERGY CONVERSION

[CASP] Victor I. Klimov

Los Alamos National Laboratory

This presentation provides a brief overview of research activities in the Center for Advanced Solar Photophysics with focus on spectroscopy of processes in semiconductor nanocrystals (NCs) of relevance to solar energy conversion. One such process is carrier multiplication (CM), or multiexciton generation, which can increase photocurrent in solar cells. Recent efforts in this area include: the development of fast, reliable screening methods for CM yields using photon counting with superconducting nanowire detectors; studies of the impact of "extraneous" processes on CM measurements and the evaluation of the effects of the NC composition, size and shape on CM yields. As part of our effort on controlling excited-state dynamics, we study hot-electron transfer in NCs. We find that the efficiency of this process can approach 10% with incidental impurity-like acceptors, suggesting that even higher probabilities are possible with appropriately engineered acceptors. We also spectroscopically probe charge transport in NC-based exploratory devices such as optical field-effect transistors, unraveling the nature of conducting states in dark and under illumination, and helping to rationalize previously observed trends in carrier mobility and in the offset between photovoltage and nominal NC band gap. These studies illustrate how key insights into the performance of nanoscale materials are gained through close integration of spectroscopic, materials and device efforts across the Center.

Parallel Scientific Session III – May 26, 2011
Grand Ballroom Central

4:00 - 4:20

T-B07 - WHAT WENT WRONG WITH PAST EFFORTS TO USE EARTH ABUNDANT ABSORBERS SUCH AS FeS_2 : THE DESIGN OF A MATERIAL FIX.

[CID] Douglas Keszler¹, John Wager¹, and Liping Yu²
¹Oregon State University ²NREL

Realizing new, efficient solar absorbers containing earth-abundant materials represents a critical element for expanding the reach of photovoltaic (PV) technologies, meeting growing energy needs, and ameliorating atmospheric CO_2 concentrations. Among all of the elements, Fe is ranked fourth in terms of abundance in the earth's crust, and it is the least expensive metallic element to extract from Nature. The use of Fe in PV was proposed more than 25 years ago in the form of FeS_2 pyrite. Unfortunately, the material has been plagued by performance problems that to this day are both persistently present and not well understood. In this contribution, we report a concerted and integrated theoretical and experimental study that provides new insight into the problem of FeS_2 . Computational results on FeS_2 reveal high formation energies for bulk point defects and small formation energies for S vacancies near the surface. These findings are consistent with the formation of metallic S-deficient binary Fe-S phases at low temperatures that affect the electrical and optical properties of thin films. We have used this new understanding to propose and implement design rules for identifying new Fe-containing materials – Fe_2SiS_4 and Fe_2GeS_4 – that may circumvent the limitations of pyrite. These ternary p-type materials have band gaps near 1.5 eV and absorption coefficients that exceed 10^5 cm^{-1} at $E_g + 0.5 \text{ eV}$.

4:20 - 4:40

T-B08 - ADVANCED PHOTOELECTRODE ARCHITECTURES FOR EFFICIENT SOLAR ENERGY CONVERSION

[ANSER] Joseph Hupp
Northwestern University

This presentation will highlight ANSER's work on designing and fabricating nanostructured photoelectrodes that enhance solar energy conversion (primarily light-to-electrical energy conversion, but also photo-oxidation of water). Described will be photo-electrode materials and architectures that allow for: a) plasmon-amplified light harvesting, b) efficient electron collection, c) permanent anchoring of molecular chromophores, even in chemically aggressive environments, d) inhibition of electrode corrosion, and e) optimal modulation of interfacial electron tunneling.

4:40 - 5:00

T-B09 - LIGHT TRAPPING AND ABSORPTION BEYOND CLASSICAL LIMITS

[LMI] Harry Atwater
California Institute of Technology

Solar energy is currently enjoying substantial growth and investment, owing to worldwide sensitivity to energy security and climate change, and this has spurred basic research on light-matter interactions relevant to solar energy. Artificial photonic materials can enhance light-trapping and absorption, as well as increase the open circuit voltage and enhance quantum efficiency in solar photovoltaic structures. We describe photonic approaches for designing thin film and wire array solar cells that have light-trapping intensity and absorption enhancements that can exceed the conventional ergodic light-trapping limit using both wave optics and ray optics methods. From thermodynamic arguments, Yablonovitch and Cody in 1982 determined the maximum absorption enhancement in the ray optics limit for a bulk material to be $4n^2$, where n is the index of refraction of the absorbing layer. In 1997 this approach was expanded to study a simple thin film waveguide structure; however, for thin film waveguide structures, the maximum absorption enhancement is $<4n^2$. Using a combination of analytical and numerical methods, we describe why these structures do not surpass the conventional ergodic limit, and show how to design structures that can. Overall, we find many opportunities for exceeding the previously anticipated intensity enhancement and light trapping factor in dispersive dielectric and metallodielectric photovoltaic structures.

5:00 - 5:20

T-B10 - ENGINEERING LIGHT-MATTER INTERACTION IN ENERGY CONVERSION DEVICES

[CNEEC] Mark Brongersma, Isabell Thomann, Chinmay Nivargi, Art Wangperawong, Steve Herron, Dong Rip Kim, Sang Moo Jeong, Vijay Parameshwaran, Xiaolin Zheng, Thomas Jaramillo, Stacey Bent, Bruce Clemens, Vardaan Chawla, Jonathan Bakke, and Carl Hagglund
Stanford

This presentation will discuss efforts within CNEEC to boost the efficiency of thin film photovoltaic (PV) and photoelectrochemical (PEC) devices by engineering new materials at the nanoscale to achieve stronger materials absorption and to enable extreme light concentration into active device regions. The driving mechanism in conventional PV and photocatalytic devices is to convert sunlight into electrons and holes and to collect them in spatially distinct regions. Unfortunately, many of the relevant materials exhibit a large mismatch between electronic and photonic length scales. The typical absorption depth in materials for photoelectrochemistry and PV is significantly longer than the electronic (minority carrier or exciton) diffusion lengths. For this reason, it is challenging to attain high operational efficiencies. Our solution to improving efficiency is to enhance light absorption in thin layers of active material. Our first strategy for this solution focuses on designing and fabricating new nanostructured materials that exploit quantum size and surface effects to enhance absorption and charge transport. Our second strategy focuses on increasing photon absorption by better managing the flow of light. This approach includes the use of nanostructuring to reduce light reflection from devices and to enhance light trapping inside the active regions.

5:20 - 5:40

T-B11 - REACHING FOR THE LIMIT: THE NEW SCIENCE TO APPROACH THE SHOCKLEY-QUEISSER LIMIT

[LMI] Eli Yablonovitch, Owen Miller, and Vidya Ganapati
UC Berkeley

The Shockley-Queisser (SQ) limit for a single junction solar cell is ~33.4%, (under the standard AM1.5 flat-plate, solar spectrum). Indeed detailed calculations show that GaAs is capable of achieving this efficiency. Nonetheless, the record GaAs solar cell had achieved only 26.4% efficiency in 2010. Previously, the record had been stuck at 26.1% for almost two decades. Why then the 7% discrepancy between the theoretical limit 33.4% versus the achieved efficiency of 26.4%? It is usual to blame material quality. But in the case of GaAs double heterostructures, the material is almost ideal with an internal fluorescence yield of >99%. This deepens the puzzle as to why the full theoretical SQ efficiency is not achieved? As solar efficiency begins to approach the SQ limit, the internal physics of a solar cell changes. Shockley and Quiesser showed that high solar efficiency is accompanied by a high concentration of carriers, and by strong fluorescent emission of photons. In a good solar cell, the photons that are emitted internally have a possibility of being reabsorbed, leading to "photon re-cycling. The SQ limit assumes 100% external fluorescence yield. We find that the failure to optimize the extraction of recycled internal photons is largely responsible for the failure to achieve the SQ limit in the best solar cells. Achieving the SQ limit requires that light extraction physics be designed into solar cells. Now new efficiency records are being broken.

5:40 - 6:00

T-B12 - EMBEDDED PHOTONIC CRYSTALS FOR HIGHER EFFICIENCY LEDs AND PHOTOVOLTAICS

[CEEM] Claude Weisbuch and Alison Matioli
University of California, Santa Barbara; MIT

Photonic crystals (PhC) may significantly improve the performance of LEDs and solar cells. Among the various possible implementations, embedded PhCs appear to increase the design parameter space to fully control the optical degrees of freedom of the devices. In LEDs, PhCs are able to extract guided optical modes trapped in the structures by diffracting such modes out of the device. However, high efficiency light extraction is only obtained if the extraction length due to the PhC is shorter than the dissipation length due to the various dissipation mechanisms. This requires structures designed to optimize the interaction of guided modes with PhCs, and embedded PhCs appear to be remarkably efficient. An additional feature is that light is extracted with a controllable directionality, which can be useful for a number of applications. In solar cells, PhCs help redirect incoming light which has been incompletely absorbed into guided modes which can be efficiently absorbed. This phenomenon is known since a long time as the Wood anomaly in gratings, but here it is optimized to enhance the bandwidth over which light is captured in the device. Embedded PhCs are particularly efficient as they additionally act as confinement layers for guided modes thus diminishing contact absorption. We describe the results of such PhC devices in GaN based materials grown by MOCVD where embedded PhCs are obtained by controlled coalescence of high quality active materials over air holes acting as PhCs.

**Parallel Scientific Session IV – May 27, 2011
Grand Ballroom Central**

8:00 - 8:20

T-B13 - ADVANCED IN CHARGE MANIPULATION IN QUANTUM DOT ARRAYS AND ARCHITECTURES FOR 3RD GENERATION SOLAR CELLS

[CASP] [Arthur J. Nozik](#)*National Renewable Energy Laboratory*

The objective of CASP development of more efficient and lower cost next-generation solar cells based on the unique properties of nanocrystals [e.g., quantum dots (QDs), wires, rods, and tubes] in arrays, which allow us to control the relaxation pathways of excited states to produce enhanced power conversion efficiency (PCE) through efficient multiple exciton generation (MEG), also termed carrier multiplication. NC-based cells will also have low cost. We studied MEG in close-packed QD arrays where the QDs are electronically coupled, yielding good carrier mobility. An understanding of transport in these QD arrays has been developed at UC Irvine and U. Minn. (Posters P2-B06 and B07). Simple, inorganic QD solar cells produce large short-circuit photocurrents ($10\text{-}35\text{ mA/cm}^2$) via nanocrystalline Schottky and p-n junctions; record certified PCEs of 4.4% have been achieved in p-n cells. We have demonstrated experimentally that the MEG efficiency (excitons/bandgap) of PbSe QDs is twice that of the parent bulk material, and the MEG efficiency is directly related to the threshold photon energy for MEG. Thermodynamic calculations show ideal MEG-based PV cells can have PCEs 34% greater than the bulk material. The maximum PCE (~43%) is achieved when the threshold photon energy for MEG is twice the QD bandgap. The effect of solar concentration on the maximum PCE of MEG PV cells is enormously enhanced compared to conventional solar cells, and the mechanism for this effect is understood.

8:20 - 8:40

T-B14 - LIGHT CAPTURE IN SILICON MICROCELL PHOTOVOLTAICS

[LMI] John Rogers

UIUC

Solar modules that involve large collections of small, ultrathin photovoltaic cells offer opportunities to address issues in materials utilization, light capture and cost in ways that are unavailable to conventional designs. This talk describes materials, assembly and optics aspects of this type of technology, implemented with monocrystalline silicon and epitaxial compound semiconductors derived from wafer-scale sources of material. We highlight recent collaborative work in our EFRC on a composite luminescent concentrator photovoltaic system that embeds large scale, interconnected arrays of microscale silicon solar cells in thin matrix layers doped with luminophores. Photons that strike the cells directly generate power in the usual manner; those incident on the matrix launch wavelength-downconverted photons that reflect and waveguide into the sides and bottom surfaces of the cells to increase further their power output, by more than 300% in examples achieved experimentally. Unlike conventional luminescent photovoltaics, this unusual design can be implemented in thin, mechanically bendable formats on sheets of plastic. Detailed studies of design considerations and fabrication aspects for such devices, using both experimental and computational approaches, provide quantitative descriptions of the underlying materials science and optics.

8:40 - 9:00

T-B15 - LIGHT HARVESTING WITH FRAMEWORK MATERIALS

[UNC] [Wenbin Lin](#)¹, [Spiros Skourtis](#)², Caleb A Kent¹, Demin Liu¹, Cheng Wang¹, Andre van Rynbach², Xiangqian Hu², Brian Mehl¹, Thomas Meyer¹, John Papanikolas¹, and David Beratan²¹*University of North Carolina at Chapel Hill*; ²*Duke University*

The chemistry of framework materials such as metal-organic frameworks (MOFs) and crosslinked polymers (CPs) has evolved rapidly in recent years. With their well-defined, repeating structures, functionalized MOFs in particular present an opportunity to design and study dimensionally controlled antenna structures. We have recently synthesized Ru(II)-bpy MOFs and observed efficient energy migration in these materials. Following MLCT excitation of Ru(II) sites in these MOFs, energy transfer occurred to lower energy (~0.5 eV), structurally isomorphous Os(II) trap sites. With their high absorptivities and facile intra-crystal energy transfer properties, these materials show great promise as antenna for sensitizing electron transfer and ultimately, catalytic redox reactions. We demonstrated the successful implementation of this strategy and the first examples of oxidative and reductive interfacial electron transfer quenching of MOF microcrystals. Individual microcrystals are highly efficient light-harvesting structures due to their high visible absorptivities, facile intra-crystal site-to-site energy migration to the MOF surface, and efficient electron transfer quenching at the MOF/solution interface. We have also developed kinetic models of energy transport in Ru-Os MOFs and considered the

effect of lattice dimension on the transport efficiency. These models are complemented by *ab initio* TDDFT calculations of the Ru-centered electronic exciton states in the different framework material.

9:00 - 9:20

T-B16 - DEVELOPMENT OF NOVEL NANOMATERIALS AS THE BUILDING BLOCKS FOR NEXT-GENERATION SOLAR CELLS

[CASP] Jeffrey M. Pietryga

Los Alamos National Laboratory

Materials engineered at the nanoscale are of tremendous interest for use in solar energy capture because the unique physics that arises at these tiny scales fundamentally changes the way such materials interact with light. At CASP, we study and develop new nanoscale materials and new methods for exploiting these unique physical effects in the context of photovoltaic conversion of sunlight into electricity. Our Novel NanoMaterials Thrust is focused in particular on solution-processable nanostructures which can be incorporated into devices via low-cost, highly scalable fabrication methods. Current efforts proceed along three basic themes, each of which emphasizes a varying collection of the advantages offered by this class of materials. In the most straightforward, we render established bulk semiconductors into quantum-confined nanocrystal form to enhance their optoelectronic properties and their flexibility toward application. A second theme is known as "band-gap engineering" which refers to controlling the nature and dynamical behavior of the excited state in heterostructured semiconductor nanocrystals by finely controlling their structure. Finally, our efforts in metal/semiconductor hybrid nanomaterials strive to create unique multifunctional superstructures that exploit metal plasmons to enhance the ability of nanocrystals to convert light into electricity in extremely thin devices. I will examine specific examples of these themes in ongoing work from across our Center.

9:20 - 9:40

T-B17 - UNDERSTANDING CARRIER DOPING AND ELECTRICAL CONDUCTIVITY OF WIDE GAP OXIDES AS TRANSPARENT CONDUCTORS FOR SOLAR PHOTO CONVERSION.

[CID] Stephan Lany¹, Andriy Zakutayev¹, Thomas Mason², John Wager³, Kenneth Poeppelmeier², John Perkins¹, Joseph Berry¹, David Ginley¹, and Alex Zunger¹

¹NREL; ²Northwestern University; ³Oregon State University

Functional oxides in optoelectronic applications are today most commonly employed in the thin-film form, e.g. in photovoltaic energy conversion technologies. The materials and device design is, however, still guided by models for defect mechanisms that were developed half a century ago for bulk materials. The conductivity of transparent conducting oxides, for example, has been described by extrinsic dopants like Sn-on-In in In₂O₃, intrinsic defects like O-vacancies, or unintentional impurities like hydrogen. Such models, however, cannot account for the observation of very high conductivities above 1000 S/cm in pure In₂O₃ thin films. By a comparison of electronic structure theory predictions with transport measurements we show here that the traditional point defect mechanism of O-vacancy formation consistently describes the behavior of pure In₂O₃ in the bulk, but that such bulk concepts are insufficient and fail for thin-films. Instead, we find that the thin-film conductivity is dominated by surface donors having particularly low formation energies. This finding implies that oxides which are non-conductive or even non-dopable as bulk materials can nevertheless become highly conductive as thin films.

C – Solar Fuels and Biomass – Mount Vernon Square/ Grand Ballroom North

Parallel Scientific Session I – May 26, 2011 Mount Vernon Square

10:15 - 10:35 (Joint with Session A in the Grand Ballroom)

T-C01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA

[CST] Xiaoyang Zhu and Jennifer Lyon

University of Texas at Austin

A memorial tribute to Paul F. Barbara (1953-2010), world-renowned laser spectroscopist, Professor of Chemistry at the University of Texas at Austin, member of the National Academy of Sciences and founding Director of the DOE Energy Frontier Research Center on Understanding Charge Separation at Interfaces in Energy Materials (EFRC:CST). Here we celebrate Paul's "lifetime in the excited state," including his numerous scientific achievements, academic developments and, above all, his tireless enthusiasm for the pursuit of fundamental scientific knowledge.

10:35 - 10:55

T-C02 - NEW AVENUES TOWARDS THE DEVELOPMENT OF A BIO-INSPIRED ARTIFICIAL OXYGEN EVOLVING COMPLEX

[BISfuel] Petra Fromme, Hao Yan, Yan Liu, Giovanna Ghirlanda, James Allen, Kevin Redding, Don Seo, Raimund Fromme, Kim Rendek, Chad Simmons, Sandip Shinde, Mingui Liu, Justin Flory, Sudipta Biswas, Xixi Wei, Angelo Cereda, Matthieu Walter, Josifina Sarrou, Wang Dong, and Palash Dutta
Arizona State University

Photosynthesis is the main process that converts light energy into chemical energy. Two large membrane protein complexes, Photosystems I and II, initialize this process through light induced charge separation. Photosystem II catalyzes the oxidation of two water molecules into O_2 plus $4 H^+$ and $4 e^-$ using earth abundant metals and driven by visible light. Our project is building an artificial oxygen-evolving complex (aOEC) that mimics nature in its ability to split water with visible light at low overpotential, but shows superior stability and efficiency. We will present two strategies to achieve this goal. The first strategy aims to build a metalloprotein-based aOEC inside DNA nanocages. The nanocages can be custom designed to harbor the peptides that assemble the mimic of the metal cluster (Mn_4CaCl) that catalyzes water oxidation in the native system. The second strategy includes development of a water-soluble mimic of the photosynthetic oxygen-evolving complex. We designed and synthesized a di-nuclear metal-binding peptide, which binds manganese with a 2:1 metal:peptide stoichiometry. Data on the interaction between the two metal sites will be presented. The ultimate goal of the Center for Bio-inspired Solar Fuel Production is to provide the scientific basis for the development of an 'artificial leaf' where a stable highly efficient aOEC is coupled to the artificial reaction center and electrons are used for production of solar based carbon neutral fuel.

10:55 - 11:15

T-C03 - BIO-INSPIRED MOLECULAR MATERIALS FOR SOLAR FUELS

[ANSER] Michael R. Wasielewski
Northwestern University

Natural photosynthesis is carried out by organized assemblies of photofunctional tetrapyrrole chromophores and multi-metallic catalysts within proteins that provide specifically tailored environments to optimize solar energy conversion. Artificial photosynthetic systems for practical solar fuels production must collect light energy, separate charge, and transport charge to catalytic sites where multi-electron, proton-coupled redox processes will occur. The primary goal of ANSER Center research in this field is to understand the fundamental principles needed to develop integrated artificial photosynthetic systems for solar fuels formation. These principles include how to promote and control: 1) energy capture, charge separation, and long-range directional energy and charge transport, 2) coupling of separated charges to multi-electron catalysts for fuel formation, and 3) supramolecular self-assembly for scalable, low-cost processing from the nanoscale to the macroscale. The central scientific challenge is to develop small, functional building blocks, having a minimum number of covalent linkages, which also have the appropriate molecular recognition properties to facilitate self-assembly of complete, functional artificial photosynthetic systems. In this lecture we will highlight ANSER Center progress to achieve these goals.

11:15 - 11:35

T-C04 - UNDERSTANDING AND CONTROLLING PROTON MOVEMENT IN MOLECULAR ELECTROCATALYSIS

[CME] R. Morris Bullock¹, Daniel L. DuBois¹, Michel Dupuis¹, James M. Mayer², Sharon Hammes-Schiffer³, Bruce A. Parkinson⁴, Jenny Y. Yang¹, Michael T. Mock¹, John A. S. Roberts¹, Simone Raugel¹, and Roger Rousseau¹
¹*Pacific Northwest National Laboratory; Pacific Northwest National Laboratory; Pacific Northwest National Laboratory;*
²*University of Washington;* ³*Pennsylvania State University;* ⁴*University of Wyoming*

Increased utilization of non-fossil fuel energy sources is necessary to address problems of escalating energy demand and increasing CO_2 emissions. Carbon-neutral, sustainable energy sources, including solar and wind power, are being actively pursued, but their intermittent nature requires a reliable method of storing the energy. Electrocatalysts for efficient conversion between electricity and chemical bonds will play a vital role in future systems for storage and delivery of energy. Research in the Center for Molecular Electrocatalysis focuses on understanding and developing catalysts for production of hydrogen, oxidation of hydrogen, and reduction of oxygen and nitrogen. Development of catalysts that achieve controlled, precise delivery of protons is a major focus of our experimental and theoretical efforts. Proton relays are functional groups that lower the barrier for delivery of protons to (or from) the active site of catalysts. The active site of the FeFe Hydrogenase enzyme in Nature uses an amine as a proton relay, and our research involves bio-inspired design of functional hydrogenase models. Nickel complexes with pendant amines as proton relays are the fastest synthetic molecular electrocatalysts for the oxidation of hydrogen and production of hydrogen. Iron catalysts for reduction of oxygen use proton relays from carboxylic acids incorporated into the porphyrin ligand. Complexes of Cr, Mo and W are being studied to understand initial steps in the reduction of N_2 .

11:35 - 11:55

T-C05 - DESIGN OF PEPTIDE-BASED CATALYSTS: DEVELOPMENT OF ARTIFICIAL HYDROGENASES

[BISfuel] Giovanna Ghirlanda, Anne K. Jones, Arnab Dutta, Anindya Roy, Sandip Shinde, and Mathieu Walther
Arizona State University

Biological systems store solar energy by fuel production, utilizing chains of reactions catalyzed by redox enzymes. Such chains are assembled through specific protein-protein interactions, or by exploiting co-localization for example in the membrane bilayer. Each catalyst is a complex enzyme consisting of a buried active site linked to the protein surface via a chain of redox active groups. Hydrogenases, the enzymes for biological hydrogen production, are examples. They are usually heteromultimeric, consisting of a buried [NiFe] or [FeFe] active site exchanging electrons with a redox partner via a chain of [FeS] clusters. Designing an artificial hydrogenase implies optimizing both the catalytic site and the redox chain that delivers electrons to that site as well as understanding how interactions between cofactors control reactivity. We are proceeding hierarchically, designing minimalist metal binding peptide units and metal-mediated interfaces that will modulate higher order assembly of the functional units. Synthetic strategies for incorporation of binuclear metalcenters related to hydrogenase active sites into peptides have been developed in small model peptides. To obtain the necessary spatial organization in an artificial hydrogenase, we have designed a family of peptides that can self assemble into large complexes functionalized with distinct active sites tailored to a specific function.

11:55 - 12:15

T-C06 - MOLECULAR ELECTROCATALYSTS FOR PRODUCTION AND OXIDATION OF HYDROGEN

[CME] Daniel DuBois, Morris Bullock, Mary Rakowski DuBois, Wendy Shaw, Aaron Appel, Stuart Smith, Jenny Yang, John Roberts, Uriah Kilgore, Doug Pool, Simone Raugei, Michel Dupuis, Roger Rousseau, Molly O'Hagan, Michael Stewart, Shentan Chen, and Monte Helm
Pacific Northwest National Laboratory

The simplest fuel generation reaction is the production of hydrogen from two protons and two electrons. Hydrogenase enzymes are highly active and efficient catalysts for this reaction, and use inexpensive metals such as iron and nickel. A key feature of these enzymes is the delivery of protons to the active site using proton relays. These considerations led our laboratories to study nickel complexes containing diphosphine ligands with pendant amines as catalysts for hydrogen production with the following three objectives: (1) to understand how proton relays can facilitate the formation and cleavage of the H-H bond and the transfer of protons between the metal center and the solution, (2) to use this understanding to design fast, efficient catalysts for hydrogen production, and (3) to extend this knowledge to catalysts for more complex multielectron and multiproton reactions. Our studies have shown that pendant bases dramatically reduce overpotentials by coupling intramolecular and intermolecular proton transfer reactions to electron transfer steps and that catalytic rates are greatly enhanced by positioning a pendant base in close proximity to the nickel center, facilitating heterolytic formation of the H-H bond. These studies resulted in catalysts for hydrogen production with turnover frequencies of 110,000 per second and an overpotential of 0.6 V compared to [FeFe] hydrogenase enzymes with rates of 10,000 per second and an overpotential of approximately 0.1 V.

Parallel Scientific Session II – May 26, 2011
Grand Ballroom North

1:45 - 2:05

T-C07 - ENGINEERING CATALYSTS AT THE NANO-SCALE FOR ENERGY CONVERSION REACTIONS

[CNEEC] Thomas F. Jaramillo, Zhebo Chen, Yelena Gorlin, Hee Joon Jung, Robert Sinclair, Jennifer Wilcox, Bruce M. Clemens, Mark Brongersma, Arthur Grossman, Fritz B. Prinz, Stacey F. Bent, and Jens K. Nørskov
Stanford University

This paper will cover current research activities at the Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, with a focus on the theme of controlling catalysis at the nano-scale. The overarching goal is to understand catalysis for energy conversion reactions at the molecular level, and then to use that insight in developing materials and processes with increased performance. To accomplish this goal, we are combining theory and experiment to understand chemical and physical processes on surfaces, nano-structured materials, and biological systems. Results will be presented in the following areas: (1) Bandgap engineering of MoS₂ through quantum confinement effects, with relevance to solar fuel synthesis, (2) Development of active and stable hydrogen evolution catalysts based on nano-structured MoS₂, (3) Development of oxygen reduction catalysts and water oxidation catalysts based on manganese oxides, combining Density Functional Theory (DFT) calculations with experimental electrochemical surface science in order to tailor surface chemistry through nano-structure, (4) DFT studies of the influence of carbon supports onto the

electronic and geometric structure of metal nanocatalysts, and (5) Investigation of photosynthetic membrane proteins by *in-situ* atomic force microscopy (AFM).

2:05 - 2:25

T-C08 - THE PHOTOSYNTHETIC ANTENNA RESEARCH CENTER: OVERVIEW AND NATURAL ANTENNAS

[PARC] [Robert E. Blankenship](#) and [Himadri B. Pakrasi](#)

Washington University in St. Louis

The Photosynthetic Antenna Research Center (PARC) is an Energy Frontier Research Center whose mission is to understand the basic scientific principles that govern solar energy collection by photosynthetic organisms. PARC plans to use this knowledge to enhance natural antenna systems and to fabricate biohybrid and bioinspired systems for light-harvesting. PARC has 17 Principal Investigators from 10 institutions in the US and the UK, as well as 14 Research Affiliate members from around the world. Research in PARC is in three major themes: 1. Natural Antennas: Structure and Efficiency; 2. Biohybrid Antennas: Organization and Implementation; 3. Bioinspired Antennas: Design and Characterization. Current studies on Natural Antennas are primarily focused on (a) examining the effects of reductions in antenna sizes as well as expanding the usable wavelength range on the physiology as well as productivities of cyanobacteria and eukaryotic algae, and (b) determination of high resolution structures and functions of diverse naturally occurring antenna systems.

2:25 - 2:45

T-C09 - DESIGN, SYNTHESIS AND CHARACTERIZATION OF BIOHYBRID AND BIOINSPIRED LIGHT-HARVESTING SYSTEMS

[PARC] [Dewey Holten](#) and [C Neil Hunter](#)

Washington University in St. Louis and University of Sheffield

Research at the Photosynthetic Antenna Research Center (PARC) aims to understand natural antenna complexes and to formulate concepts for next-generation systems for solar energy conversion. Engineered natural or synthetic antenna complexes are attached to nanopatterned surfaces; *de novo* synthesis of the tunable (bacterio)chlorin pigments enables collection of energy from untapped regions of the solar spectrum. The goal of this bottom-up approach is delivery of harvested solar energy for chemical processes or photocurrent production. PARC is developing new tools for fabrication and characterization of such nanoscale light-harvesting (LH) arrays. (1) Near-field photolithography, interferometric lithography and nanostamping to enable patterning arrays of LH complexes on surfaces in geometries such as nanoscale lines and dots. (2) Surface chemistries for attaching LH complexes to self-assembled monolayers on various substrates, and aerosol attachment of antenna complexes to TiO₂ pillars. (3) Microscopy approaches for assessing the performance of native LH complexes *in vivo*, and of patterned non-native LH arrays: scanning high resolution (~100 nm) wide-field imaging plus AFM; high resolution total internal reflection fluorescence; hyperspectral confocal fluorescence imaging. (4) Self-assembly of biohybrid and bioinspired LH complexes using native apoproteins with synthetic bioconjugatable bacteriochlorins, and synthetic peptide maquettes housing designer amphipathic chlorins.

2:45 - 3:05

T-C10 - REDESIGNING METABOLIC FLUX FOR THE PRODUCTION OF ADVANCED BIOFUELS IN CAMELINA AND ALGAE

[CABS] [Edgar Cahoon](#)

University of Nebraska

A goal of the Center for Advanced Biofuels (CABS) is to tailor the composition of storage oils in *camelina* seeds and green algae for specific biofuel applications through the use of novel metabolic engineering strategies. Both sources of vegetable oils can be propagated on land that is not suitable for production of soybean, the major U.S. source of vegetable oils for food use. *Camelina* is also an attractive platform for complex metabolic engineering because genetic transformation of this crop can be conducted rapidly and with minimal labor input. Studies are underway to engineer *camelina* oil for the accumulation of C8-C16 fatty acids to mimic the hydrocarbon content of jet fuel. This approach has yielded *camelina* oil with 30% to 40% of C8-C16 fatty acids by expression of novel fatty acid thioesterases. Ongoing work is aimed at increasing amounts of these fatty acids by introduction of specialized acyltransferases from *Cuphea* species whose seeds accumulate >90% of C8 and C10 fatty acids. To obtain aromatic hydrocarbons similar to those of jet fuel, *camelina* seeds have also been engineered to produce the monoterpene limonene at levels approaching 1% of the seed oil by metabolic redesign of the plastid isoprenoid pathway. Crossing studies will allow for the stacking of fatty acid and monoterpene traits to achieve oil compositions suitable for testing as jet fuel substitutes. Furthermore, studies have been initiated to transfer these technologies to *Chlamydomonas* to demonstrate the feasibility of these metabolic engineering strategies for the production of advanced biofuels in green algae.

3:05 - 3:25

T-C11 - COMBUSTION CHEMISTRY OF A NEW BIOFUEL: BUTANOL

[CEFRC] [William Green](#)¹, [David Davidson](#)², [Fokion Egofopoulos](#)³, [Nils Hansen](#)⁴, [Michael Harper](#)¹, [Ron Hanson](#)², [Stephen Klippenstein](#)⁵, [C.K.Ed Law](#)⁶, [C.Jackie Sung](#)⁷, [Donald Truhlar](#)⁸, and [Hai Wang](#)³¹MIT; ²Stanford; ³USC; ⁴Sandia Livermore; ⁵Argonne; ⁶Princeton; ⁷U. Connecticut; ⁸U. Minnesota

Many different potential biofuels are now being considered. Most of these have never been tested in engines, and very little is known about their combustion chemistry, making it hard to accurately predict their performance (and so their economic value). The Combustion Energy Frontier Research Center (CEFRC) is developing the methods needed to rapidly assess proposed fuels, and to construct accurate kinetic models for new fuels. Butanol is a new biofuel which is likely to be commercialized soon in gasoline-powered vehicles. Butanol has several advantages over ethanol, including improved miscibility with gasoline, less corrosion, and reduced smog-forming evaporative emissions. To facilitate the large-scale introduction of butanol, and to accurately assess its potential, the CEFRC has developed and experimentally validated a kinetic model for butanol combustion, which can be used in engine simulators. This required cooperative efforts of quantum chemists, kinetic modelers, and a broad team of experimentalists. In the course of this work, several important discrepancies between the models and the experimental data were identified, leading to significant learning, and improvements in both the models and the experiments. The efficient team process by which the butanol model was developed, which is a model for future work on alternative fuels, will also be discussed.

3:25 - 3:45

T-C12 - INTERACTIONS OF CELLULOSE WITH MATRIX POLYSACCHARIDES

[CLSF] [Yong Bum Park](#), [Akira Tabuchi](#), [Lian-Chao Li](#), and [Daniel J. Cosgrove](#)*The Pennsylvania State University*

CLSF focuses on three major themes: (1) to elucidate the synthesis of cellulose and its assembly into a crystalline ribbon; (2) to understand how cellulose interacts with matrix polymers such as pectins, hemicelluloses and lignin, to form a flexible yet strong network that is capable of expanding during cell growth, yet resists physical forces and microbial assaults and (3) to work out how the macroscopic properties of cell walls, such as tensile strength and porosity, depend on their nano-scale structure. I will highlight some of the approaches being taken by CLSF researchers in Theme 2 to investigate the molecular interactions of cellulose with matrix polysaccharides. In primary cell walls, cellulose is thought to be tethered into load-bearing networks by xyloglucans or arabinoxylans, depending of cell wall type. We have tested this model by measuring the effects of specific enzymes on cell wall mechanics. Contrary to prediction, enzymes that specifically digest xyloglucan do not loosen the cell wall, nor do enzymes that specifically digest cellulose. Only enzymes that could digest both components were capable of wall loosening. This result calls for a revised wall model. The cell walls of grasses are thought to be linked together primarily by arabinoxylan, and this simple arrangement is supported by the results of treatments with xylanases. We conclude that the mechanical linkages between cellulose microfibrils are more variable and subtle than is currently appreciated.

**Parallel Scientific Session III – May 26, 2011
Grand Ballroom North**

4:00 - 4:40

T-C13 - A ROADMAP FOR SELECTIVE DECONSTRUCTION OF LIGNOCELLULOSIC BIOMASS TO ADVANCED BIOFUELS AND USEFUL CO-PRODUCTS

[C3Bio] [Maureen C McCann](#)¹, [Mahdi Abu-Omar](#)¹, [Joe Bozell](#)², and [Peter Ciesielski](#)³¹Purdue University; ²University of Tennessee; ³NREL

The production of second-generation biofuels derived from lignocellulosic biomass via biological catalysis (microbial fermentation of sugars released from plant cell wall polysaccharides) is both carbon- and energy-inefficient. In contrast, chemical catalysis has the potential to efficiently transform biomass components (cellulose, hemicellulose and lignin) directly to alkanes, aromatics, and other useful molecules. We are developing catalytic processes to enable the extraction, fractionation, and depolymerization of cellulose and hemicellulose coupled to catalytic transformation of hexoses and pentoses into hydrocarbons. Additional catalysts may cleave the ether bonds of lignin to release useful aromatic co-products or that may oxidize lignols to quinones. Our understanding of biomass-catalyst interactions require novel imaging and analysis platforms, such as mass spectrometry, to analyze potentially complex mixtures of reaction products and transmission electron tomography to image the effects of applying catalysts to biomass and to provide data for computational modeling. By integrating biology, chemistry and chemical engineering, our data indicate how we might modify cell wall composition, or incorporate Trojan horse catalysts, to tailor biomass for optimal carbon- and energy-

conversion efficiencies. We envision a road forward for directed construction and selective deconstruction of plant biomass feedstock.

4:40 - 5:00

T-C14 - PROBING THE STRUCTURE OF CELLULOSE SYNTHASE, A KEY PROTEIN WITHIN A REMARKABLE FIBRIL-SPINNING CELLULAR NANOMACHINE

[CLSF] Candace H. Haigler¹, Rami Alkhatib¹, Mark J. Grimson², James D. Kubicki³, Le Li¹, Antonin Marek¹, Mohamed Naseer³, Ali Mohamed³, Tuyen Nguyen¹, Latsavongsakda Sethaphong¹, Abhishek Singh¹, Alex I. Smirnov¹, Maxim A. Voinov¹, and Yaroslava G. Yingling¹

¹North Carolina State University, ²North Carolina State University; ²Texas Tech University; ³The Pennsylvania State University

Plants accomplish the remarkable conversion of sugar into structural cellulose fibrils through a protein-based cellulose synthesis complex (CSC). Despite its natural and economic importance, we still need to clarify the elements of protein structure and assembly that support fibril spinning via the CSC nanomachine. We carried out theoretical modeling and experiments to elucidate the structure and function of cellulose synthase (CESA), the key protein within the CSC. We will describe efforts to: (a) apply refined methods of freeze fracture transmission electron microscopy to reveal details of CSC structure *in situ* within the plasma membrane; (b) use *ab-initio* structure prediction followed by refinement by molecular dynamics simulations to produce a 3D model of plant CESA structure; (c) perform quantum mechanical calculations of the substrate for cellulose synthesis, UDP-glucose, prior to docking into the modeled catalytic site of CESA and (d) analyze synthetic peptides representing selected CESA transmembrane helices (TMH) by spin-labeling electron paramagnetic resonance spectroscopy to assess the potential for TMH self-aggregation in a lipid context. Means of testing the putative CESA macromolecular structure and unifying results from different approaches will be discussed. Research support: US Dept. of Energy, Office of Basic Energy Sciences as part of The Center for Lignocellulose Structure and Formation, an Energy Frontier Research Center and Texas Tech University.

5:00 - 5:20

T-C15 - SELECTIVE TRANSFORMATION OF BIOMASS DERIVATIVES

[CCEI] Dion G. Vlachos
University of Delaware

In this talk, an overview of the research thrusts of the Catalysis Center for Energy Innovation (CCEI) will be given. Modern catalytic-based technologies will be presented that may overcome challenges of traditional methods in converting biomass to renewable fuels, chemicals, and electricity. Cross-cutting technologies, including hierarchical multiscale materials and models, will be reviewed. We will then review modern technologies that rely on biomass degradation to simple derivatives, such as sugars, followed by a number of reactions, such as isomerization and acid-based chemistry to convert sugars to valuable intermediates, such as furans.

5:20 - 5:40

T-C16 - IACT - GOALS AND PROGRESS IN BIOMASS REACTION MECHANISMS

[IACT] Christopher Marshall and Peter Stair
Argonne National Laboratory and Northwestern University

The Institute for Atom-efficient Chemical Transformations (IACT) is a collaboration between Argonne National Laboratory, Northwestern University, University of Wisconsin and Purdue University is focused on advancing the science of catalysis for the efficient conversion of energy resources into usable forms. Using a multidisciplinary approach involving integrated catalyst synthesis, advanced characterization, catalytic experimentation, and computation, IACT is addressing the key chemistries for the efficient removal of oxygen and the addition of hydrogen associated with the conversion of biomass into transportation fuels. This lecture will first summarize the requirements for efficient conversion of cellulosic biomass, the goals of IACT and show how the four subtasks; Catalyst Synthesis, *In situ* Characterization, Computational Modeling, and Catalytic and Chemical Reaction Science are accomplishing the research work of IACT. The members of each subtask are considered to be world class leaders in their fields and have the experience to work with members of other subtasks. Following the introduction, the talk will show how controlled synthesis coupled with *in situ* characterization and reactor testing is improving our understanding of the catalysis under these relatively harsh conditions and where we are going to improve catalyst stability and reactivity. Several examples of current research programs will be used.

5:40 - 6:00

T-C17 - CATALYSIS FOR BIOMASS REFORMING

[CCEI] Michael Saliccioli, Weiting Yu, Mark Barteau, Jingguang Chen, and Dion Vlachos*University of Delaware*

Understanding and controlling bond breaking sequences of oxygenates on transition metal catalysts can greatly impact the utilization of biomass feedstocks for fuels and chemicals. The decomposition of ethylene glycol and glycolaldehyde, as the simplest representatives of biomass-derived oxygenates, were studied via density functional theory (DFT) calculations, temperature programmed desorption (TPD) experiments and high resolution electron energy loss spectroscopy (HREELS) experiments to identify the differences in reaction pathways between Pt and the more active Ni/Pt bimetallic catalyst. Further, fundamental differences are found between the decomposition energetics of highly functionalized oxygenates compared to mono alcohols and hydrocarbons which can aid in catalyst design for biomass reforming technologies.

**Parallel Scientific Session IV – May 27, 2011
Grand Ballroom North**

8:00 - 8:20

T-C18 - COMPUTATIONAL AND ENABLING TECHNOLOGIES IN THE CENTER FOR ADVANCED BIOFUELS (CABS)

[CABS] Lisa Carey¹, Rahul Deshpande¹, David Gang², Mahmoud Gargouri², Jeong-Jin Park², Leslie Hicks³, Yair Shachar-Hill¹, Hongxia Wang³, and Baichen Zhang³¹*Michigan State University*; ²*Washington State University* ³*Donald Danforth Plant Science Center*

The computational and enabling technologies group consists of the Gang, Hicks and Shachar-Hill laboratories. We support the work of CABS in understanding and improving photosynthetic biofuel species by multi-omic analyses of plant and algal systems. Group members study wild type, mutant and transgenic strains and obtain detailed quantitative information on the levels and regulation of transcripts, proteins, metabolites, and metabolic fluxes. Our focus is on obtaining rigorous, integrated datasets from cells and tissues that will shed light on the mechanisms and potential bottlenecks of biofuel production in oilseeds and algae. We collaborate closely with other CABS groups to accelerate progress on specific research targets, and with one another to exploit the advantages of investigating metabolism and its regulation at multiple biochemical and genetic levels. This presentation will describe the establishment of analytical platforms for analyses of transcript levels by high throughput sequencing; of protein identities, modifications and quantities by proteomic mass spectrometric methods; of primary and secondary metabolites using liquid and gas chromatographic mass spectrometric platforms and of metabolic fluxes using stable isotopic labeling and computer-aided modeling. Examples of datasets from *Chlamydomonas* and *Camelina* will also be presented to illustrate our progress in identifying and quantifying changes in the biochemical networks that accompany genetic and environmental changes. Finally we will describe our plans for integrated studies of the induction of oil production in plants and algae by transgenic and environmental interventions.

8:20 - 8:40

T-C19 - PYROPROBE/TANDEM MASS SPECTROMETRY PROVIDES INSIGHTS INTO FAST PYROLYSIS OF BIOMASS

[C3Bio] Piotr Gawecki, Andrew D. Smeltz, Matthew R. Hurt, David J. Borton II, Nelson R. Vinueza, Nicholas J. Nugent, Rakesh Agrawal, W. Nicholas Delgass, Hilkka I. Kenttamaa, William E. Anderson, and Fabio H. Ribeiro*Purdue University*

Fast pyrolysis appears to be a relatively simple and scalable process to transform biomass into fuels. However, the low quality and instability of the resulting bio-oil limit its utility. Since pyrolysis lasts from seconds to minutes at temperatures high enough to sustain multiple reactions, the resulting bio-oil is a very complex mixture of primary, secondary, and later products. C³Bio has developed a novel technique utilizing a pyroprobe coupled with a tandem mass spectrometer to identify the primary reaction products of fast pyrolysis. In these experiments, sub-milligram samples were heated to 600 C at a rate of 1,000 C s⁻¹, with the reactions quenched instantly or after a specified time delay, and the products analyzed with a linear quadrupole ion trap mass spectrometer via chloride attachment atmospheric pressure chemical ionization. These experiments revealed that the major product of fast pyrolysis of cellulose is an isomer of levoglucosan, which re-polymerizes in the gas phase to predominantly yield either dimers, trimers or tetramers of this structure, depending on conditions. Similar results were obtained for intact (dried and crushed) sorghum biomass. Finally, a novel millisecond residence time "rocket" reactor capable of pyrolysing biomass at a rate of 10 grams per minute was used to determine the mass balance and demonstrate the feasibility of obtaining simple product distributions in laboratory-scale experiments.

8:40 - 9:00

T-C20 - MULTISCALE KINETIC KNOWLEDGE PROPAGATION - COMBUSTION CHEMISTRY OF SMALL HYDROCARBONS

[CEFRC] Hai Wang

University of Southern California

Chemical kinetic models have become indispensable to the design of low-emission, highly efficient engines using both conventional and bio fuels. At this time, the predictive uncertainties of these models remain large. While the validity of a reaction model can be checked usually against a set of fundamental combustion data, the underlying problem of model uncertainty is nonetheless ill-defined mathematically. The accuracy of the reaction rate parameters can be assessed, in principle, by examining the scatter in the experimental data and/or the results obtained in *ab initio* quantum chemistry methods at different levels of theory. In this talk, the rate parameter uncertainty will be illustrated using a recent theoretical study as an example. It will be shown that the best theory available still leaves a rate uncertainty as large as a factor of 3. To address the above problem, we introduce the spectral uncertainty method, and more specifically the method of Polynomial Chaos Expansions and its application in examining the effects of kinetic model uncertainty on combustion predictions. An extension of this method, termed the Method of Uncertainty Minimization, has been developed to allow for forward and backward projections of uncertainties in both the reaction model and fundamental combustion experiments. The application of this method in model reduction and in designing better combustion experiments will be discussed.

9:00 - 9:20

T-C21 - IDENTIFICATION OF NEW REGULATORY NETWORKS FOR INCREASING PLANT OIL ACCUMULATION

[CABS] Geliang Wang¹, Maoyin Li¹, Amanda Tawfall¹, Carlotta Peters¹, Brian Fanella², and Xuemin (Sam) Wang¹¹Donald Danforth Plant Science Center; ²University of Missouri

Increasing the conversion of photosynthates to oils presents an efficient way to capture solar energy to bioenergy. Lipids are the high-density and easily extractable and transportable form of biofuels. However, it has been extremely challenging to significantly increase oil content in crops because the pathways for and regulation of lipid production are not well understood. In most plant species, storage lipids accumulate primarily in the form of triacylglycerol (TAG) stored in oil bodies, but phospholipids play pivotal roles in TAG biosynthesis and accumulation. For example, phosphatidylcholine (PC) is a substrate for fatty acid desaturation and modifications and can also provide diacylglycerol (DAG) directly for TAG synthesis. Phosphatidic acid provides DAG for PC and TAG biosynthesis, and is also involved in fatty acyl movement, vesicular trafficking, and cell signaling. One of our strategies has been to study the interaction between proteomes and lipidomes involved in TAG production. The study has led to identification of new regulatory networks that potentially sense the level of lipid metabolites. Manipulation of the signaling/regulatory complexes has resulted in significant increases in seed oil content.

9:20 - 9:40

T-C22 - DESIGN, ENGINEERING, AND PHOTOPHYSICAL CHARACTERIZATION OF ARTIFICIAL LIGHT-HARVESTING COMPLEXES USING SYNTHETIC CHLORINS AND MAQUETTES

[PARC] Goutham Kodali¹, Joseph W. Springer², Olga Mass³, Lee A. Solomon¹, Tammer A. Farid¹, David F. Bocian⁴, Christine Kirmaier², Jonathan S. Lindsey³, Dewey Holten², Christopher C. Moser¹, and P. Leslie Dutton¹¹University of Pennsylvania; ²Washington University in St. Louis; ³North Carolina State University; ⁴University of California, Riverside

The design and synthesis of proteins with specific customized functions such as light-harvesting holds great promise for capturing solar light efficiently. Our laboratory introduced the concept of protein maquettes as versatile, flexible, minimal working peptide scaffolds in which to study a selected function abstracted from highly complex natural proteins. It is well established that in natural photosynthetic antenna proteins the density of cofactors, the orientation and distance between them is critical for efficient energy transfer. We have applied these principles to design and express in *E. coli* a single chain, hydrophilic maquette to incorporate light-harvesting cofactors. Incorporation attempts of different Zinc tetrapyrroles gauged their ability to bind to maquettes. Spectral shifts and binding data suggest that assembly and binding strongly depend on an amphiphilic character to the tetrapyrrole: a hydrophilic part for solubility and orientation, and a hydrophobic side for burial into the maquette core. Based on this hypothesis we have designed and synthesized novel amphiphilic zinc chlorins that successfully bind to maquettes and can be purified using size exclusion and ion-exchange chromatography. The spectroscopic properties of maquette bound chlorins were compared with those in pure solvents. This work naturally leads to new chlorins with enhanced spectroscopic properties and site selective incorporation that discriminates different chlorins in a single maquette.

D – Energy Storage and Transmission - Congressional Hall A&B**Parallel Scientific Session I – May 26, 2011
Congressional Hall A&B**

10:15 - 10:55

T-D01 - ELECTRODE REACTIONS IN LITHIUM ION BATTERIES - FUNDAMENTAL RESEARCH AT NECCES

[NECCES] Clare P. Grey¹, Anton Van Der Ven², Hui-Chia Yu², and Katsuyo Thornton²¹*Stony Brook University*; ²*University of Michigan*

NECCES' goals are to identify the key fundamental mechanisms by which electrode materials for rechargeable batteries operate and the factors that control the rate and the reversibility of these processes. This is done by investigating a series of systems (Thrusts 1 and 2, intercalation and conversion materials) and by developing novel methodologies and theoretical approaches (Thrusts 3 and 4, diagnostics and theory). This talk will provide a general overview of the activities of the center and specific examples of activities from the intercalation, diagnostics and theory thrusts. The Intercalation thrust, working closely with the theory and characterization thrusts, is focused on the elucidation of the ultimate limits of intercalation reactions for chemical energy storage, what factors prevent the limits from being reached, and how to overcome these barriers. We investigate pure intercalation systems, such as the olivine LiFePO₄, and materials that may exhibit intercalation and conversion chemistry, as well as intercalation chemistry combined with extrusion. The talk will illustrate how, by using a combination of theory -- from the atomistic level through to the continuum level -- in close concert with appropriate experiments, we can achieve a fundamental understanding of the electrochemical performance of these materials. A strong emphasis of NECCES is on the development of *in situ* and *ex situ* methods and multi-functional probes to investigate the mechanisms of electrode reactions under conditions that closely mimic those in operating batteries. Examples include the development of new *in situ* NMR and MRI approaches, the use of synchrotron sources to image electrodes by using a variety of different techniques, and approaches involving the investigation of single particles - from nanoparticles to large single crystals.

10:55 - 11:15

T-D02 - COLLABORATIVE ENERGY FRONTIER RESEARCH: CONTROLLED SILICON NANOSTRUCTURES FOR LITHIUM STORAGE

[NEES] John Cumings¹ and S. T. Picraux²¹*University of Maryland* and ²*Los Alamos National Lab*

Lithium batteries stand poised as an incipient portable energy source for electric vehicles among a variety of applications, but problems of power density stand in the way. Silicon has long been sought as a superlative storage material for lithium battery anodes, but problems of brittle pulverization limit possible applications. Recently, nanostructured anodes have emerged as a possible solution to these problems. This talk will present the research under the University of Maryland EFRC to advance the science of silicon nanostructures with the end-goals of nanostructured battery anodes. Results on the *in-situ* observation of the lithiation of silicon nanowires will be presented along with careful transport measurements of silicon nanojunctions. Implications for future directions will be discussed.

11:15 - 11:35

T-D03 - UNDERSTANDING AND DESIGNING SURFACES AND INTERFACES IN LI-ION BATTERIES FROM FIRST PRINCIPLES

[CEES] Maria Chan¹, Scott Kirklin², Hakim Iddir¹, Kah Chun Lau¹, Jishnu Bhattacharya², David Snyder², Jeff Greeley¹, Chris Wolverton², and Larry Curtiss¹¹*Argonne National Laboratory*; ²*Northwestern University*

At the Center for Electrical Energy Storage (CEES), our focus is on the fundamental understanding of processes occurring at electrode surfaces and interfaces in lithium batteries, and on using this knowledge to design novel interfaces and structures for improved performance. Towards these ends, we use first principles density functional theory (DFT) computation, which provides accurate energies, atomistic details, and electronic properties. In this talk, we give an overview of computational investigations in CEES, including the modeling of anode surfaces and the solid-electrolyte interphase (SEI), as well as the design of novel anodes and cathode coatings. As a case study, we discuss investigations of silicon as anodes, which have significantly higher capacity than currently-used carbon. DFT studies of Si lithiation and delithiation show atomistic details of the processes and reveal differences in Li insertion thermodynamics and kinetics among the different crystalline orientations. These differences may explain the observed anisotropies in microstructured Si electrodes. The effects of dopants on lithiation are also investigated using DFT in order to explain the results of electrochemical experiments. The implications of these results and understandings for the design of Si electrodes are discussed.

11:35 - 11:55

T-D04 - UNDERSTANDING THE REACTION MECHANISM OF CONVERSION REACTION IN BATTERIES - A MULTIPRONGED EXPERIMENTAL AND THEORETICAL APPROACH

[NECCES] Glenn Amatucci*Rutgers University*

A pathway to the development of higher energy density electrodes for lithium batteries lies in the successful implementation of conversion reaction to higher voltage candidate materials. In contrast to the ubiquitous intercalation reactions which dominate today's Li-ion materials which involve insertion of lithium ions into host structures, multielectron conversion materials manifest themselves as very complex 3, 4 and greater phase reactions. The product of these reactions are of extremely small nanodimensions on the order of 1-10nm thereby making the characterization and subsequent understanding of these systems an extremely complex task which no single group can elucidate on their own. Within the Northeastern Center for Electrochemical Energy Storage EFRC we have established a thrust to embark on this mission. Some of the key questions we are addressing is the pathway of electron and ion transfer through converted phases, atomic level mass transport leading to material nucleation and growth, phase evolution, catalytic properties of the nanocomposites with electrolyte and microstructure development. The basic science answers to these goals will lead to applied science pathways allowing reduced hysteresis, improved cycling and better rate capabilities. Although our initial focus are on model systems of FeF_2 , FeO_xF_2^x , and FeF_3 , these answers will be applicable to a wide range of conversion materials including oxide, chalcogenides, nitrides lithium sulfur and lithium air batteries. Finally, conversion reactions represent a unique pathway to the formation of dispersed 1-2nm metals which may be useful for other applications such as catalysts and magnetic materials This talk we focus on research completed to date related to iron fluoride and oxyfluoride nanocomposite conversion systems.

11:55 - 12:15

T-D05 - ENABLING CONCEPTS FOR SAFE, SELF-HEALING LI-ION BATTERIES

[CEES] Jeffrey S. Moore*University of Illinois Urbana Champaign*

Lithium-ion batteries degrade through a variety of chemical and physical processes including electrolyte decomposition and SEI formation, and lithium plating and subsequent corrosion. Capacity decreases from a loss of conductivity due to cracking, deterioration, and electrochemical pulverization of electrode particles. All of these events result in decreased battery performance and can cause catastrophic failure leading to unsafe thermal runaway. We are investigating new materials integrated within the battery cell to both repair electrodes and thus extend battery lifetimes, and to provide mechanisms for autonomic shutdown. Our general approach is to incorporate stimuli-responsive microspheres that supply materials, when triggered, for repair or shut down. The talk will present new thermo-responsive microspheres that release an insulating material to coat an electrode for safe termination by preventing Li-ion transport. Microspheres have been incorporated onto battery electrodes and separators and data on thermally triggered shutdown will be shown. The talk will also present new polymeric microcapsules containing conductive suspensions or a liquid metal capable of restoring electrical conductivity to damaged circuits. These capsules are being developed to restore interparticulate electrical connectivity within damaged electrodes.

**Parallel Scientific Session II – May 26, 2011
Congressional Hall A&B**

1:45 - 2:05

T-D06 - ELECTROCATALYTIC APPROACHES TO VIRTUAL HYDROGEN STORAGE

[CETM] Oana R. Luca¹, Steven J. Konezny¹, Jeremy Praetorius¹, Gary Yeager², Guillermo D. Zappi², David Simone², Grigori L. Soloveichik², John B. Kerr², Judith Stein³, Thomas Miebach², Chris E.D. Chidsey⁴, Victor S. Batista⁵, and Robert H. Crabtree⁵¹*Yale University*; ²*GE Global Research*; ³*LBNL*; ⁴*Stanford University*; ⁵*Yale University*

Energy storage is a vital part of any alternative energy economy, and more efficient methods are eagerly sought. Our proposed regenerative fuel cell [1,2] relies on reversible electrochemical hydrogenation/dehydrogenation of an organic liquid carrier or 'fuel' (L/LH₂) with Eq. 1 being the energy release step and Eq. 2 the storage step. $\text{LH}_{2n} + n/2 \text{O}_2 \Rightarrow \text{L} + n \text{H}_2\text{O}$ (1) $\text{L} + n \text{H}_2\text{O} \Rightarrow \text{LH}_{2n} + n/2 \text{O}_2$ (2) The main challenges are the choice of a suitable fuel, LH_n, and development of suitable electrocatalysts, ideally ones that can catalyze both steps: Eq 1 and 2. Each of these components must also be stable and active under the fuel cell conditions. We have computational and experimental data that incorporating N atoms into a carbocyclic framework results in suitable fuel thermodynamics. Electrocatalysts for Eq. 1-2 are entirely unknown so we have been looking at organocatalysts such as quinones, transition metal catalysts such as NNN pincer complexes and

also outer sphere electron transfer catalysts. The problem will be finding the right selectivity pattern so as to avoid overoxidation and tuning the redox potentials of catalyst and fuel so they can work in harmony. The whole team has been in close contact during the work, with regular meetings, both physical and electronic, as well as exchange of materials for testing. [1]. R. H. Crabtree, *Energy & Environmental Science*, 1, (2008), 134-138. [2] G. L. Soloveichik, J.-C. Zhao, US Patent Application 2008/0248345 (2008).

2:05 - 2:25

T-D07 - THERMODYNAMIC AND ELECTROCHEMICAL STUDIES ON ORGANIC FUELS

[CETM] Davide L. Simone¹, Thomas Miebach¹, Matthew Rainka¹, Robert H. Crabtree², and Grigori L. Soloveichik¹
¹*GE Global Research*; ²*Yale University*

The energy density of an organic fuel cell is strongly dependent on the energy barrier for fuel dehydrogenation. In order to choose a suitable organic fuel for dehydrogenation it is necessary to understand both the thermodynamic favorability and the relative speed with which the fuel is effectively dehydrogenated. An understanding of the thermodynamic driving force behind the electrochemical dehydrogenation process for various heterocycles will be presented from experiment and compared to modeling work and data on chemical dehydrogenation [1]. The interdependence of heteroatoms in fuel molecules and their role in lowering dehydrogenation barriers will be discussed as well as the ability to utilize modeling as a predictive tool. Further discussion will be focused on the solution electrochemistry of fuels in an attempt to understand substituent effects on lowering oxidation barriers while suppressing unwanted side reactions. The role of bases and their effect on fuel redox potentials will also be discussed. [1]. E. Clot O. Eisenstein R. H. Crabtree *Chem. Commun.* 2007 -22 2231.

2:25 - 2:45

T-D08 - NANOSCALE CONTROL OF THERMODYNAMIC POTENTIALS

[CNEEC] Bruce Clemens¹, Fritz Prinz¹, David Goldhaber-Gordon¹, Robert Sinclair¹, John Vajo², Ping Liu², Sung Chul Lee¹, Chia-Jung Chung¹, James Donough¹, Jang Wook Choi¹, Men Young Lee¹, James Williams¹, Phil Van Stockum¹, James Mack¹, Jun Liu², Adam Gross², Elena Sherman², and Sky Mahoney²
¹*Stanford University*; ²*HRL Laboratories*

Energy storage and conversion involve charge transport, charge storage and conversion of materials from one phase to another. Our program develops fundamental understanding of the effect of size on thermodynamics, kinetic processes, electronic structure and charge transport. The material systems considered include those used in advanced batteries, solar cells, charge storage devices and hydrogen storage. Nanostructuring offers the chance to use quantum confinement to electronic structure resulting in devices with built-in potential and high charge densities. We use *in-situ* growth using scanning tunneling microscope controlled atomic layer deposition to produce structures for high-density charge storage. We explore field-effect devices with electrolytic gates, and measure the effect of electrolyte-generated field on charge density and transport to explore transport phenomena as a function of carrier density. We also use an electrochemical synthesis approach for producing nanometer scale pores in nanowires. These structures have an extremely high surface to volume ratio for charge storage in ultracapacitor devices. We also employ nanostructured materials to control thermodynamics and kinetics of phase transformation and stability in hydrogen storage materials and in electrode materials for batteries. We use vapor phase condensation to produce size-controlled nanoparticles of relevant elements and alloys and study nanomaterials incorporated into nanoporous aerogels.

2:45 - 3:05

T-D09 - EMC²: OVERVIEW AND FUTURE PROJECTIONS

[EMC2] Hector Abruna
Cornell University

This presentation will provide a general overview of the center's activities and programmatic focus over the past year. Emphasis will be placed on the discovery and characterization of novel electrode materials for fuel cell and battery applications, computational approaches, high throughput combinatorial methods and *in-situ* techniques.

3:05 - 3:25

T-D10 - NANO-STRUCTURED SURFACES AND INTERFACES FOR EFFICIENT ENERGY STORAGE AND CONVERSION

[HeteroFoam] Matt Lynch¹, Min Kyu Song¹, Kevin Blinn¹, Lei Yang¹, Mostafa El-Sayed¹, Feng Liu², Andreas Heyden³, Anil Virkar², Ken Reifsnider³, and Meilin Liu¹*Ga Tech*; ²*University of Utah*; ³*USC; University of Utah*

The rates of many chemical and energy transformation processes are limited by the charge and mass transfer along surfaces and across interfaces. The objectives of our studies are to unravel the mechanisms of surface processes and to enhance electrode performance through surface modifications using an integrated approach involving multi-scale modeling and *in situ* characterization. Fundamental understanding of rate-limiting steps is vital to achieving rational design of new electrode materials with dramatically enhanced functionality. We have demonstrated the utility of Raman spectroscopy for probing and mapping new phases and reaction intermediates on electrode surfaces under operating conditions. We have also characterized the local structure, composition, and morphology of electrode surfaces and interfaces using synchrotron-based techniques and microscopy. These studies have helped us to develop a nanostructured, mixed-valent metal oxide electrode with the highest specific capacitance while maintaining excellent power density and long cycling life. The enhanced performance is attributed to the unique mixed-valent metal oxides of porous nano-architectures, which may facilitate rapid mass transport while promoting facile redox reactions associated with intercalation or adsorption of ions on electrode surfaces. We have also demonstrated that the electrocatalytic activity and durability of widely-used electrodes can be enhanced by the introduction of a catalytic coating.

3:25 - 3:45

T-D11 - FUEL CELLS AND BATTERY MATERIALS: CHALLENGES AND PROGRESS

[EMC2] Frank Disalvo and Michael Lowe

Cornell University

The EMC² thrust in fuel cells and battery materials involves a broad search for improved performance and durability in cathode and anode materials as well as new polymeric ionic conductors for electrode separators. We will briefly outline the synthetic and processing methods and strategies utilized in this search and the methods of characterizing such materials. Fuel cell activities include a combinatorial search for catalysts with enhanced activity, development of new methods for synthesizing complex catalysts as nanoparticles, and durable catalyst support systems that can replace carbon black. In addition, we discuss new separator materials that can enable the development of fuel cells that operate under alkaline conditions. Research on battery materials also is a broad-based investigation of cathode, anode, and electrolyte materials. Significant efforts are devoted to developing and characterizing new electrode architectures for active materials, including carbons for improved lithium-sulfur cathodes, carbon-metal oxide composites for lithium-based battery anodes, and redox-active macromolecules for supercapacitor and lithium-ion battery anodes. Concurrent development of nanoscale organic-inorganic hybrid materials is moving towards a single-ion conducting electrolyte with a large operational voltage window.

**Parallel Scientific Session III – May 26, 2011
Congressional Hall A&B**

4:00 - 4:20

T-D12 - Pincer METAL COMPLEXES AS ELECTROCATALYSTS

[CETM] Grigori L. Soloveichik¹, Mark D. Doherty¹, Oltea Siclovan¹, Kenneth P. Zarnoch¹, Alex Usyatinsky¹, Guillermo D. Zappi¹, Oana R. Luca², Steven J. Konezny², Victor S. Batista², and Robert H. Crabtree²¹*GE Global Research*; ²*Yale University*

In the proposed novel regenerative fuel cell [1,2] a hydrogenated organic liquid carrier (L^*nH_2) is electrochemically dehydrogenated at the anode of a PEM fuel cell (cell discharge), while hydrogenation of the spent organic hydride L (reverse reaction) occurs during charge (Eq. 1). $L^*nH_2 + n/2 O_2 \rightarrow L + n H_2O$ (1) Development of electrocatalysts for dehydrogenation and hydrogenation of organic hydrides, which are compatible with a low humidity proton exchange membrane, is critical for operation of the projected fuel cell. We have synthesized a series of cobalt, rhodium and iridium complexes with PCP and NNN pincer ligands as potential electrooxidation catalysts and studied those using standard electrochemical methods in different solvents. Cobalt NNN complexes demonstrate a reversible oxidation (Co^{2+}/Co^{3+}). An effect of different substituents (donor and acceptor) in the imino (pyridine) ligand on $E_{A}^{1/2}$ was analyzed. Electrochemical characteristics of rhodium and iridium pincer complexes have been evaluated. Measured redox potentials were compared with computational results based on the density functional theory calculations of free energy using the thermodynamic cycle formalism in conjunction with a continuum solvation model. Electrocatalytic properties of metal pincer complexes in

the oxidation of hydrocarbons will be discussed. 1. R. H. Crabtree, *Energy & Environmental Science*, 1, (2008), 134-138.
2. G. L. Soloveichik, J.-C. Zhao, US Patent Application 2008/0248345 (2008).

4:20 - 4:40

T-D13 - CAPACITIVE ENERGY STORAGE

[MEEM] Bruce Dunn, Yunfeng Lu, Laurent Pilon, Sarah Tolbert, and Vidvuds Ozolins

UCLA

Our research on capacitive energy storage, one of three IRGs in the MEEM program, combines experimental and computational components to achieve fundamental understanding of charge storage processes in redox-based materials. These materials offer much higher energy densities than traditional double-layer capacitors, however, there are few reports of redox-active materials achieving specific capacitances comparable to their theoretical values. In this presentation, we will briefly describe our progress in three different areas. Electrochemical studies of Nb₂O₅ nanoparticles and mesoporous films indicate that this material is a very promising one for electrochemical capacitive storage. The material, when in the appropriate crystal phase, exhibits fast redox kinetics and our analysis shows that nearly all charge storage arises from pseudocapacitive processes. The second topic involves the fabrication of electrode architectures comprised of V₂O₅ nanowires and carbon nanotubes. The CNT network enhances charge transfer to the V₂O₅ nanowires so that the nanocomposite exhibits high levels of charge storage at high discharge rates for some 10,000 cycles. The third research area concerns our work on the charge storage properties of MOFs. Our initial results indicate that redox-active MOFs exhibit capacitive charge storage well above that attained by just the framework and the linker.

4:40 - 5:00

T-D14 - LITHOGRAPHICALLY PATTERNED MnO₂ NANOWIRE ARRAYS

[NEES] Reginald Penner and Yan Wenbo

University of California, Irvine

Linear arrays of delta-phase MnO₂ nanowires have been fabricated on glass. The performance of these arrays as Li⁺ cathodes in aqueous solution has been evaluated and we report these results and our interpretation of them in this talk. Nanowire arrays (NWAs) were prepared using the Lithographically Patterned Nanowire Electrodeposition (LPNE) method. The nanowires within these arrays are millimeters in length and have a rectangular cross-section with adjustable heights and widths in the 20-60nm x 50-500nm range, respectively. The specific capacity of MnO₂ NWAs was measured by cyclic voltammetry as a function of the potential scan rate from 1 mV/s to 500 mV/s. The sp. capacity across this entire scan rate range increased with diminishing wire size and a diffusion-limited capacity was observed over this entire scan rate range for nanowires of all sizes. Accurate total mass estimates for the MnO₂ nanowires were obtained by calibrating the electrodeposition efficiency using quartz crystal microbalance gravimetry. The highest capacities observed were for the smallest nanowires - 20 nm in height x 200-300 nm in width - where 1300-1400F/g was measured at 1 mV/s and 200-400F/g was measured at 100 mV/s.

5:00 - 5:20

T-D15 - ELECTRICAL ENERGY STORAGE: USE-INSPIRED BASIC RESEARCH

[CEES] Michael Thackeray

Argonne National Laboratory

Energy storage represents an opportunity and a challenge for basic research to cross technological boundaries in bringing energy independence to the U.S. The mission of the Center for Electrical Energy Storage (CEES) is to undertake use-inspired electrochemical- and materials research, notably on lithium batteries, by leveraging the internationally recognized battery program and unique infrastructure at Argonne National Laboratory, in conjunction with complementary facilities and expertise at Northwestern University and the University of Illinois at Urbana Champaign. Control and understanding of the composition and structure of electrified interfaces are essential to overcoming present-day limitations and providing the fundamental basis for finding breakthrough technologies for the next generation of battery systems. Success in this endeavor will allow the design of new materials that can operate safely at extremely high and low redox potentials and provide, uncompromisingly, the necessary increases in energy and power. In this presentation, some of the advances made by CEES during its first two years of operation will be highlighted, including 1) the design of novel electrode materials and architectures, 2) the characterization of electrochemical phenomena at the electrode/electrolyte interface, and 3) an understanding of structure and electrochemical phenomena at the interface through complementary theoretical approaches.

5:20 - 6:00

T-D16 - CONTACT ELECTRIFICATION: SEARCHING FOR ANSWERS TO THE MILLENNIA-OLD QUESTION
 [NERC] H. T. Baytekin¹, A. I. Patashinski¹, M. Branicki², B. Baytekin¹, and B. A. Grzybowski¹
¹Northwestern University; ²NYU

When dielectric materials are brought into contact and then separated, static electricity is generated on their surfaces. Though contact electrification is very frequently encountered in everyday life and has found many applications in industry, such as electrostatic separations and electrophotography, mechanisms leading to this phenomenon are still not fully understood despite the extensive research dating back to ancient Greek. To date, it has been assumed that such contact charging derives from the spatially homogeneous material properties and that within a given pair of materials, one charges uniformly positively and the other, negatively. We have shown that this picture of contact charging is incorrect. While each contact-electrified piece develops a net charge of either positive or negative polarity, each surface supports a random "mosaic" of oppositely charged regions of nanoscopic dimensions. These mosaics of surface charge have the same topological characteristics for different types of electrified dielectrics, accommodate significantly more charge per unit area than previously thought. We have also demonstrated that it is indeed possible to convert the energy by which electrical charges form on surfaces to chemical energy and drive chemical reactions with contact electrified dielectrics. Finding answers to this millennia-old problem will help us govern the processes by which static electricity takes place, also store and use the electrical energy associated with it.

E – Energy Conservation and Efficiency - Renaissance Ballroom East

Parallel Scientific Session I – May 26, 2011 Renaissance Ballroom East

10:15 - 10:55

T-E01 - HIGH PERFORMANCE NANOSTRUCTURED THERMOELECTRIC MATERIALS (nThEM)
 [RMSSEC] Mercouri Kanatzidis¹, Vidvuds Ozolins², David Seiman¹, Chris Wolverton¹, and Sergey Barabash²
¹Northwestern University; ²UCLA

Thermoelectric materials, that convert waste thermal energy into useful electrical energy, have an important thematic role to play in the broad energy strategy. The emergence of nanostructured thermoelectrics has ushered a new era for bulk thermoelectrics, with considerable promise to enhance the "contra-indicating" parameters of high electrical conductivity (power factor) and low thermal conductivity to achieve high ZT - the thermoelectric figure of merit. We achieve this by introducing nanostructures in bulk thermoelectric host to significantly reduce lattice thermal conductivity via effective scattering of heat carrying phonon through hierarchical architecture of nanostructured thermoelectrics (nThEM). The presentation will cover recent developments in our EFRC, and future prospects for higher performance nThEM. Systems based on lead chalcogenides (e.g., PbTe, PbSe) present key science challenges with promising properties and are given particular emphasis. We have achieved excellent control of synthesis and crystal growth of such materials resulting in record enhancements ZT. These enhancements derive from very large reductions in lattice thermal conductivity with nanostructuring. We have experimentally realized concurrent synergistic effect of phonon blocking and charge transmission via the endotaxial nanostructures in thermoelectric host matrix. Theory and simulation efforts provide the basis for experimental observations, optimization and challenge the experimentalists for innovative compositions and microstructure for further enhanced performance. The presentation will highlight prospects for conversion of waste energy into useful electrical energy with bulk nThEM, and future strategies for enhancing ZT of bulk nThEM.

10:55 - 11:15

T-E02 - NEW THERMOELECTRIC MATERIALS USING RARE EARTH NANOPARTICLE FOR INCREASED SEEBECK COEFFICIENT
 [CEEM] John Bowers, Art Gossard, Chris Palmstrom, Ali Shakouri, and Shuji Nakamura
 University of California, Santa Barbara

In this work, we present research on a number of novel thermoelectric materials using semimetal-semiconductor nanocomposites grown by molecular beam epitaxy (MBE). We study several different III-V semiconductors embedded with semimetallic RE-V compounds, including ErAs:InGaAs for n type and ErSb:InGaSb for p-type thermoelectric materials. Nanostructures of RE-V compounds are formed and embedded within the III-V semiconductor matrix. The thermoelectric properties have been engineered for enhanced thermoelectric device performance. Segmented thermoelectric power generator modules using 50 μm thick Er-based nanocomposites have been fabricated and measured. Research on different rare earth elements for thermoelectrics is discussed. For high temperature thermoelectrics, two approaches are being pursued. We discuss fabrication and characterization of arrays of Si nanowires

with sub-100 nm diameters with low thermal conductivities below 10 W/m-K. Promising measurements of InGaN/GaN based thermoelectrics up to 600C will also be presented.

11:15 - 11:55

T-E03 - SOLID-STATE SOLAR-THERMAL ENERGY CONVERSION CENTER, PHONON TRANSPORT AND SOLAR THERMOELECTRIC ENERGY CONVERSION

[S3TEC] [Gang Chen](#), [Keith Nelson](#), and [Daniel Kraemer](#)
Massachusetts Institute for Technology

This talk will start with a brief introduction to the solid-state solar-thermal energy conversion center (S³TEC Center), followed by in depth discussion on phonon transport and solar thermoelectric energy conversion. The S³TEC Center aims at advancing fundamental science and developing materials to harness and convert heat from the sun into electricity via solid-state thermoelectric and thermophotovoltaic technologies. Solar thermophotovoltaics (STPV) first use solar radiation to raise the temperature of a terrestrial object, which then emits photons optimized to the bandgap of a photovoltaic cell to generate electricity. Solar thermoelectric energy conversion uses solar radiation to create a temperature difference across a solid-state material to generate electricity. For solar thermoelectric generation, the S³TEC center aims at improving thermoelectric materials through detailed experimental and theoretical studies of electron and phonon transport in nanostructures and bulk materials. First-principle based simulations carried out at the Center show phonons contributing to heat conduction in solids have a wide range of mean free path distributions, pointing to the characteristic length scales needed to reduce phonon thermal conductivity via nanostructuring that can lead to improved thermoelectric figure of merits. Optical techniques are being developed at the Center to map out the distributions of phonon mean free path experimentally. Prototype devices developed at the Center using nanostructured thermoelectric materials points to the promising future of solar thermoelectric energy conversion.

11:55 - 12:15

T-E04 - HIGHLIGHTS OF THERMOELECTRIC RESEARCH AT THE UNIVERSITY OF MICHIGAN

[CSTEC] [Ctirad Uher](#)
University of Michigan

The thermoelectric program of the University of Michigan's CSTEC-EFRC focuses on fundamental processes that determine the efficiency of thermoelectric (TE) energy conversion. The crucial material parameter that governs the efficiency of energy conversion is the thermoelectric figure of merit that combines three important transport coefficients: electrical conductivity, Seebeck coefficient and thermal conductivity. Since the transport coefficients are interdependent, it is challenging to find conditions that maximize the figure of merit. The team of Michigan scientists explores the energy conversion efficiency in a broad spectrum of materials encompassing single molecules trapped between metallic contacts, lower-dimensional structures based on MBE-fabricated thin films, and novel bulk nanocomposite materials that hold promise for applications in waste heat recovery. Our strong experimental efforts are ably supported by computational and simulation studies and the presence of CSTEC-EFRC on the campus has created a fertile ground for new and vigorous collaborations between the colleges and departments. Major scientific accomplishments supported by CSTEC-EFRC will be reviewed.

Parallel Scientific Session II – May 26, 2011
Renaissance Ballroom East

1:45 - 2:05

T-E05 - ELECTRONIC AND THERMAL TRANSPORT PROPERTY CHARACTERIZATION OF THERMOELECTRIC MATERIALS UNDER REVOLUTIONARY MATERIALS FOR SOLID STATE ENERGY CONVERSION-EFRC, AWARD NUMBER DE-SC001054

[RMSSEC] [Ctirad Uher](#)
University of Michigan

The development of novel, more efficient thermoelectric (TE) materials necessitates precision measurements of the key transport coefficients that govern the thermoelectric figure of merit $Z = s^2/k$ — the material parameter that informs on how efficiently a given material functions as a TE energy converter. As a minimum requirement, one must measure the electrical conductivity, s , Seebeck coefficient, S , and the thermal conductivity, k . In addition, it is highly desirable to measure the Hall effect which provides invaluable information on the carrier density and, in conjunction with the electrical conductivity, on the mobility of the dominant charge carriers. Measurements should be carried out over a wide range of temperatures so as to provide insight into the nature of carrier and phonon dynamics as well as to gauge the actual performance of the material in the temperature regime where it is intended to operate as an energy converter. In this

presentation I will review techniques and facilities we use to assess the performance of TE materials that are being developed as part of the Revolutionary Materials for Solid State Energy Conversion – EFRC.

2:05 - 2:25

T-E06 - EFFECT OF ELECTRODE MORPHOLOGY AND MATERIALS CHEMISTRY ON POLARIZATION IN SOLID OXIDE FUEL CELLS [HeteroFoam] Anil Virkar¹, Wilson Chiu², Kenneth Reifsnider³, Prasun Majumder³, Fazle Rabbi³, MD. Raihan³, and Qianlong Liu³

¹University of Utah; ²University of Connecticut; ³University of South Carolina

Heterogeneous Functional Materials, "HeteroFoams" are a special class of engineered materials designed to achieve specific functional properties. Their morphology and feature size over multiple scale lengths is central to their functionality involving transport and chemical/electrochemical reactions in bulk, on surfaces/interfaces, lines, and points. Thus, HeteroFoams are different from typical multi-phase materials in which 'properties' are defined in terms of phase distribution and morphology alone. In HeteroFoams, spatial locations of various constituents in relation to directions of transport are important. For example, root systems in trees and lungs in mammals are HeteroFoams. The central theme of our EFRC is science and engineering of HeteroFoams in electrochemical systems such as fuel cells, batteries, electrolyzers, and capacitors in which physical location of reacting species in relation to morphology and spatial distribution of heterogeneous functional materials is central to their performance. The general concept of HeteroFoams is applicable to physical, chemical, and biological systems which require transport of matter, charge, and heat. The principal focus of the HeteroFoam Center is to conceptualize, model and synthesize electrochemical systems based on HeteroFoam materials/systems. This paper will primarily discuss the design of electrodes for solid oxide fuel cells.

2:25 - 2:45

T-E07 - UNDERSTANDING EFFICIENCY LIMITATIONS OF LEDs FOR SOLID-STATE LIGHTING

[SSLS] Mary Crawford¹, Weng Chow¹, Daniel Koleske¹, Normand Modine¹, Andrew Armstrong¹, Tania Henry¹, Jeffrey Tsao¹, Qi Dai², Jaehee Cho², and E. Fred Schubert²

¹Sandia National Laboratories; ²Rensselaer Polytechnic Institute

Solid-state lighting is a rapidly advancing technology with potential to provide decisive energy savings and functionality well beyond traditional lighting systems. Already, the efficiency of commercial white LEDs has surpassed that of incandescents and exceeds that of compact fluorescents in particular applications. Research efforts are now focused on achieving an electricity-to-white-light conversion efficiency of ~50%; a performance target that will soundly surpass existing technologies. A roadblock to reaching this goal is the significant loss of efficiency when InGaN LEDs are operated at high currents to achieve high output powers. The origin of this "efficiency droop" is under intense debate and many mechanisms, from Auger recombination to carrier leakage, have been proposed. In this presentation, we will review efforts in our EFRC to understand the competing radiative and non-radiative mechanisms that underlie efficiency droop. We will present LED designs that allow exploration of the contributions of carrier capture, distribution, and transport in the InGaN multi-quantum well active region. We will describe an improved model for LED radiative efficiency into the high carrier density regime and demonstrate how intrinsic contributions to efficiency droop are related to bandstructure and plasma heating. Finally, we will present new insights into conditions under which non-radiative recombination at crystalline defects may also contribute to efficiency droop.

2:45 - 3:05

T-E08 - NANOSTRUCTURES FOR ENERGY GENERATION AND CONSERVATION

[CEN] P. Daniel Dapkus, Ting-Wei Yeh, Chun Yung Chi, Hyung-Joon Chu, Yenting Lin, Anuj Madaria, Maoqing Yao, Ruijuan Li, and Chongwu Zhou

University of Southern California

Semiconductor nanowires have the potential to realize both low cost solar cells and LEDs for solid state lighting. Nanowires offer the enhanced light absorption and coupling in well designed structures, the strain release between lattice mismatched materials, wider choice of substrate materials and geometries and crystalline orientations not accessible in planar thin films. The Center for Energy Nanoscience (CEN) is exploring nanowires designs as efficient LEDs in the InGaN materials system. Nanowires with nonpolar facets can be used to mitigate the causes of efficiency "droop" in blue LEDs for future solid state lighting. Thicker quantum well light emitting layers on nonpolar facets will promote efficient electron capture, reduced carrier leakage and increased quantum efficiency. Dense arrays of InGaN quantum wires have been grown that support high efficiency luminescence. Further studies of efficiency droop and its elimination are underway. CEN is also exploring nanowires for tandem solar cells. The relaxation of lattice matching constraints and the possible use of low cost substrates in their fabrication offer unique advantages in designing and fabricating these efficient devices. Uniform, dense arrays of GaAs and other III-V nanowire arrays on lattice matched and mismatched substrates

have been demonstrated. The growth mechanisms and kinetics have been modeled to demonstrate the influence of geometry and facet reactions on their formation.

3:05 - 3:25

T-E09 - BEYOND 2D: NANOWIRES FOR SOLID-STATE LIGHTING

[SSLS] [George Wang](#)

Sandia National Laboratories

This talk will provide an overview of research efforts at the Solid-State Lighting Science (SSLS) EFRC investigating III-nitride based nanowires in the context of future, higher efficiency solid-state lighting (SSL). Compared to planar films which current LEDs are based on, nanowires have several potential advantages including higher crystalline quality and reduced strain, which enables growth on arbitrary substrates as well as allowing a greater range of alloy compositions and hence wavelengths. However, before the promise of nanowire-based SSL can be fully realized, several challenges must be addressed in the areas of controlled nanowire synthesis, electrical integration, and understanding and controlling the nanowire structural, electrical, thermal, and optical properties. I will discuss our research objectives and approaches to address some of these challenges. Recent results will then be highlighted regarding the fabrication of GaN-based nanowires and nanowire LEDs by both bottom-up and top-down methods, along with insights into the nanowire properties obtained using cutting-edge structural, electrical, and optical nanocharacterization techniques. Finally, future directions will be discussed. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:25 - 3:45

T-E10 - LIGHT-MATTER INTERACTION IN SUBWAVELENGTH PHOTONIC STRUCTURES

[SSLS] [Arthur J. Fischer](#), Ganapathi Subramania, Ting S. Luk, Weng W. Chow, Eric A. Shaner, Daniel D. Koleske, and Igal Brener

Sandia National Labs

For this part of our EFRC we are investigating advanced photonic structures with the goal of demonstrating highly efficient light emission processes which one day may lead to a new generation of emitters for solid state lighting applications. Purcell effect enhancements for emitters incorporated into cavities are of particular interest for lighting applications since the fundamental radiative recombination rate can be enhanced, allowing radiative processes to beat out non-radiative processes. By carefully designing and building an appropriate subwavelength photonic structure, it is possible to beneficially alter the photonic density of states and thereby demonstrate more efficient photon emission. We have designed and fabricated a number of two-dimensional and three-dimensional photonic crystal structures with incorporated emitters and have investigated the light emission processes for these advanced emitter structures. As one increases the light-matter interaction, either by increasing the cavity quality factor or the emitter oscillator strength, it is possible to enter the strong coupling regime. Recent experiments at Sandia related to strong coupling in one-dimensional and two-dimensional semiconductor-based photonic structures will also be discussed. Although research on strong coupling phenomenon is still in its infancy, a more detailed understanding of this regime may lead to the demonstration of novel, next generation light sources.

**Parallel Scientific Session III – May 26, 2011
Renaissance Ballroom East**

4:00 - 4:20

T-E11 - SUPERCONDUCTIVITY AS AN ENERGY CARRIER

[CES] [George Crabtree](#)

Argonne National Laboratory and University of Illinois at Chicago

Superconductors carrying high density currents with little or no heating offer unique solutions to fundamental grid challenges of the 21st century: high capacity power delivery in urban areas, long distance transmission of renewable electricity from remote sources to population centers, seamless interconnection of the three national power grids, and high capacity, low weight offshore wind turbines. Wide penetration of superconducting power technologies depends on raising the performance and lowering the cost of second generation high temperature superconducting coated conductors based on $\text{YBa}_2\text{Cu}_3\text{O}_7$. The Center for Emergent Superconductivity has identified two grand challenges for advancing superconducting power applications: raising the magnitude and lowering the anisotropy of the critical current of commercial superconducting wires. Working with industry partners, we show that splayed columnar defects produced by heavy ion bombardment at Argonne's ATLAS accelerator raise the lowest critical current values of commercial

superconducting wire by a factor of two, and reduce the anisotropy from a factor of ~ 2 to a factor of ~ 1.2 . These results provide a proof of principle that splayed columnar defects are an effective route to addressing the two grand challenges of superconducting power applications.

4:20 - 4:40 T-E12 - INTERPLAY OF SYNTHESIS, CALCULATION AND CHARACTERIZATION OF HETEROGENEOUS FUNCTIONAL MATERIALS

[HeteroFoam] Emily Carter¹, Andreas Heyden², Hanno Zur Loye², Prasun Majumdar², Kyle Brinkman², and Fanglin Chen²
¹Princeton University; ²University of South Carolina

Solid oxide fuel cells (SOFCs) can directly convert the chemical energy in the fuel directly to electrical energy with very high energy conversion efficiency and fuel flexibility. Electrodes provide active sites where the electrochemical reactions taking place in SOFCs. One particular issue that arises with the use of conventional Ni-based anode in SOFCs is their dimensional instability when subjected to redox (reduction–oxidation) cycling. On the other hand, when SOFCs are operated at very high current density, O₂ partial pressure at the cathode triple phase boundary region is quite low, potentially causing partial decomposition of the conventional manganite and cobaltite-based material and thus long-term deterioration of the cell performance. In addition, if the electrode is a mixed ionic and electronic conducting material, the triple phase boundary sites can be extended beyond the physical interfaces between the electrode and the electrolyte, consequently enhancing the electrode electrochemical performance. We have recently discovered a perovskite based on Sr₂Fe_{1.5}Mo_{0.5}O_{6-d} (SFM) which has demonstrated excellent redox stability and electrochemical performance in both reducing and oxidizing environment. SFM has been applied as both anode and cathode on La_{0.8}Sr_{0.2}Ga_{0.87}Mg_{0.13}O₃ (LSGM) electrolyte supported cells, achieving a peak power density of 835 mW×cm⁻² at 900 °C using H₂ as fuel and ambient air as oxidant, in spite that the LSGM electrolyte has a thickness of 265 μm.

4:40 - 5:00

T-E13 - DEVELOPMENT OF KINETIC MODELS FOR METHYL-ESTER MOLECULES FOR BIODIESEL MODELING

[CEFRC] Pascal Divart¹, Stephen Dooley¹, Sang Hee Won¹, Frederick L. Dryer¹, Yiguang Ju¹, Emily A. Carter¹, Chung K. Law¹, Fokion Egolfopoulos², Ronald K. Hanson³, Stephen J. Klippenstein⁴, Nils Hansen⁵, and Chih-Jen Sung⁶
¹Princeton University; ²University of Southern California; ³Stanford University; ⁴Argonne National Laboratory; ⁵Sandia National Laboratories and ⁶University of Connecticut

The ignition delay time, flame speeds, extinction limit, and soot emissions of methyl ester fuels have been measured. The results show that the existing mechanisms over-predict the fuel reactivity and the burning rates. A new high temperature kinetic mechanism of methyl decanoate and methyl butanoate is constructed based on the oxidation chemistries of n-heptane, methyl butanoate, and methyl decanoate. The results show that the newly developed mechanism improves the prediction of ignition delay time and speciation time history in a jet-stirred reactor. Moreover, the new model reproduces well the measured extinction limits of methyl decanoate diffusion flames. Kinetic analysis shows that under diffusion flame conditions, the fuel is exclusively consumed by metathesis reactions with H atoms and formaldehyde is produced via two different paths: the decomposition of methyl ester function group and the small radicals in reaction zone. A transport weighted enthalpy flux is introduced to isolate the effect of transport and heating value on extinction. The results show that methyl butanoate and methyl decanoate exhibit the same extinction behavior, indicating the size of methyl-ester molecule has negligible effect on the fuel oxidation kinetics in flames. The results suggest that methyl butanoate will be an appropriate research target for understanding the kinetic mechanism of methyl esters and for the development of a validated kinetic model for biodiesel.

5:00 - 5:20

T-E14 - COMPARING IRON-BASED AND COPPER-BASED HIGH TEMPERATURE SUPERCONDUCTORS

[CES] J. C. Seamus Davis
 Brookhaven National Laboratory

We present a comparison of the electronic structure of iron-based and copper-based high temperature superconductors from its direct visualization at the atomic scale. This reveals vividly the broken electronic symmetries which disappear, in both systems, at the critical point where the superconducting critical temperature is maximum. By exploring and comparing these phenomena CES hopes to determine the essential characteristics underpinning high temperature superconductivity and to use that information to motivate improvement of present compounds and search for new Superconductors.

5:20 - 5:40

T-E15 - ENERGY FRONTIER RESEARCH UNDER HIGH PRESSURES

[EFree] Ho-kwang Mao*Carnegie Institution*

The critical shortage of abundant, affordable, and clean energy calls upon novel materials that are superior to any known material existing today with extreme properties for energy production, storage, conversion, and transfer. The extreme pressure-temperature (P-T) environments present a vast, unexplored ground to search for transformative materials and phenomena. The Center for Energy Research in Extreme Environments (EFree) sets a mission on accelerated discoveries of novel materials and phenomena in the extreme environments and recoveries of the favorable properties for energy applications. EFree has made major advanced in the scientific exploration. Novel high-pressure chemistry of hydrogen-rich materials has been revealed. New mechanism of tuning the maximum superconducting temperature has been discovered. Pressure-induced insulator-metal transitions have been investigated. Fundamental excitonic structure of solid helium has been determined at ambient temperature. Novel nano phases, mesoporous diamond, and amorphous materials have been synthesized at high pressures and preserved at ambient conditions. These achievements are preparing us to focus on two EFree grand challenges, namely the quest for metallic hydrogen which has been predicted to be a room temperature superconductor and superfluid, and the quest for superhard materials which are resistive to extreme mechanical, chemical, and thermodynamic conditions.

5:40 - 6:00

T-E16 - CES HIGH TEMPERATURE SUPERCONDUCTING MATERIALS RESEARCH, PRESENT AND FUTURE

[CES] Peter Abbamonte*University of Illinois at Urbana-Champaign*

Improving materials generally for advancing energy science is of profound importance, and superconductivity is a prime example. The long term prospects of using superconductivity to improve the efficiency of the power grid depend on our ability to identify superconducting materials with improved properties, such as higher transition temperature, higher critical current, or lower anisotropy. Here we summarize a general strategy laid out by the Center for Emergent Superconductivity for identifying superior superconducting materials, which is based on layering favorable combinations of ionic materials in a manner that optimizes conditions for superconductivity. Several recent successes in the CES involving Fe- and Cu-based materials will be described.

F – Carbon Capture and Sequestration - Renaissance Ballroom West A

Parallel Scientific Session III - May 26, 2011

Renaissance Ballroom West A

4:00 - 4:20

T-F01 - COMPUTATIONAL CARBON CAPTURE

[CGS] Berend Smit¹, Joe Swisher¹, Maciej Haranczyk², Jeff Neaton², Roberta Poloni¹, Giulia Galli³, Laura Gagliardi⁴, Allison Dzubak⁴, Jihan Kim⁵, and Richard Martin⁵¹UC Berkeley ²LBNL; ³UC Davis; ⁴U Minnesota ⁵LBNL

Metal organic frameworks are a promising class of materials for carbon capture. As one can change the metal, the linker, and the structure of these frameworks there are nearly an infinite number of possible materials that can be synthesized. To support the experimental efforts in the EFRC a computational carbon capture research program focused on finding the optimal material. The aim of the computational research is to develop the methodology to predict the properties of a metal organic framework before the material has been synthesized. To achieve this we combine quantum mechanical calculations to obtain detailed insights in the interaction of CO₂ with these materials, molecular simulations to compute those thermodynamic and transport properties that are important for the separation, and finally a simple separation design to compare energy costs of various materials for a typical flue gas separation. As we need to screen many millions of different materials chemoinformatic techniques are developed to efficiently screen so many structures. In this presentation the integration of the various approaches is illustrated with some examples of adsorption studies of mixtures of CO₂ in various materials.

4:20 - 4:40

T-F02 - CARBONATE MINERAL NUCLEATION PATHWAYS

[NCGC] A. Fernandez-Martinez¹, A. Radha², A.G. Stack³, L. Hedges¹, Y. Hu⁴, A. Loulier⁴, L. J. Banuelos³, G. Rother³, Y.S. Jun⁴, S. Whitlam¹, D. R. Cole⁵, A. Navrotsky², G.A. Waychunas¹, and J.J. DeYoreo¹¹Lawrence Berkeley National Laboratory; ²University of California, Davis; ³Oak Ridge National Laboratory; ⁴Washington University in St. Louis; ⁵Ohio State University

A key characteristic of CO₂ storage in geological reservoirs is the presence of a porous medium that confines the geological fluid. Experimental and theoretical studies in our Center aim to understand how this confinement affects nucleation of carbonate minerals - the main expected contributors to mineral trapping of CO₂ - and the extent to which these pores are available as nucleation sites. Neutron scattering experiments have shown that nucleation of CaCO₃ in model silica nano-pores is possible under mildly saturated conditions, proving that nano-confinement -and its associated solvent-structuring effects- does not prevent nucleation. Statistical mechanical models of pore nucleation reveal how pore geometries and surface characteristics control the free energy barriers to nucleation within pores as well as out into the surrounding solution. The results suggest strategies for enhancing nucleation in the experiments. In the last few decades, a new CaCO₃ nucleation pathway involving the initial formation of an amorphous phase (ACC) has been reported to occur in many systems. It has also been reported that the presence of Mg²⁺ ions in ACC increases its stability. In an effort to understand carbonate mineral nucleation pathways, we have studied the structural and energetic properties of ACC, confirming its thermodynamically metastable character and its increased stability upon dehydration, and showed how variations in the Ca-to-Mg ratio help to stabilize the amorphous phase.

4:40 - 5:00

T-F03 - MOLECULAR, CHEMICAL AND PHYSICAL PROPERTIES OF CO₂-H₂O - ELECTROLYTE-MINERAL SYSTEM[CFSES] Philip Bennett¹, Susan Altman², Bayani Cardenas¹, Randall Cygan², Eugenio Santillan¹, Matthew Kirk², Molly Kent¹, Kuldeep Chaudhary¹ and Wen Deng¹¹University of Texas at Austin; ²Sandia National Laboratories

Understanding the processes and risks associated with the geological storage of CO₂ requires an understanding of the properties and interactions of complex mixtures of reactive fluids that will fundamentally alter the preexisting steady state conditions of the subsurface environment. Dissolved CO₂ alters aqueous phase density and viscosity, and therefore its flow properties through porous media, while providing abundant acidity in the form of carbonic acid that will result in accelerated water-rock reactions and toxic metal mobilization, resulting in extreme geochemical disequilibrium extending across many orders of magnitude in length scale. This EFRC is investigating the physical, chemical, and biological consequences of geologic CO₂ storage from the molecular to basin scale, using experimental, field, and computational methods, with the goal of integration using numerical simulations. Our observations and simulations are providing insight into molecular-scale interactions of supercritical CO₂ with water and solutes, pore scale movement of CO₂ in brines, the reaction rates of CO₂ dissolution, physico-chemical properties of CO₂ in complex brines, changes in microbial activity caused by geological CO₂ storage, toxicity of CO₂ to subsurface microbial communities, and impact of subsurface biofilms in pore clogging. These data and interpretation are being incorporated into larger scale modeling to offer a realistic simulation of carbon dioxide sequestration in the subsurface

5:00 - 5:20

T-F04 - NANOPORE PROCESSES IN SEALING CAP ROCKS OF CARBON DIOXIDE STORAGE REPOSITORIES

[NCGC] Ian Bourg*Lawrence Berkeley National Laboratory*

Geological carbon sequestration (GCS) is an emerging technology that could potentially offset up to 12% of global CO₂ emissions by 2020 and up to 45% by 2050. Pilot studies have firmly established the feasibility of injecting CO₂ in geological formations in quantities of up to several megatonnes per year for durations of up to 15 years. Commercial-scale implementation of GCS will require the demonstration that much larger plumes of buoyant CO₂ (hundreds of megatonnes) can be safely stored, with negligible leakage, for durations of thousands of years, as required to achieve permanent CO₂ sequestration through naturally-occurring rock weathering reactions. A critical knowledge gap, at this point, is the long-term sealing integrity of low-permeability caprocks with respect to an underlying buoyant plume of supercritical CO₂. Here, we describe how molecular-dynamic simulations of mineral-CO₂-brine systems are contributing to reveal the molecular-scale processes (such as adsorption, diffusion, surface wetting, and capillary pressure) that determine the sealing properties of nanoporous cap-rocks.

5:20 - 5:40

T-F05 - MULTISCALE SIMULATION OF CO₂ SEQUESTRATION IN SUBSURFACE MEDIA[CFSES] Steven Bryant¹, Matt Balhoff¹, David DiCarlo¹, Sanjay Srinivasan¹, Tom Dewers², Hongkyu Yoon², Peter Eichhubl¹, Behdad Aminizadeh-Goharrizi¹, Tie Sun¹, Yashar Mehmani¹, Matt Roberts¹, and Valentina Prigiobbe¹¹University of Texas at Austin; ²Sandia National Laboratories

The long-term security of CO₂ sequestered in geologic formations is an important pre-requisite for this form of greenhouse gas mitigation. If CO₂ escapes from its storage formation, a critical question is whether the CO₂ flux becomes focused or diffused as it approaches the Earth's surface. Several physical and chemical processes occur at small scales (individual pores 10 microns across) that govern the destiny of sequestered CO₂ at much larger scales (100 m to 100 km). These processes include the geochemical alteration of sedimentary rocks as water saturated with CO₂ migrates through them and the consequent alteration of flow paths within those rocks. We present methods that account for coupled processes at the relevant scale but uniquely allow prediction of their macroscopic consequences. The coupled phenomena are overlaid on an already heterogeneous background flow field in the subsurface. We illustrate this in a geologic fault, which is potential escape route for CO₂ or CO₂-saturated water. The implications of the influence of interfacial phenomena (surface energy at the CO₂/water meniscus) on the large-scale path of the CO₂ plume are examined at the field scale. Finally we describe experimental results that validate the small scale models, and another set of experiments that show how to prevent a focused flux of CO₂ by means of emplacing water loaded with suitably treated nanoparticles.

5:40 - 6:00

T-F06 - APPROACHES TO IMPROVING CARBON DIOXIDE ADSORPTION IN MULTIVARIATE METAL-ORGANIC FRAMEWORKS

[CGS] Omar M. Yaghi

UCLA

Metal-organic frameworks (MOFs) represent an extensive class of porous crystals in which organic 'struts' are linked by metal oxide units to make open networks. The flexibility with which their building units can be varied and their ultra-high porosity (up to 10,000 m²/g) have led to many applications in gas storage and separations for clean energy production, to mention a few. This lecture will focus on two approaches for enhancing carbon dioxide adsorption. Firstly, we studied the incorporation of open metal sites into a metal organic framework. This can be done by activation of a metal site, where a tightly bound solvent molecule is removed from the metal oxide unit. The open metal sites offer a binding site for gas molecules, enhancing gas adsorption. Secondly, strategies for incorporating heterogeneity into MOF frameworks will be reviewed, as heterogeneity of functionalities has been shown to enhance carbon dioxide adsorption.

Parallel Scientific Session IV - May 27, 2011
Renaissance Ballroom West A

8:00 - 8:20

T-F07 - BASIC SCIENCE FOUNDATIONS FOR SUBSURFACE ENERGY SECURITY

[CFSES] Marianne Walck, Gary Pope, Susan Altman, and Mojdeh Delshad*Sandia National Laboratories; University of Texas at Austin; Sandia National Laboratories and University of Texas at Austin*

The Center for Frontiers of Subsurface Energy Security (CFSES) is pursuing scientific understanding of multiscale, multiphysics processes to ensure safe and economically feasible storage of carbon dioxide and other byproducts of energy production without harming the environment. We are integrating and expanding our knowledge of physical, chemical and biological processes from the molecular scale to the field scale, using both experimental and modeling approaches to better understand and quantify behavior far from equilibrium. Ultimately, we will obtain capabilities to better predict long term behavior of subsurface storage. The presentation describes foundational science activities that the Center is pursuing in order to address several questions that are critical for assessing the safety and security of subsurface disposal of energy production byproducts. How does supercritical CO₂ interact with water, brines, mineral surfaces, and bacterial growth as it flows through the subsurface? What are the relevant physics of CO₂ fate and transport in the subsurface, and how can these be synthesized, upscaled, and incorporated into more powerful continuum models? Can we engineer solutions to mitigate contaminant leakage from natural and anthropogenic leakage pathways? How can we represent the essential features of large-scale behavior (flow, transport, reaction and deformation in the Earth's subsurface) that emerge from small-scale phenomena, without resolving all small-scale features?

8:20 - 8:40

T-F08 - PROBING CO₂-RICH FLUID INTERACTIONS WITH RESERVOIR ROCKS: FROM ATOMIC TO PORE SCALES[NCGC] [Gernot Rother](#)¹, [Larry Anovitz](#)¹, [Ariel Chialvo](#)¹, [David Cole](#)², [Mirek Gruskiewicz](#)¹, [Andrew Stack](#)¹, [Lukas Vlcek](#)¹, and [Garrison Sposito](#)³¹*Oak Ridge National Laboratory*; ²*Ohio State University* and ³*Lawrence Berkeley National Laboratory*

The fate of CO₂ deposited in subsurface storage reservoirs is initially controlled by sorption and capillary trapping processes, with the possibility of formation of a buoyant plume rich in CO₂. Using a combination of experimental and simulation techniques, we study the interactions of supercritical CO₂ with reservoir and caprock materials at the nanoscale. We will discuss the properties of CO₂ in nanoporous silica materials with different nano-scale pore morphologies, which serve as proxies for natural quartz-rich rocks and sediments. Vibrating tube densimetry, excess sorption, and neutron scattering techniques are used to quantify the amount of fluid in the pore spaces and its distribution between the adsorbed and unadsorbed fluid phases, yielding a microscopic picture of pore-confined supercritical fluids. The impacts of pressure, temperature and fluid morphology will be discussed and conclusions for CO₂ storage applications drawn. Molecular-based simulations link to the experimental data and enhance our understanding of fluid-solid phenomena at the atomic level. Neutron Scattering and electron microscopy data are used to characterize the structure and pore features of natural rocks. Fractal concepts are employed to describe the multi-scale pore network. The impacts of the nano-scale pore network structure on fluid flow properties are studied by neutron tomography, addressing the mechanism of reservoir rock filling with CO₂ and migration processes of CO₂-rich plumes.

8:40 - 9:00

T-F09 - SYNTHESIS OF ZEOLITIC IMIDAZOLATE FRAMEWORKS AND THEIR GAS ADSORPTION

[MEEM] [Omar M. Yaghi](#)*UCLA*

Zeolitic Imidazolate Frameworks (ZIFs) are an important class of materials that share many of the characteristics of zeolites, in that they are porous, crystalline and have similar atom geometries. ZIFs are comprised of tetrahedral metal centers (Zn²⁺, Cd²⁺, and Co²⁺) with bridging imidazolate units. The intrinsic crystallinity and porosity of ZIF materials, combined with the many topologies that can be obtained when combining a metal tetrahedron with imidazolate, make ZIFs ideal for the study of gas adsorption. First, this talk will focus on the efficient synthesis of ZIF materials. The technique of high throughput will be highlighted as an efficient method to access a wide range of ZIF materials. Many factors, including metal center, functionality, and topology have been shown to affect gas adsorption. In our study, we chose to select ZIFs in which one aspect of the ZIF structure is altered in order to see how the gas adsorption properties change. From the wide range of ZIF frameworks that have been synthesized, we selected five ZIF materials with the same underlying topology, RHO, but with different functionalities decorating the imidazolate. The functionalities including -CHO and -NH₂, were shown to enhance CO₂ adsorption; the results are supported by computation. Finally, the talk will highlight the role topology can play on gas adsorption; two ZIF frameworks, ZIF-93 and -94, were selected because they possess identical components but have different functionalities.

9:00 - 9:20

T-F10 - TOWARD MOLECULARLY DEFINED POROUS MEMBRANE

[CGS] [Ting Xu](#)*University of California, Berkeley*

Porous thin films containing sub-nanometer channels oriented normal to the surface exhibit unique transport and separation properties and can serve as selective membranes for separation and protective coatings. However, the dimensions of individual polymer chains, the thermodynamics governing the microphase separation of block copolymers (BCPs), the surface energy required to stabilize such small pores, and the relaxation behavior of synthetic polymers pose insurmountable obstacles in extending pore diameters to the sub-nanometer level using polymer alone. While molecularly defined nanoporous inorganic materials and organic materials obtained by supramolecular assembling motifs have been extensively studied, generating flexible nanoporous thin films with highly aligned channels over large areas has been elusive. Here, by conjugating polymer chains to peptides, and co-assembling these peptide-polymer conjugates with BCPs, porous thin films are readily produced containing high-density arrays of perpendicularly oriented, hexagonally packed sub-nanometer pores that span the film. These nanoporous thin films show size-selective solution transport as well as accelerated gas transport and offer ideal platforms to understand molecular transport in sub-nanometer pores. Equally important, these porous thin films can be solution processed on different substrates, opening avenues to technologically relevant membranes.

G – Materials in Extreme Environments - Renaissance Ballroom West A**Parallel Scientific Session I - May 26, 2011
Renaissance Ballroom West A**

10:15 - 10:35

T-G01 - WHAT SUB-PICOSECOND X-RAY DIFFRACTION WILL TELL US ABOUT THE STRUCTURAL DYNAMICS OF DISPLACEMENT CASCADES

[CDP] Ben Larson, Jon Tischler, Roger Stoller, Yuri Osetskiy, Rad Radhakrishnan, Haixuan Xu, and Don Nicholson
Oak Ridge National Laboratory

One of the earliest applications of molecular dynamics (MD) was to simulate numerically the atom-by-atom trajectories of the "cascade" of lattice displacements generated when fast-neutrons collide with lattice atoms and deposit tens of keV of energy within nanometer scale volumes. Beginning 50 years ago with 500 atom cascade calculations, MD simulations can now handle tens of millions of atoms - but so far without real-time experimental measurements for comparison. With the availability of intense, 100-femtosecond hard x-ray pulses from the free-electron-laser Linac Coherent Light Source (LCLS), it will be possible for the first time to probe experimentally the ultra-fast dynamics of cascades in real time with atomic scale structural resolution. Here we discuss the experimental requirements and the type of cascade dynamics information that will be available by combining real-time experimental measurements with computational simulations of (ion-induced) cascades. X-ray diffraction calculations based on atomic positions from bulk crystal MD simulations of cascades in Fe and Cu will be used to illustrate the information possible using 100-femtosecond LCLS pulses over picosecond time scales. The extension of MD simulations and x-ray scattering calculations to surface geometry will be discussed, and the use of kinetic Monte Carlo techniques to simulate cascade evolution for comparison with experimental measurements in the nanosecond to millisecond regimes will be considered.

10:35 - 10:55

T-G02 - THE EFRC MICROSTRUCTURAL CHARACTERIZATION OF ION IRRADIATED CeO₂[CMSNF] Peng Xu¹, Clarissa Yablinsky¹, Anthony Schulte¹, Todd Allen¹, Brent Heuser², Jian Gan², In-Wook Park³, John Moore³, and Jianliang Lin³¹University of Wisconsin-Madison; ²University of Illinois; ³Idaho National Laboratory; ³Colorado School of Mines

Microstructural development in nuclear fuels has a strong impact on fuel performance. The fundamental processes governing the fuel microstructure in a reactor involve fission gas effect, displacement damage from nuclear stopping, electronic excitation from electronic stopping, chemical effect due to fission product and transmutation, and temperature gradient effect. The first part of the presentation highlights the important microstructural features observed in the irradiated UO₂ fuels under various conditions in open literature. The second part summarizes the microstructural characterization of ion irradiated CeO₂, a commonly used surrogate for UO₂. Ion irradiation experiments with well controlled parameters allow to examine the separate effects on the microstructure. The ion irradiation studies for CeO₂ consist of large grain vs. small grains for the grain size effect on defect evolution, the high energy (>102 MeV) swift ion irradiation for fission fragment effect, Kr ion irradiation for fission gas effect, and proton irradiation for fast neutron effect. Microstructures and substructures were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The experimental work and results are important to support the modeling work on the materials science of UO₂ microstructural development.

10:55 - 11:15

T-G03 - EFRC ACTIVITY AT THE SPALLATION NEUTRON SOURCE

[EFree] Guthrie Malcolm¹, Boehler Reini¹, Karotsis Georgios¹, Tulk Chris², dosSantos Antonio², Molaison Jamie², Pradhan Neelam², Somayazulu Maddury³, and Strobel Tim³¹Carnegie Institution; ²Oak Ridge National Laboratory and ³Carnegie Institution

The mission of our Energy Frontier Research in Extreme Environments EFRC is to use extreme pressures and temperatures to fabricate, modify and understand new materials for energy science. Comprehensive understanding of atomic-level structure is fundamental in this endeavor, and neutron diffraction is a vital tool, with its unique advantages for determining the structure of light-atom and non-crystalline materials and also characterizing long-range magnetic order. Correspondingly, neutron capabilities cut through a broad swath of our research program and impact many diverse projects including studies of hydrogen rich fuels, novel superconducting and magnetocaloric materials and the structural characterization of polyamorphic transitions in metallic glasses and nanomaterials. However, the conditions of most interest - pressures and temperatures sufficient to radically alter chemical bonding - can only be applied to microscopic samples, many orders of magnitude smaller than conventional neutron sources can see. However, the intense neutron

flux of the new Spallation Neutron Source at Oak Ridge National Laboratory has made these measurements feasible for the first time. The ambitious science agenda of EFree is driving a tight-knit collaboration with SNS staff, with the aim of realizing necessary breakthrough technological developments to explore these new frontiers. The latest achievements of this collaboration will be presented in terms of the impact on the science of our EFRC.

11:15 - 11:35

T-G04 - BENCHMARK PREDICTIONS OF STRUCTURAL MATERIALS: THE CASE OF ALUMINUM

[CDP] Randolph Q. Hood¹, P. R. C. Kent², and Fernando A. Reboredo³

¹Lawrence Livermore National Laboratory; ²Oak Ridge National Laboratory and ³Oak Ridge National Laboratory

The Center for Defect Physics in Structural Materials focuses on providing the fundamental knowledge to allow atomistic control and manipulation of defects, defect interactions, and defect dynamics - the very defect properties that currently limit the performance and lifetime of materials. The theory component of this research is focused on overcoming limitations of existing approaches with respect to accuracy, system size, and simulation time necessary for quantifying the unit events of defect formation, evolution, and deformation and to make direct comparisons with experiments. We use fixed-node diffusion quantum Monte Carlo (DMC) to validate and seek improvements upon existing density functional theory (DFT) approaches. Our initial focus is aluminum, which has been well studied experimentally as a "simple" metal prototype for investigating the effects of radiation damage such as void formation and helium embrittlement. Using DMC we calculate the energetics of point defects in aluminum demonstrating a very high accuracy when compared to experiment. Often accuracies at the level of milli-electronvolts are required which is not achieved even for the simple case of pairs of vacancies in aluminum using common DFTs. Perhaps surprisingly even single vacancy energies are not reliable in many simple structural materials. We also present results for the bulk properties of aluminum. These calculations bring a new level of rigor to the study of defects in metals.

11:35 - 11:55

T-G05 - COMPETING EFFECTS OF GRAIN BOUNDARIES IN RADIATION DAMAGE RESPONSE OF CU

[CMIME] Blas Uberuaga¹, Xian-Ming Bai², Richard Hoagland¹, Arthur Voter², and Mike Nastasi²

¹Los Alamos National Laboratory; ²Idaho National Laboratory

It is well accepted that grain boundaries serve as effective sinks for radiation-induced defects (interstitials and vacancies). However, insight into the atomic-scale origin of this behavior is still lacking. In order to meet the demands of future nuclear applications, the origin of this enhanced radiation tolerance must be understood. We use molecular dynamics, temperature accelerated dynamics, and molecular statics to study radiation damage phenomena near a variety of grain boundaries in Cu over three different temporal regimes: the short-time damage production phase of a collision cascade, the longer-time scales over which defect annihilation and aggregation occur, and the thermodynamic-limiting behavior of the system. We find that both the production and the subsequent annealing of the radiation-induced defects are modified significantly by the presence of the grain boundary. In particular, we identify a new mechanism by which interstitials efficiently annihilate vacancies, promoting enhanced defect recombination. We compare to previous experimental results and identify three regimes over which different thermally activated processes are active, resulting in different responses, both better and worse than large-grained counterparts, of the material to irradiation. Our results show that nanostructured materials have a very sensitive response to irradiation and offer new insights into the design of radiation tolerant materials.

11:55 - 12:15

T-G06 - TOWARD A QUANTITATIVE UNDERSTANDING OF SINGLE DEFECT PHYSICS CONTROLLING MECHANICAL BEHAVIOR

[CDP] George M. Pharr¹, Yanfei Gao¹, Easo P. George¹, K.S. Kumar², Michael J. Mills³, B.C. Larson⁴, Andrew M. Minor⁵, Ian M. Robertson⁶, and Eliot D. Specht⁷

¹University of Tennessee and Oak Ridge National Laboratory; ²University of Tennessee and Oak Ridge National Laboratory; ³Oak Ridge National Laboratory and University of Tennessee; ⁴Brown University; ⁵The Ohio State University; ⁶Oak Ridge National Laboratory; ⁷University of California Berkeley; ⁶University of Illinois and ⁷Oak Ridge National Laboratory

A primary goal of the Center for Defect Physics is to provide a fundamental understanding, at the level of unit events, of the defect interactions that determine the mechanical properties of structural materials. Since the strength of metals is controlled primarily by dislocations, quantification of single dislocation interactions with other defects is of paramount importance in understanding their mechanical behavior. Achieving this goal requires coordinated efforts from diverse research groups to develop new testing methodologies and verify their capabilities. Here, we report on progress toward these goals based on 3D X-ray Microscopy (3D-XM), a synchrotron-based technique that uses highly focused x-rays to quantify strength-controlling defects. Recent progress includes: preparation of simple dislocation configurations in hcp

metals to serve as model specimens for initial measurements; development of nanoindentation techniques to produce controlled dislocation structures for examination in both static and dynamic experiments; proof-of-principle experiments to measure lattice rotations and stresses near dislocations; development of electron tomography techniques to characterize the 3D nature of dislocation structures; verification of dynamic defect interactions by quantitative *in-situ* TEM experiments; finite element modeling to interpret the development of slip and deformation during indentation and improvements in x-ray beam focusing to enhance spatial resolution.

**Parallel Scientific Session II - May 26, 2011
Renaissance Ballroom West A**

1:45 - 2:05

T-G07 - ACTINIDE MATERIALS UNDER THE EXTREME CONDITIONS OF TEMPERATURE, PRESSURE AND INTENSE RADIATION FIELDS [MSA] Maik Lang
University of Michigan

For the future energy needs, materials must be developed that display exceptional performance under extreme conditions. At the University of Michigan, we pursue a new experimental strategy that allows us to investigate the properties of solids simultaneously under coupled extreme conditions. This approach is based on the combination of large ion accelerator facilities, diamond-anvil cells and laser-heating experiments. We are currently developing this approach for actinide-bearing materials and have completed a systemic investigation on CeO₂. The cubic structure of this analogue for U and Pu containing compounds is very resistant to phase changes under pressure or ion irradiation. Ion-beam exposure with GeV ions at ambient conditions to a fluence of up to 8Å—10¹² cm⁻² did not result in any evidence of amorphization, but a minor amount of radiation-induced fragmentation into nanocrystals was observed. In contrast, the application of high pressure in excess of 35 GPa leads to the formation of a cotunnite-like high-pressure phase. However, this behavior is significantly changed when irradiation is additionally applied at high pressure, and the transformation takes place at an unexpectedly low pressure (~15 GPa). This highlights the extreme conditions prevailing within tracks of energetic heavy ions. We have demonstrated in complex oxides (e.g., Gd₂TiO₅) that such projectiles trigger highly non-equilibrium collective processes, which result in multiple nanoscale phase transitions.

2:05 - 2:25

T-G08 - CHARACTERISTIC INTERFACES IN METALLIC COMPOSITES SYNTHESIZED BY SEVERE PLASTIC DEFORMATION [CMIME] Irene Beyerlein¹, Nathan Mara¹, Jian Wang¹, Jon Ledonne², Tony Rollett², Nhon Vo³, Pascal Bellon³, Bob Averbach³, Ruiheng Zhang⁴, and Keonwook Kang⁴
¹*Los Alamos National Laboratory* ²*Carnegie Mellon University*; ³*University of Illinois*; ⁴*Los Alamos National Laboratory and Los Alamos National Laboratory*

The goal of the severe plastic deformation (SPD) team of the CMIME EFRC is to determine the class of bi-metal interfaces that will create composite materials with extraordinary failure resistance under extreme mechanical strains. In SPD applications, the bi-metal interface will be exposed to a high flux of crystal dislocations (line defects in metallic crystals). To prevent instability, the bi-metal interface must be able to trap and remove incoming dislocations and other defects, not allowing them to accumulate in the material and act as stress concentrators. In the past year, Cu-Nb interfaces were studied in sheets of Cu-Nb multi-layered composites synthesized using an SPD technique called accumulative roll bonding (ARB). Individual layer thicknesses ranged from the submicron-scale to the nano-scale (10 nm). Deformation texture analysis shows that a steady-state texture develops once the layer thicknesses reduce below 50 nm. In particular this characteristic texture exhibits features not expected in rolling of single-phase metals. A newly developed 5-parameter heterophase interface analysis is applied, and the results strongly suggest that most of the interfaces in the ARB material are {112}fcc//{112}bcc with a Kurdjumov-Sachs orientation relationship. Atomistic simulation, dislocation theory, and polycrystal plasticity modeling are employed to determine the structural aspects that make this characteristic {112}fcc//{112}bcc interface stable under SPD.

2:25 - 2:45

T-G09 - NUCLEAR FUEL THERMAL CONDUCTIVITY INSIGHTS FROM PHONONS IN UO₂ [CMSNF] Judy Pang¹, Aleksandr Chernatynskiy², Bill Buyers³, Mark Lumsden⁴, Bennett Larson⁵, and Simon Phillpot²
¹*Oak Ridge National Laboratory*; ²*University of Florida*; ³*National Research Council*, ⁴*Chalk River Laboratories, Canada*

Understanding thermal transport in nuclear fuel will require accounting for a wide range of phonon scattering processes, including anharmonic as well as radiation induced phonon scattering mechanisms. Over the last five decades there have been relatively few fundamental studies of phonons in the context of thermal conductivity in uranium oxide considering its widespread use as a reactor fuel. We have made high-resolution inelastic neutron scattering measurements of phonon

dispersion, lifetimes, and group velocities in single crystal uranium oxide at ambient and high temperature, 1200K. In contrast to conventional expectations, the phonon lifetimes at high temperature were found to depend strongly on wavevector, and it was inferred that longitudinal optical and transverse acoustical phonons contribute as strongly as longitudinal acoustical phonons to thermal transport at high temperature. Lattice dynamics simulations of phonon lifetimes in this project predict non-monotonic, wavevector dependent lifetimes for uranium oxide at high temperature, in qualitative agreement with the neutron scattering results. However, the strong thermal conductivity inferred for the longitudinal optical and transverse acoustical modes are in stark contrast to recent first principles calculations. These measurements provide benchmarks for lattice dynamics simulations and input for Boltzmann transport equation thermal modeling.

2:45 - 3:05

T-G10 - ENABLING ATOMIC-SCALE DESIGN OF RADIATION-RESISTANT NANOCOMPOSITES BY TAILORING INTERFACES

[CMIME] [Michael Demkowcz](#)¹, Amit Misra², Michael Nastasi², and Richard Hoagland²

¹MIT; and ²Los Alamos National Laboratory

Certain heterophase interfaces are highly efficient sinks for radiation-induced defects. Thus, nanocomposites with a high density of such interfaces exhibit enhanced resistance to radiation compared to their component materials. To maximize the stability and efficacy of such interfaces, however, the processes by which they respond to radiation must be controlled at the atomic level. This talk will describe how the Center for Materials at Irradiation and Mechanical Extremes (CMIME) is systematically laying the foundations for atomic-scale design of interfaces that may impart radiation resistance to materials for advanced nuclear energy applications. This material is based upon work supported as part of the Center for Materials at Irradiation and Mechanical Extremes, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number 2008LANL1026.

3:05 - 3:25

T-G11 - A NOVEL SUPERHARD SP³-BONDED NON-CRYSTALLINE CARBON ALLOTROPE

[EFree] [Yu Lin](#), Li Zhang¹, Ho-kwang Mao², Paul Chow³, Yuming Xiao³, Maria Baldini³, Jinfu Shu, and Wendy L. Mao¹

¹Stanford University; ²Carnegie Institution of Washington; ³Carnegie Institution of Washington

Compressing glassy carbon above 40 GPa, we have observed a new carbon allotrope with a fully sp³-bonded glassy structure and a diamond-like strength. Synchrotron x-ray Raman spectroscopy revealed a continuous pressure-induced sp²-to-sp³ bonding change, while x-ray diffraction confirmed the perseverance of the amorphous structure. The transition was reversible upon releasing the pressure. Used as an indenter, the glassy carbon ball demonstrated its exceptional strength by reaching 130 GPa with a confining pressure of 60 GPa. Such extremely large stress difference of >70 GPa has never been observed in any material except diamond, thus offering the exciting potential as a pressure-hardened superhard glass.

H – Effective and Sustainable Materials Design: Integration of Computation, Theory and Experiment Renaissance Ballroom West A

Parallel Scientific Session I - May 26, 2011 Renaissance Ballroom West A

10:15 - 10:55

T-H01 - INTEGRATION OF NOVEL SYNTHESSES, EXPERIMENTS AND MOLECULAR MODELING REVEALS FUNDAMENTAL PROPERTIES OF ELECTRODE/ELECTROLYTE INTERFACES

[FIRST] [David J. Wesolowski](#)¹, [Sheng Dai](#)¹, and [Peter T. Cummings](#)²

Oak Ridge National Laboratory and Vanderbilt University

The next generation of electrical storage devices with superior performance will require a fundamental knowledge of the nanoscale architecture of the interface, the effect of nanotexture on interfacial properties, and the structural and dynamic changes that occur during charge and discharge cycles. What is required is an atomistic understanding of the individual processes associated with ion and solvent transport at nanotextured interfaces. Nanotextured carbon surfaces with well-defined pore sizes and topologies provide ideal model systems for investigating the general issue of interfacial and nanoconfined fluid structures and dynamics. Carbon materials with controlled pore structures and topologies are synthesized for probing interfacial chemistries related to energy storage. These newly developed carbon materials feature ultrahigh surface areas, tunable pore sizes, and high electric conductivities. We are developing our fundamental understanding of these systems through a highly integrated experimental and computational approach in which molecular and atomic probes (such as -ray reflectivity, elastic, inelastic and quasi-elastic neutron scattering and NMR) are used to

validate computational approaches based on *ab initio* and classical molecular dynamics. Hence, the breadth and depth of the knowledge gained in the FIRST Center is being encapsulated into publicly available computational models that will ultimately be used to design and optimize next generation electric storage devices.

10:55 - 11:15

T-H02 - POWER GENERATION FROM SOLID FUELS IN SOLID OXIDE FUEL CELL WITH MOLTEN ANTIMONY ANODE

[CCEI] Abhimanyu Jayakumar¹, Rainer Kangas¹, Sounak Roy², Ashay Javadekar², Douglas J. Buttrey², John M. Vohs³, and Raymond J. Gorte³

¹University of Pennsylvania; ²University of Delaware; ³University of Pennsylvania

It would be extremely attractive to convert solid, carbonaceous fuels directly to electrical energy using electrochemical methods, since this could be very efficient and allow for easy CO₂ capture. Although first attempts have been made in the development of Direct Carbon Fuel Cells (DCFC), the performance levels reported so far are insufficient to make this technology commercially viable. Here we demonstrate the generation of electricity at high power densities, >300 mW/cm² at 973 K, from solid fuel (sugar char) in a Solid Oxide Fuel Cell (SOFC) using a molten Sb anode. These power densities are comparable to state-of-the-art H₂-fuelled SOFCs. The anode design is simple and capable of operating continuously on a wide range of carbonaceous fuels, including sugar, rice starch, carbon black, and graphite.

11:15 - 11:35

T-H03 - MODELING Li⁺ DIFFUSION IN BATTERY MATERIALS

[CST] Graeme Henkelman, Phani Dathar, Penghao Xiao, Keith J. Stevenson, Arumugam Manthiram, and John B. Goodenough

University of Texas at Austin

During the development process of new battery materials, calculations are used to help understand what is observed in experiments. Two specific examples are given. For the layered cathode Li₂MnO₃, oxygen is seen to evolve from the material in the first charge cycle. Substitution of Ti in place of Mn is seen to reduce oxygen loss whereas Co increases it. This trend is understood with calculations of the electronic band structure in which a correlation is found between the band gap and the stability of oxygen. In a second example, potassium niobate (KNb₅O₁₃) was investigated as a possible anode material because the Li insertion potential is above that of solid-electrolyte interface formation. Experiments of charge/discharge cycling show a surprisingly large hysteresis in both the Li potential and the lattice parameters of the material. Calculations of Li intercalation show that while Li diffuses along channels in the crystal, there are additional binding sites in the framework which can be accessed from the channel. We suggest a model in which the channel is both filled first and emptied first, giving rise to the observed hysteresis.

11:35 - 11:55

T-H04 - ELECTROCATALYTIC REDUCTION OF CO₂ TO METHANOL AT CU-BASED SURFACES

[CALCD] John Flake¹, Maoming Ren¹, Ziyu Zhang¹, Minh Le¹, Phillip Sprunger¹, Richard Kurtz¹, Gregory Griffin¹, Ullie Diebold², Susan Sinnott³, Aravind Asthagiri⁴, and Michael Janik⁵

Louisiana State University; ²Vienna University of Technology; ³University of Florida; ⁴Ohio State University and ⁵Pennsylvania State University

An efficient method to convert CO₂ to fuels using renewable energy could displace crude oil and provide high-density energy storage reservoirs similar to liquid fuels or batteries. Although photoelectrochemical conversion of CO₂ is possible, typical efficiencies are lower than the combination of conventional photovoltaics (up to 40% efficiency) and electrochemical cells (up to 80% Faradaic efficiency). In the electrochemical case, electrical energy from renewable sources may be converted to hydrocarbons or alcohols using electrocatalysts. Here, we examine the conversion of CO₂ to methanol at copper/metal oxide electrodes from a unified theoretical and experimental perspective. The objective is to leverage a fundamental understanding of electrocatalytic mechanisms to create "electrocatalysts by design". Single crystal ZnO(10-10) surfaces with Cu, CuO_x nanoclusters are considered for their potential as electrocatalysts. Electronic-structure calculations show a potential pathway for CO₂ reduction on Cu/ZnO(10-10) surfaces including a facile downhill pathway to a methoxy intermediate. *In-situ* FTIR and *ex-situ* HREELS are used to identify intermediates and support model predictions. Further work to unify experiment and simulation using empirical potentials allows larger-scale modeling of atomic scale CO₂ interactions with Cu and ZnO. Progress towards a fundamental understanding of CO₂ reduction mechanisms and selectivity as a function of electrocatalyst surfaces is discussed.

11:55 - 12:15

T-H05 - HOMOGENEOUS AND HETEROGENEOUS METAL OXO INTERMEDIATES IN PHOTOCATALYTIC AND HIGH-TEMPERATURE HYDROCARBON FUNCTIONALIZATION CYCLES

[CCHF] William Goddard¹, Robert Bergman², Robert Crabtree³, Thomas Cundari⁴, John Groves⁵, Brent Gunnoe⁶, and Thomas Meyer⁷¹California Institute of Technology; ²University of California at Berkeley; ³Yale University; ⁴University of North Texas; ⁵Princeton University; ⁶University of Virginia and ⁷University of North Carolina

As part of the DOE EFRC Center for Catalytic Hydrocarbon Functionalization we have been collaborating on several strategies for forming important molecules for energy and industry from CH₄ and other alkanes. The two key aspects are activating CH₄ at low temperature to avoid free radical processes that hinder selectivity to the desired products and the functionalization by forming new C-O and C-C bonds. The focus in this talk is achieving C-O bond formation by building catalysis with active M=O bonds. Here we are pursuing several strategies involving homogenous systems with oxo bonds, particularly porphyrin based systems and heterogenous systems with multiple types of oxo bonds. We have achieved promising results with both strategies as will be described.

**Parallel Scientific Session II - May 26, 2011
Renaissance Ballroom West A**

1:45 - 2:05

T-H06 - CHEMICAL NETWORKS: THE WIRED" UNIVERSE OF ORGANIC CHEMISTRY"

[NERC] Kyle J.M. Bishop¹, Aaron M. Drews¹, Mikolaj Kowalik¹, and Bartosz A. Grzybowski²¹Pennsylvania State University; ²Northwestern University

For over two centuries, chemists all over the world have applied their expertise and creativity to the synthesis of new molecules. Today, this cumulative effort can be summarized most concisely as a large network of chemical reactions. In this way, more than 10 million synthetic compounds are connected to one another through an even greater number of chemical reactions, in which they participate. Using this representation, the synthesis of one or more desirable chemicals from available starting materials can be described by a collection of "paths" along the reaction network. Importantly, as the number and complexity of the desired chemical products increases, the number of possible paths - i.e., synthetic strategies - can become astronomically large. Therefore, we have developed methods for identifying "optimal" reaction pathways within such complex networks. Depending on the context, optimal pathways are those that minimize the cost of the chemical process, maximize its energy efficiency, or minimize its environmental impact.

2:05 - 2:25

T-H07 - COMPUTATIONAL MODELING OF ACTINIDE COMPOUNDS: FROM CLUSTERS TO COMPLEX CRYSTAL STRUCTURES

[MSA] Mark Asta¹, Udo Becker², Laura Gagliardi³, Niels Gronbech-Jensen⁴, Ed Maginn², and William J. Weber⁵¹University of California, Berkeley and ²University of California, Davis; ³University of Michigan; ⁴University of Minnesota; ⁵University of California, Davis; ⁵University of Notre Dame

Computational research in the MSA-EFRC is reviewed its three focus areas. (1) Thermodynamic and kinetic properties of ThO₂ and UO₂ solid solutions. Mixing energetics with homovalent cations in these fuel materials are dominated by elastic contributions arising from cation size mismatch. Solutions with relevant transuranic elements have weakly positive mixing energies of a few kJ/mole. The addition of CeO₂ into ThO₂ decreases the oxygen vacancy formation and migration energies, leading to a minimum migration energy of 0.2 eV for 75 % Ce content. (2) Formation of nanoscale cage clusters based on uranyl ions. The U-O₂-U interaction has been considered in clusters of interest for nanoscale control of actinide chemical reactions. A covalent interaction causes the U-O₂-U dihedral angle to be bent, encouraging curvature and cluster formation. New candidate actinide groups for the formation of complex clusters are identified. (3) Pressure effects on pyrochlore compounds. Phase transitions and defect structures are investigated in pyrochlore compounds of interest as an inert matrix fuel or nuclear waste forms. Transitions to the defect-cotunnite structure are predicted at 43.6 GPa for Gd₂Ti₂O₇ and 13 GPa for Gd₂Zr₂O₇. In Gd₂Ti₂O₇, the dominant defect type is a cation anti-site defect, while in Gd₂Zr₂O₇, anion Frenkel-pair defects are favored at all pressures and the dominant defect type involving a cation is a coupled defect of a cation anti-site and an anion Frenkel pair.

2:25 - 2:45

T-H08 - CAN MATERIALS BE DESIGNED FOR SPECIFIC TARGET PROPERTIES?

[CID] Alex Zunger, David Ginley, and Larry Kazmerski*NREL*

The history of material science has generally proceeded via accidental discoveries of materials with interesting physical properties and their subsequent optimization. Thus, you can speculate if equally by accident, we have missed the right materials. Given the (i) sensitivity of material properties to structure, and (ii) current laboratory capabilities to explore many different atomic structures, it is interesting to enquire if one could first articulate the desired target physical property, then search for the material composition and structure that has this property? We will explore this proposition for (a) Transparent Conducting Oxides employed as contacts in photovoltaics, flat panel displays and electrochromic windows by design. The next step is to validate the theoretical predictions by exploring the relevant region of phase space using both combinatorial high-throughput and targeted synthesis approaches which can map in parallel larger numbers of samples and keep up with the theory predictions. Once identified then targeted synthesis can produce high quality samples of single composition and structure for detailed evaluation. We will illustrate this approach specifically on the development of new p-type TCO materials for contacts in renewable energy technologies such as the emerging area of earth abundant PV materials. This is the focus of our Center for Inverse Design (CID) involving collaboration with NREL's Solid State Theory Staff, NCPV staff, Stanford SLAC, Northwestern University, and Oregon State University.

2:45 - 3:05

T-H09 - ETHANOL SYNTHESIS FROM SYN-GAS: HOW SURFACE DIFFUSION OF INTERMEDIATES IMPACTS THE PRODUCT

DISTRIBUTIONS PREDICTED FOR BIMETALLIC CATALYSTS

[CALCD] David Bruce, Ming He, and James McAliley*Clemson University*

A major challenge associated with the synthesis of ethanol from syn-gas is an inability to find a low-cost catalyst that promotes the proper combination of CO dissociation and CO insertion steps, so as to yield ethanol as the primary reaction product and inhibit the formation of methane, longer chain alkanes, and other coking reaction products. For this purpose, quantum mechanical simulations were used to evaluate the catalytic activity of a series of bimetallic clusters that range in size from 13 to 38 metal atoms. DFT simulations and Bronsted-Evans-Polanyi (BEP) relations were used to map out the full reaction mechanism from syn-gas to ethanol for each of these materials. Microkinetic models were built, considering the reaction steps as well as the diffusion of intermediate species between different metal surface sites. These simulations indicate specific metal combinations that are ideally suited for ethanol production and how the selection of metals impacts the minimum energy structure of the resulting nanocluster.

3:05 - 3:25

T-H10 - IACT - COMPUTATION AND THEORY FOR CATALYST DESIGN

[IACT] Linda Broadbelt

Northwestern

Computation and theory are being used in concert with experimental methods in IACT to provide fundamental insight at the atomistic level of the catalytic properties of new materials to achieve controlled insertion or removal of oxygen atoms in organic molecules. The computational effort is targeted to systems where state-of-the-art theory can be closely coupled with experiment to effectively model the catalysts and reaction mechanisms. Three complementary components are being applied to attain a comprehensive fundamental understanding of the catalysts and reactions being studied in this Center: electronic structure theory, dynamics, and complex reaction networks. Electronic structure calculations are used to obtain a fundamental understanding at the atomistic level and provide input to the other two components. The dynamical studies involve large-scale molecular dynamics (MD) trajectory simulations based on computationally efficient semiempirical many-body potentials and development of accurate potentials. The information from the density functional theory calculations, dynamical simulations, as well as existing literature data including experimental, are utilized in the modeling of complex reaction networks. This involves generation and evaluation of known and novel reaction networks. Accomplishments that will be highlighted in this talk will focus on the conversion of glucose to an array of intermediates and catalyst design efforts to achieve the most attractive pathways.

3:25 - 3:45

T-H11 - EXPLORING GRAPHENE MOIRE-SUPPORTED CLUSTERS AS A NEW CATALYTIC MATERIAL PLATFORM

[CALCD] D. Wayne Goodman¹, Li Liu¹, Zihao Zhou¹, Feng Gao¹, Lymarie Semidey-Flecha², Ye Xu², Dieh Teng³, David Sholl³, Philip Sprunger⁴, and Ward Plummer⁴¹Texas A&M University; ²Oak Ridge National Laboratory ³Georgia Institute of Technology; ⁴Georgia Institute of Technology; ⁴Louisiana State University

Nano-clusters possess unique catalytic and energy conversion properties that are distinct from bulk materials. The fabrication of dense arrays of uniformly sized clusters nonetheless remains a challenge. A promising approach involves the use of metal-supported graphene moire as template for the nucleation and growth of cluster arrays. To explore the potential of this new class of material, we are investigating clusters of different metals that form on graphene moire supported on Ru(0001) and other metal surfaces. *In situ* imaging and spectroscopic techniques, including variable temperature scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and angle-resolved photo-emission spectroscopy (ARPES), combined with computational modeling are being applied to characterize the geometric and electronic structures and the thermal/chemical stability of these nano-materials, and to identify synthesis strategies to achieve cluster arrays on graphene moire. In this talk we will present our recent results on the synthesis and characterization of several unique graphene moire-supported metal nano-materials, and the insights generated by multi-scale computational modeling into the nucleation and growth behavior of the clusters and the roles played by the graphene moiré and the support metal in these processes.

I – New Tools and Methods for Materials Synthesis and Characterization Renaissance Ballroom West B

Parallel Scientific Session III - May 26, 2011
Renaissance Ballroom West B

4:00 - 4:20

T-I01 - MODULATING THE REACTIVITY OF MOLECULAR CATALYSTS FOR CH FUNCTIONALIZATION BY PROTON TRANSFER WITH NON-INNOCENT LIGANDS

[CCHF] Roy A. Periana¹, Brian G. Hasihiguchi¹, Steven M. Bischof¹, Kapil S. Lokare¹, Claas H. Hovelmann¹, Robert J. Nielsen², Kenneth J. H. Young³, and William A. Goddard, III²¹The Scripps Research Institute; ²California Institute of Technology; ³University of Southern California

The solvent is usually the largest volume species present in a reaction system. Consequently, utilizing the solvent could provide a powerful method of modulating the reactivity of soluble, molecular catalysts. One of the most powerful ways to modulate the reactivity of any species, in this case, catalysts, is by enabling proton transfer between the catalyst and the solvent. The most common mode of this type of reported modulation is with acid solvents that facilitate substrate coordination and increase catalyst electrophilicity through protonation of "non-innocent" ligands of the catalyst. The role of this type of acid modulated catalysis will be reviewed for the CH activation systems that we have developed. Since proton transfer between the catalyst and the solvent can take place in either direction, we have been exploring the use of basic solvents to modulate the catalyst by, in this case, deprotonation of now protic "non-innocent" ligands. Intuitively, it would be expected that strongly basic solvents can inhibit substrate coordination. However, we will show that ligand deprotonation in basic solvents can actually facilitate substrate coordination. Additionally, complimentary to the role of acid solvents to increase electrophilicity, we will discuss the possibility that ligand deprotonation by basic solvents can increase reactivity by increasing the nucleophilic character of the coordinatively unsaturated metal center.

4:20 - 4:40

T-I02 - SYNTHESIS OF NANOSTRUCTURED CATALYSTS FOR BIOMASS CONVERSION

[IACT] Christopher Marshall¹, Eric Stach², Fabio Ribeiro³, Jeffrey Greeley¹, Justin Notestein⁴, Kenneth Poepelmeier¹, Larry Curtiss¹, Mayfair Kung⁴, Peter Stair⁴, Randy Winans⁴, SonBinh Nguyn⁴, and Jeffrey Elam¹¹Argonne; ²BNL; ³Purdue; ⁴Argonne; ⁴Northwestern

The successful transition to an energy economy based on biomass will require radical advances in catalyst science. This challenge demands a new paradigm in catalyst synthesis whereby inorganic components can be assembled at the atomic scale to yield complex, multifunctional catalysts rivaling Nature's enzymes in their specificity. To this end, we have developed a novel approach combining templated synthesis for shape-selectivity with the atomically-precise positioning of discrete functionalities. In this approach we begin with a supporting scaffold for catalyst growth upon which we chemically attach molecular templates. Next, atomic layer deposition is used to build a structure around each template in an

atomically precise, layer-by-layer fashion where the thickness and composition can be tuned at each layer. Finally, the template is removed yielding a "nanobowl" defining a structured catalytic environment. The molecular template can be synthesized to contain bulky organic ligands surrounding a catalytic atom or cluster which remains anchored to the bottom of the bowl after ligand removal. Furthermore, one or more layers in the bowl wall can be selected to serve as a co-catalyst (e.g. Lewis acid group) positioned at a well-defined distance from the catalyst at the bottom of the bowl. This presentation will review our recent progress synthesizing, characterizing, modeling, and testing these unique catalytic materials.

4:40 - 5:00

T-I03 - DEVELOPMENT OF CATALYSTS FOR SELECTIVE FUNCTIONALIZATION OF HYDROCARBONS

[CCHF] T. Brent Gunnoe¹, Jeremy Andreatta¹, Bradley A. McKeown¹, Victor S.-Y. Lin², Brian G. Trewyn², Hung-Ting Chen², and Thomas R. Cundari³

¹University of Virginia; ²Iowa State University; ³University of North Texas

Catalysts that selectively convert hydrocarbons into value added materials are central to the chemical industry and energy sector. For example, alkyl arenes are produced and used on a multi-billion pound scale annually. Work in the CCHF seeks to exploit expertise in homogeneous catalysis, materials design/characterization and computational modeling to develop new catalysts for the production of alkyl arenes. Groups at the U. of Virginia and U. of North Texas have demonstrated that Pt(II) complexes supported by bipyridyl ligands catalyze the hydroarylation of olefins. For example, [(tbp)Pt(Ph)(THF)]⁺ (tbp = 4,4'-di-tert-butyl-2,2'-bipyridyl) serves as a catalyst for using unactivated substrates (e.g., benzene, ethylene, propylene). Previous studies show that the Pt(II) catalysts operate by olefin coordination and insertion into the Pt-Ph bond followed by benzene C-H activation. Using methods for the preparation of nanomaterials developed at Iowa State U., single-site catalysts in which (bpy)Pt(Ph)₂ catalyst precursors are tethered to mesoporous silica nanoparticles (MSNs) have been prepared. These materials exhibit enhanced stability compared to analogous homogeneous catalysts, and the selectivity of the homogeneous catalyst is effectively transferred from the homogeneous system to the MSN-supported catalyst. The long-term goal is to tailor the MSN to control substrate selectivity for olefin hydroarylation and other hydrocarbon functionalization reactions.

5:00 - 5:20

T-I04 - SEEING CELLULOSE IN PLANT CELL WALLS AND LIGNOCELLULOSIC BIOMASS -- SUM-FREQUENCY-GENERATION (SFG) VIBRATION SPECTROSCOPY STUDY

[CLSF] Seong H. Kim¹, Christopher Lee¹, Anna L. Barnette¹, Yong Bum Park¹, Daniel J. Cosgrove¹, Jin Gu¹, Jeffrey M. Catchmark¹, Sunkyu Park¹, Candace Haigler² and Eric Roberts³

¹The Pennsylvania State University ²North Carolina State University; ³Rhode Island College

The crystalline cellulose structures are usually studied with x-ray diffraction (XRD) and solid-state ¹³C nuclear magnetic resonance (NMR); but these techniques suffer from weak signals or interferences from other components present in cell walls. Thus, they require separation of crystalline cellulose from other components of cell walls for structural study. We recently discovered that the non-centrosymmetric crystal structures of cellulose give unique non-linear optical responses, which allows selective detection of the crystalline cellulose in plant cell walls without interferences from hemicelluloses, pectin, lignin, and other cell wall components. Thus, SFG will be a new complementary analytical tool that can reveal structural information of cellulose inside plant cell walls that has been inaccessible in the past with conventional analytical tools such as IR, Raman, XRD, and NMR. This talk will present some of the new insights that SFG finds about cellulose in plant cell walls. For example, it was observed that when non-cellulosic components are extracted, the cellulose remaining in plant cell walls may undergo structural changes. SFG also revealed drastic differences between two naturally-produced allomorphs (I₁ and I₂) and changes in cellulose structures as the plant cell grows.

5:20 - 5:40

T-I05 - DYNAMICS OF VOID GROWTH IN IRRADIATION

[CMSNF] Thomas Hochrainer¹, Abdel-Rahman Hassan¹, Peng Xu², Todd Allen², and Anter El-Azab¹

¹Florida State University; ²University of Wisconsin-Madison; ³Florida State University

We are investigating the fundamental physics of void nucleation and growth in irradiated materials, by both theory and experiments. A critical step in the investigation is to understand interactions of defects with void surfaces and capture details of void growth. In oxide fuels like UO₂, defect interactions at the void surface are governed by electrochemical reactions. To develop mesoscale models of void nucleation and growth in irradiated materials, requires a detailed understanding of the defect interactions with and across the surface. We present a unified method for how defect reactions at free surfaces, which govern the growth kinetics of voids and gas filled bubbles, can be obtained from thermodynamics. This leads to requirements on transition state theoretical models of reactions at the surface which are

not considered in the literature. The reaction rates at the surface define dynamic boundary conditions for the evolution of defect density fields. These equations were solved numerically as a free boundary value problem. We use these calculations to determine parameters of a phase field formulation of the same problem. The calibrated phase field simulations are used in large scale simulations of void nucleation and growth under irradiation. A key finding is that defect-surface interactions play an essential role in the growth rate of voids under irradiation. We discuss experiments currently set up to characterize the defect interactions at the surface of UO_2 .

5:40 - 6:00

T-106 - NDTB-1: A SUPERTETRAHEDRAL CATIONIC FRAMEWORK MATERIAL FOR SELECTIVE TRAPPING OF RADIOISOTOPES [MSA] Shao Wang¹, Evgeny V. Alekseev², Juan Diwu¹, William H. Casey³, Brian L. Phillips⁴, Wulf Depmeier² and Thomas E. Albrecht-Schmitt¹

¹University of Notre Dame; ²University of Kiel and University of Notre Dame; ³University of California, Davis; ⁴SUNY-Stony Brook

We have recently undertaken the study of the preparation, structure elucidation, and physico-chemical property measurements of actinide borates. During the course of these studies a highly unusual thorium borate was discovered, $[\text{ThB}_5\text{O}_6(\text{OH})_6][\text{BO}(\text{OH})_2] \cdot 2.5\text{H}_2\text{O}$ (Notre Dame Thorium Borate-1). The structure of NDTB-1 is a porous supertetrahedral 3D framework. Six channels form a network that pierces the whole structure, and allows facile anionic and molecular transport for exchange processes. When the single crystal X-ray data and solid-state NMR spectroscopy are taken together, we can conclude that NDTB-1 is an exceedingly rare example of a cationic framework with extraframework borate anions residing in the centers of the gates being used to maintain charge neutrality. Anion exchange experiments were conducted with a variety of common anions. These studies revealed that not only does anion exchange take place, but that the structure remains intact throughout the exchange. Exchange experiments were conducted with a variety of highly colored anions and the single crystals show the color of the transition metal anions rapidly. The critical anion exchange experiments are replacing the extraframework borate anions with TcO_4^- . These studies with NDTB-1 show rapid uptake of TcO_4^- from solution. NDTB-1 selectively removes pertechnetate from nuclear waste streams despite massive excesses of nitrate, nitrite, and chloride in these streams.

Parallel Scientific Session IV - May 27, 2011 Renaissance Ballroom West B

8:00 - 8:20

T-107 - ELECTROCHEMICAL STRAIN MICROSCOPY: A NEW PROBE OF LI-ION DYNAMICS IN ELECTRODE MATERIALS

[FIRST] Nina Balke, Leslie Adamczyk, Nancy Dudney, and Sergei Kalinin

Oak Ridge National Laboratory

The development of the capability for probing ion transport on the nanometer scale is a key challenge for development of energy storage and generation systems including Li-ion batteries, and can potentially unravel complex interplay between structure, functionality, and performance in these systems. Up to now, the unique capability of Scanning Probe Microscopy to measure bias induced phase transitions on a local scale as it is common in other fields like ferroelectrics is not used in the field of energy storage. Consequently, the nanoscale mechanisms underpinning battery functionality remain unexplored, precluding developing strategies for improvement of energy and power densities and life times of these devices. The strong strain-bias coupling in electrochemical materials is used to develop the capability for mapping electrochemical reactions on the nanometer scale, and hence get insight into the mechanisms of battery operation. The developed technique, Electrochemical Strain Microscopy (ESM) allows to probe ionic transport in battery materials on length scales 100 times smaller than with other characterization methods. ESM will be demonstrated on LiCoO_2 thin films as an example for cathode materials for Li-ion batteries. In addition, it will be demonstrated how ESM can be used to investigate the Li-ion flow through a $\text{LiCoO}_2/\text{Lipon}/\text{Si}$ system thin film battery with a sub-10 nm resolution and correlate it directly to the microstructure of the battery.

8:20 - 8:40

T-108 - NANOSCALE STUDIES OF BATTERY ELECTROCHEMISTRY: IN-SITU TEM AND SPM AND ATOMISTIC MODELING

[NEES] John Sullivan, Jian Yu Huang, Kevin Zavadil, Kevin Leung, Xiao Hua Liu, Arunkumar Subramanian, Nicholas Hudak, and Yang Liu

Sandia National Labs

In this presentation, we describe our work within the NEES EFRC in developing new tools and models for examining nanoscale Li-ion battery materials and their electrolyte interfaces. This work includes *in-situ* TEM and SPM and *ab initio* molecular dynamics (MD) in the liquid state. Specifically, we describe our *in-situ* TEM analysis of the morphology and

kinetics of lithiation in nanoscale anodes based on tin oxide or silicon nanowires when these are electrochemically cycled inside a TEM (for these studies, we assembled an *in-situ* cell consisting of tin oxide or silicon nanowires, an ionic liquid-based electrolyte, and an electrode of lithium cobalt dioxide). We will also describe our new, sealed *in-situ* TEM platforms that enable the use of volatile electrolytes inside the TEM. For *in-situ* STM and AFM studies, we have synthesized isolated crystalline particles of Li manganese oxide supported on graphite surfaces. This characterization tool is ideal for examining the surface morphology and the morphology of electrolyte decomposition products at the electrode-electrolyte interface. Lastly, we will describe *ab initio* MD modeling of ethylene carbonate reduction at Li-ion battery anode surfaces and the new understanding of the initial reaction pathways for electrolyte reduction. The goal of this research is fundamental understanding of electrode electrochemistry which should lead to new materials or additives that will improve battery performance and/or lifetime.

8:40 - 9:00

T-109 - COMPLEX OXIDES AND COMPUTATIONAL STUDIES

[EMC2] Joel Brock, Kendra Weaver, Ravishankar Sundararaman, and Tomas Arias

Cornell University

Our goal is to understand and control, via nanostructuring and interface engineering, the interplay between the diverse microscopic degrees of freedom prevalent in complex oxide systems in order to create new materials heterostructures for use as catalyst supports, and catalysts in fuel cell and battery applications. Oxide heterostructures are of great interest both because they exhibit emergent behaviors not observed in the corresponding bulk parent compounds and because recent experimental advances in thin film science allow complex oxides to be synthesized with atomic precision, allowing properties to be tailored and enhanced at the nanoscale. So where do we begin? Researchers can synthesize these compounds but what specifically should they be growing? Our approach to answering these questions is two-fold. We develop and apply novel experimental tools for probing the dynamics and kinetics of structure and chemistry at interfaces, in films, and in working devices. And, we develop and employ computational and modeling platforms to understand the fundamentals underlying oxide/electrolyte, interfaces and their relationships to energy generation, conversion and storage. As a specific example, we present a novel description of water which allows the first *a priori* studies of catalysis in aqueous electrochemical environments. With our novel extensions to Joint Density Functional Theory, we can accurately predict solvation energies of small organic molecules. We also present applications to a variety of aqueous electrochemical systems. Our overarching goal is to establish the opportunities for – and the fundamental limitations of – energy generation, conversion and storage technologies.