

EFRC and DOE Research and Networking Poster Reception

Thursday, May 26, 2011, 6:00 – 7:30 pm

Department of Energy Programs

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P1-J1 Advanced Research Projects Agency – Energy (ARPA-E)

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Website: <http://arpa-e.energy.gov/>

ARPA-E is a new agency of the Department of Energy, designed to identify and support next generation disruptive technologies across the entire energy landscape. During our first year of existence ARPA-E awarded \$350M in grants to support work in areas as diverse as batteries (both for transportation and grid-scale storage), renewable energy, biofuels, power electronics, and HVAC, to name a few. ARPA-E's 4th round of funding focuses on rare earth alternatives, breakthroughs in biofuels, thermal storage, grid controls and solar power electronics. Additional details regarding both ARPA-E and the projects we support is available at our website.

P1-J2 Office of Energy Efficiency and Renewable Energy, Biomass Program

Contact: Paul F. Bryan, Program Manager

Website: www.biomass.energy.gov

P1-J3 Office of Energy Efficiency and Renewable Energy (EERE), Office of Vehicle Technologies, Batteries for Advanced Transportation Technologies (BATT)

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The Batteries for Advanced Transportation Technologies (BATT) Program is the premier research program focused on developing the next generation battery chemistries for use in vehicle applications. The focus of the program is presently on developing safe, long lasting batteries with adequate performance and low cost for use in plug in hybrid electric vehicle (PHEV) and electric vehicle (EV) applications. BATT is managed by the Lawrence Berkeley National Lab for the Department of Energy and funded by the Office of Vehicle Technologies in EERE. 40 PIs across various National Labs, Industry, and Universities work in a coordinated fashion to enable breakthroughs in energy storage. The focus is on translation research that links the fundamental material properties to performance. BATT coordinates with other applied offices (e.g., ARPA-E) and with the Office of Science EFRCs in energy storage.

BATT research is presently focuses predominantly on Li-ion batteries. New materials for use as anodes, cathodes, and electrolytes are an active area of research. These developmental efforts are supported by novel theoretical tools, diagnostics, and cell designs. BATT's structure allows exploratory research into new materials and designs, while also allowing a focused research effort to be conducted that can solve the problems that cut across many batteries. In FY2011, BATT research is focused on developing a high voltage spinel cathode and in enabling the use of silicon as an anode material. The coordinated approach ensures success in the short/intermediate term while also seeding developments that can impact the long-term.

P1-J4 Office of Environmental Management, Office of Technology Innovation & Development

P1-J5 Office of Fossil Energy

DIVISION OF ADVANCED ENERGY SYSTEMS

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DIVISION OF CARBON CAPTURE AND STORAGE

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DIVISION OF CROSSCUTTING RESEARCH

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Secure, affordable, and environmentally acceptable energy sources are essential to the nation's security and economic prosperity. The Fossil Energy Research and Development (FE R&D) program advances technologies related to the reliable, efficient, cost-effective, and environmentally sound use of fossil fuels, which provide about 83 percent of U.S. energy consumption. To help meet this demand, the program is developing fuel systems and practices that will provide current and future generations with clean, efficient, reasonably priced and reliable energy from the nation's abundant fossil fuel resources. Consequently, the mission of the program is to create technology and technology-based policy options for public benefit by enhancing U.S. economic, environmental, and energy security. This mission is achieved by developing technologies to enable the clean use of domestic fossil fuels with the goal of achieving near-zero atmospheric emissions power production, including a specific focus on dramatic reductions of global carbon emissions at acceptable cost.

P1-J6 National Nuclear Security Administration, Office of Inertial Confinement Fusion, Laboratory for Laser Energetics at the University of RochesterContact: David D. Meyerhofer, dmd@lle.rochester.eduWebsite: www.lle.rochester.edu

The Laboratory for Laser Energetics (LLE) at the University of Rochester is supported by the Office of Inertial Confinement Fusion (ICF) within NNSA to perform ICF and High Energy Density Physics (HED) research. LLE operates the Omega Laser Facility that contains two of the world's largest HED laser systems. The OMEGA Laser is a 60 beam, 30 kJ (UV) system that provides a flexible platform for HED research, including spherical implosions. The OMEGA EP laser system has four beamlines that can each produce 6.5 kJ (UV) in single sided target illumination. Two of the beamlines can be operated as high energy Petawatt (HEPW) lasers in the infrared, each with up to 2.6 kJ in 10 picoseconds. The HEPW beamlines can be used in either the OMEGA or OMEGA EP target chambers. Omega is operated as a National User Facility supporting both programmatic and basic science research.

LLE's primary research activities include the development of the direct-drive ICF concept and participating in the National Ignition Campaign to demonstrate ICF ignition on the National Ignition Facility at Lawrence Livermore National Laboratory. Other activities include the development of laser, materials, and target technologies to support the ICF program and the education and training of students. LLE is NNSA's largest laboratory located at a University.

P1-J7 Office of Nuclear Energy, Fuel Cycle Technology

MICROCALORIMETRY FOR ULTRA HIGH RESOLUTION SPECTROSCOPY

Daniel Vega, daniel.vega@nuclear.energy.govwww.lanl.gov

FUEL RESOURCES

Dr. Sheng Dai, National Technical Director, Dais@ornl.gov

Creating a new supply of uranium at competitive cost would eliminate concerns over long-term fuel availability for nuclear power production. One intriguing approach is the extraction of uranium from seawater. The Japanese have demonstrated technology that makes this possible by developing uranium-selective polymeric adsorbents and methods for deployment in a marine environment. The Fuel Resources Program has established a core research team to investigate how to increase the efficiency and stability of the adsorbent material to make the process more economical. To provide a baseline for assessing improvements, the team has prepared the Japanese adsorbent and confirmed the reported uptake of uranium. The adsorbent is made by grafting short ligand-bearing polymers onto existing polymeric supports. A dual approach toward improving adsorbent performance involves chemical modification to the uranium binding sites to obtain more efficient uptake and enhanced stability, as well as the use of high surface area support materials to increase the porosity and binding site density. To provide a basis for chemical modification, studies of the current adsorbent are underway on the thermodynamics and kinetics of uranium adsorption, selectivity for uranium over other metal ions, chemical stability of the binding sites, and how the binding sites interact with uranium. Fabrication of novel adsorbents, made by grafting binding sites to both high surface area polyethylene fibers and mesoporous carbon supports, are also under investigation.

P1-J8 Office of Nuclear Energy, Office of Space and Defense Power Systems

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For the last 50 years, first as the Atomic Energy Commission, the Department of Energy has provided systems powered by plutonium-238 to federal agencies and the National Aeronautics and Space Administration. Radioisotope Power Systems are ideally suited to very long missions that require reliable and predictable power and performance in harsh and remote environments – such as space. Missions in these environments are enabled by Radioisotope Power Systems because other sources of power – such as solar panels or chemical batteries - are impractical for these kinds of environments. The Nation will be forced to terminate its exploration of deep space unless the United States begins producing plutonium-238, which is required for a radioisotope power system. In fact, the Nation's planned activities are already being impacted by the limited availability of plutonium-238.

P1-J9 Office of Science, Advanced Scientific Computing Research

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Website: <http://science.energy.gov/ascr/>

The mission of the Advanced Scientific Computing Research (ASCR) program is to discover, develop, and deploy computational and networking capabilities to analyze, model, simulate, and predict complex phenomena important to the Department of Energy (DOE). A particular challenge of this program is fulfilling the science potential of emerging computing systems and other novel computing architectures, which will require numerous significant modifications to today's tools and techniques to deliver on the promise of exascale science.

ASCR provides high performance and leadership class computing facilities and advanced scientific networks along with programs to utilize these facilities.

High performance and leadership class computers, by every definition describes machines that employ very large numbers of processors in parallel to address scientific and engineering challenges. "Massively parallel processing" splits up a task or problem and parcels it out to multiple processors that work simultaneously but in concert to quickly supply results. High-performance computers link hundreds or thousands of processors - the computer chips that perform most calculations - in massively parallel configurations. Some of the processors in high-performance computers are specially designed for their purpose. In others, the processors are similar to the commercially available ones found in home computers, but they're linked by custom-made hardware and software that lets them work together quickly and efficiently.

ASCR's supercomputers carry out trillions or even quadrillions of calculations each second - powerful enough to simulate the most complex physical, biological and chemical phenomena. Supercomputers help scientists understand these processes at unprecedented levels - from individual atoms for nanoscale engineering to the entire planet for global climate studies. High-performance computers also are powerful enough to provide insight into systems and process by simulating them with great detail over relatively long times.

THE PRIMARY FACILITIES FUNDED AND MANAGED BY ASCR INCLUDE:

OAK RIDGE LEADERSHIP COMPUTING FACILITY

The Oak Ridge Leadership Computing Facility (OLCF) at Oak Ridge National Laboratory provides the one of the world's most powerful computing resources for open scientific research. The OLCF's 2.33 petaflop Cray XT system has 37,376 AMD six-core Opteron processors, for a total of 224,256 processing cores, and features 300 terabytes of memory and a 10-petabyte Lustre-based shared file system.

ARGONNE LEADERSHIP COMPUTING FACILITY

The Argonne Leadership Computing Facility (ALCF) provides the computational science community with a world-leading computing capability dedicated to breakthrough science and engineering. The major resource at the ALCF is an IBM Blue Gene/P system with a peak speed of 557 Teraflops and 40,960 nodes, each with four processors or cores for a total of 163,840 cores and 80 terabytes of memory.

NERSC

The National Energy Research Scientific Computing Center (NERSC) is a supercomputing center funded and maintained by ASCR at the Lawrence Berkeley National Laboratory to support basic scientific research in support of DOE's missions. NERSC provides capacity computing through a 1.28 Petaflop Cray XE6 with 6,384 compute nodes each containing 2 twelve-core AMD MagnyCours processors for a total of 153,216 processor nodes, 212 TB of memory and 2 petabytes of online disk storage. Additional NERSC resources include a 352 teraflop Cray XT4 with 38,128 compute cores and an 400 compute node IBM iDataPlex system.

P1-J10 Office of Science, Basic Energy Sciences, Nanoscale Science Research Centers

CENTER FOR FUNCTIONAL NANOMATERIALS

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CENTER FOR INTEGRATED NANOTECHNOLOGIES

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CENTER FOR NANOPHASE MATERIALS SCIENCES

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CENTER FOR NANOSCALE MATERIALS

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THE MOLECULAR FOUNDRY

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The five Nanoscale Science Research Centers (NSRCs) are DOE's premier user centers for interdisciplinary research at the nanoscale, serving as the basis for a national program that encompasses new science, new tools, and new computing capabilities. Each center has particular expertise and capabilities in selected theme areas, such as synthesis and characterization of nanomaterials; catalysis; theory, modeling and simulation; electronic materials; nanoscale photonics; soft and biological materials; imaging and spectroscopy; and nanoscale integration. The centers are housed in recently-constructed and custom designed laboratory buildings near one or more other major Office of Science facilities for x-ray, neutron, or electron scattering, which complement and leverage the capabilities of the NSRCs. These centers contain clean rooms, nanofabrication resources, one-of-a-kind signature instruments, and other instruments not generally available except at major user facilities. The facilities are routinely made available for use by the research community.

THE FIVE CENTERS ARE:

- CENTER FOR FUNCTIONAL NANOMATERIALS AT BROOKHAVEN NATIONAL LABORATORY
- CENTER FOR INTEGRATED NANOTECHNOLOGIES AT LOS ALAMOS AND SANDIA NATIONAL LABORATORIES
- CENTER FOR NANOPHASE MATERIALS SCIENCES AT OAK RIDGE NATIONAL LABORATORY
- CENTER FOR NANOSCALE MATERIALS AT ARGONNE NATIONAL LABORATORY
- THE MOLECULAR FOUNDRY AT LAWRENCE BERKELEY NATIONAL LABORATORY

P1-J11 Office of Science, Basic Energy Sciences, Electron-Beam Microcharacterization Centers

ELECTRON MICROSCOPY CENTER FOR MATERIALS RESEARCH (EMCMR)

Dean J. Miller, Director, miller@anl.gov
<http://www.msd.anl.gov/groups/emc/>

NATIONAL CENTER FOR ELECTRON MICROSCOPY

Ulrich Dahmen, Director, udahmen@lbl.gov
<http://ncem.lbl.gov/>

SHARED RESEARCH EQUIPMENT (SHARE) USER FACILITY

Karren More, Director, morek1@ornl.gov
<http://www.ornl.gov/sci/share/>**P1-J12 Office of Science, Basic Energy Sciences, Neutron Scattering Facilities**

SPALLATION NEUTRON SOURCE (SNS)

Judy Trimble, User Program Manager, trimblej@ornl.gov
<http://neutrons.ornl.gov/facilities/SNS/>

HIGH FLUX ISOTOPE REACTOR (HFIR)

Judy Trimble, User Program Manager, trimblej@ornl.gov
<http://neutrons.ornl.gov/facilities/HFIR/>

LOS ALAMOS NEUTRON SCIENCE CENTER (LANSCE)

Kurt Schoenberg, kurts@lanl.gov

www.lansce.lanl.gov

The Los Alamos Neutron Science Center (LANSCE) provides the scientific community with intense sources of neutrons with the capability of performing experiments supporting civilian and national security research. LANSCE remains a premier accelerator-based user facility for national security and fundamental science. Five major experimental facilities operate simultaneously at LANSCE: The Lujan Neutron Scattering Center delivers one of the highest-peak neutron fluxes in the world. The Weapons Neutron Research (WNR) Facility enables nuclear measurements for the weapons program, civilian applications, and basic nuclear physics research. The Proton Radiography (pRad) Facility provides a proton pulse trains allow observation of dynamic events on the microsecond timescale. The Isotope Production Facility (IPF) produces radioisotopes for both research and nuclear medicine. The Ultra-Cold-Neutron Source (UCN) produces ultra-cold neutrons, which are an ideal system for high-precision tests of weak interaction.

P1-J13 Office of Science, Basic Energy Sciences, X-Ray Light Sources

ADVANCED LIGHT SOURCE (ALS) AT LAWRENCE BERKELEY NATIONAL LABORATORY

Scientific Contact: Roger Falcone, RWFalcone@lbl.gov

User Program: Susan Bailey, sbailey2@lbl.gov

<http://www-als.lbl.gov/>

ADVANCED PHOTON SOURCE (APS) AT ARGONNE NATIONAL LABORATORY

Scientific Contact: Dennis Mills, dmm@aps.anl.gov

User Program: Susan Strasser, strasser@aps.anl.gov

<http://www.aps.anl.gov/>

LINAC COHERENT LIGHT SOURCE (LCLS) AT SLAC NATIONAL ACCELERATOR LABORATORY

Scientific Contact: Uwe Bergmann, bergmann@slac.stanford.edu

User Program: Cathy Knotts, knotts@slac.stanford.edu

<http://lcls.slac.stanford.edu/>

NATIONAL SYNCHROTRON LIGHT SOURCE (NSLS) AT BROOKHAVEN NATIONAL LABORATORY

Scientific Contact: Qun Shen, qshen@bnl.gov

User Program: Kathy Nasta, nasta@bnl.gov

<http://www.nsls.bnl.gov/>

STANFORD SYNCHROTRON RADIATION LIGHTSOURCE (SSRL) AT SLAC NATIONAL ACCELERATOR LABORATORY

Scientific Contact: Mike Toney, mftoney@slac.stanford.edu

User Program: Cathy Knotts, knotts@slac.stanford.edu

<http://ssrl.slac.stanford.edu/>

The five light sources operated by the DOE Office of Science are the nation's premier arsenal of tools to study materials at all length scales. The light produced by these facilities—light that ranges from the infrared through the ultraviolet to extremely short x-rays—enables advanced research into the structure, composition, and dynamics of materials in virtually every major scientific discipline, including materials science, physics and chemistry, metrology, geoscience, environmental science, biology, medicine, and pharmaceutical research. The three broad categories of synchrotron techniques (spectroscopy, scattering, and imaging) correspond roughly to the parameters we use to perceive the physical world (energy, momentum, and position). By exploiting the short pulse length of synchrotron radiation, it is also possible to watch the dynamics of materials as they change—for example, research at light sources is now examining how high-tech batteries discharge their energy in order to find longer-lasting, more efficient materials. The newest light source, the Linac Coherent Light Source (LCLS), is the world's first hard free electron x-ray laser facility and provides x-ray light 10 billion times brighter than any existing light source. With this powerful beam, scientists can take stop-motion pictures of atoms and molecules in action, shedding light on the fundamental processes of chemistry, technology, and life itself.

THE FIVE FACILITIES ARE:

- ADVANCED LIGHT SOURCE, LAWRENCE BERKELEY NATIONAL LABORATORY
- ADVANCED PHOTON SOURCE, ARGONNE NATIONAL LABORATORY
- NATIONAL SYNCHROTRON LIGHT SOURCE, BROOKHAVEN NATIONAL LABORATORY
- STANFORD SYNCHROTRON RADIATION LIGHTSOURCE, SLAC NATIONAL ACCELERATOR LABORATORY
- LINAC COHERENT LIGHT SOURCE, SLAC NATIONAL ACCELERATOR LABORATORY

P1-J14 SunShot Initiative

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The DOE SunShot Initiative is a collaborative national initiative to make solar energy technologies cost-competitive with other forms of energy by reducing the cost of solar energy systems by about 75% before 2020. Reducing the total installed cost for utility-scale solar electricity to roughly 6 cents per kilowatt hour without subsidies will result in rapid, large-scale adoption of solar electricity across the United States. Reaching this goal will re-establish American technological leadership, improve the nation's energy security, and strengthen U.S. economic competitiveness in the global clean energy race.

EFRC Research Posters
Thursday, May 26, 2011, 6:00 – 7:30 pm

P1-A01 - POLARITON LASING BY INTRA-CAVITY PUMPING AND APPLICATIONS TO ULTRA-FAST OPTICAL MODULATION

[CE] Gleb Akselrod¹, Elizabeth Young¹, Scott Bradley¹, and Vladimir Bulovic¹

¹*Massachusetts Institute of Technology*

The Center for Excitonics is focused on examining the interaction of light and photosensitive materials to produce excitons, and the subsequent manipulation of these excitons. A newly emerging branch of this endeavor is the study of strong coupling between excitons and photons in a confined optical resonator, forming quasi-particles called polaritons. Polariton microcavities offer exciting possibilities for the study of condensation, superfluidity and other condensed matter phenomena, and show promise as a radically new class of ultra-fast, low energy optoelectronic devices based on the macroscopic coherence of light and matter. In particular, organic materials allow for strong coupling and polariton condensation to be achieved at room temperature. Here we demonstrate room temperature polariton lasing in a lambda-thick microcavity where a highly absorbing thin film of J-aggregates serves as the strong coupling material. A new pumping scheme is employed known as intra-cavity pumping which circumvents annihilation losses inherent to organic materials at high excitation densities. Finally, we propose how such a polariton laser can be used as all-optical switch and present preliminary results.

P1-A02 - NONDIABATIC QUANTUM MOLECULAR DYNAMICS SIMULATIONS OF RAPID ENERGY TRANSPORT IN LIGHT-HARVESTING MOLECULES

[CEN] Aiichiro Nakano¹, Rajiv. K. Kalia¹, and Priya Vashishta¹

¹*University of Southern California*

We have developed a metascalable algorithmic framework that is likely to scale on future exaflops computing platforms. The framework has achieved parallel efficiency over 0.95 on 212,992 IBM BlueGene/L processors for 1.68 trillion electronic degrees-of-freedom quantum molecular dynamics (QMD) simulation. We have used the framework to design a nonadiabatic QMD simulation algorithm for the study of photoexcitation dynamics in hybrid organic-inorganic nanostructures based on the linear-response time dependent density functional theory by Casida and the fewest-switches surface-hopping method by Tully. We have performed NAQMD simulations of a conjugated light-harvesting molecule consisting of a zinc-porphyrin core connected to a benzyl ether-type antenna. Simulation results show that the rapid transfer of a photoexcited electron from the antenna to the porphyrin core is assisted by the crossing of energy levels and the overlap of wave functions between electronic orbitals. These, in turn, are assisted by thermal motion of the molecule. Specifically, we have found that the fluctuation of key energy levels is caused by the vibrational motion of the aromatic rings in the peripheries.

P1-A03 - PROBING NANOMETER-SCALE ENERGETICS AND ORIENTATION OF MOLECULES AT INTERFACES

[CISSEM] Bradley MacLeod¹, Matthew Schalnaf², Dallas Matz², David Ginger¹, Jeanne Pemberton², Sergio Paniagua³, Seth Marder³, Ajaya Sigdel⁴, Joseph Berry⁴, Mariola Macech², Hong Li³, and Jean-Luc Bredas³

¹*University of Washington*; ²*University of Arizona*; ³*Georgia Institute of Technology* and ⁴*National Renewable Energy Laboratory*

Surface composition of metal and metal oxide contacts in PV platforms are critical determinants of energy conversion efficiency. We focus on understanding chemistries at interfaces between metals and active layers, and between transparent conducting oxides (TCOs) and surface modifiers and active layers. We focus here on studies which feature techniques probing molecular composition and molecular orientation, and their relationship to electrical properties of these interfaces. For organic/metal interfaces our primary tools include high vacuum Raman spectroscopies, revealing a rich assortment of chemical processes occurring when reactive metals are deposited on a variety of molecular semiconductors. For oxide/organic interfaces our work has focused on dipolar small molecule modifiers, which provide tunability of the effective work function (wf) over a range of ca. 1.5eV, while significantly lowering the surface free energy. Near-edge X-ray absorption fine structure (NEXAFS at SLAC), X-ray reflectivity (XRR), and polarization-modulated infrared reflection/absorption spectroscopies (PM-IRRAS) have been used as a complimentary techniques to investigate orientation of these molecular modifiers. Changes in wf at TCO/organic interfaces have also been investigated in photodiodes using electroabsorption spectroscopy (EAS), which probes the formation of charged species at oxide/organic interfaces, demonstrating the importance of interface composition on charge injection and harvesting.

P1-A04 - FULLERENE SELF-ASSEMBLY AS A MEANS TO CONTROL MORPHOLOGY IN POLYMER/FULLERENE BULK HETEROJUNCTION SOLAR CELLS

[MEEM] Christopher Tassone¹, Alexander Ayzner¹, Robert Kennedy¹, Yves Rubin¹, Benjamin Schwartz¹, and Sarah Tolbert¹
¹UCLA

The efficiency of bulk hetero-junction (BHJ) photovoltaics is very sensitive to the nanoscale morphology that evolves during fabrication, and is particularly sensitive to the level of nanoscale phase segregation between the donor, polymer, and acceptor, fullerene, components. We have synthesized a novel series of penta-aryl fullerene derivatives as a means to explore how the fullerene component of the BHJ can control the degree of phase segregation. Through a combination of grazing incidence small angle x-ray diffraction (GISAXD) and atomic force microscopy (AFM) we are able to see two distinct nanoscale morphologies emerge across the series. The morphological control we observe is achieved through tuning the propensity of these penta-aryl fullerene molecules to self-assemble and thus direct the solid state film morphology. Furthermore, we investigate the device physics using i-v characterization, light intensity dependence as well as fluorescence quenching studies and are able to correlate the physical device properties to their respective morphologies. Finally we propose a mechanism by which self-assembling fullerenes can drive an order of magnitude increase in device efficiency over their non-assembled counterparts within our penta-aryl fullerene series.

P1-A05 - P3HT/PCBM BULK HETEROJUNCTION ORGANIC PHOTOVOLTAICS: CORRELATING EFFICIENCY AND MORPHOLOGY

[PHaSE] Dian Chen¹, Atsuhiko Nakahara², Dongguang Wei³, and Thomas P. Russell⁴
¹U Mass Amherst; ²Kurashiki Research Center; ³Carl Zeiss NTS LLC and ⁴U Mass Amherst

Controlling thin film morphology is key in optimizing the efficiency of polymer-based photovoltaic (PV) devices. The morphology and interfacial behavior of the multicomponent active layers confined between electrodes are strongly influenced by the preparation conditions. The results quantitatively show the photovoltaic device performance was strongly affected by the nanoscopic morphology, crystal orientation, composition distribution and the interdiffusion behavior of the photoactive layer. To better understand the physics of the photoactive layer in the organic photovoltaic devices, it is necessary to gain a quantitative understanding of the morphology and the manner in which it develops. A key element in the kinetics associated with the structure development is the interdiffusion of the components. To that end we used P3HT/PCBM bilayers as a model to investigate the interdiffusion of the components and its role in the development of the morphology. A detailed description of the diffusion behavior and the morphology developed from a layer of P3HT in contact with a layer of PCBM during thermal annealing is given. Amorphous P3HT and PCBM are shown to be highly miscible and PCBM can penetrate into the P3HT layer through the P3HT amorphous region and form the bulk heterojunction structure within a few second of annealing at 150 °C. Finally, we put forth an alternative mechanism, namely a competitive crystallization/diffusion argument, to describe the origin of the morphology.

P1-A06 - SELF-ASSEMBLY OF MIXTURES OF NANORODS IN BINARY, PHASE-SEPARATING BLENDS

[PHaSE] Anna Balazs¹, Li-Tang Yan¹, Egor Maresov¹, and Gavin A Buxton²
¹Univ of Pittsburgh and ²Robert Morris University

Aligned nanorod inclusions have the potential to significantly improve both photovoltaic and mechanical properties of polymeric materials. Establishing facile methods for corralling' nanorods to self-assemble into aligned morphologies could facilitate fabrication of robust devices. We modeled self-assembly of a mixture of A-coated and B-coated rods in an AB phase-separating blend. Dissipative particle dynamics (DPD) simulations show that steric repulsion between ligands causes the coated rods to preferentially align end-to-end within the minority phase of the binary blend. A coarse-grained approach (Cahn-Hilliard model for the polymer blend Brownian dynamics simulation for the rods) simulating a rod-filled 30 : 70 AB thin film indicates that a small volume fraction of B rods in the majority B phase promotes percolation of A-like rods within A. The percolation threshold for the A-rods is significantly lowered. If the number of B nanorods in the B phase exceeds a particular volume fraction the B particles inhibit percolation of the A rods. Thus there is an optimal volume fraction of B nanorods for beneficial effects. Nanorods oriented along the tensile direction enhance the macroscopic mechanical properties of the material. A multi-scale approach (microscopic mesoscopic and macroscopic) greatly helps determination of structure-property relationships in nanocomposites.

P1-A07 - DESIGN, SYNTHESIS, AND CHARACTERIZATION OF CHEMICALLY TAILORED SEMICONDUCTOR NANOPARTICLES

[RPEMSC] Brandi Cossari¹
¹Columbia University

Colloidal quantum dot (QD) materials have been of tremendous importance for energy harvesting systems, but even the best QD syntheses yield a distribution of nanoparticle sizes with a variety of defect and trap states. The EFRC is developing synthesis for small inorganic QD compounds with identical size, structure, and stoichiometry. Such uniformity

makes these nanostructures a valuable model system by which to investigate the chemistry and photophysical properties of their larger nanocrystal relatives. We have found that a benzoate-terminated CdSe cluster molecule can be readily synthesized and isolated with the empirical formula $[(\text{CdSe})_4\text{Cd}(\text{OC}(\text{O})\text{Ph})_2(\text{H}_2\text{NR})_2]_n$ ($n = 6-9$). Using a combination of nanosecond and femtosecond resolution measurement techniques we have quantified exciton lifetimes in these materials and demonstrated a competition between band-edge and trap state luminescence.

P1-B01 - NEW TYPE OF SEMICONDUCTOR NANOCRYSTALS AND SEMICONDUCTOR-METAL NANOHYBRIDS FOR EFFICIENT CAPTURE OF SOLAR RADIATION

[CASP] Anshu Pandey¹, Liang Li¹, Bishnu P. Khanal¹, Hsinhan Tsai¹, Hsing-Lin Wang¹, Jeffrey M. Pietryga¹, and Victor I. Klimov¹

¹Los Alamos National Laboratory

At CASP, we are developing novel, inexpensive solution-processable nanomaterials to enable cost-effective capture of solar radiation. In this poster, we describe the synthesis of novel semiconductor nanocrystals (NCs) and metal-semiconductor hybrids. Copper Indium Sulfide (CIS) NCs have a band-gap energy well suited for applications in thin-film photovoltaics. We have developed a new synthesis of CIS NCs using a scalable, virtually waste-free approach. The growth of an inorganic shell boosts emission quantum yields to 90%, indicating excellent surface passivation. We study the role of defects in these NCs and demonstrate that the emission occurs through the recombination of a conduction-band electron with a localized hole. These results help to rationalize a significant difference between electron and hole conductivities in CIS nanocrystal films. In a separate effort, we synthesize and study hybrid structures that combine semiconductor NCs with nanoscale metals. Metal plasmons can significantly modify the behavior of proximal NCs, e.g., enhancing absorption and modifying emission and energy transfer rates. The goal of our study is to develop solution-processed hybrid materials with optical responses useful for light harvesting. We will discuss the synthesis and optical properties of tunable hybrid structures with a focus on novel features associated with strong semiconductor-metal coupling.

P1-B02 - CHEMICAL MODIFICATION OF PbSE QUANTUM DOT ARRAYS TO ENHANCE MULTIPLE EXCITON GENERATION AND IMPROVE DEVICE EFFICIENCY

[CASP] Octavi E. Semonin¹, Joseph M. Luther¹, Jianbo Gao¹, Sukgeun Choi¹, Matthew C. Beard¹, and Arthur J. Nozik¹

¹National Renewable Energy Laboratory

At CASP, we are pursuing revolutionary approaches in order to lower the cost/watt for photovoltaic energy generation. Quantum dots (QDs) offer the potential to utilize inexpensive materials and low-cost scalable manufacturing to arrive at devices that convert light to electricity at extremely high efficiency. Due to quantum confinement effects, multiple exciton generation (MEG), in which absorbed high energy photons generate more than one band-edge excitation, has been shown to be more efficient in QDs than bulk materials, leading to theoretical efficiencies for a single-junction device above the Shockley-Queisser limit. However, MEG has not been observed in an efficient solar cell, leading to some debate about its effectiveness. In this work, we present an improved PbSe QD layer that produces robust, stable, high-current devices. This results in a large increase in the 1-sun efficiency from previous work, and it yields a high internal quantum efficiency. Optical modeling and progress towards quantifying MEG in this solar cell will be presented.

P1-B03 - INGAN/GAN QUANTUM WELL SOLAR CELLS FOR MULTI-JUNCTION CONCENTRATOR APPLICATION

[CEEM] Carl Neufeld¹, Samantha Cruz¹, Robert Farrell¹, Michael Iza¹, Stacia Keller¹, Shuji Nakamura¹, Steven DenBaars¹, James Speck¹, and Umesh Mishra¹

¹UCSB

To increase the efficiency of solar cells, new materials will have to be developed which can efficiently capture the high-energy portion of the solar spectrum. The excellent material properties of the InGaN material system have made it a promising candidate for use in high efficiency solar cells. These properties include the wide range of band gap energies (0.7 eV for InN to 3.4 eV for GaN) available and a high absorption coefficient which allows for significant absorption of light in very thin epitaxial layers. This wide band gap range makes III-N semiconductors an ideal material for the high-energy cell of a multijunction concentrator solar cell, especially for band gap energies above 2.2 eV for which few materials are viable. Current state-of-the-art high-efficiency solar cells containing 3 junctions consisting of InGaP/InGaAs/Ge have attained conversion efficiency of over 40%, but next-generation devices will require more junctions with larger band gap energies to increase efficiency over 50%. In this work we report on our recent progress on InGaN/GaN quantum-well based solar cells with Indium fraction of 27% and long-wavelength absorption edge of 500 nm. The devices have open circuit voltage of 2 V and fill factor of 63% leading to a 1 sun (AM1.5G) efficiency of 2.6%. Thermal measurements show an increase in output power up to 115 C indicating InGaN may perform well under high concentration where thermal degradation can dominate performance.

P1-B04 - THREE-DIMENSIONAL NANOJUNCTION DEVICE ARCHITECTURES FOR THIN-FILM PHOTOVOLTAICS

[CNEEC] Artit Wangperawong¹ and Stacey F. Bent¹¹Stanford University

A model is developed to describe the behavior of three-dimensionally nanostructured photovoltaic devices, distinguishing between isolated radial pn junctions and interdigitated pn junctions. We examine two specific interdigitated architectures, the point-contact nanojunction and the extended nanojunction, which are most relevant to experimental devices reported to date but have yet to be distinguished in existing works. The model is also applied to polycrystalline CdTe devices with inverted grain boundaries. We demonstrate that for CdTe/CdS solar cells using low-quality materials, the efficiency of the extended nanojunction geometry is superior to other designs considered.

P1-B05 - GIANT ANHARMONIC PHONON SCATTERING IN PbTe: INELASTIC NEUTRON SCATTERING AND PHONON CALCULATIONS

[S3TEC] Olivier Delaire¹, Karol Marty¹, Jie Ma¹, Andrew May¹, Michael McGuire¹, Mao-Hua Du¹, David Singh¹, and Brian Sales¹¹ORNL

Understanding the microscopic processes affecting the bulk thermal conductivity is crucial to develop more efficient thermoelectric materials. PbTe is currently one of the leading thermoelectric materials, largely thanks to its low thermal conductivity. However, the origin of this low thermal conductivity in a simple rocksalt structure has so far been elusive. Using a combination of inelastic neutron scattering measurements and first-principles computations of the phonons, we identify a strong anharmonic coupling between the ferroelectric transverse optic mode and the longitudinal acoustic modes in PbTe. This interaction extends over a large portion of reciprocal space, and directly affects the heat-carrying phonons. This anharmonic coupling is likely to play a central role in explaining the low thermal conductivity of PbTe. The present results provide a microscopic picture of why many good thermoelectric materials are found near a lattice instability of the ferroelectric type.

P1-C01 - ULTRAFAST ELECTRON TRANSFER AND PHOTOCHEMICAL HYDROGEN PRODUCTION VIA COVALENT CHROMOPHORE-HYDROGENASE MODEL COMPLEX ASSEMBLIES

[ANSER] Samuel, Amanda P. S.¹, Co, Dick T.¹, Poddutoori, Premaladha¹, Vagnini, Michael T.¹, and Wasielewski, Michael R.¹¹Northwestern University

While electrocatalytic proton reduction using diiron complexes modeled on the [FeFe] hydrogenase active site has received a great deal of interest in recent years, the field of photodriven hydrogen generation by systems that incorporate these complexes is significantly less developed. One of the main challenges is that many of these catalysts are difficult to photoreduce using chromophores that absorb visible light. To address this issue, we developed a diiron complex that utilizes an electron-poor naphthalene monoimide (NMI) ligand (NMI-Fe₂S₂(CO)₆). The NMI moiety results in a reduction potential that is sufficiently mild such that photodriven electron transfer from a Zn porphyrin chromophore to the diiron complex in a covalently-linked porphyrin-diiron complex dyad (ZnP-NMI-Fe₂S₂(CO)₆) is achieved. Selective photoexcitation of the Zn porphyrin results in ultrafast charge separation, which was monitored using both visible and infrared femtosecond time-resolved transient absorption spectroscopy. To extend the lifetime of the catalytically-relevant reduced diiron state an electron donor-acceptor triad consisting of NMI-Fe₂S₂(CO)₆, a Zn porphyrin, and a ferrocene secondary donor was prepared. In this triad the lifetime of the fully charge separated state is extended by a factor of >1000 relative to that of the dyad. Additionally, photoexcitation of both the dyad and triad in the presence of trifluoroacetic acid was shown to generate H₂.

P1-C02 - TAILORING THE ARCHITECTURE OF LIGNIFIED WALLS

[C3Bio] Jeong Im Kim¹, Joe Cox¹, Anna Olek¹, Nick Carpita¹, Maureen McCann¹, Dan Szymanski¹, and Clint Chapple¹¹Purdue University

The toolkit of plant molecular biology allows modification of biomass composition by manipulating gene expression. In C³Bio, we are using a synthetic biology approach to introduce novel genes and pathways to tailor biomass for catalytic and thermal transformations. For example, iron is a useful co-catalyst both in thermal processing and in enzymatic saccharification of cell walls. Iron co-catalyst pretreatments are elucidated and quantified by electron tomography, which gives a 3-D, nano-scale image of cell wall architecture. We show that iron is an effective catalyst for "fibrillating", or delaminating, cellulose microfibril bundles in the secondary walls of energy grasses. However, the iron atoms contact very limited surfaces of cell wall. We aim to integrate metal catalysts into the cell wall throughout development. We have fused Fe-binding domains of non-plant proteins with cellulose- and carbohydrate-binding modules (CBMs) and introduced them in *Arabidopsis* by Agrobacterium-mediated transformation. We show that *Arabidopsis* plants expressing the fluorescent protein mCHERRY fused to a CBM is targeted to the cell wall and attaches to the planar face of crystalline cellulose. We

explore metal-binding peptides for fusion to CBMs that bind at acidic pHs. We are targeting selected lignin precursors and artificial aromatic catalysts to the cell wall to enhance catalytic conversion of the lignocellulosics into advanced biofuels and valuable co-products.

P1-C03 - REDUCTIVE ACTIVATION OF FATTY ACID SYNTHASE - A MECHANISM OF REGULATING FATTY ACID BIOSYNTHESIS

[CABS] Hui Chen¹, Huimin Man¹, Jinxia Wu¹, and Oliver Yu¹

¹*Donald Danforth Plant Science Center*

In plants, many metabolic enzymes including plastidic acetyl-CoA carboxylase (ACCase) are posttranslationally regulated by thioredoxin, a cysteine thiol-disulfide reductase. Previous studies indicate that *Arabidopsis* enoyl-ACP reductase (ER, At2g05990), one of the key components of fatty acid synthase complex, is a potential target of thioredoxin y2 (Trx y2, At1g43560) (Marchand et al. 2010). In addition, ER (MOD1) was identified by proteomic screening as a putative disulfide-bonded protein in vivo (Alvarez et al. 2009). However, there has been no report on the verification of these proteomic results. Nor the physiological function of the redox-regulation of ER is known. Here we provide evidence to show that ER and Trx y1/y2 physically interact with each other in a yeast-two-hybrid assay. We also demonstrate that CuCl₂ could partially oxidize recombinant ER expressed in *E. coli* and decrease its activity. In contrast, the ER-C198A mutant did not show these responses to CuCl₂ treatment. We also found that ER activities in the crude extracts from leaves, flowers and seeds were enhanced if the crude protein extracts were preincubated with dithiothreitol (DTT), indicating that ER catalyzed reaction is a regulatory step in fatty acid biosynthetic pathway. Transgenic *Arabidopsis* and *Camelina* overexpressing ER-C198A mutant under the control of 35S or seed-specific glycinin promoter were obtained. Several lines with higher ER activity were identified. The phenotypes and seed oil contents of these transgenic plants are under investigation.

P1-C04 - USING COMBINED OMICS TOOLS TO INVESTIGATE REGULATION OF METABOLISM IN CHLAMYDOMONAS

[CABS] Jeong-Jin Park¹, Mahmoud Gargouri¹, and David R. Gang¹

¹*Washington State University*

Photosynthetic organisms such as higher plants and algae produce a large array of compounds from many different compound classes. Because of their role as primary solar energy assimilators, the metabolic responses of plants to different light conditions, particularly responses to light/dark cycles, are of great interest. Using the model organism, *Chlamydomonas reinhardtii*, we are working to identify target genes and proteins that play important roles in regulating and controlling flux and partitioning through networks leading to production of potentially valuable metabolites. In this study, we compare the metabolomic and proteomic changes occurring in *C. reinhardtii* under mixotrophic and heterotrophic culture conditions, with the ultimate goal of generating a working model that will aid in predicting metabolic responses to genetic alterations or environmental stimuli. Protein expression and metabolite accumulation data are clustered using a self-organizing tree algorithm and visualized as heat maps in order to accurately group metabolites that exhibit similar patterns under each growth condition or in each strain. Optimization of metabolic networks is an important component of efforts to increase the efficiency of solar energy conversion into biofuel components.

P1-C05 - POROUS ANTIMONY TIN OXIDE AS A CONDUCTIVE HOST FOR A FUNCTIONALIZED DNA NANOCAGE

[BISfuel] Chad R. Simmons¹, Xixi Wei¹, Alex Volosin¹, Dominik Schmitt¹, Dong-Kyun Seo¹, Yan Liu¹, and Hao Yan¹

¹*Arizona State University*

A functionalized tetrahedral DNA nanocage has been designed to serve as a stable three-dimensional scaffold for the coordination of electron transfer mediators, nanoparticles, and peptides. The design is ideal in that it provides us with the ability to spatially control and optimize position on the framework to facilitate effective electron transfer to electrodes. A conductive mesoporous antimony tin oxide (ATO) powder has been prepared using the sol gel method. It contains an extensive matrix of porous cavities within the metal oxide that possesses the capability of hosting a variety of molecules such as our tetrahedral nanocage with high affinity. Furthermore, during the synthesis of the ATO material, we have shown that the pore sizes of the matrix are highly tunable with sizes on the nanoscale (i.e. 5-25 nm). This has provided us with the ability to selectively absorb or exclude our DNA nanostructure from the metal oxide surface within the porous substrate. To demonstrate this, confocal microscopy and solution FRET experiments have been employed to show the size selectivity of the cavities, while maintaining the integrity of the DNA structure. This work opens up exciting new possibilities for the use of functionalized DNA architectures as guest molecules for mesoporous conductive metal oxides such as ATO, which may lead to development of applications such as electrodes for photovoltaic and light emitting diode devices, sensors, and potentially solar fuel cells.

P1-C06 - TOWARDS BIO-INSPIRED MANGANESE-CALCIUM BIMETALLIC CENTERS FOR ELECTROCATALYTIC WATER OXIDATION [BISfuel] Matthieu Koepf¹, Benjamin D. Sherman¹, Ana L. Moore¹, Devens Gust¹, and Thomas A. Moore¹
¹Arizona State University

Ditopic ligands derived from porphyrins bearing a coordination site for spherical cations have been prepared and their ability to bind alkali and alkaline-earth metals investigated. The ligands were designed to assemble a manganese-calcium bimetallic center as a simple synthetic model for the Mn-Ca motif found in the oxygen evolving complex of the natural photosynthetic water oxidation system (PSII). In the proposed architectures, the porphyrin ring, which can coordinate a Mn ion, was either capped or decorated with (cyclic) polyether moieties and carboxylic groups were further introduced at the meso position of the porphyrin ring to form a binding site for alkali and alkaline-earth cations. Because the complexation of Mn(III) in porphyrins is well established, the design of an adequate Ca binding site to form such a ditopic ligand is crucial for the preparation of molecular electrocatalysts for water oxidation. Preliminary ¹H-NMR studies indicated that the capped porphyrins may be too constrained to bind efficiently a Ca ion within the polyether strap, whereas structures containing flexible polyether chains are more promising candidates. The synthesis of the different ligands as well as initial Ca-binding studies will be reported.

P1-C07 - MOLECULAR SIEVE CATALYSTS AND ADSORBENTS FOR EFFICIENT SYNTHESIS AND PURIFICATION PROCESSES OF 5-HYDROXYMETHYL FURFURAL AND ITS ETHERS [CCEI] Nafiseh Rajabbeigi¹ and Michael Tsapatsis¹
¹University of Minnesota

A promising furanic biofuel or biofuel precursor which can be produced from sugars or hydroxymethyl furfural (HMF) is ethoxymethylfurfural (EMF). We investigate the synthesis and purification of EMF from HMF, fructose and glucose. In this poster we will discuss the kinetics of EMF formation from HMF using certain zeolite catalysts. We will also present preliminary results on the formation of EMF directly from glucose and fructose as well as by a process that combines conversion of sugars to HMF followed by HMF adsorption on a selective sorbent and the subsequent HMF conversion to EMF.

P1-C08 - ACCURATE COMPUTED THERMOCHEMISTRY AND KINETICS FOR THE REACTION BETWEEN N-BUTANOL AND THE HYDROPEROXYL RADICAL [CEFRC] Ionut Alecu¹, Tao Yu¹, Jingjing Zheng¹, and Donald Truhlar¹
¹University of Minnesota

The hydrogen-atom abstraction reaction $\text{CH}_3(\text{CH}_2)_3\text{OH} + \text{HO}_2 = \text{CH}_3(\text{CH}_2)_2\text{CHOH} + \text{HOOH}$ is an important process that drives the low temperature chemistry in the combustion of n-butanol, a promising biofuel that will soon be used in combustion engines on a commercial scale. Thermal rate coefficients are calculated using multi-structural variational transition state theory (MS-VTST). This new formulation of VTST integrates multi-structural partition functions that account for torsional anharmonicity, canonical VTST with a curvilinear dividing surface, and a multidimensional treatment of tunneling, to conveniently and accurately obtain the rates of reactions involving complex molecules possessing multiple torsions which can combine to give rise to many structures (i.e., conformers). The M08-SO hybrid meta-GGA density functional, validated against the highly-accurate CCSD(T)-F12a explicitly-correlated method paired with the efficient jul-cc-pVTZ basis set, is used to compute the properties of all stationary points and the energies and Hessians of a few non-stationary points along the reaction path, which are then used to efficiently generate a reliable potential energy surface via the multi-configuration Shepard interpolation method (MCSI).

P1-C09 - NANOMECHANICAL IMAGING AND MAPPING OF PLANT CELL WALLS BY ATOMIC FORCE MICROSCOPY [CLSF] Sahar Maghsoudy-Louyeh¹, Tian Zhang¹, Yong Bum Park¹, Daniel J. Cosgrove¹, and Bernhard R. Tittmann¹
¹The Pennsylvania State University

The structure of plant cell walls is important as a determinant of plant growth and tissue mechanics and has a major impact on the conversion of cellulosic biomass to biofuel. Plant cell walls consist of cellulose nanofibrils embedded in polysaccharides, structural protein, and (sometimes) lignin. With atomic force microscopy (AFM) operating in peak-force tapping mode, we characterized the topography of primary cell walls at the surface closest to the plasma membrane, visualizing the arrangement of cellulose fibrils in the native wall, without artifacts induced by dehydration or extraction of matrix components. We visualized individual fibrils as small as 2-3 nm in diameter and bundles of many fibrils that split or merged in complicated patterns. These images suggest that fibril bundling is of key significance for wall structure and cohesiveness. With AFM we can also probe cell wall mechanics and surface properties at nm resolution and analyze the effects of enzymes that depolymerize or unlink specific structural components of the cell wall. In initial trials we examined the effect of pectin lyase and a beta-1,4-endoglucanase on wall mechanics and wall structure at the nm scale and compared these values with changes in axial force-extension curves at large (mm) scale. The two sets of measurements

differ in time scale and the force direction, thus complicating their comparison. With these combined approaches we are set to test current models of plant cell wall structure.

P1-C10 - MOLECULAR ELECTROCATALYSTS FOR HYDROGEN PRODUCTION AND OXIDATION

[CME] Jenny Y. Yang¹, Uriah J. Kilgore¹, Monte Helm¹, Stuart E. Smith¹, John A. Roberts¹, Michael P. Stewart¹, Douglas P. Pool¹, Daniel L. DuBois¹, Mary Rakowski DuBois¹, and R. Morris Bullock¹

¹*Pacific Northwest National Laboratory*

Catalysts capable of inter-converting electrical energy and chemical fuels are important for a future flexible and sustainable energy supply. Hydrogen has been proposed as a medium for energy storage, transport, and as a chemical reductant to generate other chemical fuels. The design of efficient and fast inorganic catalysts with abundant, inexpensive metals for hydrogen production and utilization requires consideration of both the first and second coordination spheres. Both of these are known to be essential to the active sites of Hydrogenase enzymes found in Nature. Our research has focused on nickel bis(diphosphine) complexes with pendant nitrogen bases incorporated into the ligand backbone. Pendant amines functioning as proton relays in the secondary coordination sphere are essential to controlling the proton inventory at the nickel active site. The highly modular nature of the ligands has permitted synthetic modifications that affect thermodynamic and proton transport properties, and has resulted in improvements in both efficiency and rate for hydrogen production and oxidation electrocatalysis. The elucidation of the structure function relationships has been enhanced by detailed NMR spectroscopic studies that expand our understanding of the mechanism and rate of intra- and intermolecular proton transfer. This has led to new ligand designs that display catalyst activities that exceed the rates observed for the Hydrogenase enzymes for hydrogen production.

P1-C11 - Ni(II) COMPLEXES FOR HYDROGEN OXIDATION AND HYDROGEN PRODUCTION: AN AB-INITIO MOLECULAR DYNAMICS INVESTIGATION

[CME] Raugei Simone¹, Chen Shentan¹, Ho Ming-Hsun¹, Rousseau Roger¹, Dupuis Michel¹, DuBois Daniel, and Bullock R. Morris¹

¹*Pacific Northwest National Laboratory*

Recent advances in Ni-based bio-inspired catalysts prepared in the Center for Molecular Electrocatalysis demonstrated the possibility of cleaving H₂ or generating H₂, with high turnover frequencies. In these catalysts the transformation between H₂ and protons involves the interaction of H₂ with both the Ni(II) center and pendant amines incorporated in a six-membered ring, which act as proton relays. By using DFT calculations and hybrid QM/MM simulations, we have characterized both catalysts for H₂ oxidation and H₂ production designed at our EFRC. Results indicate that for H₂ oxidation, the loss of H₂ translational entropy upon binding to the metal center is a major energetic bottleneck. Conversely, the entropic gain upon release of molecular hydrogen is an important driving force for H₂ production. In the case of H₂ oxidation, once the H₂ molecule enters the coordination sphere of the metal, it quickly forms a Ni(II) proton-hydride species with N-H and Ni-H bonds, which further evolves with an even lower barrier toward a Ni(0) di-proton intermediate. The same species are also involved in the H₂ production. The overall chemistry of the Ni[P₂N₂]₂ complexes is understood in terms of the ability of the P and N substituents to tune the pK_a of the amines and the metal center hydricity. [1] Yang et al. Chem. Commun., 46, 8618 (2010). [2] Chen et al. J. Phys. Chem. A 114, 12716 (2010). [3] Dupuis et al. J. Phys. Chem. A (in press).

P1-C12 - TEMPERATURE AND IONIC STRENGTH EFFECTS ON THE CHLOROSOME LIGHT-HARVESTING ANTENNA COMPLEX

[PARC] Joseph K.-H. Tang¹, Liyong Zhu¹, Volker S. Urban², Aaron M. Collins¹, Pratim Biswas¹, and Robert E. Blankenship¹

¹*Washington University in St. Louis* and ²*Oak Ridge National Laboratory*

Chlorosomes, the peripheral light-harvesting antenna complex from green photosynthetic bacteria, are the largest and one of the most efficient light-harvesting antenna complexes found in nature. In contrast to other light-harvesting antennas, chlorosomes are constructed from more than 150,000 self-assembled bacteriochlorophylls, and contain relatively few proteins, which play secondary functional roles. These unique properties have led to chlorosomes as an attractive candidate for developing biohybrid solar cell devices. Here, we investigate the temperature and ionic strength effects on the viability of chlorosomes from the photosynthetic green bacterium *Chloroflexus aurantiacus* using small-angle neutron scattering and dynamic light scattering. Our studies indicate that chlorosomes remain intact up to 75 °C, and that increases in ionic strength induce the formation of large aggregates of chlorosomes. No internal structural changes are observed for the aggregates. The salt-induced aggregation, which is a reversible process, is more efficient with divalent metal ions than with monovalent metal ions. Moreover, with treatment at 98 °C for 2 minutes, the bulk of the chlorosome pigments are undamaged, while the protein baseplate is destroyed. Chlorosomes without the baseplate remain rod-like in shape, but are 30-40% smaller than with the baseplate attached. Further, chlorosomes are stable from

pH 5.5 to 11.0. Together, our studies have enabled elucidation of properties that are not only important to understanding the functionality of chlorosomes but also useful in designing biohybrid devices for effective light harvesting.

P1-C13 - SYNTHESIS AND CHARACTERIZATION OF NANO-BIOHYBRID LIGHT HARVESTING COMPLEXES FOR SOLAR UTILIZATION [PARC] Woo-Jin An¹, Joseph K.H. Tang¹, Robert E. Blankenship¹, and Pratim Biswas¹

¹Washington University in St. Louis

Dye-sensitized solar cells (DSSCs) were inspired by photosynthesis which converts solar energy into photochemical energy.¹ For highly efficient energy conversion, it is necessary to harvest light over a wide spectrum. However, DSSCs usually employ a single dye molecule that can only absorb photons within a limited light spectrum in the visible light range. Chlorosomes, which are natural photosynthetic assemblies, are perfectly suited to capture photons and funnel them towards a reaction center for charge separations. Recently, a novel biohybrid light harvesting complex was designed and employed in a photovoltaic cell device.² Artificial reaction centers, black dye molecules, and natural light-harvesting antenna complexes, chlorosomes were sequentially deposited onto the TiO₂ surface by electrospray. This combination of a black dye molecule and a chlorosome satisfied the FRET (Förster resonance energy transfer) model, absorbing photons ranging from UV (ultraviolet) to NIR (near infrared) light spectrum. Quantum dots (QDs) are strong candidates for serving as artificial reaction centers. The light absorption spectrum of QDs can be tuned to accept energy transferred from chlorosomes by changing its size. In this study, the electrospray system was employed to characterize the size of QDs as well as deposit them onto the nanostructured metal oxide surface. Using an electrospray system, deposition of quantum dots can be precisely controlled. Furthermore, innovative and improved design of the bio-hybrid solar cells will be presented. REFERENCES [1] O'Regan, B. and Grätzel, M. A low-cost and high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* 353, 737-740 (1991). [2] Modesto-Lopez, L. B., Thimsen, E. J. Collins, A. M., Blankenship, R. E. and Biswas, P. Electrospray-assisted characterization and deposition of chlorosomes to fabricate a biomimetic lightharvesting device. *Energy & Environ. Sci.* 3, 216-222 (2010).

P1-C14 - STRUCTURE-PROPERTY RELATIONSHIPS OF PHOSPHONATE-BASED RUTHENIUM(II) BIPYRIDINE DYES ON NANOCRYSTALLINE TiO₂ IN AN AQUEOUS ENVIRONMENT

[UNC] Kenneth Hanson¹, M. Kyle Brennaman¹, Hanlin Luo¹, Mike Norris¹, Christopher Glasson¹, Javier J. Concepcion¹, Wenjing Song¹, and Thomas J. Meyer¹

¹UNC

In dye-sensitized solar cells (DSSCs) and dye-sensitized photoelectrosynthesis cells (DSPECs), light absorption and charge separation events occur at a chromophore bound to a metal oxide film. Charge separation efficiency, rate, and lifetime depend intimately on molecule-metal oxide interfacial structure. A single chromophore, e.g. ruthenium tris(bipyridine), can have a number of different possible binding modes to the metal oxide particle which can have a significant impact of the performance of DSSCs and DSPECs. In this poster we present a comparative study of various phosphonated [Ru(bpy)₃]²⁺ derivatives on nanocrystalline TiO₂ focusing on mono, bis and tris 4,4'-phosphonated bipyridine derivatives with and without a methylene spacer between the ligand on ruthenium and the phosphonate linker. How these different binding motifs affect surface coverages, adsorption affinities, injection yields, back electron transfer rates, and photo/electrochemical stabilities in aqueous environments are presented.

P1-D01 - AUTONOMIC PROTECTION, REPAIR, AND SHUTDOWN OF LI-ION BATTERIES

[CEES] B. Blaiszik¹, M. Baginska¹, S. Odom¹, E. Jones¹, S. Kang¹, A. Abouimrane², W. Weng², Z. Zhang², J. Moore¹, S. White¹, N. Sottos¹, and K. Amine¹

¹University of Illinois Urbana Champaign and ²Argonne National Laboratory

In natural materials, external stimuli autonomically trigger dynamic responses from the biological system (i.e. self-healing, cooling, cell removal) to maintain internal homeostasis. In most synthetic materials, similar responses do not exist. However, a new class of synthetic materials incorporates autonomic functionality to address a broad spectrum of engineering challenges. In this work, we investigate the application of this material concept to Li-ion batteries. The research presented in this poster is divided into three sections: 1) self-repair and protection of Li-ion batteries for increased lifetime, 2) autonomic shutdown of overheating Li-ion batteries for enhanced safety, and 3) investigation of electrode mechanical behavior for an improved understanding of failure mechanisms. The key accomplishments featured in this poster include the demonstration of thermally-induced shutdown of Li-ion coin cells operating above a target temperature, the preparation of microcapsules containing conductive cores, the first demonstration of autonomic restoration of conductivity in a damaged electronic circuit, the synthesis of new additives for the stabilization of high-energy cathodes, and the development of new redox shuttles for batteries operating in overcharge conditions.

P1-D02 - CENTER FOR ELECTRICAL ENERGY STORAGE: AN OVERVIEW

[CEES] M. Thackeray¹, P. Fenter¹, J. Elam¹, L. Curtiss¹, H. Kung², M. Hersam², A. Gewirth³, and J. Moore³
¹Argonne National Laboratory; ²Northwestern University and ³University of Illinois Urbana Champaign

The Center of Electrical Energy Storage (CEES) seeks to acquire, through experiment and theory, a fundamental understanding of interfacial, transport and associated bulk phenomena controlling electrochemical processes that ultimately will enable dramatic improvements in the safety and performance of energy storage devices, notably lithium batteries. The CEES research program is organized into four inter-related efforts: the design, synthesis, and electrochemical evaluation of three-dimensional electrode/electrolyte interfaces; the safe shutdown of dangerously operating batteries and the extension of battery lifetime through protection using redox shuttles and additives and with electronic self-healing; the development of a direct understanding of the structure and processes that take place at the electrode-electrolyte interface through modeling and *in-situ* measurements and a cross-cutting theory effort that seeks to model the structure and processes that take place at the electrode-electrolyte interface. These efforts seek to identify approaches and concepts that may radically improve the synthesis and design of novel, stabilized electrode-electrolyte architectures and the characterization of electrochemical processes at the interface.

P1-D03 - 'CLICK' IMMOBILIZATION OF CATALYSTS ON ELECTRODES

[CETM] Christopher E. D. Chidsey¹, Vadim R. Ziatdinov¹, and Ali Hosseini¹
¹Stanford University

The Cu(I)-catalyzed azide alkyne coupling (CuAAC) reaction to form 1,2,3-triazole linkers [1,2] is a fast, mild and selective 'click' reactions for the covalent attachment of molecular electrocatalysts to electrode surfaces [3]. We have investigated the kinetics and ability to control of the CuAAC reaction. We find the reaction can be switched on electrochemically by reduction of Cu(II) to Cu(I), but that the dependence of the rate on the copper concentration shows as yet unexplained threshold and saturation behaviors. The azide-modification of graphitic carbon electrodes with iodine azide [4] has been adapted to a simple vapor-deposition procedure immediately following heat-treatment of the carbon. This method has been shown to install azide groups cleanly on glassy carbon surfaces for convenient electroanalytical studies of electrocatalysts and on carbon black powders (Vulcan XC-72R) for use in polymer electrolyte fuel cells. [1] Rostovtsev, V. V., Green, L. G., Fokin, V. V., and Sharpless, K. B., *Angew. Chem., Int. Ed.*, 41, 2596-2599, (2002). [2] Tornøe, C. W., Christensen, C., and Meldal, M., *J. Org. Chem.*, 67, 3057-3064, (2002). [3] Collman, J. P., Hosseini, A., Eberspacher, T. A., and Chidsey, C. E. D., *Langmuir*, 25, 6517-6521, (2009). [4] Devadoss, A., and Chidsey, C. E. D., *J. Am. Chem. Soc.*, 129, 5370-5371, (2007)

P1-D04 - SURFACE-MODIFIED SILICON NANOSTRUCTURES FOR ENHANCED ENERGY STORAGE

[CST] Justin T. Harris¹, Sankaran Murugesan¹, Anthony Dylla¹, Aaron M. Chockla¹, Keith J. Stevenson¹, and Brian A. Korgel¹
¹University of Texas at Austin

High energy density storage materials are crucial for numerous battery applications, including electric vehicles, and there has been big impetus to increase both the specific energy density and power in such batteries. Silicon has the largest known specific capacity per weight of any material (4,200 mAh/g). However, if used in a Li-ion battery, bulk silicon degrades significantly upon reversible alloying/dealloying with lithium due to large volumetric changes. This work reports on the synthesis and characterization of surface-modified silicon nanostructures, which offer several advantages including: (1) enhanced charge transfer kinetics and reduced charge transfer resistance, (2) more reversible and increased charge storage capacity, and (3) improved tolerance to volumetric expansion/contraction processes. In particular, we describe the development of a surface metallization process to facilitate the formation of electronically conducting networks that lead to an enhanced charge storage capacity of a factor of 10 over that observed for pristine Si nanostructures. We also present high-resolution interfacial spectroelectrochemical studies involving both Raman and FTIR spectroscopies for elucidation of failure mechanisms of silicon based electrodes that provide insight for solving the problem of low Coulombic efficiency and capacity fading on cycling, which have now enabled new materials design strategies for utilization of these energetic materials for advance energy storage.

P1-D05 - COMPUTATIONAL MODELING OF CAPACITIVE CHARGE STORAGE IN NANOSTRUCTURED OXIDES

[MEEM] Fei Zhou¹ and Vidvuds Ozolins¹¹UCLA

We have studied the supercapacitive energy storage in hydrous RuO₂, a prototypical and high-performing supercapacitor material, with first-principles calculations. First, we have studied the surface redox reaction of RuO₂ with proton, and discovered that the surface is oxygen-covered at normal conditions. The computed surface redox voltage is in good agreement with experiment. Our theory predicts that the kinetics of proton transport is hindered by high activation barrier of hydroxyl dimer rotation in ruthenia, implying that charge storage is likely limited to sub-surface redox reactions. Another accomplishment is to clarify the structure of hydrous RuO₂, which has not yet been settled definitively in experiment. Knowledge about this structure is crucial to understand the charge storage and transport process. We find that water incorporation into the bulk RuO₂ oxide is energetically highly unfavorable. Instead, water is predicted to agglomerate outside bulk RuO₂, supporting the picture of microscopic charge transport with nanocrystalline RuO₂ cores and structural water at the grain boundaries. The interfacial energy of RuO₂ oxide and water is estimated to be very low, which may explain the large surface area of ruthenia oxide in the hydrated form.

P1-D06 - EXPLORING ELECTROCHEMICAL PROCESSES OF METAL FLUORIDE/OXYFLUORIDE NANOCOMPOSITES AS CATHODE MATERIALS FOR LI ION BATTERIES

[NECCES] Lin-Shu Du¹, James P. Pastore¹, Clare P. Grey¹, Feng Wang², Yimei Zhu², Jason Graetz², Andrew Gmitter³, Nathalie Pereira³, Glenn G. Amatucci³, Olaf Borkiewicz¹, Karena W. Chapman¹, and Peter J. Chupas¹¹Stony Brook University; ²Brookhaven National Laboratory and ³Rutgers University

Carbon metal fluoride/oxyfluoride nanocomposites are potential positive electrode materials in rechargeable Li ion batteries due to their high energy densities [1]. These materials react via conversion reactions which involve multi-electron transfers per redox center during lithiation. Although they have shown promising specific capacities, there are still issues, such as poor capacity retention, which prevent commercialization. Details of the electrochemical processes, phase distributions are valuable information to understand how to maintain Li ion and electron percolation throughout the phase evolution. Nuclear magnetic resonance (NMR) spectroscopy and pair distribution analysis (PDF) are essential methods for probing short- and intermediate-range structure, making them ideal tools for exploring the electrochemistry of these nanocomposites [2,3]. In this study, ¹⁹F NMR techniques were performed to monitor the speciation of metal fluorides/oxyfluorides and electrochemically formed lithium fluoride (LiF) during cycling. The evolution of the degree of disorder and phase transformation of the electrode materials upon cycling were further examined by PDF analysis. The phase distribution between metal oxyfluoride/fluorides and LiF can be probed by 2-D magnetization exchange NMR experiments. Transmission electron microscopy, electron energy-loss spectroscopy can provide high-resolution (at 1 nm scale) compositional mapping of the primary phases in the pristine and fully discharged electrode materials [4]. In iron fluoride and tin fluoride systems, metal/metal fluoride and lithium fluoride domains are well dispersed, whereas they are well separated in copper fluoride and bismuth fluoride systems.[1] G.G. Amatucci, N. Pereira, C. J. Fluorine Chem., 128, 243 (2007).[2] N. Yamakawa, M. Jiang, and C.P. Grey, Chem. Mater., 21, 3162 (2009). [3] N. Yamakawa, M. Jiang, B. Key, and C.P. Grey, J. Am. Chem. Soc., 131, 10525 (2009). [4] F. Wang, et. al., Conversion Reaction Mechanism in Lithium Ion Batteries: Study of the Iron (II) Fluoride Electrode, submitted to J. Am. Chem. Soc.

P1-E01 - HIGH EFFICIENCY NONPOLAR AND SEMIPOLAR INGAN LEDs

[CEEM] James Speck¹, Ravi Shivaraman¹, Elison Matioli¹, Dobri Simenov¹, Steve DenBaars¹, Shuji Nakamura¹, and Claude Weisbuch¹¹UCSB

In this poster we review highlights of our work on nonpolar and semipolar GaN-based light emitting diodes. We focus on understanding fundamental issues in compositional homogeneity of the InGaN quantum wells in reference c-plane, nonpolar and semipolar full LED structures. We have investigated, by Local Electrode Atom Probe Analysis, the Indium incorporation and homogeneity as well as the physical roughness and chemical diffuseness of the GaN/InGaN interface in the case of various InGaN quantum wells grown on m-plane, c-plane and semipolar (20-21) GaN templates. The Indium distribution in the InGaN quantum wells was found statistically homogeneous in all cases. However, in most cases the top interface was found to possess greater roughness and larger value for the 90%-10% Indium interfacial width than the bottom one. Additionally, we present results on photonic crystals in m-plane LEDs that have both high light extraction efficiency and additionally preserve light polarization. Finally, we demonstrate a method for bonding nitride based LEDs to antimony doped tin oxide templates. The resulted LEDs exhibit electrical properties on parity with conventional LEDs with indium-tin-oxide transparent contacts. The forward voltage at 20 mA is 3.96 V and differential resistance at 100 mA is as low as 16 Ω . This current-carrying bonding procedure is interesting both for fabrication of more complex LEDs and solar cells.

P1-E02 - TOWARDS ACCURATE THERMOCHEMICAL KINETICS OF BIODIESEL COMBUSTION FROM MULTIREFERENCE CONFIGURATION INTERACTION CALCULATIONS

[CEFRC] Victor Oyeyemi¹, Ting Tan¹, Michele Pavone¹, and Emily A. Carter¹
¹Princeton University

Biodiesel has recently re-emerged in importance as a renewable transportation fuel. Biodiesel is ideally carbon neutral and it has the attractive feature of burning in a cleaner fashion than petro-diesel. However, the details of biodiesel combustion are still uncertain. To elucidate the detailed chemistry, chemical kinetics models are constructed in concert with measurements. These models are made up of elementary reactions whose thermochemical parameters must be known accurately. To this end, we report the development and validation of an *ab initio* approach to determine these parameters with deviations no greater than ~ 1 kcal/mol from experiments. We use the multireference singles and doubles configuration interaction method with complete basis set extrapolation for electronic energies, together with the B3LYP exchange-correlation density functional within density functional theory for molecular structures and vibrational frequencies. We do not resort to any empirical parameter to correct energies, in contrast to methods that are currently standard for thermochemistry. We first focus on the prediction of a key thermochemical parameter, the bond dissociation energy (BDE). Validation against reliable experimental values shows that our scheme approaches chemical accuracy on average. Directions for further improvement of our method performance are also outlined. Finally, we report accurate BDEs for biodiesel surrogate molecules, including methyl crotonate and methyl butanoate.

P1-E03 - THERMAL ANALYSIS OF HIGH INTENSITY OLEDs USING A TRANSMISSION MATRIX APPROACH

[CEN] Xiangfei Qi¹ and Stephen Forrest¹
¹University of Michigan

We introduce a general model to determine the thermal excursion of organic light-emitting diodes (OLEDs) under high current normally encountered in ultra-bright illumination conditions using a transmission matrix approach. This new approach facilitates the calculation of transient coupled heat transfer in a complex, multi-layer composite characteristic of high intensity OLED structures. It is based on a method of converting the partial differential equations governing heat transfer into a simplified algebraic form. Model calculations are compared with experimental data on a set of 25cm^2 OLEDs under various current pump conditions. This model is easily extended to study complex OLED structures under a wide variety of conditions that include heat removal via conduction, radiation and convection. We discuss the effects of using high-thermal-conductivity substrates, transient thermal response under pulsed current operation, and multi-junction (i.e. stacked) emitters.

P1-E04 - PAIRS AND VORTICES ABOVE AND BELOW T_C [CES] Wai-Kwong Kwok¹, Ulrich Welp¹, George Crabtree¹, Mike Norman¹, Juan Atkinson¹, Dale Van Harlingen², Raffi Budakian², Gregory Polshyn², Peter Johnson³, and Seamus Davis^{3,4}
¹Argonne National Laboratory; ²University of Illinois at Urbana-Champaign; ³Brookhaven National Laboratory and ⁴Cornell University

Superconductors are described by an order parameter (OP) defined through its amplitude and a phase. Vortices are defects in the OP characterized by the "winding" of the OP phase in quantized units of 2π around the vortex core. This quantization reflects the fact that the quantum mechanical wave function of the Cooper pairs is coherent in the region surrounding the vortex core. In the cuprate superconductors, there exists a hierarchy of temperature scales characterizing the emergence of the superconducting state. At the highest temperatures, local Cooper pairing begins. At lower temperatures, diamagnetic fluctuations begin. Below T_c , phase rigidity appears over macroscopic lengthscales. It is thought above T_c , in the pseudogap (PG) regime, rapid phase fluctuations disrupt long-range phase coherence and destroy superconductivity. Understanding the connection between the PG regime and the superconducting states may point to a way of stabilizing superconductivity to much higher temperatures. To understand the nature of the PG state, we have assembled a diverse suite of complementary experimental techniques capable of probing PG regime. Scanning tunneling microscopy will be used to provide local spectroscopic information in the PG regime. Vortices provide an ideal lens to probe phase coherence in a microscopic region of the sample. To search for the existence of vortices, various transport geometries as well as ultrasensitive cantilever magnetometry measurements will be employed.

P1-E05 - NEW SUPERCONDUCTORS BY DESIGN

[CES] Wai Kwon Kwok¹, Tony Leggett², Laura Greene², Philip Phillips², Cedomir Petrovic³, Ivan Bozovic³, Peter Abbamonte², Mao Zheng², Weicheng Lee², Yize Li², James Lee², and Jim Eckstein²

¹Argonne National Lab; ²University of Illinois, Urbana-Champaign and ³Brookhaven National Lab

There are now two distinct paradigms for designing a high-temperature superconductor: 1) copper-based or 2) iron-based. This diverse group is interested in answering the question: Are there additional pathways by which the superconducting transition temperature can be increased? While several approaches are being explored, the most promising involves an approach which attempts to combine the distinct elements of the copper and iron-based materials into a single superconductor. Copper-based superconductivity arises from a single d-electron per copper that strongly interacts with all the other electrons. In the iron-based systems, several d-electrons are present and the interactions are considerably weaker. The open question is what happens when these two ingredients are combined. To this end, we are exploring ways to engineer strongly correlated multi-d electron systems that exhibit superconductivity. Promising materials being studied include $A_v\text{Fe}_{2-x}\text{Te}$ (A=Ti, Cs, K) and $A_2\text{O}_3\text{Fe}_2\text{M}_2$ (A=La, Y) and (M=Se, S, Te). Several doping schemes are being explored and interfacial systems based on multi-orbital Mott physics will also be synthesized.

P1-E06 - ATOMIC CONFIGURATION STUDIES IN CUBIC AND TETRAGONAL YTTRIA-STABILIZED ZIRCONIA

[HeteroFoaM] Hepeng Ding¹ and Feng Liu¹

¹University of Utah

YSZ is the leading choice of material used as electrolyte in SOFC. However, many fundamental properties of YSZ associated with its fuel cell application are not fully understood. For example, the YSZ exhibits the maximum ionic conductivity at 15%-18% $\text{YO}_{1.5}$, which was suggested to have two possible origins: 1) the number of high-energy Y-Y pathways increases with the increasing Y concentration; 2) oxygen vacancies form ordered alignments which inhibit the diffusion of oxygen vacancy at high Y concentration. However, there still exist large amount of discrepancies among the existing theoretical and experimental works in the literature. In this work, we have performed extensive first-principles DFT calculations to investigate the detailed atomic configurations of defects in cubic and tetragonal phases of YSZ, as a function of Y concentration. Furthermore, we reveal a correlation between the atomic configuration of O vacancy and the stability of YSZ as a function of Y concentration, which helps to better understand the phase transition from the cubic to tetragonal phase at certain Y concentration range.

P1-E07 - SOLID-STATE LIGHTING: AN ENERGY ECONOMICS PERSPECTIVE

[SSLS] JY Tsao¹, HD Saunders², JR Creighton¹, ME Coltrin¹, and JA Simmons¹

¹Sandia National Laboratories and ²Decision Processes Incorporated

Artificial light has long been a significant factor contributing to the quality and productivity of human life. As a consequence, we are willing to use huge amounts of energy to produce it. Solid-state lighting is an emerging technology that promises performance features and efficiencies well beyond those of traditional artificial lighting, accompanied by potentially massive shifts in (a) the consumption of light, (b) the human productivity and energy use associated with that consumption, and (c) the semiconductor chip area inventory and turnover required to support that consumption. In this paper, we provide estimates of the baseline magnitudes of these shifts using simple extrapolations of past behavior into the future. For past behavior, we use recent studies of historical and contemporary consumption patterns analyzed within a simple energy-economics framework (a Cobb-Douglas production function and profit maximization). For extrapolations into the future, we use recent reviews of believed-achievable long-term performance targets for solid-state lighting. We also discuss ways in which the actual magnitudes could differ from the baseline magnitudes of these shifts. These include: changes in human societal demand for light; possible demand for features beyond lumens and guidelines and regulations aimed at economizing on consumption of light and associated energy.

P1-E08 - ON THE SYMMETRY OF EFFICIENCY-VERSUS-CARRIER-CONCENTRATION CURVES IN GAINN/GAN LIGHT-EMITTING DIODES AND RELATION TO DROOP-CAUSING MECHANISMS

[SSLS] Qi Dai¹, Qifeng Shan¹, Jaehee Cho¹, E. Fred Schubert¹, Mary H. Crawford², and Daniel D. Koleske²

¹Rensselaer Polytechnic Institute and ²Sandia National Laboratories

Lighting technologies based on GaN light-emitting diodes (LEDs) offer unprecedented promises that include three major benefits: (i) Gigantic energy savings enabled by efficient conversion of electricity to light; (ii) Substantial positive contributions to sustainability through reduced emissions of global-warming gases and toxic substances and (iii) The creation of new paradigms in lighting driven by the unique controllability of solid-state lighting sources. Due to the powerful nature of these benefits, the transition from conventional lighting sources to solid-state lighting is very likely. One of the preeminent technical obstacles of GaN-based LED is the "efficiency droop". The efficiency droop is the gradual decrease of the internal quantum efficiency (IQE) as the carrier concentration (n) in the active region of a LED increases. The IQE-

versus-n curves of GaN-based light-emitting diodes have been frequently described by the ABC model: $IQE = Bn^2 / (An + Bn^2 + Cn^3)$. We show that this model predicts IQE-versus-n curves that have even symmetry. Phase-space filling makes the B and C coefficients concentration-dependent. We also show that IQE-versus-n curves that take into account phase-space filling possess even symmetry. In contrast, experimental IQE-versus-n curves exhibit asymmetry. The asymmetry requires a 4th-power or higher-power contribution to the recombination rate and provides insight into the droop-causing mechanisms.

P1-F01 - MULTISCALE NUMERICAL METHODS FOR MODELING THE EARTH'S SUBSURFACE

[CFSES] Benjamin Ganis¹, Gergina Pencheva¹, Mary Wheeler¹, Todd Arbogast¹, Hailong Xiao¹, Guangri Xue¹, Mojdeh Delshad¹, and Xianhui Kong¹

¹University of Texas at Austin

The challenges associated computational modeling of CO₂ sequestration involve complex phenomena over disparate length and time scales at conditions far from equilibrium. In this poster we showcase three computational developments to cope with the size, difficulty, and accuracy of these systems: (1) A Homogenization-Based Mortar Domain Decomposition Method gives an efficient parallel algorithm for computing an accurate flow velocity; (2) A Frozen Jacobian Preconditioner for Nonlinear Interface Problems gives a way to speed up the convergence of a complex interface iteration with multiphase flows and (3) Modeling the Effect of Interfacial Tension on CO₂ Trapping and Migration shows how we can incorporate a critical microscopic scale phenomena that strongly affects the behavior and distribution of CO₂ in large-scale geologic systems.

P1-F02 - THE COUPLED EFFECTS OF MICROBIAL AND PHYSIC-CHEMICAL PROCESSES ON GEOLOGICAL CARBON STORAGE

[CFSES] Matthew Kirk¹, Susan Altman¹, Philip Bennett², Bayani Cardenas², Thomas Dewers¹, Mojdeh Delshad², Eugenio Santillan², Wen Deng¹, Kuldeep Chaudhary¹, and Hongku Yoon¹

¹Sandia National Laboratories and ²University of Texas at Austin

Geological carbon storage has been identified as a strategy to help limit accumulation of carbon dioxide in the atmosphere. The long-term success of storage in reservoirs will depend heavily on the chemical and physical properties of the subsurface. Biological controls are also important to consider, however, because microorganisms strongly influence the chemical and physical properties of the subsurface. Our research examines the interplay between carbon storage and microbiology from both sides. We consider: (1) whether the ability of bacteria to survive stress due to high carbon dioxide levels will vary with reservoir mineralogy, (2) if geochemical changes resulting from carbon injection can alter the balance between subsurface microbial reactions, and (3) whether microbial biofilms attached to the reservoir solid matrix will have significant effects on brine and supercritical CO₂ flow through pores. We are also developing numerical simulations that will improve our understanding of biofilm growth in porous medium and how to apply pore-scale observations to field scale applications. Our ultimate goal is to contribute to strategies that will enhance carbon storage by learning about the fundamental relationships between subsurface microbiology and injected carbon dioxide.

P1-F03 - FLEXIBLE POROUS FRAMEWORK MATERIALS FOR CARBON CAPTURE

[CGS] Daqiang Yuan¹, Jinhee Park¹, Weigang Lu¹, Jian-Rong Li¹, and Hong-Cai Zhou¹

¹Texas A&M University

Flexible porous framework materials are excellent candidate for the separation for CO₂. Recently, we designed and synthesized some novel flexible MOFs, which can respond to external stimuli, such as pressure, temperature, light, and guest molecules. Firstly, temperature-responsive selective gas adsorption was observed in some MAMS materials, and these properties were further demonstrated to be related to the activation conditions of the material. Based on detailed activation-adsorption investigations, a mechanism for explaining the observed selective adsorption properties for these materials was proposed, as "diffusion-controlled kinetic gating effect". Secondly, a rare flexible MOF with optically and thermally controllable gas uptake is presented. Azobenzene moiety which can switch its conformation upon light irradiation or by heat is introduced to the organic linker. The gas accessible site change during the isomerization of the ligand in a MOF-5 type crystal is achieved and confirmed by gas adsorption measurement. Finally, a type of pure-organic porous materials with high stability and tailorability, called porous polymer networks (PPNs), has been developed for gas separations. Three new PPNS with functionalized pore surface were revealed to be highly selective for CO₂ over N₂ adsorption at room temperature. Breakthrough experiments also showed the high separation ability of these materials for the mixed gases.

P1-F04 - SUB-NANOMETER POROUS MEMBRANES WITH MOLECULAR LEVEL CONTROL OVER PORE CHEMISTRY FOR GAS SEPARATION

[CGS] Rami Hourani¹, Nana Zhao¹, Rob van der Weegen², Beverly Zhang¹, Brett A. Helms², and Ting Xu^{1,2}
¹University of California, Berkeley and ²Lawrence Berkeley National Laboratory

Thin films containing sub-nanometer channels aligned normal to the surface constitute promising materials for selective separation and transport to meet growing demands in renewable energy, environmental sustainability and life sciences. As membrane selectivity is determined by the shape, size, and surface chemistry of the channels, fabricating membranes with molecular level control over transport is highly desirable, yet non-trivial. We have developed a new approach to generate sub-nanometer porous membranes by co-assembling cyclic peptide nanotubes with diblock copolymers in thin films. This process takes full advantage of nanoscopic assembly of copolymers and the reversibility of organic nanotube growth. Our recent efforts aim to design and synthesize cyclic peptide nanotubes with tunable size, shape and surface chemistry. As a first demonstration, an artificial amino acid was incorporated in the primary peptide sequence. NMR, CD and TEM confirmed molecular modifications of the interior of nanotubes with diameters ranging from 0.4-1.5nm. This new family of peptide nanotubes exhibit reversible assembly process, and is fully compatible with polymer processing, thus opens up new avenues toward molecularly defined organic nanotubes for polymeric membrane fabrication.

P1-F05 - BIOLOGICAL AND BIOMIMETIC APPROACHES TO CONTROL CARBONATE MINERALIZATION

[NCGC] Jenny Cappuccio¹, Chun-Long Chen¹, Joanne Emerson², Jillian Banfield², Jim DeYoreo¹, Ronald Zuckermann¹, and Caroline Ajo-Franklin¹
¹Lawrence Berkeley National Laboratory and ²University of California, Berkeley

Geologic CO₂ sequestration will be an essential component of global climate change mitigation. Carbonate minerals are an effective form of stable CO₂ storage, but their formation occurs on a geologic, rather than a human timescale. This work explores biological and biologically-inspired approaches towards enhancing carbonate mineralization so as to improve CO₂ storage security. We take a two-pronged approach to explore how biological systems can be used to control mineralization. First, we have initiated studies examining microbial communities from both naturally-occurring CO₂ rich environments and CO₂ sequestration sites. Secondly, we have explored how different environmentally prevalent bacteria affect mineralization rates. We find that many microbial surfaces bind Ca²⁺ and thus accelerate the rate at which calcite nucleates. Our data suggest that many microbes will have a profound impact on the kinetics of carbonate mineralization in geologic reservoirs. In our biomimetic approach, we have shown that non-natural polymers, peptoids, impact CaCO₃ mineralization by controlling crystal growth morphology. The CaCO₃ crystals grown in the presence of peptoid variants exhibit a number of unique morphologies ranging from elongated spindles to spheres. In addition to altering morphology, peptoids dramatically impact growth rates at low concentrations. Thus, our data suggest that peptoid-based biomimetics can be developed to direct the timing and rate of carbonate crystallization

P1-G01 - SYNTHESIS AND CHARACTERIZATION OF HCP METALS WITH CONTROLLED DISLOCATION STRUCTURES

[CDP] Masafumi Tsunekane¹ and Sharvan Kumar¹
¹Brown University

The overall objectives of this research effort are to i) synthesize and characterize single and bicrystals of a model HCP metal like Mg, ii) design appropriate specimen geometry, and iii) determine suitable deformation conditions that will enable measuring the field of a stationary and a moving dislocation in the crystal and its interaction with another defect such as a grain boundary. Thus, Mg single crystals have been deformed off C-axis to activate basal slip only and the resulting dislocation structures are being characterized by TEM to determine spacing between loops on a single slip plane as well as between parallel planes. We also propose to use a sharp notch in a single crystal as a dislocation source, align the basal planes at an angle to the notch and take advantage of the fact that stress decays ahead of the notch tip with distance. White light interferometry/AFM methods will be used to map surface relief where dislocations have emerged from the specimen surface after loading. This will provide a "marker" for subsequent *in-situ* experiments in the synchrotron beamline and enable identifying an appropriate location for focusing the beam to enhance the probability of encountering a single dislocation about to emerge at the surface. A similar geometry is also being designed for a bicrystal to address unit dislocation-grain boundary interaction. Progress to date in these areas will be presented.

P1-G02 - ELECTROCALORIC EFFECT IN LiNbO₃ AS FUNCTIONS OF PRESSURE AND TEMPERATURE

[EFree] Ronald Cohen¹, Maimon Rose¹, Qing Peng², and P. Ganesh³
¹Carnegie Institution of Washington; ²RPI and ³ORNL

First-principles computations within density functional theory (DFT) have given many insights into the properties of active materials, and have been used successfully to design new materials and predict their properties. Generally these computations are done at zero temperature, but there are questions that depend completely on the effects of temperature.

The electrocaloric effect (ECE) is the change in entropy with electric field, and clearly depends on being able to compute accurate thermal properties. The ECE can be used for a potentially very useful new energy technology. Heat pumps and refrigeration based on ECE can be chip mounted with essentially no moving parts, and actively pump heat away from heat producing circuit elements. We use a potential model fit to first-principles results, and then use molecular dynamics to find thermal properties. We have fit a shell model potentials to first-principles computations for LiNbO_3 and have successfully computed the electrocaloric effect in this way. Here we concentrate on the effects of pressure on the ECE in LiNbO_3 . Pressure has been shown to be a useful tool to better understand how to tune properties for a higher, more useful response. We show that the ECE is greatest in the phase transition region, and near critical curves in the response, and points towards the ability to optimize ECE materials for energy applications.

P1-G03 - AN INVESTIGATION OF RADIATION DAMAGE EFFECTS ON MAGNETIC STRUCTURE OF IRON

[CDP] Yang Wang^{1,2}, Malcolm Stocks³, Don Nicholson³, Roger Stoller³, and Aurelian Rusanu³

¹Pittsburgh Supercomputing Center, ²Carnegie Mellon University and ³Oak Ridge National Laboratory

A fundamental understanding of the radiation damage effects in solids is of great importance in assisting the development of improved materials with ultra-high strength, toughness, and radiation resistance for nuclear energy applications. In this presentation, we show our recent theoretical investigation on the magnetic structure evolution of bulk iron in the region surrounding the radiation defects. We applied the locally self-consistent multiple scattering method (LSMS), a linear scaling ab-initio method based on density functional theory with local spin density approximation, to the study of the magnetic structure in a low energy cascade in a 10,000-atom sample for a series of time steps for the evolution of the defects. The primary damage state and the evolution of all defects in the sample were simulated using molecular dynamics with empirical, embedded-atom inter-atomic potentials. We also discuss the importance of thermal effect on the magnetic structure evolution.

P1-G04 - MD SIMULATIONS OF FREE SURFACE EFFECTS ON ATOMIC DISPLACEMENT CASCADES.

[CDP] Yury Osetskiy¹, Andy Calder², and ¹Roger Stoller

¹ORNL and ²University of Liverpool

Recent MD simulations of cascades in bulk iron have demonstrated that a sub-picosecond shock-front is responsible for the creation of large interstitial clusters and that the major damage is created before the thermal spike phase of the cascade. A decelerating supersonic front from the primary recoil event produces an expanding volume of destroyed lattice. Modeling of surface damage has shown that the damaged microstructure depends on interaction of supersonic shock with a surface. If a shock is decelerated below sonic speed before it reaches free surface a normal bulk-like displacement cascade is formed. Large self-interstitial clusters form on the transonic boundary of this zone if a peripheral hypersonic recoil has created a secondary zone just ahead of this boundary. If a supersonic shock becomes sonic near the surface many atoms are pushed out, creating a large number of adatoms on the surface and large vacancy loops below the surface. However, if the shockwave is still supersonic when it intersects the surface, it creates a deep crater with a large rim of adatoms and less damage below the surface. Many other details are observed and discussed. An attempt is made for a direct comparison with experimental results on ion-irradiated films from earlier TEM studies and current picosecond-to-microsecond time-resolved x-ray scattering measurements of displacements.

P1-G05 - SIMULATION OF DISPLACEMENT CASCADE EVOLUTION USING MONTE CARLO METHODS

[CDP] Haixuan Xu¹, Yury Osetsky¹, and Roger Stoller¹

¹Oak Ridge National Lab

The long-term evolution of mobile point defects created in atomic displacement cascade in BCC iron is investigated using kinetic Monte Carlo (KMC) simulations. Parameters such as fraction of the initially created self-interstitial atoms that escape from the cascade region are determined. The effects of temperature, simulation box size, and rotation of interstitials are evaluated and their relative importance is discussed. Nevertheless, standard KMC techniques are insufficient to fully model the process; the evolution of complex interstitial clusters or the interaction between interstitial clusters and dislocations cannot be accurately described. To overcome these limitations, the framework of a new method including multiple techniques is developed. The new approach employs an off-lattice atomistic KMC method to evolve the system, with the evolution at each time step dictated by a saddle point search that identifies possible atom movements. In contrast to conventional KMC models, the new approach is self-evolving and any physically relevant motion or reaction may occur. Application of this self-evolving atomistic kinetic Monte Carlo (SEAK-MC) approach is illustrated by predicting the evolution of a complex interstitial cluster obtained in a molecular dynamics simulation (MD) of displacement cascades in Fe. The direct comparison with MD modelling confirms the atomistic fidelity of the new approach, while enabling much longer simulation times.

P1-G06 - LARGE SCALE DENSITY FUNCTIONAL THEORY MODELING OF MAGNETIC PROPERTIES OF SCREW DISLOCATIONS IN ALPHA-IRON

[CDP] Khorgolkhuu Odbadrakh¹, Aurelian Rusanu¹, George Stocks¹, Yang Wang², German Samolyuk¹, and Don Nicholson¹¹ORNL and ²PSC

Dislocations are central to the deformation behavior of crystalline Fe. The local magnetic moments contribute to the interactions between dislocations and between dislocations and other defects. The magnetic changes are most pronounced near the dislocation core and decay as the strain field induced by the dislocation decreases with distance. We have implemented a coarse graining procedure in order to calculate the local moments in large simulated dislocation structures from the first principles. In this scheme large a number of atoms apart from dislocation cores are represented by few real atoms, thus reducing computational costs substantially. The local moments are calculated using the Locally Self-consistent Multiple Scattering (LSMS) method. The boundary conditions for these simulations include free surfaces in order to model open boundary conditions. The LSMS is used in a manner that allows application of the LDA-DFT to the magnetic and electronic structure within a sub-volume of the much larger simulation cell. The influence of various boundary conditions on the electronic /magnetic structure are taken into account by modifying the Madelung procedure to treat periodicity in 1,2, and 3 dimensions.

P1-G07 - FOUR-DIMENSIONAL CHARACTERIZATION OF DISLOCATION-DEFECT INTERACTIONS IN THE TEM

[CDP] Virginia McCreary¹, Grace S. Liu¹, Martha Briceno¹, and Ian M. Robertson¹¹University of Illinois, Urbana

The interactions between glissile dislocations and stacking-fault tetrahedra have been investigated by conducting time-resolved experiments *in-situ* in the transmission electron microscope from ambient temperature to 700K. With increasing temperature, the interaction can result in total annihilation of both perfect and truncated tetrahedra or can transform them into another defect. Computer simulations suggest the outcome of the interaction is dependent on the dislocation type, the type of tetrahedron and the location on the tetrahedron at which the dislocation intersects it. The spatial information is not available in conventional electron microscopy. We introduce a new method for viewing the tetrahedra distribution throughout the foil along with the relative position of the dislocations using electron tomography. This three-dimensional visualization technique along with dynamic deformation experiments *in-situ* in the TEM provides the ability to discern the interactions between dislocations and obstacles in four dimensions. The results from these experiments will be presented and the implication on the formation of defect-free channels and the models for predicting mechanical properties will be discussed.

P1-G08 - QUANTITATIVE TENSILE TESTING OF MO-ALLOY NANO-FIBERS IN A TEM

[CDP] Chisholm, Claire^{1,2}, Bei, Hongbin², Oh, Jason⁴, Syed Asif, S.A.⁵, Warren, Oden L.⁵, Shan, Zhiwei^{5,6}, George, Easo P.^{4,7}, and Minor, Andrew M.^{1,2}¹University of California, Berkeley ²Lawrence Berkeley National Laboratory; ⁴Oak Ridge National Laboratory; ⁵Hysitron Incorporated; ⁶Xi'an Jiaotong University and ⁷University of Tennessee

In situ transmission-electron-microscopy (TEM) tensile testing is a powerful tool for revealing the underlying physical mechanisms of deformation in materials. Here we will discuss the development of a novel technique for quantitative, *in-situ* tensile testing of nano-structured materials inside a TEM. Molybdenum alloy nano-fibers, with tailored dislocation densities, were loaded onto a microfabricated "push-to-pull" (PTP) device and pulled in tension with a quantitative *in-situ* nanoindentation/nanocompression holder. The PTP device allows for quantitative load-displacement data to be obtained in parallel with real time images of the microstructural behavior. Results from the uniaxial tensile testing of Mo-alloy nano-fibers will be presented including observations of exhaustion hardening. With this *in situ* testing method it is possible to observe the defect evolution and directly correlate the observations with the mechanical data. The results from these quantitative *in situ* tensile tests will be discussed in relation to current models of small-scale plasticity.

P1-G09 - ATOMISTIC MODELING AND LASER EXPERIMENTS ON SHOCKED CU/NB NANOLAYERED COMPOSITES

[CMIME] Timothy C. Germann¹, Ruifeng Zhang¹, Jian Wang¹, Xiang-Yang Liu¹, Shengnian Luo¹, Weizhong Han¹, Irene Beyerlein¹, and Amit Misra¹¹LANL

Classical molecular dynamics (MD) simulations and laser and gas gun experiments are used to study the shock response of Cu-Nb nanolayered composites. We describe the development of an interatomic potential which provides an accurate description of deformation twinning in bcc Nb under compression, slip in fcc Cu, and the interface structure of Cu-Nb interfaces with the Kurdjumov-Sachs (KS) orientation relationship. The MD simulations provide insight into the role of atomic Cu-Nb interface structures on the nucleation, transmission, absorption, and storage of dislocations during shock

compression, and their role as dislocation sinks upon release. This, together with the effects of confined layer slip and twinning, leads to a greater degree of recovery as compared to either constituent Cu or Nb single crystal for layer thicknesses down to 5 nm, an effect seen both in our simulations and in companion shock experiments.

P1-G10 - GRAIN BOUNDARY RESPONSE IN SHOCKED COPPER MULTICRYSTALS: TEM CHARACTERIZATION AND ATOMISTIC MODELING

[CMIME] Alejandro Perez-Bergquist¹, Christian Brandl¹, Juan Pablo Escobedo¹, Carl Trujillo¹, Ellen Cerreta¹, George Gray III¹, and Timothy Germann¹
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To understand the role of interface structure in the extreme environment of shock loading, four different Cu grain boundaries (GBs) were studied experimentally and through atomistic simulations. These GBs were characterized prior to deformation using electron back scattered diffraction (EBSD) and transmission electron microscopy (TEM) to determine axis/angle pair relationships, interface planes, and GB structure. Samples containing these GBs were then subjected to incipient spall at 2.5 GPa and shock loading at 10 GPa, respectively, then soft recovered and characterized post-mortem via EBSD and TEM. Molecular dynamics (MD) simulations were also performed where GBs representative of those present in the experimental samples were subjected to shock loading conditions. Given similar strain rates between experiments and simulations, MD provides perspective into *in situ* damage mechanisms within the shocked crystals and also allows for improved atomic-scale GB structure analysis in conjunction with TEM. Preliminary results show that typical GBs are subject to failure during shock loading but special boundaries, such as twin boundaries, are resistant to failure. Specifically, MD simulations and experimental post-mortem GB characterization suggest that asymmetric S3 GBs can plastically relax the applied stress state by coupled GB motion, which is a possible deformation mechanism beyond direct dislocation-interface interactions such as dislocation transmission and nucleation.

P1-G11 - MICROSTRUCTURAL AND INTERFACIAL EVOLUTIONS OF CU-NB COMPOSITES SUBJECTED TO SEVERE PLASTIC DEFORMATION

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Nanolayered composite materials are promising materials for applications requiring high resistance to radiation damage or shock loading. Atomistic simulations suggest that the model system Cu/Nb can offer such properties when prepared with special interface orientation relationships such as Kurdjumov-Sachs (KS), owing to their high efficiency for absorbing point defects, He atoms, and dislocations. These nanolayered composite structures may be subjected to severe plastic deformation (SPD) either during their synthesis, for instance by accumulative roll bonding (ARB), or in service. One of the main questions addressed by the Severe Plastic Deformation (SPD) Team at CMIME is thus to assess the stability of nanocomposites of immiscible metallic elements, such as Cu and Nb, subjected to SPD. Molecular dynamics simulations indicate that the stability of Cu/Nb interfaces varies greatly with the fcc-bcc orientation relationship and interface habit plane. In this work we employ high-pressure torsion (HPT) to subject Cu/Nb nanocomposites to shear strains up to 500. Two types of Cu/Nb nanocomposites are used as starting materials, (i) nanolayered ARB Cu/Nb with average layer thicknesses of 40 nm and 10 nm, for the Cu and Nb phase respectively, and predominant KS interfaces with {112} habit planes; (2) 3D Cu/Nb nanocomposites obtained by mechanical alloying by ball milling followed by heat treatment. These materials have been characterized by X-ray diffraction and transmission electron microscopy (TEM). At shear strain of 400, the initial Nb layers in the ARB sample are no longer present and diffraction patterns indicate that significant mixing and texturing has taken place. Our initial results will be compared to our MD simulations.

P1-G12 - THE ROLE OF GRAIN BOUNDARIES IN RADIATION DAMAGE EVOLUTION IN SrTiO₃ AND TiO₂

[CMIME] Aylin Karakuscu¹, Blas Uberuaga¹, and Chris Stanek¹
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Radiation tolerant ceramics have been extensively studied in recent years since they are central for numerous nuclear energy applications, including the fuel itself and nuclear waste forms. Radiation can cause severe effects on ceramics especially at the microstructural level, possibly leading to radical degradation in mechanical properties. However, interfaces can also significantly improve the radiation tolerance of a material and offer one potential route for designing radiation tolerant materials. Therefore, understanding the relation between defects generated by irradiation and multidimensional defects such as interfaces and grain boundaries is a key aspect for developing radiation tolerant materials. In this study we focus on radiation effects in SrTiO₃ and TiO₂. Polycrystalline SrTiO₃ and TiO₂ samples are produced by the novel flash sintering method and compared to the corresponding single crystals. Samples are structurally

characterized by grazing-incidence x-ray diffraction and transmission electron microscopy; both before and after irradiation with energetic ions. In addition, new ultrafast laser spectroscopy techniques are used to characterize the properties of the irradiation-induced defects. The results show significant difference in radiation tolerance of polycrystalline samples as compared to the single crystals. The grain boundaries preserve their shape and prevent the amorphization even at high radiation doses; whereas, single crystal is amorphous.

P1-G13 - ANALYTICAL PREDICTIONS OF HETEROINTERFACE INTERACTIONS WITH DEFECTS

[CMIME] Kedarnath Kolluri¹, Aurelien Vattre¹, Abishek Kashinath¹, and Michael J. Demkowicz¹

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Using theory and atomistic simulations, we demonstrate that the interaction of defects with interfaces depends on interface structure. Furthermore, we show that the structure of semicoherent heterointerfaces can be predicted analytically, making it possible to design interfaces that have tailored interactions with defects, such as those created by radiation. We illustrate our findings on three examples: trapping of implanted helium at interfaces, migration of interface vacancies and interstitials, and effect of misfit dislocation character on interface shear resistance. 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

P1-G14 - HELIUM BUBBLE FORMATION AT GOLD TWIST BOUNDARIES

[CMIME] Michael Nastasi¹, Zengfeng Di¹, Qiangmin Wei¹, Amit Misra¹, Richard Hoagland¹, Yongqiang Wang¹, Jonghan Won¹, Xian Ming Bai¹, Blas Uberuaga¹, Enrique Saez¹, Jeffery Hetherly¹, and Alfredo Caro¹

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Helium bubble nucleation at low-angle twist boundaries in gold has been investigated. It is found that the helium bubbles preferentially nucleate at screw dislocation nodal points and result in helium bubble superlattice formation, which is completely isomorphic with the screw dislocation network along the twist grain boundary. Molecular statics calculations reveal that defect formation/solution energies along the screw dislocations, especially at the nodal points, are lower than their bulk counterparts. It is believed that this driving force is responsible for the helium bubble superlattice formation. Our study suggests that grain boundary engineering via adjustable twist angles in parallel boundaries to form tunable 3-D bubble superlattices could afford a very promising approach for design of radiation tolerant materials.

P1-G15 - EFFECTS OF RADIATION AND ANNEALING ON MICROSTRUCTURE AND THERMAL TRANSPORT IN CeO₂

[CMSNF] Clarissa Yablinsky¹, Peng Xu¹, Anthony Schulte¹, David Hurley², Jian Gan², and Todd Allen³

¹*University of Wisconsin-Madison*; ²*Idaho National Laboratory* and ³*University of Wisconsin-Madison*

The material response to irradiation damage is of prime importance in nuclear fuels. Experimental and theoretical efforts can be combined to model material response to ion bombardment. In this study, polycrystalline CeO₂, a common surrogate material for UO₂, was used in two forms: bulk CeO₂ and thin film CeO₂ on a silicon substrate. Two different grain sizes were investigated: thin film samples with ~500 nm grain size, and bulk samples with ~5µm grain size. Samples were exposed to a range of energies and ions to fluences of no less than 1E10 ions/cm² to investigate defects, defect formation, and how the defects influence thermal conductivity. Additionally, a bulk sample was annealed at 1500C for 5 hr. Investigated defects include dislocation arrangements, and ion track size and structure. Microstructures and substructures were investigated using scanning electron microscopy and transmission electron microscopy (TEM). Thermal transport was measured on a subset of samples using laser based spatially resolved thermal wave microscopy.

P1-G16 - CHARACTERIZATION OF NUCLEAR FUEL WITH 3D ATOM PROBE

[CMSNF] Hunter Henderson¹, Billy Valderrama¹, and In-Wook Park²

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Precise and accurate characterization of materials is of paramount importance to the field of nuclear, especially for theory validation and damage assessment. The complex and convoluted microstructural evolution of materials under irradiation is often hampered by uncertainties associated with the quantification of properties at the atomic scale. Historically, Transmission Electron Microscopy has been the tool of choice for analyzing nanoscale damage features, but in the last 10 years, 3D Atom Probe technology has matured to the point where it can gather information otherwise unobtainable. Advantages and disadvantages of Atom Probe, with respect to nuclear fuel technology, are discussed, as well as worthwhile complementary techniques.

P1-G17 - DEPOSITION AND POST-ANNEALING OF CERIA FILMS DEPOSITED BY PULSED UNBALANCED MAGNETRON SPUTTERING [CMSNF] In-Wook Park¹, John Moore¹, Jianliang Lin¹, Michele Manuel², Anter El-Azab³, Todd Allen⁴, Peng Xu⁴, David Hurley⁵, Marat Khafizov⁵, and Jian Gan⁵

¹Colorado School of Mines ; ²University of Florida ; ³Florida State University ; ⁴University of Wisconsin-Madison and ⁵Idaho National Laboratory

Ceria films, used as a UO₂ surrogate, were deposited on silicon wafers in an argon-oxygen atmosphere using pulsed unbalanced magnetron sputtering from a metallic Ce target. Ceria films were annealed using rapid thermal annealing in a range of room temperature to 1100 deg. C. Crystallinity of the annealed samples was characterized by x-ray diffraction (XRD). The XRD results indicated the as-deposited ceria films have a cubic CeO₂ phase with (111) or (222) preferred orientations. However, post-annealed ceria films have a hexagonal Ce₂O₃ phase with a (002) preferred orientation after RTA at 1000 deg.C for 5 min. This phase transformation, from cubic CeO₂ (111) to hexagonal Ce₂O₃ (002), is probably due to the Ce⁴⁺ to Ce³⁺ cation transformation by the formation of oxygen vacancies. X-ray photoelectron spectroscopy was performed to confirm the chemical status of Ce (e.g., Ce⁴⁺, Ce³⁺, etc) and O of the ceria samples. Nano-indentation analysis was performed to obtain mechanical values of nanohardness and Young's modulus. The nanohardness & Young's modulus of the as-deposited CeO₂ films were 11.7GPa and 241GPa, respectively. However, nanohardness & Young's modulus of the post-annealed ceria films were reduced to about 7.5GPa & 150GPa, respectively, caused by an increase in oxygen lattice defects with the phase transition from CeO₂ to Ce₂O₃. In the present work, microstructural changes & mechanical properties of the ceria films were investigated & correlated with deposition parameters.

P1-G18 - STRUCTURE AND DYNAMICS OF IONIC LIQUID-RHODAMINE 6G SOLUTIONS: NMR, FLUORESCENCE CORRELATION SPECTROSCOPY AND MOLECULAR MODELING

[FIRST] Jianchang Guo¹, Kee Sung Han¹, Song Li², Guang Feng², P. Ganesh³, Paul R.C. Kent³, Sheng Dai³, Peter T. Cummings², Shannon W. Mahurin³, Edward W. Hagaman³, and Robert W. Shaw³

¹Oak Ridge National Laboratory; ²Vanderbilt University and ³Oak Ridge National Laboratory

Room temperature ionic liquids (RTILs) and their applications have been a subject of intense interest in recent years. However, the local liquid structures and microscopic dynamics of RTILs are relatively unexplored. Here, we demonstrate the utility of NMR, fluorescence correlation spectroscopy (FCS) and molecular modeling to investigate solvent/solute diffusion and rotational dynamics for elucidating RTIL local liquid structures. In studying a series of [C_nMPy][Tf₂N] RTILs containing trace concentrations of rhodamine 6G, biphasic rhodamine 6G solute diffusion dynamics were observed; both the fast and slow diffusion coefficients decrease with increasing alkyl chain length, with the relative contribution from slow diffusion increasing for longer-chain [C_nMPy][Tf₂N]. We propose that the biphasic diffusion dynamics of rhodamine 6G originate from self-aggregation of the nonpolar alkyl chains in the cationic [C_nMPy]⁺, generating two unique environments for the dye molecule. This is consistent with the molecular dynamics simulation results. The diffusion coefficients of the ionic liquid [C₄MPy][Tf₂N] measured by PFG-NMR is much faster than that for rhodamine 6G. The Stokes-Einstein equation, $D = k_B T / 6\pi\eta r_s$ states that the diffusion coefficient is inversely proportional to the size of molecules, where r_s is the hydrodynamic radius. This difference in solvent/solute diffusion is attributed to the larger size of the dye molecule. The effect of charge state of probe dyes on rotational dynamics will be also discussed, comparing the time resolved fluorescence anisotropy of negative, neutral, and positively-charged rhodamine dyes in [C_nMPy][Tf₂N].

P1-G19 - ACTINIDE MATERIALS UNDER EXTREME CONDITIONS: AN EXPERIMENTAL AND COMPUTATIONAL APPROACH

[MSA] Fuxiang Zhang¹, Maik Lang¹, Jiaming Zhang¹, Jianwei Wang¹, Udo Becker¹, and R.C. Ewing¹

¹University of Michigan

We have investigated the behavior of actinide-bearing materials, garnet, brannerite and UO₂, under the extreme conditions of high pressures and temperatures combined with high-energy ion irradiation. Garnet, A3B2X3O12, can incorporate long-lived actinides, e.g., 239Pu and 237Np. The susceptibility of the garnet structure, doped with actinides, to radiation damage has been investigated by self-radiation damage from \hat{I}_{\pm} -decay of 244Cm and 1 MeV Kr²⁺ ion-irradiations. The similarity of the radiation response for different compositions suggests that radiation damage to the garnet structure is topologically constrained. The monoclinic brannerite structure, AB2X6, can incorporate actinides on the A-site. Pressure-induced structural changes of three brannerite compositions were studied at pressures up to 50 GPa. Above 20 GPa, brannerite becomes amorphous. UO₂ can be nonstoichiometric. The electronic structure and high-pressure phase transitions of stoichiometric UO₂ and hyperstoichiometric UO_{2.03} have been investigated by first-principles calculations in order to understand the effect of oxygen interstitials on the stability of the structure. The dramatic increase in transition pressure for the hyperstoichiometric uranium dioxide is related to the structural incompatibility of the interstitial oxygen in the high-pressure, cotunnite-like orthorhombic structure.

P1-G20 - NANO-SCALED MATERIALS UNDER HIGH PRESSURES

[EFree] Lin Wang¹, Wenge Yang¹, Yang Ding¹, Yugang Sun², Wendy L. Mao³, and ⁴Ko-Kwang Mao¹*Carnegie Institution of Washington*; ²*Argonne National Laboratory*; ³*Stanford University* and ⁴*Carnegie Institution of Washington*

Nano-scaled materials have greater potential applications and were expected to have higher efficiencies, thus save more energy than their bulk counterparts. Revolutionary improvements in the applications and efficiencies of nano-scaled materials depend on a detailed knowledge of phase stabilities of the materials. Here, we present our recent studies on phase stabilities of several energy related nano-materials. Nano-scaled Y_2O_3 has potential applications as red-emitting phosphor material with higher efficiency and resolution. We studied a series of n- Y_2O_3 with particle sizes ranging from 5 nm to 1 μ m at high pressure using x-ray diffraction and Raman spectroscopy techniques. N- Y_2O_3 particles are shown to be more stable than their bulk counterparts, and a grain size-dependent crystalline-amorphous transition was discovered in these materials. N-Ag has been found to have higher efficiency and more other advantages in its applications in water purification, electronics industry, automotive industry etc. In our high pressure studies, two distinct structural transformation processes have been, for the first time, discovered in Ag nanoplates under nonhydrostatic pressures. The results also indicate that Ag nanocrystals can undergo phase transformations at much lower external pressures in comparison with their counterpart.

P1-G21 - HIGH PRESSURE DISCOVERY OF RhH_2 AND AMBIENT PRESSURE RECOVERY[EFree] Bing Li¹, Yang Ding¹, Wenge Yang¹, and Ho-Kwang (Dave) Mao¹*Geophysical Lab Carnegie Institution of Washington*¹

Heavy metal hydride is of great scientific interest as both a potential high T_c superconductor and hydrogen storage material. Rhodium metal, as a member of platinum group metals, is the second one to be discovered after palladium metal to form its hydride. At ambient condition, rhodium metal adopts FCC structure and it forms hydride under high hydrogen pressure around 3.8 GPa. This hydride (RhH_1) remains in FCC structure but expands a lot from its Rhodium metal matrix. To further explore rhodium-hydrogen system, we performed higher pressure experiments. We discovered that RhH_1 will transform to RhH_2 at around 8 GPa, and this new hydride still has FCC structure. Compared with the first volume change, which is from Rhodium metal to RhH_1 , the formation of RhH_2 has much larger volume expansion (~ 1.7 times larger than the first one). Thermodynamic stability study of RhH_2 shows that it can be quenched up to liquid nitrogen temperature and ambient pressure. This result indicates the practical application with much higher hydrogen storage capability of RhH_2 at ambient pressure.

P1-G22 - PERSISTENCE OF JAHN-TELLER DISTORTION UP TO THE INSULATOR TO METAL TRANSITION IN $LaMnO_3$ [EFree] Maria Baldini¹, Viktor V. Struzhkin¹, Alex F. Goncharov¹, Paolo Postorino², and Wendy L. Mao³¹*Carnegie Institution of Washington*; ²*University Sapienza* and ³*Stanford University*

The origin of high pressure driven insulator to metal transition (IMT) in $LaMnO_3$, the role played by electron-electron and electron-lattice interactions have been the subject of a large number of experimental [1-3] and theoretical [4,5] studies. Despite the considerable efforts, the key question of whether $LaMnO_3$ is a classical Mott-Hubbard insulator or not remained unresolved. In this study we performed high pressure Raman measurements up to 34 GPa over several low temperature cycles which provide the first evidence for persistence of the Jahn Teller (JT) distortion over the entire stability range of the insulating phase [6]. This result suggests that the IMT is related to the disappearance of the JT distortion and conclusively resolves the ongoing debate, demonstrating that $LaMnO_3$ cannot be considered a classical Mott insulator. Evidence for the formation of domains of JT distorted and symmetric octahedral was found from 3 to 34 GPa suggesting that $LaMnO_3$ enters the metallic state when the fraction of undistorted octahedra domains increases beyond a critical threshold. In this scenario, it is interesting to consider whether or not the CMR effect may be induced in an undoped sample as $LaMnO_3$ by applying P. [1] I. Loa, et al., Phys. Rev. Lett. 87, 125501 (2001). [2] A.Y. Ramos et al., Phys. Rev. B 75, 052103(2007). [3] A.Y. Ramos et al., J. Phys. Conf. Ser. 190, 012096 (2009). [4] A. Yamasaki et al., Phys. Rev. Lett. 96, 166401 (2006). [5] J. D. Fuhr et al., Phys. Rev. Lett.

P1-G23 - MELTING OF REFRACTORY MATERIALS IN EXTREME ENVIRONMENTS

[EFree] Amol¹, Liuxiang¹, and Reinhard¹Karandikar¹; Yang¹ and Boehler¹¹*Carnegie Institution of Washington*

Knowledge of the physical properties, in particular, the strength of refractory transition metals (Mo, Ta, W, Re, etc.) is essential to many research fields monitoring the material behavior under extreme conditions. A considerable amount of experimental melting measurements using laser heated diamond anvil cell and shock-wave experiments have been made for transition metals, providing new insights into the systematic behavior of these metals at extreme pressures and

temperatures. However, a large discrepancy of several thousand degrees exists between static and shock melting. We pursue three novel experimental ways of detecting melting of these transition metals using synchrotron X-ray diffraction, Scanning electron Microscopy and pulsed laser techniques to tackle the challenges in producing accurate data.

P1-G24 - MAKING SUPERCONDUCTING TRANSITION TEMPERATURE HIGHER FOR ENERGY APPLICATION

[EFree] Xiao-Jia Chen¹, Viktor V. Struzhkin¹, Alexander F. Goncharov¹, Russell J. Hemley¹, and Ho-Kwang Mao¹
¹*Carnegie Institution of Washington*

Superconductivity offers powerful new opportunities for restoring the reliability of the power grid and increasing its capacity and efficiency. The key issue in superconductivity research is to find materials with high critical temperatures so that all operations can be done at ambient conditions. Currently, cuprate superconductors remain the superconducting materials having highest transition temperatures both at ambient condition and under pressure. We perform extensive investigations in order to explore effective ways to enhance superconductivity in these materials. One of our experimental findings is that one can enhance remarkably transition temperature through the suppression of competing order in the inner copper-oxygen plane(s) of multilayer cuprates and through the optimization of two competing energy scales (pairing and phase ordering) of different copper-oxygen planes. These results have important implications for designing and engineering superconductors with much higher transition temperatures at ambient conditions.

P1-G25 - HIGH PRESSURE CHEMISTRY WITH PERIODIC MESOSTRUCTURES

[EFree] Kai Landskron¹, Paritosh Mohanty¹, Manuel Weinberger¹, Yingwei Fei², Ho-Kwang Mao², Dong Li, Tianbo Liu¹, Neil Coombs¹, Ilke Arslan³, Nigel Browning⁴, and Volkan Ortolan⁴
¹*Lehigh University*; ²*Carnegie Institution of Washington*; ³*University of Toronto* and ⁴*University of California at Davis*

Periodic mesoporous silicas with crystalline channel walls are interesting target materials for hydrocarbon cracking applications. Nanocasting at high pressure is a suitable synthetic method to produce such materials. A periodic mesostructured silica/carbon composite is prepared at ambient pressure and then subjected to high-pressure high-temperature conditions at which the crystallization of the silica phase takes place. After the high-pressure synthesis the carbon phase is removed by oxidation. The product materials show excellent hydrothermal stability. Mesoporous silica with crystalline channel walls can also be made directly from periodic mesoporous silica because mesopores can undergo elastic pore collapse when exposed to high pressure. A similar route is furthermore suitable for the production of mesoporous diamond from periodic mesoporous carbon.

P1-H01 - SYNTHESIS, MODELING AND APPLICATION OF MIXED RARE EARTH OXIDES

[CALCD] Kerry Dooley¹, Michael Janik², Adam Mayernick², Rui Li¹, Matthew Krcha², Joseph Bridges¹, Sumana Adusumilli¹, and Weishi Kong¹
¹*Louisiana St. Univ.* and ²*Pennsylvania St. Univ.*

The goal of this project is to design a rare-earth oxide (REO)/transition metal catalytic system capable of reforming/cracking typical tar components (e.g., naphthalene) at <850 °C in a realistic biomass/coal gasifier effluent containing water, H₂, CO, CO₂ and H₂S. Computational studies are used to help identify optimal transition metals and composition ranges. Both Mn and Fe look like good candidates with CeO₂/La₂O₃ or CeO₂/ZrO₂ based REOs, but recent computational work on methane activation and on reduction of doped CeO₂ surfaces suggests that Pd, V or Re dopants may be superior. These computational studies are guiding the materials design. The sorbent/catalyst materials are tested for both adsorption of H₂S at 600-650 °C (where the Mn-containing materials are definitely superior) and for reforming of naphthalene at similar temperatures. We found that the temperature range 600-650 °C is the best compromise between high conversion of the naphthalene model "tar" and extended catalyst lifetime. We also found that while CO₂ inhibits tar reforming under these conditions, CO promotes it, or at least extends catalyst lifetimes. Supporting the rare earths on stable high temperature supports greatly increases sulfur adsorption capacity on a rare earth atom basis. The surface chemistry of encouraging sorbent/catalyst compositions is being characterized by combined XANES, EXAFS, XRD, XPS and TPR studies.

P1-H02 - A COMPUTATIONAL APPROACH TO EVALUATING CATALYST PARTICLE SIZE AND STRUCTURE EFFECTS: COMPARISONS OF HOMOGENEOUS 13-ATOM AND CORE-SHELL 38-ATOM BIMETALLIC CLUSTERS

[CALCD] Ming He¹, James McAliley¹, and David Bruce¹
¹*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.

P1-H03 - ROOM TEMPERATURE WATER SPLITTING AT THE SURFACE OF MAGNETITE

[CALCD] Gareth Parkinson¹, Zbynek Novotny¹, Peter Jacobson¹, Michael Schmid¹, and Ulrike Diebold¹

¹TU Wien

This poster will report a hitherto unobserved adsorption behavior for water, which has been observed at the (001) surface of magnetite (Fe₃O₄). Initially, water adsorbs dissociatively at room temperature, as it does on many oxide surfaces, but high-resolution STM images and isotopically labeled LEIS results show that only a single proton from each molecule is adsorbed on the surface. The resulting surface is indistinguishable from that obtained through atomic H deposition [1]. Several important aspects of the work will be described in detail, including the influence of the Jahn-Teller distorted surface [2] on the adsorption geometry, the surface chemistry defining the fate of the missing OH species, and the observation that light annealing renders magnetite the first known example of a material being reduced by exposure to water vapor. [1] Parkinson, G. S. et al. Semiconductor-half metal transition at the Fe₃O₄(001) surface upon hydrogen adsorption. Phys. Rev. B 82, 125413 (125415 pp.), (2010) [2] Pentcheva, R. et al. Jahn-Teller stabilization of a polar metal oxide surface: Fe₃O₄(001). Phys. Rev. Lett 94 126101 (2005).

P1-H04 - MULTI-SCALE MODELING OF CATALYSTS FOR CO₂ REDUCTION TO ALCOHOLS

[CALCD] Aravind Asthagiri¹, Susan Sinnott², Tao Liang², Tzu-Ray Shan², Bryce Devine², Donghwa Lee², Yu-Ting Cheng², Beverly Hinojosa², Simon Phillpot², Michael Janik³, and John Flake⁴

¹The Ohio State University; ²University of Florida; ³Penn State University and ⁴Louisiana State University

Within the CALCD EFRC we have an integrated experimental and theoretical effort to develop novel catalysts for the electrochemical reduction of CO₂ to alcohols. There are several challenges to accurately model these systems such as the aqueous electrochemical environment, the changes to the catalyst structure under reaction conditions, the multiple possible reaction pathways and possible catalyst candidates. In this poster, we will present a multi-scale modeling framework to tackle these challenges. We have focused on understanding CO₂ reduction on Cu/ZnO catalysts, which experimental results in our EFRC shows to be selective to methanol with improved activity versus Cu metal and Cu oxides. We have applied density functional theory (DFT) with free energy corrections for the aqueous electrochemical environment to examine CO₂ reduction pathways on various models of Cu on ZnO(10-10). While these DFT studies provide insight into possible critical mechanisms on Cu/ZnO, they suffer from the computational cost of electronic-structure calculations. To be able to probe more realistic models of Cu on ZnO in a rapid manner we are developing charge optimized many body (COMB) potentials to describe hydrocarbon chemistry on Cu/ZnO interface. These COMB potentials will be ultimately combined with adaptive kinetic Monte Carlo to model Cu growth on ZnO and rapidly screen potential pathways for CO₂ reduction on these surfaces.

P1-H05 - A DENSITY FUNCTIONAL THEORY STUDY OF SYNGAS CLEANUP WITH CERIA-BASED RARE EARTH OXIDES

[CALCD] Matthew Krcha¹, Adam Mayernick¹, Rui Li², Kerry Dooley², and Michael Janik¹

¹Pennsylvania State University and ²Louisiana State University

Biomass conversion to liquid fuels may be accomplished through gasification to syngas (CO+H₂) followed by fuel synthesis processes, enabling a renewable energy source of liquid fuels. Prior to fuel synthesis catalysts, the syngas must be cleaned of sulfur and tar species. In a Department of Energy forecast for 2012, approximately 50% of the cost to produce ethanol from biomass is involved in syngas cleanup. Mixed Rare-Earth Oxides (REOs) have shown promise in both desulfurization and hydrocarbon conversion. Our goal is to design a REO catalyst to reform large hydrocarbons into CO and H₂ and remove sulfur at high temperatures, thus making biomass gasification-based processes viable for sustainable liquid fuel production. Density functional theory (DFT+U) is used to generate composition-function relationships of mixed REOs for H₂S adsorption and hydrocarbon conversion. Initial efforts have examined the H₂S adsorption and incorporation process. Oxygen vacancy sites in the doped oxide are active for H₂S adsorption and dissociation. Relative rates of the initial H₂S activation step predict trends in experimental H₂S adsorption capacity over a series of dopants in ceria, suggesting surface kinetic rates impact the adsorption capacity. As an indicator of methane reforming and tar cracking activity, the C-H bond activation energy of ceria based catalysts doped with transition metals is correlated with the surface reducibility. DFT findings are compared with experimental data.

P1-H06 - AB INITIO CALCULATION OF REDOX POTENTIALS IN TRANSITION METAL COMPLEXES

[CETM] Steven J. Konezny¹, Mark D. Doherty², C. Moyses Araujo³, Oana R. Luca³, Robert H. Crabtree³, Grigori L. Soloveichik², and Victor S. Batista³

¹Yale University; ²GE Global Research and ³Yale University

The prediction of electrochemical properties of redox-active transition metal complexes is essential to gaining insight into catalytic mechanisms and guiding the design and development of efficient electrocatalysts for renewable energy. We used combination of theoretical and electrochemical studies to calculate absolute values of redox potentials. Here we report the characterization of redox properties of transition metal complexes in non-aqueous solutions by using density functional theory (DFT) methods and direct comparison with cyclic voltammetry measurements of benchmark redox couples, including $[MCp_2]^{0/+}$, $[MCp^*_2]^{0/+}$ and $[M(bpy)_3]^{2+/3+}$, with M = Fe, Co, and Ru, in various non-aqueous solvents, as well as Co and Ni complexes with various NNN pincer ligands. We find that agreement between theory and experiment can be significantly improved compared to previous studies when the redox potential is referenced to a transition metal complex couple measured under the same solvent and electrolyte conditions. Other important considerations include changes in redox-active ligands and dimerization process induced by charge transfer interactions.

P1-H07 - INVERSE BAND STRUCTURE OF NANOSTRUCTURES: FINDING ATOMIC CONFIGURATIONS OF SI AND GE THAT PRODUCE DIRECT GAP SUPERSTRUCTURES

[CID] Mayeul d'Avezac¹, Jun-Wei Luo¹, Alex Zunger¹, and Stephan Lany¹

¹NREL

The fact that Silicon is the paradigm semiconductor -- readily dopeable by either electrons or holes and protected from environmental scatterers by a native oxide passivation layer -- is unfortunately not matched by the additional virtue of being able to strongly emit and absorb light. Nevertheless, one of the most promising research axis of the CMOS industry relies on the integration of optical and electronic functions on single Silicon wafer. Indeed, the ability to replace copper interconnect within and between processors with optical connectors is a key strategy for the industry to keep up with its obsessive chase of Moore's law. However, Silicon remains an indirect-gap material and a fairly poor light emitter, despite the resources and ingenuity deployed to improve its opto-electronic properties. We provide an unexpected solution to a classic problem, by spatially melding two indirect-gap materials (Si and Ge) into one strongly dipole-allowed, direct-gap, and CMOS-compatible material. We use a combination of genetic algorithms with a pseudopotential Hamiltonian to search through the astronomic number of possible variants of $Si_n/Ge_m/\dots/Si_p/Ge_q$ superstructures grown on (001) $Si_{1-x}Ge_x$. This search reveals a robust configurational motif -- $SiGe_2Si_2Ge_2SiGe_n$ on (001) $Si_{1-x}Ge_x$ substrate ($x < 0.4$) -- which presents both a direct and dipole-allowed gap by coupling the CBM at Γ with the direct transition state at Γ .

P1-H08 - COMPUTATIONAL DISCOVERY AND HIGH THROUGHPUT SYNTHESIS OF NEW A_2BX_4 AND ABX SEMICONDUCTORS FOR SOLAR ENERGY

[CID] Vladan Stevanovic¹, Xiuwen Zhang¹, Andriy Zakutayev¹, David Ginley¹, and Alex Zunger¹

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The A_2BX_4 and ABX are important classes of ternary materials, spanning a significant range of physical properties. Members of these families include transparent conductors, topological insulators, ferromagnetic, and thermoelectric materials, etc. However, a large percentage of A_2BX_4 and ABX combinations have never been experimentally synthesized. We used a computational discovery in conjunction with high throughput synthesis to examine these missing materials in the light of potential solar energy applications. To discover missing A_2BX_4 ($X = O, S, Se, Te$) and ABX ($X = O, S, Se, Si, N, P, As$) compounds, we used a systematic theoretical approach, which consists of two steps: 1) running a set of high-throughput *ab-initio* calculations to find the lowest-energy structure; 2) testing the stability of a given material against all possible combinations of known compounds involving the same elements. We predicted about 100 A_2BX_4 and about 60 ABX new stable compounds and calculated their heats of formation. To validate the theoretical predictions for both A_2BX_4 and ABX classes, we used high-throughput combinatorial approach, which consists of two steps: 1) depositing thin films of A-X and B-X binaries or A, B and X elements with a controlled gradient of chemical composition; 2) mapping crystallographic structure and relevant physical properties as a function of chemical composition. Preliminary synthesis and characterization results for one prototypical material from each family will be presented.

P1-H09 - WILL A DOPED WIDE GAP MATERIAL CONDUCT? POLARON VS. BANDS IN SOLAR OXIDES

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In the development of new p-type transparent conducting oxides for solar applications, a critical question is whether the hole conductivity is small polaron-like with limited mobility or band-like with potentially high mobility. Focusing on A_2ZnO_4 ($A=Rh,Co$) p-type spinels, we show how the combination of first-principles theory and in-depth experimental electrical characterization updates the traditional approach and provides new insights into conduction mechanisms. We applied traditional small polaron analysis to our *in situ* high temperature simultaneous conductivity and thermopower measurements, finding internal consistency with the small polaron mechanism. However, applying recent density functional based theory tools, which allow the quantitative prediction of hole localization, to a number of different oxides, we find that holes localize (self-trap) in the prototypical case of TiO_2 , but in Rh_2ZnO_4 self-trapped holes are unstable against delocalization into the valence band. Hence, we predict band conductivity in Rh_2ZnO_4 , which is corroborated by high-field Hall effect measurements that yield a mobility consistent with band conduction. These findings are reconciled in the traditional analysis when we correct for the temperature dependence of the effective density of states. In the case of $Co_{3-x}Zn_xO_4$, neither the measured Hall mobility nor the correction for the temperature dependence of the effective density of states rules out the possibility of small polaron conduction.

P1-H10 - DESIGN AND DISCOVERY OF A NEW CLASS OF A_3BO_4 P-TYPE CONDUCTORS

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New p-type transparent conducting oxides (TCOs) are often produced by reacting the prototype binary p-type oxides, i.e., Ag_2O and Cu_2O , with binary oxides of other transition metals or main-series elements. Yet, so far only a small part of all the multi-cation Cu and, in particular, Ag oxides have been assessed as candidate p-type TCOs. Furthermore, numerous multi-species Cu and Ag oxide systems are poorly characterized, which leaves ample scope for discovery of yet unknown compounds belonging to them, and, likely, of unsuspected new TCOs, too. Here, we survey a complete database of known multicomponent Ag and Cu oxides, without restrictions on element composition, to search for new candidate TCOs. We indexed all the compounds in this database by applying selected crystal structure descriptors as structure type, stoichiometry, and coordination environment of the Cu and Ag cations. Chemical insight points to a significant likelihood that 2- and 4-fold coordination of the noble metal cations yield band structure properties suitable for the transparency and hole conductivity needed in TCOs. We scanned the indexed database to find compounds that could match these requirements and identified a set of materials that could be interesting candidate p-type TCOs.

P1-H11 - PHONON LIFETIMES AND THERMAL CONDUCTIVITY IN UO_2 : AN INTEGRATED SIMULATION AND EXPERIMENTAL APPROACH

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There are more than twenty different interatomic potentials for UO_2 in the literature. Atomistic simulation methods are used to determine the predicted phonon dispersion curves, phonon densities of states, and thermal conductivities for each potential. In order to investigate the phonon properties, a powerful new simulation code based on the solution of the Boltzmann Transport Equation (BTE) at the level of the three-phonon scattering processes is applied to UO_2 and extended to allow the determination of the phonon lifetimes. Technical details of the implementation of the solution to the BTE are discussed. In particular, a comparison between three different solution methods (relaxation time approximation, iterative and variational methods) is presented. For those interatomic potentials that best reproduce the experimentally established phonon dispersions and thermal conductivities, the phonon lifetimes are also determined as a function of wave vector and polarization. These are compared to the phonon lifetimes calculated from neutron scattering experiments.

P1-H12 - ORDER-DISORDER TRANSITIONS OF FILLER SPECIES IN SKUTTERUDITES

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Binary skutterudites are one of the promising thermoelectric (TE) materials and an example of 'Phonon Glass Electron Crystal' paradigm because they possess high charge carrier mobilities and reduced phonon conductivity upon filling their structural voids. We analyze the Ba-vacancy ordering of the filler sites of $Ba_xCo_4Sb_{12}$ in order to understand the effect of order and disorder on the scattering of phonon conductivity. In order to find the effect of the Ba-vacancy order on the filler

species sites, the cluster expansion (CE) method was used. The CE was parameterized by the formation energy of Ba-vacancy configurations calculated from the *ab initio*. Below $x < 0.5$, we identified three ground-state ordered phases and two-phase regimes exist between the two phases. From the results of phase diagram, the phonon conductivity was calculated using the equilibrium molecular dynamics and the Green-Kubo autocorrelation. For the solid solution structure, the phonons propagate through the ordered CoSb_3 and the thermally distributed Ba atoms act as point defects (Regime-I). In the two-phase mixture (Regime-II), the mixture of two ordered phases causes significant two-phase scattering. We conclude that these two regimes characterize the scattering mechanisms. The long-range acoustic phonon transport decreases most noticeably by the two-phase scattering. Therefore, the suppression of long-range acoustic phonon transport causes the observed reduced phonon conductivity in two-phase mixtures.

P1-H13 - THEORETICAL DEVELOPMENTS AND COMPUTATIONAL MATERIALS SCIENCE FOR ENERGY SYSTEMS

[EMC2] Robert Berger¹, Kendra Weaver², Ravishankar Sundararaman², Tomas Arias², Craig Fennie², and Jeff Neaton¹
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This poster highlights two projects in the theory objective of the Energy Materials Center at Cornell (EMC²). In the first, the Arias group has developed a joint density functional theory, which bridges a microscopically accurate continuum description of the aqueous environment with standard density-functional theory (DFT), to study catalyst surfaces and interfaces in electrochemical cells. In the second, the Neaton group has used DFT and many-body perturbation theory to examine electronic trends in strained and layered modifications of SrTiO_3 , with an eye toward optimizing the band gap and band-edge energies for solar absorption and water splitting

P1-H14 - DYNAMICS OF CONFINED WATER AND ELECTROLYTES

[FIRST] Suresh M. Chathoth¹, Eugene Mamontov¹, Alexander I. Kolesnikov¹, Gernot Rother¹, Michael Rouha², Peter T. Cummings², Pasquale Fulvio¹, X. Wang¹, Sheng Dai¹, Jake McDonough³, Volker Presser³, and Yury Gogotsi³
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Molecular dynamic (MD) simulation, inelastic (INS), spin-echo (NSE) and quasi-elastic (QENS) neutron scattering have been used to study the dynamics of water and electrolytes in confinement. The confining media were carbon materials produced at Drexel University and Oak Ridge National Laboratory. INS data of water confined in sub-nanometer pores of carbide-derived-carbon exhibit acoustic vibrational modes, which confirms that water in the pores is in the form of clusters, and interaction of water and CDC pore walls is hydrophobic. QENS studies on water in the same confinement shows a dynamic transition temperature of 190 K, similar to that found in 16 Å... diameter carbon nanotubes. This shows that the dynamical behavior of water remains qualitatively unchanged in, perhaps, the smallest hydrophobic pores which water can enter under the ambient conditions. The QENS experiments show a strong increase in the mean dynamics of cations in a room temperature ionic liquid, [bmim][Tf₂N] confined in the carbon mesopores as compared that in the bulk. The NSE measurements indicate slowing down of dynamics in the same confined system. Using atomistic molecular modeling strongly attractive pore-fluid interactions were found, and led to the formation of an immobile fluid layer at the pore walls. This sorption phase is in contact with a free fluid phase with faster dynamics.

P1-H15 - STRUCTURE OF ELECTROLYTES AT CARBON ELECTRODE SURFACES: COUPLING X-RAY AND NEUTRON SCATTERING WITH MOLECULAR MODELING

[FIRST] Hua Zhou¹, Paul Fenter¹, Volker Presser², Jake McDonough², Yury Gogotsi², Matthew Wander², Kevin Shuford², P. Ganesh³, Paul R.C. Kent³, De-en Jiang³, Gernot Rother³, Ariel Chialvo³, Pasquale Fulvio³, Sheng Dai³, Michael Rouha⁴, Guang Feng⁴, and Peter T. Cummings⁴
¹Argonne National Laboratory; ²Drexel University; ³Oak Ridge National Laboratory and ⁴Vanderbilt University

An understanding of the interactions of electrolytes with carbon electrode surfaces is essential to provide a full description of the processes in electrochemical energy storage systems. We review our efforts to obtain a molecular-scale perspective of these systems at ambient conditions. Structures of various electrolytes including aqueous solutions and room temperature ionic liquids (RTILs) on planar (free-standing and epitaxial graphene) and imbedded in the nanopores of novel carbon electrodes have been systematically investigated by coupling high-resolution X-ray and neutron scattering measurements with various molecular modeling-simulation approaches. X-ray studies in combination with *ab-initio* molecular dynamics indicate that water interacting with epitaxial buffer layer graphene (on SiC) is more hydrophilic with strong localization effects due to the presence of substrate and surface defect sites, in contrast with that observed on free-standing graphene. A strong cation-specific pore densification was found for RTILs in disordered mesoporous carbon by small-angle neutron scattering, as comparable to simulation results. The distributions of adsorbed ions in aqueous solutions and molecular layering in RTILs on both graphene and glassy carbon as a function of surface potentials have also been explored by both techniques. These results provide a base-line for understanding the carbon-electrolyte interactions relevant to energy storage systems (e.g., supercapacitors).

P1-H16 - A QUANTUM CHEMICAL STUDY OF URANYL-PEROXIDE NANOCLUSTER GROWTH MECHANISMS

[MSA] Bess Vlasisavljević¹, Pere Miro¹, Christopher Cramer¹, Peter C. Burns², and ¹Laura Gagliardi
¹University of Minnesota and ²University of Notre Dame

The uranyl ion, $[\text{UO}_2]^{2+}$, is central in aqueous hexavalent uranium chemistry. Our goal is to understand the formation of novel polyperoxouranates. A departure from typical uranyl crystal topologies, the clusters grow readily when uranyl reacts with hydrogen peroxide in the presence of an alkali base.¹ The synthesis of a variety of clusters containing twenty to sixty uranium atoms has been achieved, showing that these clusters are not only present as crystals, but persist in solution.¹⁻³ Still many questions remain regarding cluster formation. Previous work⁴⁻⁶ has shown that structures containing two, four, and five uranyl groups likely exist in solution and are proposed building blocks of the nanoclusters. While our overall focus is the growth of the large clusters, the initial steps can be understood by studying smaller clusters. Using density functional theory, free energy barriers are examined for the formation of the monomer, $(\text{UVIO}_2)_2\text{O}_2\text{L}_3$, and dimer, $(\text{UVIO}_2)_2\text{O}_2\text{L}_{4-6}$, with various equatorial ligands, L (L=water, hydroxyl, or oxalate). Monomer formation is preferred over the dimer in the absence of counteranions as the dimerization barrier is prohibitively high. When ion pairing between the two reactants and the cation is included, a stable adduct is formed. Additionally, the presence of the cation lowers the barrier. Adduct formation and a lower dimerization barrier show the important role of cations in favoring dimer growth.

P1-H17 - NANOSCALE CONTROL OF ACTINIDE MATERIALS

[MSA] Peter C. Burns¹, Ginger E. Sigmon¹, Daniel K. Unruh¹, Jie Ling¹, Jie Qiu¹, Christine Wallace¹, and Jennifer E.S. Szymanowski¹
¹University of Notre Dame

Polyhedra containing uranium (VI), present as the linear dioxo cation, typically link to form extended structural sheets as well as chains and frameworks. Where uranyl ions are bridged through bidentate peroxide ligands a bent configuration is favored by a partially covalent interaction. This favors assembly of nano-scale cage clusters rather than extended structures. More than 60 topologically distinct clusters self-assemble in aqueous solutions under ambient conditions. Some contain only uranyl polyhedra, whereas others contain bridges such as oxalate, pyrophosphate, and various transition metal polyhedra. The cage clusters contain as many as 128 uranyl polyhedra and exceed three nanometers in diameter. They have been characterized in solution using small-angle X-ray scattering and electrospray ionization mass spectroscopy, and have been crystallized for full structure characterization using X-ray diffraction. Clusters of uranyl polyhedra adopt a myriad of different topologies that can be synthesized in aqueous systems with pH ranging from 3 to 13. Current efforts are focused on understanding the reaction pathways of self-assembly, the aqueous solubility of the nano-scale clusters, the heats of formation of the clusters, and their aggregation under different conditions. These clusters present the possibility of controlling the composition of materials at the nano-scale. They are effective for the removal of uranium from solutions through molecular weight filtration.

P1-H18 - OXYGEN-EXCHANGE STUDIES OF URANYL COMPLEXES BY NMR

[MSA] Rene L. Johnson¹, Stephen J. Harley¹, C. Andre Ohlin¹, Adele F. Panasci¹, and William H. Casey¹
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There is little information about the mechanisms of reactions involving aqueous actinide elements and high-pressure ¹⁷O- and ¹³C-NMR methods are particularly useful; we these we can sample the transition states in elementary aqueous reactions. We used the methods to probe the activation properties of the $[\text{UO}_2(\text{OH})_4]^{2-}_{(\text{aq})}$ ion and the rates of isotope exchange in the apical oxygens in alkaline solution from 0.1 to 350 MPa at 333 K. Using NMR saturation-transfer techniques we measured an activation volume (\hat{V}^\ddagger) of $-9.8 \pm 0.8 \text{ cm}^3/\text{mol}$ for the reaction, which indicates a strongly associative pathway. We are now extending the work to examine the pressure dependence of ¹³C and ¹⁷O exchange in the $[\text{UO}_2(\text{CO}_3)_3]^{4-}_{(\text{aq})}$ ion over the range 5 to 350 MPa, which has two known pathways of isotope exchange that differ in how protons are involved. In addition we are establishing the stability of U(VI)-catecholate complexes and measuring the rates of ligand substitution. We also study the aqueous chemistry of larger uranyl complexes, most notably the U₂₈ cluster (and others) prepared in collaboration with Dr. May Nyman of Sandia National Laboratory. We find that the U₂₈ compound synthesized with ¹⁷O-enriched uranyl nitrate was only slightly soluble and that the compound was not stable in solution over timescales of days; apparently new products form. Finally, in collaboration, we reported ⁹⁹TcO₄⁻ signals in the NDTB-1 material. Two sites of reaction were indicated that differ in steric chemistry.

P1-H19 - TEMPLATING EFFECTS ON ASSEMBLY OF ACTINIDE NANO-CAPSULES

[MSA] [May Nyman](#)¹¹*Sandia National Laboratory*

The U₂₈ nanosphere, [UO₂(O₂)_{1.5}]₂₈ self-assembles with a central anionic template that is surrounded by four large alkali templates (Rb⁺ or Cs⁺) and twelve smaller alkali templates (Na⁺ or K⁺). In turn, the larger alkalis assemble four hexagonal uranyl peroxide rings, and the smaller alkalis assemble twelve pentagonal uranyl peroxide rings: these link together to form the U₂₈ capsule. Successful anionic templates include Nb(O₂)₄³⁻, Ta(O₂)₄³⁻, UO₂(O₂)₃⁴⁻ and VO_{4-x}(O₂)_x³⁻. These templates along with utilization of monomeric precursors (alkali uranyl peroxides) provide opportunity to synthesize high yields of pure and stable materials, which in turn has facilitated a variety of collaborations and studies, both computational and experimental. Ongoing collaborations within the EFRC include: 1) thermochemical measurements on both the monomers and capsules to determine their thermodynamic stability (U.C. Davis), 2) Oxygen-isotope exchange studies on the cluster in aqueous solution (U.C. Davis), 3) Extending this chemistry to trans-uranium actinides (SRNL). At Sandia National Laboratories, we are utilizing solution and solid-state, multi-nuclear NMR techniques to study ion-exchange between the U₂₈ capsule and aqueous media. We are also developing non-aqueous chemistry of the nanospheres, which greatly facilitates investigating redox behavior.

P1-H20 - IRRADIATION-INDUCED GRAIN GROWTH IN NANOCRYSTALLINE CERIA

[MSA] [Yanwen Zhang](#)^{1,2}, [Philip Edmondson](#)¹, [Tamas Varga](#)³, [Sandra Moll](#)³, [Fereydoon Namavar](#)⁴, and [William J. Weber](#)^{1,2}¹*Oak Ridge National Laboratory and* ²*University of Tennessee, Knoxville;* ³*Pacific Northwest National Laboratory and* ⁴*University of Nebraska Medical Center*

Cubic ceria (CeO₂) is a well known ionic conductor that is isostructural with urania, plutonia, and thoria nuclear fuels. In the context of nuclear fuels and actinide inert matrices, CeO₂ is a nonradioactive model system for evaluating the role of nanograined structures on radiation effects, and the ability to engineer material properties by ion beams may be critical to developing other clean energy sources. The response of nanocrystalline cubic CeO₂ films to ion-beam irradiation was studied using 330 nm thick films prepared by ion-beam-assisted deposition and irradiated with 3.0 MeV Au ions at 160, 300 and 400 K to doses up to 100 displacements per atom. The elemental composition and film thickness were characterized by Rutherford and non-Rutherford backscattering spectroscopy. Grain growth and phase stability under irradiation was characterized by glancing-incident angle X-ray diffraction, cross-sectional transmission electron microscopy and selected-area electron diffraction. Characterization of the as-deposited CeO₂ films confirmed the cubic structure and a fine-grained nanocrystalline film with an O/Ce ratio of 2 and an average grain size of about 6 nm. Thermal annealing of as-deposited films at 400 K revealed no measurable grain growth. However, under irradiation, grain growth exhibits a power-law dependence on dose at all three temperatures. The increased saturation grain size with increasing temperature suggests a radiation-enhanced growth process.

P1-H21 - USING ATOMIC LAYER DEPOSITION TO HINDER SOLVENT DECOMPOSITION IN LITHIUM ION BATTERIES: FIRST PRINCIPLES MODELING AND EXPERIMENTAL STUDIES

[NEES] [Kevin Leung](#)¹, [Yue Qi](#)², [Kevin Zavadil](#)¹, [Yoon Seuk Jung](#)³, [Ann Dillon](#)³, and [Andrew Cavanaugh](#)⁴¹*Sandia National Laboratories;* ²*General Motors;* ³*National Renewable Energy Laboratory and* ⁴*University of Colorado*

Passivating lithium ion battery electrode surfaces to prevent electrolyte decomposition is critical for battery operations. Recent work on conformal atomic layer deposition (ALD) coating of anodes and cathodes has shown significant technological promise. ALD further provides well-characterized model platforms for understanding electrolyte decomposition initiated by electron tunneling through a passivating layer. Using density functional theory (DFT) calculations, the interactions between alumina-coated, lithium-intercalated graphite anode surfaces and ethylene carbonate (EC, a main component of commercial electrolyte) are compared with EC reactions on Li metal surfaces. EC accepts electrons from Li metal and decomposes within picoseconds, whereas constrained DFT (cDFT) calculations in an ultra-high vacuum setting suggest that, on the oxide coatings, electron tunneling to adsorbed EC falls into the non-adiabatic regime. Here the molecular reorganization energy, computed in the harmonic approximation, plays a key role in slowing down tunneling. *Ab initio* molecular dynamics simulation results emphasize that reactions and electron transfer occurs right at the interface, although a widely used DFT functional is found to underestimate tunneling barriers. X-ray photoelectron spectroscopy and electrochemical microgravimetric measurements indicate reduced electrolyte decomposition compared to uncoated anodes and corroborate the theoretical results.

P1-H22 - ELECTRONIC STRUCTURE AND TRANSPORT IN HEUSLER ALLOYS WITH PSEUDO-GAPS*

[RMSSEC] S. D. (Bhanu) Mahanti¹¹Michigan State University

Heusler alloys have been studied extensively since they were first discovered by Heusler in 1903. Among those Fe₂VAl and Fe₂TiSn became interesting when they showed heavy fermion characteristics without containing f electrons. Several experiments have indicated that these systems are semimetals with finite density of states (DOS) at the Fermi energy. *Ab initio* electronic structure calculations within LDA/GGA show that they are pseudo-gap systems with small DOS near the Fermi energy but sharp edges in the DOS near the Fermi level, making them promising thermoelectric materials.

Transport measurements in n-doped Fe₂VAl indeed show rather large power factors. We have carried out systematic studies of the electronic structure and thermopower (S) in this system using *ab initio* density functional theory (GGA) and Boltzmann transport theory to understand the experimental results, focusing on the carrier concentration and temperature dependence of S. These systems contain d electrons and since for the d-electrons which are localized, LDA and GGA do not give an accurate picture of the band structure, we have used GGA+U theory to investigate the effects of intra-site Coulomb repulsion (U) on the band structure and S. Effect of U and defects (vacancies and anti-site) on the detailed electronic structure and thermopower will be discussed. Work done in collaboration with Do Thanh Dat and Mal Soon Lee, and supported by the US Department of Energy, Office of Basic Energy Sciences as pa

P1-H23 - COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF METAL-MEDIATED C-O BOND FORMATION

[CCHF] Joanna R. Webb¹, Travis M. Figg², Mark J. Pouy¹, Bruce M. Prince², T. Brent Gunnoe¹, Thomas R. Cundari², and John T. Groves³¹University of Virginia; ²University of North Texas and ³Princeton University

Selective catalysts for the partial oxidation of hydrocarbons could provide more efficient routes for the production of commodity chemicals and fuels. In particular, conversion of the abundant hydrocarbon feedstock methane (natural gas) into a liquid such as methanol would have numerous benefits for the chemical and transportation sectors. Catalysts for hydrocarbon oxidation must be able to perform two key chemical steps, carbon-hydrogen bond activation and carbon-oxygen bond formation. Our strategy is to combine these two fundamental steps into a single catalytic cycle through carbon-hydrogen activation across a metal-alkoxide bond [M-OR + R'-H → M(ORH)(R')] followed by oxygen insertion into the newly formed metal-carbon bond. Carbon-hydrogen bond activation by addition across transition metal-heteroatom bonds has precedent in previous research by the Gunnoe and Cundari groups, as well as the Periana and Goddard groups. New routes for carbon-oxygen bond formation are most acutely needed to complete a viable catalytic cycle for conversion of methane to methanol. Recently, Periana and Goddard reported the insertion of an oxygen atom into the rhenium-methyl bond of methyltrioxorhenium. The current work builds upon these prior efforts by our CCHF collaborators. Through a synergism of theory and experiment, several novel carbon-oxygen bond formation pathways have been identified; chemical factors that favor one mechanism over the other have been delineated.

P1-H24 - LIGHT INDUCED SELF ASSEMBLY OF SWITCHABLE COLLOIDS

[NERC] Prateek Jha¹, Vladimir Kuzovkov², Bartosz Grzybowski¹, and Monica Olvera de la Cruz¹¹Northwestern University and ²University of Latvia

Dynamic self-assembly aims at producing ordered structures in otherwise disordered materials by controlled energy influx into the system. This strategy has been widely successful in the design of nanoscale components - where the conventional mechanical design methods cannot be used. From a theoretical perspective, dynamic self-assembly processes pose several difficulties because of their intrinsic non-equilibrium nature, since the well-established toolset of equilibrium thermodynamics cannot be applied. Non-equilibrium thermodynamics is a field in its infancy, and one is often faced with computational challenges associated with tracking the dynamics of infinitely many particles, that are needed to explain the mesoscale behavior of systems. We are working on a novel method of kinetic Monte Carlo simulations, applied to the study of aggregation phenomenon in a model system of colloidal particles under periodic light forcing.

P1-H25 - SELF-ASSEMBLY OF SWITCHABLE COLLOIDS

[NERC] Antonio Osorio¹, Igal Szleifer², and Sharon Glotzer¹¹University of Michigan and ²Northwestern University

With recent developments in experimental techniques, we can start to consider the synthesis and fabrication of switchable building blocks that can dynamically switch between two or more states and assemble into novel structures. In this work, we present some novel steady-state structures predicted by computer simulation to assemble in systems of switchable building blocks. We discuss tools for characterizing the resulting patterns, explore approaches to analyze the dissipative nature of the system, and provide a mapping to experimental colloidal systems where these concepts could be implemented.

P1-I01 - MULTIMODAL IMAGING AND MODELING OF LIGNOCELLULOSIC BIOMASS

[C3Bio] [Lee Makowski](#)¹, Mike Crowley², Michael Himmel², Shi-You Ding², Bryon Donohoe², Jeremy Madden³, Garth Simpson³, Jyotsana Lal, and Ross Harder

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Multiple imaging modalities are being used to monitor the deconstruction of lignocellulose during processing. Recalcitrance of biomass to physical and chemical processing is a major obstacle for biomass utilization as a feedstock for chemical or fuel production. Development of environmentally benign approaches requires detailed information about the effects of processing on the nanoscale structures within plant cell walls. No individual imaging method is capable of providing all the required information. Here we describe the coordinated use of transmission electron microscopy, atomic force microscopy, coherent x-ray diffraction imaging, and coherent second harmonic generation microscopy for the characterization of biomass deconstruction. Introduction of metallic catalysts into biomass either through environmental or genetic manipulations leads to modulation of the effects of deconstructive processes. Imaging of the biomass during deconstruction is generating detailed information about the effect of catalysis on nanoscale features of the biomass, thereby providing guidance for the development and refinement of novel catalytic approaches to biomass deconstruction.

P1-I02 - HIGH-RESOLUTION X-RAY IMAGING OF DISLOCATIONS AND THEIR INTERACTIONS

[CDP] [Eliot Specht](#)¹, Jon Tischler¹, Ben Larson¹, Matt Brandes², Jonghan Kwon², Michael Mills², Wenjun Liu³, and Gene Ice¹

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X-ray microbeam diffraction is being developed as a tool to nondestructively measure the three-dimensional position and motion of dislocations and other lattice defects, along with the deformation and stress fields that mediate the interactions of these defects. This microscopic information is needed to develop a fundamental understanding of the macroscopic deformation and mechanical reliability of materials. Since lattice rotations and elastic strains decrease rapidly as a function of distance from dislocations, submicron spatial resolution structural probes are needed to detect and track dislocations. We report ~300 nm resolution x-ray diffraction dislocation maps on thin (<1 micron) Ti-7%Al samples that were pre-measured by TEM to map the location and determine the type of dislocation structures. Local lattice tilts were measured using white-beam three-dimensional x-ray microscopy (3D-XM) on Sector-34 ID-E at the Advanced Photon Source (APS), which uses Kirkpatrick-Baez mirror optics, area detectors, and white-beam Laue diffraction. In addition to presenting results for 300 nm resolution, we discuss the impact of advanced Montel mirror optics with 150 nm focus that are under development in collaborations with the APS, and even higher-resolution optics in the planning stage. The potential for characterizing dislocation-defect interactions by mapping strain and lattice rotations using coherent as well as incoherent x-ray optics techniques will be considered.

P1-I03 - A NEW APPROACH TO MODELING PORE-SCALE REACTIVE TRANSPORT PROCESSES

[NCGC] [Sergi Molins-Rafa](#)¹, David Trebotich¹, Chaopeng Shen¹, and Carl Steefel¹

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Mineral precipitation (or dissolution) modifies the geometry of the pore space in subsurface sediment with continuously evolving solid-liquid boundaries. In turn, changes in the pore space alter the groundwater flow through the sediment, which ultimately affects the continuum scale reaction rates that are relevant for field applications such as carbon sequestration. We have developed a new suite of simulation tools for direct numerical simulation of reactive transport processes associated with CO₂ sequestration at the pore scale. Building on high performance computations of microscale flows in complex geometries developed at LBL in the Chombo software framework, we use operator splitting to couple it with the geochemical code CrunchFlow to perform high resolution calculations of reactive transport at the pore scale. Solution of flow and transport employs higher-order algorithms based on adaptive mesh refinement and finite volume methods. The capability has been validated against a single pore calcite dissolution problem published in the literature. Current work focuses on experimental validation of 3D packed bed systems with idealized flow domains where microspheres are packed in a cylinder. Pore scale modeling is used to gain insights into the scale dependence of such parameters as permeability and reactive surface area as they affect CO₂ sequestration, with an objective of upscaling these to the continuum scale.

P1-I04 - PROBING AND MAPPING ELECTRODE PROPERTIES USING RAMAN SPECTROSCOPY

[HeteroFoaM] Kevin Blinn¹, Xiaxi Li¹, Samson Lai¹, Mostafa El-Sayed¹, Andreas Heyden², and Meilin Liu¹
¹Georgia Institute of Technology and ²University of South Carolina

In situ characterization of the structure, morphology, and chemistry of fuel cell electrode surfaces and interfaces would provide information missed by conventional electrochemical analysis, such as new phases and intermediate species that form during anode contamination processes. Unfortunately, surface analysis methods such as XPS, LEED, and AES are not suitable for such studies because they require high vacuum in order to operate. One route for further analyzing electrode surfaces *in situ* is Raman spectroscopy. With the correct setup, this technique would allow for the tracking of the evolution of different species as well as new phases at electrode surfaces and interfaces while they are subject to various temperatures, atmospheres, and electrochemical stimuli. Raman methodologies have shown significant promise in characterizing the surface and interface structure and chemistry of solid oxide fuel cells. *In situ* experiments with controlled atmosphere have been shown to yield pertinent information on key surface species and phases for fuel cell processes, i.e. carbon build-up from anode coking. Enhanced Raman methods can increase sensitivity and potentially improve spatial resolution to the nm scale. This information, complemented by electrochemical measurements, surface morphology characterization (i.e. AFM), and DFT calculations, aim towards helping to unravel the mechanisms of the electrode reactions and thus offer better insights vital to design of better electrodes.

P1-I05 - EXPLORING CELLULOSE STRUCTURE BY SFG SPECTROSCOPY

[CLSF] Seong H. Kim¹, Christopher Lee¹, Daniel J. Cosgrove¹, Yong Bum Park¹, Jeffrey M. Catchmark¹, Jin Gu¹, Anna Barnette¹, and Laura Bradley¹
¹The Pennsylvania State University

Lignocellulose, an agriculture feedstock containing semi-crystalline cellulose, hemicellulose and lignin, is economically appealing for energy demands because it is highly renewable and globally available. For the first time it is possible to selectively detect crystalline cellulose in lignocellulosic biomass using sum-frequency-generation vibrational spectroscopy (SFG). Non-centrosymmetric ordering of glucosyl residues in crystalline cellulose yields a unique SFG profile. Amorphous hemicellulose and lignin do not contribute a SFG signal. Understanding synthesis and alteration of crystalline cellulose is dependent upon the capability of the technique employed. Conventional methods are limited to strong background interference, low sensitivity to crystallite size, and require chemically altered samples. However, SFG is effective on intact biological samples, without chemical modifications. SFG can quantitatively determine the amount of crystalline cellulose, and display significant spectral distinctions between 1alpha and 1beta native cellulose. SFG is sensitive to changes in crystalline cellulose due to: hemicellulose and water interactions, orientation of microfibrils, development of primary and secondary cell wall tissues, and chemical treatments for biofuels.

P1-I06 - REVEALING SOLAR FUEL GENERATION PATHWAYS USING X-RAYS

[ANSER] Lin X. Chen^{1,2}, David M. Tiede¹, Michael Mara¹, Jier Huang², and Oleksandr Kokhan¹
¹Argonne National Laboratory and ²Northwestern University

Resolution of structural dynamics at the atomic scale is fundamental for identifying mechanisms in solar fuels generation and for the design of efficient new catalysts. The ANSER (Argonne Northwestern Solar Energy Research) Center is addressing this challenge using synchrotron X-rays for determining static and transient structures involved in solar fuels catalysis. In particular, a facility at the Advanced Photon Source is being developed where a laser pulse mimicking the solar photons at a particular wavelength is used to create the initial excited-states of light-harvesting chromophores, while an X-ray pulse interrogates the reaction with adjustable time delays from the laser pulse to probe transient structures and electron transfer events that follow photoexcitation. Two structural methods are currently used to capture the structural transformation on different length scales. X-ray transient absorption spectroscopy is used to resolve transient local structures of metal catalysts, including coordination geometry, oxidation state and electronic configuration. Transient wide angle X-ray scattering is used to resolve atomic pair correlations at multiple length scales. These methods are combined with *in-situ* spectroelectro-XAS and WAXS to provide insightful information regarding the stability and efficiency of the catalysts and reveal the mechanisms of the reaction. Examples related to ANSER projects will be presented along with the description of the facility.

P1-I07 - DESIGN AND CONTROLLED SYNTHESIS OF SINTERING-RESISTANT CU/ZNO METHANOL SYNTHESIS CATALYSTS
NANOCONFINED IN MESOPOROUS HOSTS

[CALCD] Dr. Gonzalo Prieto¹, Jovana Zecevic¹, Dr. Heiner Friedrich¹, Prof. Krijn P. de Jong¹, and Dr. Petra E. de Jongh¹
¹Utrecht University (The Netherlands)

Metal sintering is a common deactivation pathway for many industrial catalysts applied to energy-related processes of utmost importance. Particularly relevant is the Cu-catalysed methanol synthesis from syngas. Under standard plant conditions, catalysts deactivate due to sintering of Cu nano-crystallites. Here, we report a fundamental study on the effects of confinement in mesoporous SiO₂ hosts, displaying different pore morphologies, on the deactivation behavior of Cu/ZnO catalysts under realistic catalytic conditions. Of special interest are liquid crystals-templated "caged" mesostructures, such as SBA-16, which display a 3D arrangement of mesocavities (6-15 nm) exclusively connected by narrower necks (< 4 nm). Highly dispersed SiO₂-supported Cu/ZnO catalysts are obtained through NO-mediated nitrate activation. Nano-confined catalysts display catalytic activities (per Cu mass) comparable to a benchmark Cu/ZnO(Al₂O₃) catalyst. Under "severe" methanol synthesis conditions (T=533K, P=40bar), catalysts "encaged" in SBA-16 cavities show an enhanced stability as compared to the benchmark counterpart or to Cu/ZnO catalysts confined in SiO₂-gel or channel-like SBA-15 hosts of similar pore dimensions (ca. 10 nm). Smaller cage/neck sizes provide further stabilization. Electron Tomography, applied to ultramicrotomed catalyst sections, offers 3D and quantitative information on the spatial location of metal species inside the 3D arrangement of mesocavities, at the nanoscale.

P1-I08 - CROSS-CUTTING RESEARCH THRUSTS IN THE CATALYSIS CENTER FOR ENERGY INNOVATION

[CCEI] Jingguang Chen¹

¹University of Delaware

The mission of the Catalysis Center for Energy Innovation (CCEI) is (1) to develop the enabling science leading to improved or radically new catalytic technologies for viable and economic operation of biorefineries from various biomass feedstocks, (2) to educate the workforce needed to further develop and implement these new technologies, which in turn will lead to further sustainable economic growth and reduced energy dependence of the U.S., and (3) to pursue technology transfer strategically via multi-institutional collaborations and joint ventures with industrial partners to impact the U.S. economy more quickly and efficiently. The goals of CCEI are (1) to transform biomass and/or its derivatives into valuable chemicals, fuels and electricity through a fundamental understanding of the chemistry and catalyst performance, (2) to design novel hierarchical multiscale materials with nanoscale resolution suitable for processing derivatives from complex, multiphase media of biomass to ensure efficient, highly selective and benign processes, and (3) to promote catalyst design and technology advancement through novel theoretical and multiscale simulation platforms and cutting-edge characterization tools. In this poster, we present cross-cutting computational, characterization and materials synthesis tools that are developed in CCEI to enable the development of efficient, selective, and benign conversion of biomass to chemicals and fuels.

P1-I09 - FULLY PHASE-COHERENT MULTIDIMENSIONAL SPECTROSCOPY: NOVEL METHODS FOR EXPLORING EXCITON DYNAMICS

[CE] Patrick Wen¹, Dylan H. Arias¹, Katherine W. Stone¹, and Keith A. Nelson¹

¹Massachusetts Institute of Technology

After the absorption of solar radiation, energy is quickly redistributed in photovoltaics, on the timescale of femtoseconds (10⁻¹⁵ seconds). Understanding the dynamics that occur on this timescale should provide essential details for engineering more efficient photovoltaics. One method toward this goal is employing femtosecond pulses of light to excite systems followed by pulses of light to take snapshots of the system dynamics via changes in its spectrum. However, there are several shortcomings of this method, including overlapping peaks, ambiguous relationships between peaks, and an inability to directly resolve the correlated dynamics between multiple excited states. Over the last fifteen years, multidimensional spectroscopy of electronic states has been developed to overcome these difficulties. The key innovation in multidimensional spectroscopy is that after initially exciting the sample with a pulse of light, the influence of each initially excited state is correlated to changes in each peak recorded in subsequent emission spectra, overcoming the aforementioned shortcomings. Multidimensional electronic spectroscopy is particularly challenging to implement because phase stability between pulses of light is required. We demonstrate fully phase-coherent multidimensional electronic spectroscopy by shaping each pulse of light with a spatial light modulator. The newly built instrument is shown to be robust and versatile.

P1-I10 - ADVANCED TOOLS FOR THE DEVELOPMENT OF NOVEL PHOTOVOLTAIC MATERIALS: COMBINATORIAL DEPOSITION AND ANOMALOUS X-RAY DIFFRACTION

[CID] Joanna Bettinger¹, Yezhou Shi¹, Andriy Zakutayev², Paul Ndione², Philip Parilla², John Perkins², David Ginley², and Michael Toney¹

¹SLAC National Accelerator Laboratory and ²NREL

Accelerating the search for new energy materials requires advances in both sample growth and characterization. Combinatorial deposition allows for high-throughput fabrication of thin films with varying compositions, thus allowing an optimal stoichiometry to be found more readily. Anomalous X-ray diffraction (AXRD), a synchrotron technique, probes the lattice site-occupancy. Together, these tools enable detailed correlation of the atomic structure with the electronic properties and hence robust experimental tests of our Inverse Design approach to materials development. We have grown thin-film composition-gradient samples of Co-Zn-O, a candidate for p-type transparent conductor. Several combinatorial libraries were grown and characterized for their electrical, optical, and structural properties at each composition. "Best-in-class" films at a uniform composition were then grown for characterization at the Stanford Synchrotron Radiation Lightsource with AXRD. The spinel structure symmetry dictates that the (222) reflection probes only octahedral sites and the (422) reflection probes only tetrahedral sites. The AXRD diffraction peak intensities as a function of energy around the Co and Zn K absorption edges were fit to determine the site occupancy, or the amounts of Zn and Co on the tetrahedral and octahedral sites. Comparisons of AXRD to electronic structure results allow us to correlate the site occupancy to the conductivity in combinatorial films.

P1-I11 - THE TOOLS OF INTERFACE CHARACTERIZATION: THE CENTER FOR INTERFACE SCIENCE: SOLAR ELECTRIC MATERIALS

[CISSEM] Neal Armstrong¹, Mariola Macech¹, Gordon MacDonald¹, Samuel Graham², Yongjin Kim², Jeanne Pemberton¹, Oliver Monti, Anne Simon¹, Brooke Beam¹, Scott Saavedra¹, Bradley Macleod¹, and David Ginger³

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All emerging thin-film photovoltaic (PV) technologies which use organic materials as active layers, and PV platforms with active layers based on combinations of semiconducting polymers and semiconducting nanocrystals and/or nanoporous metal oxides, rely upon high efficiencies of charge formation and charge harvesting that compete favorably with recombination, to ensure high power conversion efficiencies. Understanding composition and energetics of these interfaces, at nanometer length scales, requires the optimization of established surface science techniques, and the development of entirely new interface characterization technologies and protocols. Certain metal oxide combinations (nanolaminates) have demonstrated properties which make them promising candidates for barrier films, which requires characterization tools to understand the interfaces in these new barrier films. This presentation will summarize the new tools of interface science being developed by CISSEM, and their impact on enabling the development of new PV technologies.

P1-I12 - SPATIALLY RESOLVED THERMAL TRANSPORT IN SURROGATE NUCLEAR FUEL MATERIALS WITH ENGINEERED MICROSTRUCTURES

[CMSNF] Marat Khafizov¹, David Hurley¹, In-Wook Park², John Moore², Jianliang Lin², Ryan Deskins³, and Anter El-Azab⁴

¹Idaho National Laboratory; ²Colorado School of Mines; ³Florida State University and ⁴Florida State University

Understanding thermal conductivity of nuclear fuels is important for development of more efficient, safer and longer lifetime nuclear fuels. We study phonon mediated thermal transport in ceria, as a surrogate material for oxide fuels. Polycrystalline ceria thin films with engineered microstructure are deposited on silicon substrates using pulsed unbalanced magnetron sputtering. Thermal transport properties are measured using laser based thermal wave microscopy (TWM). In TWM, the sample is heated by a strongly focused, amplitude modulated laser beam. Thermal wave profiles are recorded by scanning the probe beam across the surface and monitoring temperature induced reflectivity change as a function of modulation frequency. Thermal transport properties are extracted from the analysis of the measured temperature profile using a continuum based model. Utilizing this approach, we perform temperature dependent measurements of thermal conductivity in ceria thin films. A thermal transport model based on the Boltzmann transport equation that explicitly incorporates the influence of grain boundaries is compared with our experimental results. We conclude that thermal conductivity in these samples is strongly influenced by phonon scattering at grain boundaries.

P1-I13 - PHASE FIELD MODELING OF VOIDS NUCLEATION AND GROWTH IN IRRADIATED MATERIALS

[CMSNF] Srujan Rakkam¹, Thomas Hochrainer¹, Todd Allen², and ³Anter El-Azab¹Florida State University; ²University of Wisconsin-Madison and ³Florida State University

We have developed a mesoscale phase field model for the collective dynamics of defects and nucleation and growth of voids in a single component material, as a basis to achieve the same for UO₂. We treat both nucleation and growth processes simultaneously in a spatially resolved fashion, thereby providing insight into the space and time coupling of microstructural evolution. Using principles of irreversible thermodynamics, the vacancy and interstitial fluxes and concentrations are described by Cahn-Hilliard type equations. The dynamics of void growth are obtained in terms of the evolution of a non-conserved order parameter field, whose evolution is prescribed by an Allen-Cahn type equation. Point defects generated by atomic displacement cascades are introduced as stochastic point processes which are random in space and time. The interactions between point defects and with extended defects are given as reaction terms entering the evolution equations. We illustrate model capabilities with regard to void nucleation and growth in the presence of interacting point-defects, defects interacting with lattice sinks (such as grain boundaries). Effect of irradiation rate and thermal fluctuations on void nucleation and growth is investigated. A key scientific finding is that the material swelling due to irradiation is associated with the migration of interstitial and vacancies to sinks, as opposed to the nucleation and growth of voids.

P1-I14 - CONTROLLED NANOSTRUCTURE FABRICATION FOR PHOTOVOLTAICS AND STORAGE USING STM-ALD

[CNEEC] Philip Van Stockum¹, James Mack¹, and Fritz Prinz¹¹Stanford University

We have designed and constructed a combined scanning probe microscope (SPM) and atomic layer deposition (ALD) system in order to explore the physical parameter space of nanostructures for applications in energy conversion and storage devices. The SPM-ALD system is a low noise, high vacuum system capable of atomic resolution scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and atomic force microscopy (AFM). In addition, the system can be used for tip-based lithography using ALD precursors in order to fabricate nanostructures from a wide variety of materials with control of position, shape, and size. The system has the capability to operate at sample temperatures between -200 and 200 degrees Celsius, with a high vacuum sample turnaround time of about two hours. Some of the energy-related features of nanostructures which we plan to explore with this tool are band gap tuning, stable exciton formation in adjacent nanostructures, and control of intermediate states for up/down conversion and multiple exciton generation.

P1-I15 - STRUCTURE OF Li[LIM]O₂ ELECTRODES FOR LITHIUM-ION BATTERIES[CST] Karalee Jarvis¹, Zengquiang Deng¹, Eun Sung Lee¹, Penghao Xiao¹, Graeme Henkelman¹, Arumugam Manthiram¹, and Paulo Ferreira¹¹University of Texas at Austin

With an aim to increase the energy density of lithium-ion batteries, lithium-rich layered oxides with the general formula Li[M_{1-x}Li_x]O₂ (M = Mn, Co, and Ni) have become appealing recently as they exhibit much higher capacities (250 mAh/g) relative to that of LiCoO₂ (140 mAh/g). However, as the structure of these materials is very complex, a major debate is ongoing on whether the material is composed of two layered phases or a single-phase solid solution. Of particular interest is whether the Li[M_{1-x}Li_x]O₂ material must be composed of two phases to exhibit high reversible capacity. Much of the reported structural analysis techniques have led to different interpretations by different groups. We examined the atomic structure of Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ using, for the first time, a combination of advanced characterization techniques, namely aberration-corrected scanning transmission electron microscopy (STEM) image simulations and a newly developed diffraction scanning transmission electron microscopy (D-STEM) method. These studies show unambiguously that Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ is a solid solution with C2/m monoclinic symmetry and multiple planar defects, suggesting that the Li[M_{1-x}Li_x]O₂ type materials can be single-phase and still exhibit high reversible capacity.

P1-I16 - INSTRUMENTATION FOR NANOSCALE THERMOMETRY AND PICOWATT CALORIMETRY

[CSTEC] Pramod Reddy¹, Seid Sadat¹, Yi-Jie Chau¹, and Aaron Tan¹¹University of Michigan

Probing temperature fields with nanometer resolution is critical to understanding nanoscale thermal transport as well as dissipation in nanoscale devices. We present an atomic force microscope (AFM) based technique capable of mapping temperature fields in metallic films with ~10 mK temperature resolution and <100 nm spatial resolution. A platinum coated AFM cantilever placed in soft mechanical contact with a metallic (gold) surface is used to sequentially create point contact thermocouples on a grid. The local temperature at each point contact is obtained by measuring the thermoelectric voltage of the platinum-gold point contact and relating it to the local temperature. We have also developed a calorimeter capable

of <4 pW resolution, which represents an order of magnitude improvement over state-of-the-art room temperature calorimeters. This is achieved by the incorporation of two important features. First, the active area of the device is suspended by thin and long beams making it possible to achieve a thermal conductance (G) as low as ~600 nW/K.

Further, a bimaterial cantilever thermometer is integrated into the device, which when combined with a phase locked loop measurement scheme enables temperature measurements with a resolution (ΔT_{res}) of ~4 μ K and a noise floor of ~6.4 μ K. The small thermal conductance coupled with the excellent temperature resolution enable measurement of modulated heat currents ($q = G \times \Delta T_{res}$) with a resolution better than 4 pW.

P1-I17 - BEAM-ASSISTED NANOSTRUCTURING IN THIN FILMS FOR THERMOELECTRICS

[CSTEC] Michael Warren¹, Yuwei Li¹, Vladimir Stoica¹, Lynn Endicott¹, Guoyu Wang¹, Adam Wood¹, Justin Canniff¹, Roy Clarke¹, Ctirad Uher¹, and Rachel Goldman¹

¹University of Michigan

Due to the possibility of simultaneously enhancing the electron density of states and reducing the thermal conductivity, nanocomposite materials have been identified as promising candidates for high figure-of-merit thermoelectrics. Although nanocomposites have been fabricated using epitaxial growth and chemical synthesis followed by ball-milling, the high predicted thermoelectric performance has not yet been achieved. We are investigating alternative approaches to nanocomposite synthesis using ion and ultra-fast laser beams. Using ion beams, we fabricate ultra-small nanocrystallites within amorphous matrices, via a process termed "matrix-seeded growth"[1]. Using In⁺ implantation, we are studying the matrix-seeded growth of InAs nanocrystals in GaAs. To maximize the implanted [In] by minimizing sputtering, we use a "sputter mask" approach consisting of AlAs/GaAs bilayers. We will discuss the influence of In⁺ dose and annealing on nanostructure formation, as well as on the T-dependence of the resistivity and Seebeck coefficient of the GaAs:In structures. Using ultra-fast laser-light, we are also investigating the formation of "nanotracks" on the surface of Sb₂Te₃ thin films [2]. We will discuss the influence of laser fluence and scan speed on nanotrack formation and dimensions. [1] X. Weng, W. Ye, S.J. Clarke, R.S. Goldman, V. Rotberg, A. Daniel, R. Clarke, J. Appl. Phys. 97, (2005). [2] Y. Li, V.A. Stoica, L. Endicott, G. Wang, C. Uher, R. Clarke (to be published).

P1-I18 - UNIQUE CAPABILITIES AND TECHNIQUES: REAL-TIME HIGH-ENERGY X-RAY DIFFRACTION AND REAL-TIME STEM

[EMC2] Jun Young Ko¹, Yingchao Yu¹, Manuel Plaza¹, Xin Huang¹, Alexander Kazimirov¹, Huolin Xin¹, Robert Hovden¹, Megan Holtz¹, Julia Mundy¹, David Muller¹, Joel Brock¹, and Hector Abruna¹

¹Cornell University

X-ray: We purchased a 40 cm x 40 cm area detector (GE Inspection Technologies) that is ideal for high energy (60-80 keV) X-ray diffraction studies. The main advantage of the detector is a substantial reduction in data acquisition time due to parallel collection and a fast read-out time (30 Hz). To match its full capabilities, we are building a high-energy micro-diffraction station at Cornell High Energy Synchrotron Source (CHESS) to increase the X-ray flux by 1000x. With this upgrade, we plan to perform real-time structural characterization of interfaces, novel materials, and processes associated with energy materials. STEM: We are implementing an *in-situ* liquid cell for the field-emission scanning transmission electron microscope (STEM). There are three *in-situ* capabilities which are to be fulfilled: (a) nanomaterial heating, (b) liquid flow, and (c) electrochemical scan. The *in-situ* heating enables us to reveal the growth mechanism of nanoparticle upon heating, providing some insight into the synthesis of energy materials. The *in-situ* liquid cell design allows for flowing of liquids into the TEM chamber, and has been used to study reactions of energy materials, such as chemical delithiation. With (a) and (b) completed, the next generation will include patterned electrodes for *in-situ* electrochemistry.

P1-I19 - IN-SITU S/TEM CHARACTERIZATION OF ELECTRODE/ELECTROLYTE INTERACTIONS FOR ENERGY STORAGE APPLICATIONS

[FIRST] Raymond R. Unocic¹, Leslie A. Adamczyk¹, Nancy J. Dudney¹, P. Ganesh¹, Paul R.C. Kent¹, De-en Jiang¹, and Karren L. More¹

¹Oak Ridge National Laboratory

In lithium ion batteries, it is the interfaces that play an active role in controlling the electrochemical energy conversion process. Of most crucial importance to the performance is the formation of a passive nanometer-scaled film that forms along the electrode/electrolyte (solid/liquid) interface as a result of electrolyte decomposition. Termed the solid electrolyte interphase (SEI), this layer acts to protect the active electrode materials from degradation while simultaneously regulating the transport of Li ions. In order to gain fundamental insight into the atomic-scale processes we have developed an *in-situ* characterization device that has the unique capability of capturing dynamic processes occurring along electrode/electrolyte interfaces during electrochemical cycling. The electrochemical cell *in-situ* TEM holder is comprised of removable Si chips with electron transparent SiN viewing windows and a liquid delivery system. SEI formation at the graphite interface was studied during charging in an electrolyte consisting of LiClO₄ in EC:DEC. To better understand the

physics of SEI formation and to compare with experimental observations, quantum molecular dynamics simulations was used to study interfacial reactions and breakdown of the electrolyte. It is expected that the outcome of this research will undoubtedly shed new light on the fundamental physical and chemical processes that control electrical energy generation and storage.

P1-I20 - SYNTHESIS OF OXIDE 'NANOBOWLS' AND 'ARMOR-COATED' ACTIVE SITES BY TEMPLATED ALD: A NEW PARADIGM IN HETEROGENEOUS CATALYST SYNTHESIS

[IACT] Canlas, Christian P.¹, Lu, Junling², Ray, Natalie¹, Lee, Sungsik², Winans, Randall², Elam, Jeffrey², Stair, Peter¹, and Notestein, Justin¹

¹Northwestern University; ²Argonne National Laboratory

One of the most important goals in heterogeneous catalyst development is to increase selectivity and stability. Here, we utilize atomic layer deposition, which has been used for years in microelectronics fabrication but only recently applied to heterogeneous catalysts synthesis, to grow thin oxide layers perforated with cavities over an existing oxide catalyst. We call these <2 nm deep nanometer cavities 'nanobowls'. Their presence introduces a size-sieving feature to an existing catalyst surface, and they can 'armor-coat' individual active sites on a surface. In this study, the nanobowls are generated by using a molecular template immobilized on a surface before ALD. They are deposited on oxide supports and a wall of oxide is grown around the immobilized template molecule by ALD. Template removal generates the nanobowl. The existence of the nanobowls is elucidated by *in-situ* QCM studies, SAXS and TEM. Size selectivity of the catalysts is demonstrated through selective photooxidation of benzyl alcohol, 1-hexanol and 2-adamantanol over a traditionally non-selective titania photocatalyst. For ALD films, bulky secondary alcohols like 2-adamantanol are able to access fewer active sites on the titania surface than do terminal alcohols like benzyl alcohol and 1-hexanol. This selective photocatalytic oxidation of alcohols demonstrates how nanobowls can discriminate size on an arbitrary catalyst surface and introduces a new paradigm in heterogeneous catalyst synthesis.

P1-I21 - STABILIZATION OF SUPPORTED METAL NANOPARTICLE CATALYSTS USING ATOMIC LAYER DEPOSITION

[IACT] Junling Lu¹, Hao Feng¹, Peter C. Stair², and ¹Jeffrey W. Elam

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Catalyst deactivation is costly in industrial applications due to the necessity of catalyst regeneration or replacement and the accompanying process shutdown. For supported metal catalysts, one major cause of deactivation is metal sintering. Methods have been developed to encapsulate noble metal NPs in various types of porous materials using techniques such as chemical vapor deposition, grafting, micro-emulsion, dendrimer encapsulation, etc. to form core-shell structures. Encapsulated NPs showed good sintering resistance up to 800 °C. However, in most cases there is a decrease in catalytic activity due to the mass transfer resistance associated with the protective shell (usually tens of nm's thick). Atomic layer deposition (ALD) provides the possibility for post-synthesis modification of supported catalysts by applying protective layer with precise control over thickness and composition. Very recently, we demonstrated that ALD alumina over-coating on Pd catalysts could effectively prevent the sintering of Pd NPs under reaction conditions, while preserving the catalytic activity. Using CO as a probe molecule, we found that the ALD alumina over-coat layers preferentially nucleate at corners, steps, and edges on the Pd NPs while leaving the catalytically active Pd (111) facets accessible. This preferentially blocking feature on metal NPs might point out a new way to enhance the selectivity in catalytic reactions, especially those sensitive to the shape and facets of NPs.

P1-I22 - DIRECT-WRITE ASSEMBLY OF TRANSPARENT CONDUCTING ELECTRODES FOR FLEXIBLE PHOTOVOLTAICS

[LMI] Bok Y. Ahn¹, David Lorang¹, Ralph G. Nuzzo¹, and Jennifer A. Lewis¹

¹University of Illinois

The ability to pattern functional materials in planar and three-dimensional forms is of critical importance for several emerging applications, including flexible electronics, photovoltaics, and optical displays. Direct-write assembly enables one to rapidly fabricate diverse classes of materials in arbitrary shapes without the need for expensive tooling, dies, or lithographic masks. In this poster, we highlight the fabrication of transparent conductive electrodes by direct writing of concentrated silver nanoparticle and tin-doped In₂O₃ (ITO) inks. This maskless, etch-free patterning approach is used to produce well-defined, two-dimensional periodic arrays composed of conductive silver features with center-to-center separation distances of up to 400 μ m and an optical transmittance as high as 94.1%. In addition, we demonstrate a facile route to patterning transparent conductive oxides in planar arrays and spanning architectures. These conductive metallic and oxide grids may find potential application in large-area, flexible photovoltaic devices.

P1-I23 - LIGHT-INDUCED PATTERN FORMATION DURING THE GROWTH OF CHALCOGENIDE FILMS

[LMI] Bryce Sadtler¹, Joseph Beardslee¹, and Nathan Lewis¹¹California Institute of Technology

Processes for light-driven material synthesis can enable energy conversion materials to develop their own complex architectures in response to illumination conditions. We have developed a method to spontaneously create nanoscale patterns in semiconductor selenium-tellurium (Se-Te) alloy films by shining light on the film as it grows. The patterns emerge within minutes while the films grow under a photon flux comparable to that of solar radiation. While no pattern is observable for Se-Te films prepared in the dark, those deposited under illumination display an ordered honeycomb network of pores. At longer deposition times lamellae develop via growth of material between the pores. The amplitude and periodicity of the honeycomb and lamellar patterns can be tuned with the intensity, wavelength, and coherency of the illumination source. We propose a mechanism where the patterns arise from the nonlinear photoresponse of the chalcogenide material, which acts to modulate the light intensity through the film and produce an ordered network of photogenerated charge carriers. The long lifetime of excited electrons in the Se-Te film inhibits film growth in the vicinity of trapped charges. This light-driven growth technique opens up the possibility for optimizing the absorption and transmission characteristics of a material by using light in a feedback loop to direct its structure and morphology.

P1-I24 - THERMOCHEMICAL STUDIES OF ACTINIDE MATERIALS

[MSA] T. Shvareva¹, C. Armstrong¹, T.J. Park¹, B. Hanken¹, and A. Navrotsky¹

University of California, Davis

The knowledge of the thermodynamic stability of actinide materials, from perspectives as promising nuclear fuels and as potential waste forms, is essential and urgent need. The highest research priorities in this EFRC are the energetics of fluorite-structured oxides, uranyl peroxide cluster compounds, and uranyl hybrid materials. Mixing enthalpies for La³⁺-, Y³⁺- and Ce⁴⁺-doped ThO₂ are calorimetrically determined and supported by DFT calculations (M. Asta's group). Energetics of water adsorption on ThO₂ are measured and reveal exothermic chemisorption of eight water molecules per nm² of surface (in agreement with computational studies, M. Asta's group). Surface enthalpies of ThO₂ are 0.92 ± 0.10 J/m² for hydrous and 1.24 ± 0.16 J/m² for anhydrous surfaces. Energetics of uranyl clusters and their monomeric precursors have been measured. Alkali-bearing peroxide cluster compounds are thermodynamically stable in air, even without the presence of excess peroxide in solution (collaboration with M. Nyman's group and P. Burns' group). Measured enthalpies of formation for hybrid organic-inorganic actinide materials with similar uranyl coordination units but variable ligand bonding suggest that ligand structure and bonding do not impact the energetics of selected uranyl-organic materials; however there appears to be a relationship between density and stability (collaboration with C. Cahill's group)

P1-I25 - CHARGE-STORAGE PROCESSES IN MODEL MnO₂-LI-HOPG SYSTEMS: ELECTROCHEMICAL SPM AND UHV-STM INVESTIGATIONS[NEES] Satyaveda C. Bharath¹, Wentao Song¹, Janice E. Reutt-Robey¹, and Kevin R. Zavadil²¹University of Maryland and ²Sandia National Laboratories

Nanostructured materials have the potential to substantially improve the speed, efficiency, and cyclic lifetime of energy storage systems such as the lithium-ion battery (LIB). Nanometer-scale oxide cathode elements allow for greater extent of lithium incorporation due to improved strain accommodation relative to conventional cathode structures. Exposed surface facets in structures with high surface/volume ratio will act as gateways to lithium insertion, playing an important kinetic role in charge storage. However, detailed mechanisms of lithium insertion and their dependence on oxide facet orientation and grain size and shape are largely unknown. As a platform for fundamental investigations of charge-transfer processes in nanocrystalline materials, we have developed a MnO₂-Li-HOPG model system. This system consists of low-dimensional beta-MnO₂ and cubic spinel Li_{1+x}Mn_{2-x}O₄ nanocrystallites, synthesized by the reactive co-deposition of elemental Mn and molecular oxygen on native and modified graphite (C(0001)) supports under ultrahigh vacuum conditions. Nanocrystallite phase and composition has been confirmed using single particle electron diffraction, as well as TOF-SIMS and scanning AES. Morphology of individual nanocrystallites, and their registration to the C(0001) support, have been determined with ambient AFM and UHV STM methods. The morphological response of beta-MnO₂ nanocrystallites to Li⁺ insertion has been preliminarily explored under electrochemical conditions with *in-situ* electrochemical STM/AFM and under solid-state conditions with UHV-STM. The sensitivity of these methods are currently limited by low beta-MnO₂ - C(0001) electrical conductivity, and efforts to overcome this limitation will be described. Additionally, alkali seeded growth of MnO₂ nanocrystals will be presented as a means to guide the formation of alternative MnO₂ polymorphs. Supported by Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under award DESC0001160.

P1-I26 - LASER ENHANCED ATOM PROBE (LEAP) TOMOGRAPHY

[RMSSEC] Ivan D. Blum¹, Jiaqing He¹, John Androulakis¹, David N. Seidman¹, Vinayak P. Dravid¹, and Mercouri G. Kanatzidis¹

¹Northwestern University

Characterization of nanostructured thermoelectric materials is necessary to understand the effect of nanostructures on the thermoelectric properties and how to control these nanostructures to improve the figure of merit. Laser-enhanced atom-probe (LEAP) tomography [1] enables composition measurements in three-dimensions and often at the sub-nanometer scale, unlike conventional microscopy techniques like transmission electron microscopy (TEM). Samples are prepared for LEAP analysis employing dual-beam focused ion-beam microscopy: micron-size pieces of material are extracted from bulk specimens and sharpened to a local radius of less than 50 nm. The combination of a high dc electric-field and ultraviolet (wavelength = 355 nm) laser pulsing enables atom-by-atom dissection of the microtip. Identification of the evaporated ions allows three-dimensional reconstruction of the analyzed volume of material. We employ LEAP tomography to characterize PbTe-K_{1.25mol%}-Na_{1.4mol%}, which is known to exhibit a high figure of merit [2]. The analysis reveals the presence of nanometer-size Na-rich precipitates. In combination with TEM, LEAP tomography is shown to be a promising technique for the characterization of nanostructured thermoelectric materials. [1] D. N. Seidman and K Stiller, MRS Bulletin, 34(10) (2009) 717. [2] J. Androulakis, I. Todorov, D. Y. Chung, S. Ballikaya, G. Y. Wang, C. Uher, M. Kanatzidis, Physical Review B, 82 (2010) 115209.

P1-I27 - STRUCTURE OF INTERFACES FOR ORGANIC PHOTOVOLTAIC MATERIALS

[RPEMSC] Theanne Schiros¹

¹Columbia University

New directions for the design of organic photovoltaic devices (OPV) with improved functional performance are demonstrated based on exploitation of molecular shape complementarity and self-assembly. Synchrotron-based surface-sensitive techniques, including grazing incidence x-ray diffraction (GIXD), near edge x-ray absorption fine structure (NEXAFS), and x-ray photoelectron (XPS) and resonant photoemission (RESPES) spectroscopy provide powerful probes of the microstructure, interfacial composition, molecular orientation and electronic interaction at the donor-acceptor interface in the OPV active layer. With these techniques, we demonstrate that doubly-concave donor molecules (hexabenzocoronene) form nested "ball-and-socket" interfaces with fullerene acceptors leading to improved exciton dissociation at the interface. Improved charge transport is realized with a dibenzotetrathienocoronene (DBTTC) that undergoes a heat-induced assembly process to form supramolecular cables and a 3-D reticulated donor/acceptor heterojunction with C60. Simultaneous control over the crystal growth, molecular packing, and charge (hole) transport directions has been demonstrated with the growth of vertical nanocrystals directly on graphene. These findings open new opportunities in nanotemplated architectures for OPVs, advantaged by high surface area, excellent crystallinity, and pi-stacking in the direction of charge transport, as well as the use of graphene as a transparent contact.

P1-I28 - STUDYING THE FUNDAMENTALS OF HEAT TRANSPORT AT SHORT DISTANCES

[S3TEC] Jeremy Johnson¹, Kara Manke¹, Jeffrey Eliason¹, Alexei Maznev¹, Keith Nelson¹, Austin Minnich¹, Maria Luckyanova¹, Kimberlee Collins¹, Gang Chen¹, Adam Jandl¹, Mayank Bulsara¹, Eugene Fitzgerald¹, and Mildred Dresselhaus¹

¹MIT

In many materials relevant for thermoelectric or nano-electronic applications, lattice vibrations known as acoustic phonons are responsible for the majority of thermal transport. Thermal conductivity is directly related to the frequency-dependent mean free paths (MFPs) that acoustic phonons travel before being scattered in other directions or converted into other phonons. We usually think of heat flowing diffusively to cooler regions in a material, but when measured on length scales shorter than the phonon MFP, at distances important for nanostructured materials and devices, heat travels ballistically at the sound speed without scattering, rather than diffusively. We used optical spectroscopy techniques to observe departure from diffusive transport in Si and GaAs at experimentally specified length scales in the micron range, even at room temperature where textbook MFP values are ~ 40 nm. It is understood that MFPs decrease sharply as acoustic frequencies increase to the GHz and THz regime, but in fact are poorly characterized at such high phonon frequencies important to thermal transport. We also demonstrated optical generation and measurement of GHz-THz acoustic phonons in nanostructured materials and made preliminary measurements of phonon MFP values in this frequency range as well as thermal transport in different directions. The experimental studies are essential to developing a more complete understanding of thermal transport over short distances.

P1-I29 - WORLD-CLASS INSTRUMENTATION FOR DISCOVERING THE FUNDAMENTALS OF PHOTOVOLTAIC AND SOLAR FUELS DEVICES

[UNC] Kyle Brennaman¹, John Papanikolas¹, Thomas Meyer¹, Andrew Moran¹, Christopher Fecko¹, and Malcolm Forbes¹
¹UNC Chapel Hill

The development of viable next-generation photovoltaic and solar fuels devices requires ground-breaking fundamental research made possible only with world-class instrumentation capable of tracking electron and energy transfer events on a variety of timescales. As presented here, the UNC EFRC has assembled an impressive array of experiments and established user facilities in: Spectroscopy, Photolysis, Device Fabrication and Analysis, and Gas Chromatography/Mass Spectrometry (GC-MS). In the Spectroscopy Laboratory, UV-NIR absorption spectral monitoring is available from femtoseconds to seconds. Additional capabilities exist or are in construction for time-resolved experiments with IR, EPR, and Raman monitoring. Special capabilities are under construction that will allow for increased sensitivity, faster time resolution, simultaneous collection of temporal and spectral data on a functioning device, and monitoring sequential photon events. The Photolysis Laboratory provides capabilities for photolysis and photochemical or photoelectrochemical excitation with a variety of light sources with solar fuels analysis given by the GC/MS Facility. Capabilities include photocurrent efficiency and I-V measurements on working devices. The Device Fabrication and Analysis Laboratory houses facilities for the synthesis of thin film semiconductor electrodes. Mott-Schottky analysis and temperature-controlled UV-VIS-NIR absorption & emission are available for semiconductor defect measurements.

P1-I30 - FACILE PT-TO-PT METHYL GROUP TRANSFER IN O₂²⁻(DPMS)Pt^{II}Me(X)- SYSTEMS IN WATER (X = OH⁻, I⁻)

[CCHF] Anna V. Sberegaeva¹ and Andrei N. Vedernikov¹
¹University of Maryland

Catalytic CH activation of methane with PtII compounds has been reported by Shilov et al. back in 70's, since then many research groups have focused on improving catalyst activity and selectivity of the Shilov system. Some groups also investigated O₂ as a terminal oxidant (Shilov, Sen, Neumann, Bao to name a few) or metal oxo species (Crabtree, Groves, Gunnoe, Periana) for oxy-insertions into M-R bonds. Despite these efforts achieving appropriate reaction selectivity proved challenging. Previously our group introduced a family of di(2-pyridyl)methanesulfonate (dpms) ligands that enable transformation of (dpms)Pt^{II}Alk(HX) to (dpms)Pt^{IV}Alk(X)OH with O₂ and subsequent reductive elimination of oxygenated alkane derivatives such as alcohols, ethers, epoxides, from the latter. The nature of the XH ligand (XH = water, alcohols or primary amines) and reaction pH have profound influence on the rate of Pt^{II} -> Pt^{IV} transformation and product distribution. The proposed mechanism of the oxidation includes deprotonation of XH as the step immediately preceding O₂ activation with an anionic [(dpms)Pt^{II}(Alk)X] . The oxidation step is studied in this work in more detail. It was found that (dpms)Pt^{II}Me(OH₂) undergoes facile Pt-to-Pt methyl group transfer in the presence of iodide anion or in the absence of iodide but at high solution pH. Results of a kinetics study and isotopic labeling experiments will be reported and the mechanism of the Pt-to-Pt methyl group transfer will be discussed.

P1-I31 - MSN SUPPORTED PT COMPLEXES FOR OLEFIN HYDROARYLATION

[CCHF] Jeremy R. Andreatta¹, Hung-Ting Chen², T. Brent Gunnoe¹, Victor S.-Y. Lin³, and Brian G. Trewyn³
¹University of Virginia; ²Iowa State University and ³Iowa State University

The catalytic hydroarylation of olefins provides an atom economical route to alkyl arenes. For many years, the use of acidic Friedel-Crafts catalysts has been a dominant route for the preparation of alkyl arenes. Recently, the Gunnoe group has reported the development of non-Friedel-Crafts catalysts such as Ru(II) and Pt(II) systems. For example, TpRuPh(NCMe)(CO) (Tp = hydridotris(pyrazolyl)borate) and [(tbpy)Pt(Ph)(L)][BARF₄] (tbpy = 4,4'-di-tert-butyl-2,2'-bipyridine; L = THF, NCMe or NC₅F₅, BARF₄ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) catalyze the conversion of benzene and ethylene to ethylbenzene under relatively mild reaction conditions. The preparation of single-site catalysts supported on mesoporous silica nanoparticles (MSNs) is being pursued in collaboration with the group of Dr. Brian Trewyn (Iowa State University). The initial strategy is to incorporate functionality at the 4 and 4' positions of the bipyridyl ligand of the Pt(II) system that can be used to provide a covalent attachment of the catalyst to the MSN. Preliminary studies demonstrate that this strategy is successful, including control experiments that are consistent with catalysis originating from supported material rather than leaching of Pt. Direct comparison of homogeneous and MSN-supported Pt catalysts reveals very similar selectivity and an enhancement of catalyst lifetime for the single-site MSN material.

P1-I32 - HYDROCARBON OXIDATION IN AQUEOUS AND NONAQUEOUS MEDIUM BY METAL OXO CATALYSTS

[CCHF] Amit Paul¹, Aaron K. Vannucci¹, Jonathan F. Hull¹, Zuofeng Chen¹, Daniel H. Ess², Michael R. Norris¹, Javier J. Concepcion¹, and Thomas J. Meyer¹

¹UNC Chapel Hill and ²Brigham Young University

Benzyl alcohol oxidation in aqueous medium was studied by Ru^{IV}=O²⁺ and Ru^V=O³⁺ forms of the water oxidation catalyst [Ru(Mebimpy)(bpy)(OH₂)²⁺]. Three different pathways were identified for oxidation by Ru^{IV}=O²⁺: i) C-H insertion in acid-neutral solutions, ii) a novel base-assisted concerted hydride proton transfer (HPT), iii) deprotonation and hydride transfer oxidation of the alkoxide. A significant rate enhancement was found for benzyl alcohol oxidation by Ru^V=O³⁺ compared to Ru^{IV}=O²⁺. Oxidation of hydrocarbons- ethylbenzene, toluene, cumene- were studied by Ru^V=O³⁺ in propylene carbonate/water solvent mixtures. The relative reactivity order was ethylbenzene > toluene > cumene. Mechanisms of oxidation reactions are currently under investigation in collaboration with Daniel H. Ess and William A. Goddard of the CCHF.

P1-I33 - A BV TYPE OXIDATION FOR RE-ARYL OXY-FUNCTIONALIZATION

[CCHF] Steven M. Bischof¹, Mu-Jeng Cheng², Robert J. Nielsen², T. Brent Gunnoe³, William A. Goddard III², and Roy A. Periana¹

¹The Scripps Research Institute; ²California Institute of Technology and ³University of Virginia

The design of homogeneous C-H activation and functionalization catalysts based on 2nd and 3rd row transition metals (Re, Ru, Os, and Ir) has not been well explored. Bond polarization of the metal-carbon intermediate generated from C-H activation of alkanes in these systems is believed to contain a negatively polarized (M-C⁻) intermediate. Typical functionalization strategies (oxidative addition/reductive functionalization) characteristic of later transition metal catalysts based on Pt, Pd, Au, and Hg where a positively polarized (M-C⁺) intermediate is formed are not applicable to the earlier transition metal catalysts due to their reduced electrophilicity and oxidation potential. Therefore, the development of new strategies for the functionalization of M-C intermediates will be required to utilize the known C-H activation systems. We report the study of Re-aryl oxo complexes to generate the respective phenols by a high yield and selective Baeyer-Villager type oxidation reaction. The reaction occurs selectively at the ipso carbon to generate the phenol in high yields based on Re. A variety of oxidants are capable for this reaction including DMSO and pyridine N-oxide, which could be regenerated by air and a requirement for commercialization. Density Functional Theory calculations show a mechanism that involves coordination of oxidant to an unsolvated Re-aryl trioxo complex, followed by aryl transfer and then substrate protonation to generate the phenol.

P1-I34 - THINKING LIKE NATURE: MAKING AND BREAKING STRONG BONDS WITH SYNTHETIC METALLOPORPHYRINS

[CCHF] Thomas P. Umile¹, Wei Liu¹, Erika M. Milczek¹, Rodney D. Swartz, II¹, Dawn Wallace¹, and John T. Groves¹

¹Princeton University

Nature has evolved an array of enzymes for functionalizing unactivated carbon-hydrogen bonds using molecular oxygen and a host of cheap, abundant, first-row transition metals. Taking this as our inspiration, our lab has pioneered efforts in the Center for Catalytic Hydrocarbon Functionalization (CCHF) to develop synthetic metalloporphyrins as both model systems and practical oxidation catalysts. Our experimental studies with manganese porphyrins have provided not only a fundamental understanding of the energetics of reactive metal-oxo species but also catalytic systems capable of functionalizing strong C-H bonds. Complementary theoretical work provided through the CCHF continues to inform the development of manganese as well as novel vanadium and iridium catalysts on this front. In a related thrust, we have explored with colleagues biologically-inspired flavin analogues for use as co-catalysts in the generation of reactive metal-oxo and other species directly from molecular oxygen. Approaching C-H functionalization from a different perspective, our group has worked with others in the CCHF to synthesize alkyl-rhodium and -cobalt compounds and have demonstrated their ability to generate new carbon-heteroatom bonds. Similar rhodium compounds directly activate methane suggesting that development of these complexes may afford methane-functionalization catalysts. As with the metal-oxo systems, CCHF-funded theoretical work provides insight into these experimental results.

P1-I35 - DIANIONIC PYRIDINE LIGANDS FOR CH AND O₂ ACTIVATION AT A SINGLE PALLADIUM CENTER

[CCHF] Dao-Yong Wang¹ and Andrei N. Vedernikov¹

¹University of Maryland

P1-I36 - *IN-SITU* NANOELECTROCHEMISTRY

[NECCES] Dongli Zeng¹, Feng Wang¹, Yimei Zhu¹, Jason Graetz¹, Y. Shirley Meng², Thomas McGilvray², Ming-Che Yang², and Danijel Gostovic²

¹Brookhaven National Laboratory and ²University of California, San Diego

The development of new and safer electrode materials for lithium batteries requires a better understanding of the physical and chemical processes that occur during charge and discharge. However, the identification and characterization of the nano-scale structural and chemical inhomogeneities, which often govern the thermodynamic and kinetic behavior of electrodes, remains a challenge. Transmission electron microscopy and energy-loss spectroscopy (TEM-EELS), owing to its unique capability in probing atomic-level structure and electronic properties of solids, is powerful for local structural and chemical analysis. However most of the TEM-EELS studies have been performed *ex-situ*. Since electrodes in an electrochemical system operate under conditions that are far from equilibrium, the materials studied *ex-situ* may not capture the processes that occur *in-situ* in a working battery. The capability to perform *in-situ* TEM measurements would be extremely useful to track the structural/chemical evolution that occurs in the electrodes and at interfaces during dynamic charge/discharge cycling. We will report the results of our efforts to develop *in-situ* TEM capabilities, including (i) solid-state nano-battery fabrication and *in situ* monitoring of electrochemistry (ii) custom designed TEM sample grids that enable robust electric contacts and electrochemical testing, and (iii) coupled imaging, diffraction and spectroscopy for comprehensive structural and chemical analysis of nano-batteries under biasing. In addition, we hope to use Li K-edge spectroscopy and elemental mapping to characterize the Li bonding state and track the Li transport. We will also discuss strategies for optimizing experimental conditions for quantitative TEM analysis and other critical issues such as radiation damage of lithium-containing materials.

P1-I37 - NANOMATERIALS SYNTHESIS WITH DNA-PROGRAMMED NANOPARTICLE ASSEMBLY

[NERC] Macfarlane, Robert¹, Jones, Matthew¹, and Mirkin, Chad¹

¹Northwestern University

DNA is an attractive tool in the creation of nanoscale assemblies, as its programmable recognition capabilities allow for the assembly of nanomaterials into complex architectures that can be varied via simple changes to the DNA ligands. Recent advancements in our understanding of both the fundamental forces assembling the DNA-functionalized nanoparticles and the pathway of crystallization have enabled the synthesis of a diverse array of nanoparticle superlattices. We now have established the design rules for working with different DNA lengths and nanoparticle sizes, demonstrating nanometer-scale precision in the placement of nanoparticles in three dimensions. In addition, we have extended this technique to form ordered assemblies of anisotropic particles, including rods, rhombic dodecahedra, octahedra, and triangular prisms. Finally, we have developed methods to utilize programmable oligonucleotide interactions, elements of both thermodynamic and kinetic control, and an understanding of the dominant forces that are responsible for particle assembly with this class of materials to design and deliberately make a wide variety of crystallographic symmetries.

P1-I38 - HIGH-PRESSURE SYNCHROTRON X-RAY SPECTROSCOPIC METHODS FOR STUDYING 3D AND 4F ELECTRONIC TRANSITIONS [EFree] Yang Ding¹, Daniel Haskel², Jungho Kim², Michel Van Veenendaal², Paul Chow¹, Yuming Xiao¹, and Ho-kwang Mao¹

¹Carnegie Institution of Washington; ²Argonne National Laboratory

The electron correlated materials could be greatly superior to conventional materials, which is of great significance across the energy sciences and engineering. Pressure, with its unique ability to tune the electron correlation in a clean and theoretically transparent manner, now is being applied to not only as a direct and effective means for manipulating the behavior of electrons, but also to discover novel materials existing at extreme conditions that are not available at ambient conditions. Revolutionary improvements in the efficiencies of production and application of correlated materials depend on a detailed knowledge of electronic and magnetic structure, which can be obtained by modern high-pressure synchrotron x-ray spectroscopic technique.

P1-I39 - FIRST VIBRATIONAL SUM FREQUENCY SPECTROSCOPIC STUDIES OF ENERGY-RELEVANT ORGANIC SPECIES ON HIGHLY ORDERED PYROLYTIC GRAPHITE

[FIRST] [Jennifer L. Achtyl](#)¹, Daniela M. Anjos², Avram M. Buchbinder¹, Yu Cai³, Matthew Neurock³, Steven H. Overbury², and Franz M. Geiger¹

¹Northwestern University; ²Oak Ridge National Laboratory and ³University of Virginia

Carbon surfaces are important for a variety of applications in energy, environmental, and materials chemistry but are notoriously difficult to study with vibrational spectroscopy. Here, vibrational sum frequency generation (SFG) is successfully employed to gain a molecular level understanding of the interfacial environment on carbon substrates while avoiding optical damage. We focus on understanding the nonlinear optical properties of carbon substrates, in particular highly ordered pyrolytic graphite (HOPG), and obtaining molecular level vibrational signatures of a prototypical aromatic hydrocarbons namely toluene and 1,10-phenanthrenequinone (PQ), adsorbed to their surfaces. The SFG signal of SPI-2 grade HOPG is dominated a large non-resonant (NR) response which is attributed to the mobile π -electrons. The NR response was found to be invariant with azimuthal rotation of the substrate due to the substrate's crystal domains, having 3m symmetry, being smaller than the focal spots of the incident beams. While we find that bare HOPG does not exhibit vibrational CH stretching modes, vibrational signatures of hydrocarbons adsorbed onto the surface are successfully resolved by employing IR-upconverter time-delay methods. For toluene the NR SFG response is almost quantitatively suppressed with a 500 fs time delay to resolve CH_3 vibrational resonances while for PQ spectroscopic signatures of aromatic CH stretches are resolved with a 1150 fs time delay. We explore orientation analysis of both toluene and PQ on the surface utilizing a null angle technique. The implications of our results for fluid-solid interface chemistry are discussed.

Poster Session #2

Friday May 27, 2011, 10:00 – 11:30 am

P2-A01 - UPDATING THE ROAD TO A 10% EFFICIENT ORGANIC PHOTOVOLTAIC: DEVELOPING A MODEL OF EXCITON DISSOCIATION APPROPRIATE TO THE ORGANIC HETEROJUNCTION

[ANSER] Brett Savoie¹, Jon Servaites¹, Mark Ratner¹, and Tobin Marks¹
¹*Northwestern University*

Despite impressive empirical gains to efficiency in the past decade, further progress in organic photovoltaics must proceed from a fundamental understanding of the recombination processes that limit device performance. In particular, the large band-offset currently employed to effectively split excitons continues to represent a crippling loss channel that distinguishes organic technology from its inorganic, non-excitonic counterparts. For this reason, efforts toward viability must focus on reducing the energy lost during the exciton splitting process and achieving high quantum efficiencies for low band-offset materials combinations. We present a model for exciton dissociation that directly accommodates the band-offset and offers strategies to minimize this loss. Our model for exciton dissociation is coupled to a simple device model that enables us to make predictions about the limiting efficiency of the current generation of devices. We focus on the role of band-offset and mobility on exciton dissociation, and suggest synthetic design rules on the basis of our results. Our results suggest that the most direct route to >10% efficiency doesn't lie in the continued tuning of energy levels and red-shifted bandgaps, but engineering the heterojunction interface.

P2-A02 - TOWARDS THE RECONSTRUCTION OF EXCITON DYNAMICS VIA FLUORESCENCE AND TRANSMISSION MULTIDIMENSIONAL ELECTRONIC SPECTROSCOPY

[CE] Alejandro Perdomo-Ortiz¹, Joel Yuen-Zhou¹, Sangwoo Shim¹, Geoffrey A. Lott², Andrew H. Marcus², Jacob J. Krich¹, Jacob Sanders¹, Patrick Reberstrost¹, Stephanie Valleeau¹, and Alan Aspuru-Guzik¹
¹*Harvard University* and ²*University of Oregon*

Nonlinear optics experiments are valuable techniques for unveiling the dynamics of complex systems. These techniques have been used to study excitonic coherences in photosynthetic systems and in general to study relaxation and dissipation processes in mesoscopic systems. Here, we focus on the fundamental differences between four-wave mixing techniques such as 2D Photon Echo (2DPE) and the fluorescence-detected technique called Phase-Modulation 2D Fluorescence Spectroscopy (PM-2DFS). Supported by experimental results, we will show how PM-2DFS can be used to resolve structural parameters, such as electronic couplings and dipole orientation between chromophores, in molecular environments where FWM experiments might yield poor resolution of the same molecular properties. Additionally, we propose a new set of ultrafast 2DPE experiments to extract the model-independent dynamical information about the energy transfer process from combinations of several ultrafast experiments designed to invert this quantum process matrix (quantum process tomography). We also employ several techniques ranging from quantum master equations to atomistic simulations and develop measures of efficiency, partitioning of contributions to quantum transport, and non-Markovianity. The aim of these theoretical and experimental efforts is to unravel the fundamental mechanisms for excitonic energy transfer in potential light harvesting devices.

P2-A03 - ULTRAFAST EXCITONIC PROPERTIES IN SOLAR ENERGY MATERIALS REVEALED BY MULTIDIMENSIONAL SPECTROSCOPY

[CE] Dylan Arias¹, Patrick Wen¹, Kathy Stone¹, Brian Walker¹, Sebastiaan Vlaming¹, Mounqi Bawendi¹, Robert Silbey¹, Vladimir Bulovic¹, Jeremy Baumberg², and Keith Nelson¹
¹*MIT* and ²*University of Cambridge*

J-aggregates and strongly-coupled exciton-polariton systems are promising candidates for a variety of applications requiring unique and tunable optical properties. However, before successfully designing devices with these materials for applications such as photovoltaics, optical switches, low-threshold lasers, and optical gain, the fundamental physics governing exciton properties and energy transfer and relaxation must be thoroughly understood. We used two-dimensional pulse shaping to enable multidimensional electronic spectroscopy experiments on these systems. We applied two-dimensional photon echo (2D PE) spectroscopy to elucidate the properties of singly excited states in J-aggregates by separating different types of dephasing mechanisms and unambiguously displaying coherent coupling between different excitons. We were thus able to extract the temperature-dependence of the exciton coherence length and its relation to both static and dynamic disorder. In addition to 2D PE, we performed multiple-quantum 2D spectroscopy experiments designed specifically to study directly the dynamics and correlations derived from the interactions of multiple excitons with one another. We've applied this technique to measuring the correlations and many-body interactions between exciton-polaritons in quantum wells embedded in an optical microcavity, revealing how the interactions depend on the exciton-photon coupling strength and the density of particles excited.

P2-A04 - SOLAR POWERED LASERS

[CE] Carmel Rotschild¹, Phil Reuswig¹, Matt Tomes², Hiroshi Mendoza¹, Trisha Andrews¹, Tim Swager¹, Tal Carmon², and Marc Baldo¹

¹MIT and ²University of Michigan, Ann Arbor

The brightness of solar powered lasers can be orders of magnitude larger than conventional solar concentrators, and can effectively transform sunlight into a coherent source, enabling much more efficient wavelength conversion. The challenge is that sunlight is a weak pump and consequently solar powered lasers must be based on very high quality (high-Q) factor resonator. Such lasers must be exceptionally transparent at their emission wavelength. But if high-Q lasers exhibit correspondingly weak absorption at the pump wavelengths, they are challenging to excite. Here, we demonstrate micro-ring lasers that exhibit $Q > 5.2 \times 10^6$ and a finesse of $> 1.8 \times 10^4$ with a direct-illumination, non-resonant pump. The micro-rings are coated with a combination of three organic dyes. This cascaded combination of near and ultimately far field energy transfer reduces material-losses by a factor of more than 10^4 , transforming incoherent light to coherent light with high quantum-efficiency. The operating principle established here is general and can enable efficient solar powered lasers for use in solar concentrators or efficient upconversion for photovoltaics.

P2-A05 - SINGLET FISSION IN ORGANIC SEMICONDUCTOR SOLAR CELLS

[CE] Priya Jadhav¹, Aseema Mohanty¹, Jason Sussman¹, Jiye Lee¹, and Marc Baldo¹

¹Massachusetts Institute of Technology

Single junction solar cells are limited to an efficiency of 31% due to thermalization and bandgap losses. Stacked multijunction organic solar cells exhibit higher efficiencies but each cell in the multijunction must satisfy current matching constraints, and the complete device can be challenging to fabricate, especially using solution-processing. Here, we demonstrate that singlet exciton fission in organic molecules promises single-layer organic solar cells with efficiencies beyond the single junction limit. We report solar cells comprised of tetracene, copper phthalocyanine and the buckyball C₆₀. Short wavelength light generates singlet excitons in tetracene. These are subsequently split into two triplet excitons and transported to the junction via the phthalocyanine. In addition, the phthalocyanine contributes to the photocurrent by absorbing longer wavelengths. We measure a singlet fission efficiency of (71±18)% in 2-nm-thick films of tetracene, and comparable singlet fission efficiencies in tetracene-C₆₀ blends, demonstrating that exciton fission is compatible with blended, single-layer devices, and potentially enabling low cost, higher efficiency organic solar cells.

P2-A06 - SINGLE INFRARED-EMITTING NANOCRYSTAL FLUORESCENCE DYNAMICS USING SUPERCONDUCTING NANOWIRE DETECTORS

[CE] Raoul E. Correa¹, Eric A. Dauler¹, Gautham Nair¹, Si A. Pan¹, Danna Rosenberg¹, Andrew J. Kerman¹, Francesco Marsili¹, Xiaolong Hu¹, Karl K. Berggren¹, and Mounsi G. Bawendi¹

¹Massachusetts Institute of Technology

A tremendous amount of work detailing the "exciton lifecycle" within colloidal semiconductor nanocrystals (NCs) has emerged over the past 15 years as a result of our ability to optically interrogate them one at a time using fluorescence microscopy. Unfortunately, a dearth of photon detectors with high detection efficiencies and low noise in the shortwave infrared (SWIR, 1-2 μm) has prevented the community from extending single NC studies to the lead chalcogenides, indium arsenide and other narrow-band-gap material systems. Here we present a new approach that utilizes highly-efficient, multi-element superconducting nanowire single-photon detectors (SNSPDs) for imaging single SWIR-emitting NCs. Upon isolating each NC, we measure the photoluminescence intensity as a function of time and determine the statistics of their intermittency, or "blinking". In addition, emission photon events are recorded in time-tagged-time-resolved (TTTR) mode, allowing us to calculate second-order intensity correlations in order to determine the extent of antibunching from single SWIR NC emitters. This proof-of-concept experiment demonstrates that measuring single molecule dynamics is feasible in the SWIR, and is a vital first step towards single emitter spectroscopy at these wavelengths.

P2-A07 - DEVELOPMENT OF TRANSITION METAL OXIDE CONTACTS FOR HIGH PERFORMANCE ORGANIC PHOTOVOLTAICS

[CEEM] Andres Garcia¹, Thomas Vanderpoll², Gregory C. Welch², Sergio Paniagua-Barrantes³, Seth Marder³, Guillermo C. Bazan², David S. Ginley¹, Joseph J. Berry¹, and Dana Olson¹

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The development and application of transition metal oxide (TMO) hole and electron transport layer (HTL and ETL) contacts with attractive and advantageous properties for organic photovoltaics (OPVs) are reported. Un-modify and surface modify solution process nickel oxide (NiOx) and zinc oxide (ZnO) contacts with organic self assemble monolayers (SAMs) are investigated and observed to allow the tuning of physical and electronic properties. ZnO ETL contacts modify

with alkanethiol SAMs are shown to not significantly alter work function but drastically decrease surface energy. The modify surface energy is believe to be more compatible with the organic active layers in OPVs and is observed to improve the performance in P3HT:PCBM bulk heterojunction (BHJ) inverted OPV devices. Similar improvements are also observed in recently developed small-molecule OPV devices which are more prone to film forming issues than polymers. Surface modification of NiO_x HTL contacts with aromatic phosphonic acids are also shown to alter surface energy and work function. NiO_x HTLs are in general observed to be more compatible with small-molecule BHJs than widely use PEDOT:PSS leading to drastic improvement in PV behavior and performance. These results demonstrate that electronic properties and surface chemistry of TMOs contacts can be easily tune and utilize to improve OPV performance when the electronic and/or physical properties are not ideal or appropriately match to the BHJ layer.

P2-A08 - A MODULAR MOLECULAR FRAMEWORK FOR UTILITY IN SMALL-MOLECULE SOLUTION-PROCESSED ORGANIC PHOTOVOLTAIC DEVICES

[CEEM] Gregory Welch¹, Yangming Sun¹, Wei Lin Leong¹, Alan Heeger¹, and Gui Bazan¹
¹UCSB

Solution processed organic photovoltaic devices (OPVs) have emerged as a promising energy technology due to their ease of fabrication, potential to enable low-cost manufacturing, and ability to be incorporated onto light-weight flexible substrates. Conjugated polymer based OPVs have by far been the most studied. This considerable world-wide effort in both industry and academia has resulted in power conversion efficiencies (PCEs) from 6-8% for polymer:fullerene bulk heterojunction (BHJ) devices. Solution-processed small molecule BHJ (SM-BHJ) devices have in contrast received less attention. The SM-BHJ active layers can offer advantages relative to their polymer counterparts, in that the materials have well defined structures, are easily functionalized, can be readily purified by standard organic chemistry techniques, and do not suffer from the batch-to-batch variations typical of synthetic polymers. The material presented will cover the design and synthesis of a modular molecular framework that allows for the generation of a large family of efficient light harvesting small molecules. Utility of the novel molecular materials as the donor component in solution processed SM-BHJ solar cells, yields devices with power conversion efficiencies over 5%.

P2-A09 - SEMI-RANDOM MULTICHROMOPHORIC RR-P3HT ANALOGUES FOR SOLAR PHOTON HARVESTING

[CEN] Beate Burkhart¹, Petr P. Khlyabich¹, and Barry C. Thompson¹
¹University of Southern California

Organic solar cells have been a subject of growing research interest as they promise to be low cost, lightweight, flexible and easy to incorporate into existing infrastructure. Published champion level efficiencies are around 8% but it is generally agreed that further increases in efficiency will be required before these organic solar cells can become competitive with their inorganic counterparts. A new family of semi-random hexyl-thiophene based donor-acceptor copolymers was synthesized. The restricted linkage pattern of monomers retains a high degree of structural order in the polymers preserving attractive properties of rr-P3HT while also taking advantage of the multichromophoric nature of random polymers, which allows broad spectral absorption of light. Stille-polymerization was used to synthesize six novel donor-acceptor polymers containing benzothiadiazole, thienopyrazine or diketopyrrolopyrrole as acceptors and hexyl-thiophene as the common donor. All semi-random polymers show considerably broadened absorption (up to 1000 nm) while retaining a semicrystalline morphology and hole mobilities matching P3HT. Diketopyrrolopyrrole based semi-random polymers show efficiencies between 3.6 and 4.9 %, exceeding the efficiency of P3HT based solar cells. These results show that the semi-random approach to donor-acceptor copolymers is a very attractive route to effective polymers for solar cells which also benefits from a modular and straightforward synthesis.

P2-A10 - IMPORTANCE OF THE ORGANIC/INORGANIC INTERFACE IN HYBRID SOLAR CELLS

[CEN] Matthew J. Greaney¹, David H. Webber¹, Petr Khlyabich¹, Barry C. Thompson¹, and Richard L. Brutchey¹
¹University of Southern California

Hybrid solar cells based on bulk heterojunctions of conjugated polymers with semiconducting quantum dots (QDs) are appealing because they incorporate low-cost solution processibility of the polymers with the tunable photophysical properties of QDs. Critical to device performance is the interface between the organic and inorganic domains at which exciton separation occurs. Careful selection of ligands and tailoring of surface chemistry on the inorganic nanoparticles may enhance current densities in devices and dispersibility within polymer matrices. In addition, the potential exists for using surface ligands to tune nanoparticle band levels and improve donor-acceptor alignment for enhancement of charge transfer. Using the well-developed CdSe nanoparticle platform for proof of principle, we have investigated new ligand systems on the basis of small size and extended conjugation or the ability to undergo thermal decomposition. Our goal is to develop ligand systems from these criteria that produce materials with increased conductivity while maintaining nanoparticle stability and dispersibility, ultimately leading to improvements in device characteristics.

P2-A11 - UNDERSTANDING THE INTERPLAY OF SINGLET AND TRIPLET EXCITONS IN SENSITIZED SINGLET FISSION MATERIALS [CEN] Sean T. Roberts¹, R. Eric McAnally¹, Cody W. Schlenker¹, Vincent Barlier¹, Joseph N. Mastron¹, Yuyuan Zhang¹, Mark E. Thompson¹, and Stephen E. Bradforth¹
¹*University of Southern California*

First observed in anthracene crystals in the late 1960s, singlet fission (SF) is a form of multiexciton generation in which a singlet exciton divides itself to form two triplet excitons located on neighboring molecules. Renewed interest in SF within the context of organic photovoltaics (OPVs) has occurred due to the potential to circumvent the Shockley-Queisser limit by pairing a SF material with a near-infrared absorber. Here, we report the results of femtosecond transient absorption and time resolved fluorescence experiments carried out on diphenyl tetracene (DPT) based films that monitor the interplay of singlet and triplet excitons within the material. Unlike tetracene which tends to form crystalline domains, vapor-deposited DPT films are largely amorphous. However, despite the large disorder in this material, we find that within 1 ns, ~50% of the initial singlet excitations prepared in the film have undergone SF. To extend the absorption breath of DPT based films (400-500 nm), we have prepared films doped with Platinum tetraphenyl-benzylporphyrin (PtTPBP), which absorbs intensely from 600-630 nm and has a higher triplet energy than DPT. Photoexcitation of PtTPBP leads to the formation of a singlet state that rapidly intersystem crosses to form a PtTPBP triplet exciton that passes with high efficiency (85%) to DPT. Unfortunately, singlet energy transfer from DPT to PtTPBP is also highly efficient and out-competes SF.

P2-A12 - WAVEGUIDE SPECTROSCOPIES TO CHARACTERIZE ORGANIC THIN FILM/TRANSPARENT CONDUCTING OXIDE INTERFACES [CISSEM] Anne Simon¹, Zeynep Ozkan Araci¹, Hsiao-Chu Lin¹, Neal Armstrong¹, Scott Saavedra¹, Nate Polaske¹, Dominic McGrath¹, Ajaya Sigdel², Joseph Berry², O'Neil Smith³, Yanrong Shi³, and Seth Marder³
¹*University of Arizona*; ²*National Renewable Energy Laboratory* and ³*Georgia Institute of Technology*

The charge collection rate at organic donor/ transparent conducting oxide (D/TCO) interfaces is a key parameter controlling the overall efficiency of organic solar cells (OPVs). Studies of hole harvesting and hole injection processes in OPVs, and correlating the rates of these processes with D/TCO interface composition, is essential for optimization of OPV efficiency. Visible light attenuated total reflectance (ATR) spectroelectrochemistry is a powerful tool to characterize thin molecular films adsorbed on or tethered to TCO-coated waveguides. We have developed steady-state, time-domain, and frequency-domain ATR spectroelectrochemical techniques to probe thin films of redox-active chromophores which are models for organic donor layers in OPVs and photosensitizers in hybrid photoelectrochemical cells. The enhanced pathlength of the multiple reflection waveguide geometry provides for sensitive characterization of adsorption kinetics, surface coverage, and molecular orientation, while the elimination of non-Faradaic background allows studies of samples that would be very difficult to address using electrochemical methods. Examples of these ATR techniques to study charge transfer and charge recombination events at D/TCO interfaces will be presented, including potential-modulated ATR and transient ATR spectroscopies.

P2-A13 - TOWARDS UNDERSTANDING STRUCTURE OF DONOR/ACCEPTOR ORGANIC INTERFACES IN ORGANIC PHOTOVOLTAIC SYSTEMS [CISSEM] Benjamin Wunsch¹, Mariacristina Rumi¹, David Bucknall¹, Seth Marder¹, Jeremy Gantz², Xerxes Steirer², and Neal Armstrong²
¹*Georgia Institute of Technology* and ²*University of Arizona*

In organic solar cells (OPVs), structure at the organic-organic interface - at nanometer to mesoscopic length scales - strongly influences the charge generation process as well as subsequent charge trapping and recombination. Learning how the molecular properties of organic semiconductors affect the formation, organization, and electrical characteristics of these interfaces is important for understanding solar cell operation. We have recently focused on the study of structure-property relationships of organic/organic' interfaces using new organic semiconductors (both donors and acceptors), new approaches to materials characterization, and correlation of molecular structure at the interface with OPV performance. We are using a novel blend of small molecule donor / polymer acceptor for which thermodynamic data shows significant intermolecular interactions. The organic interfaces in thin films were studied by atomic force microscopy and grazing incidence x-ray scattering. The experimental results suggest that molecular interactions affect the extent and orientation of the organic interfaces in these blends, leading to different domain structures as a function of blend compositions. We will present preliminary work showing the screening of new OPV blends in laboratory-scale platforms to select the most promising small molecule donor/acceptor blends for further structural studies.

P2-A14 - NEW PHTHALOCYANINE MATERIALS FOR ORGANIC PHOTOVOLTAICS AND INTERFACE MODIFICATION

[CISSEM] Edgardo Hernandez¹, Mayank Mayukh¹, Clarissa Sema¹, Jessica Roberts¹, Nate Polaske¹, Dominic McGrath¹, Diogenes Placencia¹, Neal Armstrong¹, Hsiao-Chu Lin¹, Scott Saavedra¹, and Erin Ratcliff¹

¹University of Arizona

Phthalocyanines (Pcs) are robust, near-IR absorbing dyes used as donors in organic solar cells (OPVs). There is interest in extending the absorptivity of these donor layers far into the near-IR, and in creation of Pcs which can function as interface modifiers of oxide contacts and interlayers. We have recently developed a unique and versatile synthetic route to near-IR absorbing, octasubstituted tri- and tetravalent metal phthalocyanines (MXPc, MX = AlCl, GaCl, InCl, V=O, Ti=O) using a "solvent-free" methodology. Pcs containing an intrinsic dipole moment in the axial direction, orthogonal to the molecular plane, exhibit higher photoactivity and a greater propensity to form near-IR absorbing polymorphs, compared to divalent metal phthalocyanines MPc (M = Cu, Ni, etc.) making them better candidates as donors in OPVs. These new Pcs have been evaluated in both planar and bulk heterojunction OPV platforms, with promising near-IR photo-electroactivity. We also show here the synthesis of a new class of asymmetric Pcs, with phosphonic acid linkers in the fourth quadrant, providing for their attachment to transparent conducting oxide (TCO) and oxide interlayer surfaces, at coverages that make them interesting as potential modifiers of wettability, work function, and rates of charge transfer. To date we have seen that these molecules bond to TCO surfaces in two distinct sub-populations, which can be resolved electrochemically and spectroscopically (refer to CISSEM poster P2-A12).

P2-A15 - ENERGETICS OF OXIDE SELECTIVE INTERLAYERS AND TRANSPARENT CONDUCTING OXIDES

[CISSEM] Jens Meyer¹, Erin Ratcliff², Ajaya Sigdel³, Xerxes Steirer², Andres Garcia³, Joseph Berry³, David Ginle³, Dana Olson³, Paul Ndione³, Edwin Widjonarko³, Neal Armstrong², and Antoine Kahn¹

¹Princeton University; ²University of Arizona and ³National Renewable Energy Laboratory

Charge extraction in organic photovoltaic cells (OPVs) is affected by the mismatch between band edge energies in the contact, in interlayer materials, and the frontier orbital energies in organic active layers. Earth-abundant, electrically homogeneous transparent conducting oxides (TCOs) are needed to extract charge efficiently in all PV platforms, and transparent metal oxide (TMO) interlayers are increasingly added to PV platforms to mitigate problems with contact electrical heterogeneity, and to enhance selectivity in charge harvesting. We are focusing on understanding the energetics of organic/oxide interfaces, as revealed by photoemission (XPS, UPS) and inverse-photoemission spectroscopies (IPES), electrochemistry, and scanning probe microscopies, and the impact of changes in interface composition on charge extraction/injection efficiencies in diode and OPV platforms. For example, solution processed TMOs MoO₃ and NiO_x are hole-extraction interlayers which function with very different mechanisms. MoO₃ is a high work function oxide which can p-dope organic hole-transport layers, leading to efficient hole-extraction. NiO_x is a lower work function, p-type oxide, can be more charge selective, but its efficacy is dependent on control of complex nickel oxide surface chemistries. Surface modification strategies are also presented for systematically varying energetic alignment and controlling charge transfer rates at TCOs.

P2-A16 - INVESTIGATING TRANSPARENT CONDUCTING OXIDES, AND THE SURFACE INITIATED GROWTH AND CHARACTERIZATION OF POLYMER BRUSHES ON METAL OXIDES

[CISSEM] Judith Jenkins¹, Joseph Berry², Natalia Doubina³, Sergio Paniagua⁴, Neal Armstrong¹, Antoine Kahn⁵, Jens Meyer⁵, Seth Marder⁴, Christine Luscombe³, Ajaya Sigdel², Paul Ndione², and Erin Ratcliff¹

¹University of Arizona; ²National Renewable Energy Laboratory; ³University of Washington; ⁴Georgia Institute of Technology and ⁵Princeton University

Realization of efficient photovoltaic organic (OPV) technologies is limited by gaps in understanding molecular-level processes at interfaces between organic active layers and transparent conductive oxide (TCO) contacts and/or transparent metal oxide (TMO) charge-selective interlayers. We focus here on tailoring TCOs from earth-abundant materials that are conductive and transparent over important regions of the solar spectrum. Composition and processing conditions are correlated to physical properties using electrochemistry, photoelectron spectroscopy, scanning probe microscopies, and characterization in prototype OPV platforms. Chemical modification of TCOs can be essential to tune their compatibility with organic layers, and to optimize interface energetics relative to the transport orbital energies of the active layers. A new strategy developed in CISSEM involves surface initiated growth of poly(3-methylthiophene) (P3MT) from indium-tin oxide. "Surface-grafting" yields well defined polymer films which can be oxidatively doped providing fine control of effective work function and conductivity. "Bottom up" design of new TCO and TMO thin-film materials which provide for molecular modification promises the formation of robust heterojunctions exhibiting seamless transitions of physical and chemical properties optimized rates of charge harvesting and improved OPV efficiencies.

P2-A17 - MICROSCOPIC THEORY OF EXCITON DISSOCIATION

[CST] Adam P. Willard¹, Loren Kaake¹, Jonathan Moussa¹, Xiaoyang Zhu¹, James R. Chelikowsky¹, and Peter J. Rossky¹
¹University of Texas at Austin

Results are presented pertaining to the dynamics and dissociation of photo-generated excitons at a donor-acceptor interface consisting of conjugated organic molecules. The results emerge as a collaboration between experiment and theory in which time-resolved second-harmonic generation is used as an experimental probe of charge dynamics. Nonadiabatic excited state simulations in conjunction with the results of high-level *ab-initio* simulations are used to generate a molecular-level interpretation of experimental results.

P2-A18 - PROBING THE ORIGINS OF CONJUGATED POLYMER MORPHOLOGY: SINGLE MOLECULE STUDIES OF CHAIN INTERACTION IN A P3HT DERIVATIVE TRIBLOCK COPOLYMER

[CST] Johanna Brazard¹, Robert J. Ono¹, Takuji Adachi¹, Songsu Kang¹, Joshua C. Bolinger¹, Christopher W. Bielawski¹, Paul F. Barbara¹, and David A. Vanden Bout¹
¹University of Texas at Austin

Conjugated polymers are promising materials for organic photovoltaic devices due to their low-cost power generation and their ease of process. While it has been demonstrated that the nanoscale morphology of thin films can greatly affect solar cell efficiency, a fundamental understanding of how chain interactions and packing affect charge separation, recombination, and mobility is lacking. To probe the role of interchain interactions, we synthesized two new, highly purified conjugated triblock copolymers composed of a central block (poly(acrylic acid), PAA, or poly(butadiene)) and two poly(3 hexylthiophene) P3HT blocks. In a good solvent (toluene), the spectra of P3HT chains in the PAA triblock resemble the spectrum of the P3HT homopolymer. When a poor solvent (methanol) is added, the interaction of the two P3HT chains in a single PAA triblock leads to absorption and emission characteristics that are nearly identical to those of bulk P3HT. In contrast, when two P3HT chains are separated by a rod linker, as is the case with the poly(butadiene) triblock, they do not generate a stable complex in presence of methanol and precipitate. Single molecule fluorescence excitation spectroscopy was used to characterize the efficiency of interchain interactions for single triblock copolymers, and the results show that both triblock systems are highly polarized and weakly interacting. Most recently, we have used solvent vapor annealing to induce interchain interactions in the PAA triblock.

P2-A19 - NEW SYNTHETIC METHODOLOGIES FOR THE PREPARATION OF DONOR-ACCEPTOR BLOCK COPOLYMERS

[CST] Robert J. Ono¹, Jonathan D. Radcliffe¹, Songsu Kang¹, Young-Gi Lee¹, Zong-Quan Wu¹, Zicheng Li¹, and Christopher W. Bielawski¹
¹University of Texas at Austin

Controlling the active layer morphology of organic photovoltaic (OPV) devices is a critical challenge that must be addressed in order to reach theoretically predicted photoconversion efficiencies. Currently, the best OPV devices consist of heterogeneous, solution-processed blends of a conjugated polymer and a C₆₀ derivative, which function as donor and acceptor components, respectively. However, due to their inherent non-equilibrium nature, these types of active layers lack well-defined, reproducible structures, and are susceptible to coarsening of phase-separated domains, which adversely affects device stability. A higher degree of morphological control is therefore still quite desirable. Recently, the use of block copolymers that self-assemble into ordered structures has emerged as a promising approach toward overcoming these challenges; however, available methods for the syntheses of such materials are laborious, often resulting in impure materials. We have developed new tools for the synthesis of highly pure, optically active block copolymers which are capable of self-assembling into higher order structures on length scales commensurate with charge separation and transfer processes occurring in OPV devices. Here we highlight the development of an unprecedented, one-pot synthesis of block copolymers comprised of mechanistically distinct polymers via sequential monomer addition, including block copolymers which carry both electron-donor and -acceptor functionalities.

P2-A20 - HIGH EFFICIENCY ORGANIC NANOCRYSTALLINE SOLAR CELLS BASED ON SQUARINE MATERIALS

[CSTEC] Guodan Wei¹, Siyi Wang², Xin Xiao¹, C. Kyle Renshaw¹, Mark E. Thompson², and Stephen R. Forrest²
¹University of Michigan and ²University of Southern California

Organic photovoltaics (OPV) have been considered as a potential low-cost solar energy conversion solution for a clean, safe, affordable and sustainable energy future. They have attracted tremendous academic and industrial interests in recent years, which stems from the deposition flexibility of lightweight organic thin films on a variety of very-low-cost substrates such as glass, plastic or metal foils. Currently, there are three main ongoing avenues to improve the power conversion efficiency of OPVs: the development of new organic materials, improved process control and novel device architecture design. Through molecular design with chemical modification of functional organic molecules, a family of new highly absorptive squaraine (SQ) materials has been systematically synthesized and explored to improve the sunlight

harvesting and charge transport. The spin-cast SQ donors are then coated with fullerene acceptors to form a unique nanocrystalline OPV device. This combination of a novel and efficient family of SQ donors, a unique device architecture and optimized fabrication processes leads to high efficiency solar cells. For example, solar cells with efficiencies of ~6.0 % and a fill factor ~0.74 are achieved, which to our knowledge both are the highest numbers reported to date for small molecule OPVs.

P2-A21 - PLASMON-ENHANCED EXCITON GENERATION IN ORGANIC PHOTOVOLTAICS

[CSTEC] Matt Sykes¹, Kwang Hyup An¹, Brian Roberts¹, Pei-Cheng Ku¹, and Max Shtein¹

¹University of Michigan

Absorption efficiency in organic thin-film solar cells can be enhanced via surface plasmon polariton (SPP) resonance, potentially allowing the organic layer thickness to be reduced to improve exciton and charge transport. Here we demonstrate a scheme for SPP-enhanced exciton generation through the use of metal-dielectric-metal (MDM) microcavities, where an optical spacer layer is used to reduce exciton quenching on one of the metal electrodes. The spacer also allows the anode workfunction to be modified, increasing the built-in potential of the cell. We excite the transverse magnetic SPP mode via a standard Kretschmann geometry using a monochromated light source. The strong optical coupling between the symmetric metal contacts of our devices produces a single propagating plasmonic mode across the entire visible spectrum, both on- and off-resonance. SPP coupling to excitons peaks at shorter wavelengths where a stronger resonance coupling exists between the active layer dipoles and the plasmon mode. Using this approach, we observe record external quantum efficiencies measured for the conversion of surface plasmons to useable photocurrent, without the need for nanopatterning of the SPP generating metal layers.

P2-A22 - TITANIA BOUND FULLERENES AS CHARGE-TRANSFER MEDIATORS IN ORGANIC PHOTOVOLTAICS

[MEEM] Jordan C. Aguirre¹, Bertrand Tremolet de Villers¹, Krastina Petrova¹, Robert Thompson¹, Benjamin J. Schwartz¹, Yves Rubin¹, and Sarah H. Tolbert¹

¹UCLA

It has been reported that charge transfer from photoexcited poly (3-hexylthiophene) to titania anatase limits the production of photocurrent in mixed organic inorganic photovoltaics. To improve this process we have coated the surface of titania with fullerenes, which are known to have a near 100% quenching efficiency. Through steady state and time resolved fluorescence we have shown that the fullerene surface modifiers improve charge transfer in thin films of titania and in titania nanorods incorporated into a bulkheterojunction geometry. Furthermore we have used this data to calculate an exciton diffusion length that is 2-3 times longer than previously reported.

P2-A23 - ENHANCING EFFICIENCIES IN DYE SENSITIZED SOLAR CELLS USING NOVEL MOLECULAR ADDITIVES

[PHaSE] Jayant Kumar¹, Akshay Kokil¹, J. Matthew Chudomel², Paul Hornick², and Paul M. Lahti²

¹UMass Lowell and ²UMass Amherst

Polymeric and molecular photovoltaic cells are promising alternative energy sources. Dye sensitized solar cells (DSSCs) have reported power conversion efficiencies (PCEs) up to 12%. However, there has been limited improvement in DSSC efficiencies in nearly two decades ago. A variety of N-heterocycle electrolyte additives such as 4-tert-butylpyridine were reported to improve open circuit voltage (VOC); but, short circuit current density (JSC) were reportedly not improved. We found significant improvement in DSSC performance, by using novel intramolecular charge transfer (ICT) molecules as additives in the electrolyte containing iodide/triiodide redox couple. Our design strategy is attractive because (1) the additives are in solution and not attached to the nanoporous anatase titania electrode, hence multiple processing steps are not required; (2) combination of the additives can be readily utilized in the electrolyte, allowing electrolyte composition to be tailored according to the requirements and (3) the design strategy is versatile and can be utilized for a variety of electrolytes. This strategy gave improved short circuit current density (JSC), with PCE improvements of up to 33% relative to controls.

P2-A24 - NANOCOMPOSITES FOR SOLAR CELL APPLICATIONS

[PHaSE] Emily Pentzer¹ and Todd Emrick¹

¹University of Massachusetts Amherst

Given the rising global demand for energy and growing environmental concerns, a major challenge facing scientists is the realization of cost effective, highly efficient energy sources. These needs could be met by organic photovoltaic (OPV) devices which harvest the energy of the sun and convert it to an electric current. OPVs are easily processible and produce lightweight, flexible devices, but their commercial success is currently limited by low power conversion efficiencies (PCE). While many approaches are being taken to improve the PCEs of OPVs, this poster will focus on facilitating the electronic communication between n-type and p-type materials, controlling the assembly of the two materials into optimally sized

domains, and stabilizing the domains once formed. Specifically, the presentation will include studies on the formation of poly(3-hexyl thiophene)-based fibrils and their assembly with electron-accepting materials, as well as the stabilization of these fibrils through chemical modification. Furthermore, this poster will report the use of hybrid n-type/p-type materials as compatibilizers which segregate at the domain interface and control phase separation.

P2-A25 - OPTICAL PROBES OF EXCITON DYNAMICS AND CORRELATION WITH INTERNAL STRUCTURE IN ORGANIC/INORGANIC SEMICONDUCTING NANOPARTICLES

[PHaSE] Joelle Labastide¹, Mina Baghgar¹, Austin Cyphersmith¹, Harihara Venkatraman¹, D. Venkataraman¹, and Michael D. Barnes¹

¹UMass Amherst

The short distance scale (~ 5-10 nm) associated with exciton dissociation in organic semiconductors represents a significant obstacle to achieving higher charge-harvesting efficiency in organic-based optoelectronic and photovoltaic systems. This has prompted significant new research aimed at structural and morphological control of conjugated polymers on a comparable length scale in order to compete favorably with radiative decay processes. In contrast with metallic or inorganic semiconductor systems that exhibit more-or-less well defined boundaries in terms of photophysical properties with respect to atomic, molecular, cluster, nanoparticle size regimes, organic semiconductors - by virtue of the large structural parameter space - have rather blurred photophysical distinctions between oligomeric, single polymer chain, and aggregated forms, depending on the choice of material and casting process. The time- and polarization-resolved photoluminescence from P3HT nanoparticles was probed as a function of particle size and internal structural order. Using time-tagged/time-resolved photon counting in which the nanoparticle luminescence is resolved in both time and polarization (resolution of ~ 4 picoseconds), exciton diffusion dynamics within a single nanoparticle are directly probed. These dynamics are correlated with particle size and internal structural order.

P2-A26 - THERMODYNAMIC STABILITY AND SELF-ASSEMBLY OF HETEROGENEOUS SEMICONDUCTOR QUANTUM DOTS FOR PHOTOVOLTAIC APPLICATIONS

[PHaSE] Sumeet C. Pandey¹, Jun Wang¹, T. J. Mountziaris¹, and Dimitrios Maroudas¹

¹University of Massachusetts Amherst

We have combined first-principles density functional theory (DFT) calculations, atomistic simulations based on Monte Carlo (MC) methods, colloidal synthesis, and materials characterization in order to establish structure-property relationships in ternary compound semiconductor QDs. We have addressed the following problems. Thermodynamic Stability of ZnSe/ZnS Core/Shell QDs: The nm-scale diffusion lengths in QDs introduce an interesting interplay between the kinetic and thermodynamic stability of core/shell interfaces. We investigate the thermodynamic stability of ZnSe/ZnS core/shell QDs based on DFT calculations combined with XPS and PL spectra. Our findings explain the possibility of compositional redistribution that may induce changes in electronic properties of QDs over time. Self-Assembly of Core/Shell-like QDs: We report results of equilibrium surface segregation in $\text{ZnSe}_{1-x}\text{Te}_x$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ QDs that identify the size and composition ranges that allow for self-assembly of hetero-nanostructures characterized by a deficient core and a rich shell in one of the constituents. Additionally, we demonstrate that equilibrium concentration profiles may also be approximated through a phenomenological continuum mass transport model. Composition-based Control of Electronic Properties: We present qualitative trends elucidating the effects of compositional distribution on the band gaps of core/shell and alloyed QDs that provide an interpretation for the observed peak shifts in PL.

P2-A27 - NANOSTRUCTURED ORGANIC PHOTOVOLTAICS FROM CONTORTED CORONENES

[RPEMSC] Alon Gorodetsky¹

¹Columbia University

I will discuss our efforts toward efficient organic photovoltaics that take advantage of the complementary geometry of contorted donor molecules and spherical acceptor molecules. We have designed, synthesized, and characterized a new class of contorted donor materials. Such molecules demonstrate favorable properties, including environmentally sensitive shape-shifting, templated assembly of robust organic/organic interfaces, and the formation of three-dimensional crystalline networks. These supramolecular features have enabled us to design and fabricate devices with power conversion efficiencies that approach state-of-the-art values for small molecule bulk heterojunction organic photovoltaics. Overall, our findings may hold significant implications for inexpensive and efficient solar energy conversion technologies.

P2-A28 - RE-DEFINING PHOTOVOLTAIC EFFICIENCY THROUGH MOLECULE SCALE CONTROL

[RPEMSC] James Yardley¹, Louis Brus¹, and Tony Heinz¹
¹*Columbia University*

This poster will present an overview of the Columbia University EFRC: Re-Defining Photovoltaic Efficiency Through Molecule Scale Control. Partners in this EFRC include Brookhaven National Laboratories, Purdue University, University of Texas, and Tel Aviv University.

P2-A29 - MEASUREMENTS OF EXCITON DYNAMICS AND SYMMETRIES IN NANOMATERIALS

[RPEMSC] Jonathan Schuller¹
¹*Columbia University*

We have been synthesizing molecular cluster compounds which potentially can offer the absorption and charge transfer control of quantum dot materials but with materials that are well defined chemically. We have synthesized both CdSe cluster compounds and a series of Cobalt Telluride cluster compounds. We have initiated studies of the optical, photodynamic, and charge generation characteristics of these materials.

P2-A30 - NEW CONDUCTING MATERIALS FOR PHOTOVOLTAICS

[RPEMSC] Marshall Cox¹
¹*Columbia University*

In this past year, we demonstrated the use of graphene as an unmodified cathode in an OPV cell, establishing that contact adjusts graphene's effective work function to serve as a transparent cathode. Our results indicate that graphene offers two potential advantages over conventional photovoltaic electrode materials: work-function matching via contact doping and increased power conversion efficiency due to transparency. These findings portend favorably for flexible, light-weight all carbon solar cells.

P2-B01 - SPECTRAL PHONON TRANSPORT PROPERTIES OF THERMOELECTRIC MATERIALS FROM FIRST-PRINCIPLES CALCULATIONS

[S3TEC] Keivan Esfarjani¹, Zhiting Tian¹, Takuma Shiga², Tengfei Luo¹, Junichiro Shiomi², Jivtesh Garg¹, Olivier Delaire³, and Gang Chen¹
¹MIT; ²U Tokyo and ³ORNL

We are interested in understanding the properties of and designing new materials for thermoelectric applications. A parameter-free calculation of lattice thermal conductivity is very challenging. Semi-empirical potentials are not accurate enough to reproduce thermal conductivity of bulk crystals. Using harmonic and anharmonic force constants extracted from density functional theory calculations within a supercell, we have developed a relatively simple but general method to compute the thermodynamic and thermal properties of any crystal. As a test, these methods are first applied to bulk silicon (Si) and the results reach decent agreement with experimental data. Moreover, the detailed phonon mean free path distribution and mode dependent contributions to the total thermal conductivity have been explored. We apply the same approach to examine the spectral phonon transport properties of GaAs, half-heusler (ZrCoSb), lead telluride (PbTe), bismuth telluride (Bi₂Te₃) and lead selenide (PbSe). This methodology paves the way for a systematic approach to model heat transport in solids using multiscale modeling.

P2-B02 - PLANAR DYE-SENSITIZED PHOTOVOLTAICS: CAVITY MODE ENHANCEMENT TO 1.0 V

[ANSER] Alex Martinson¹, Noel Giebink¹, Gary Wiederrecht¹, Daniel Rosenmann¹, Michael Pellin^{1,2}, and Michael Wasielewski^{1,2}
¹Argonne National Lab and ²Northwestern University

Dye-sensitized solar cells (DSSCs) differ from other photovoltaics in that they rely on a large area nanoparticle network to achieve sufficient absorption of solar radiation. Although highly successful to date, this approach limits the opportunities to reduce the potential loss inherent in conventional DSSC design. We will describe a resonantly coupled cavity scheme that demonstrates precise multilayer DSSCs with a 30-fold increase in monochromatic incident photon to current efficiency compared to the planar control. Under resonance conditions we observe record open-circuit voltages that approach the theoretical limit set by the traditional Ru-dye and iodide-based electrolyte. These results provide insight into the large number of co-dependent system components that govern dye-sensitized solar cell performance.

P2-B03 - PLASMONIC NANOARCHITECTURES IN PHOTOVOLTAIC AND PHOTOELECTROCHEMICAL DEVICES: ENHANCING LIGHT ABSORPTION THROUGH LOCALIZED SURFACE PLASMON RESONANCE

[ANSER] Erica DeMarco¹, Patrick Shively¹, Michael DeVries¹, Hanning Chen¹, George Schatz¹, Michael Pellin², and Joseph Hupp¹

¹Northwestern University and ²Argonne National Laboratory

Incorporation of metallic nanostructures into the photoelectrode of a dye-sensitized solar cell (DSSC) leads to amplification of light absorption by the dye sensitizer through localized surface plasmon resonance (LSPR). This presentation will show that dye absorption enhancement, and thus photocurrent enhancement, is achievable for a broad range of dye sensitizers using colloidal silver nanoparticles as plasmonic optical elements of the photoanode. Use of different metal oxide films grown by atomic layer deposition is employed to investigate the influence of dielectric environment on photocurrent enhancement in dye cells containing colloidal silver nanoparticles. Finite-difference time-domain and Mie-based computational methods are used to model these experimental systems and predict photoanode conditions that yield maximum dye absorption enhancement. This includes examining the effects of the extent of silver oxidation on dye enhancement. Nanostructure size, shape, and pitch are also examined in optimizing the plasmon-dye interaction for the current champion Ruthenium-based sensitizers for DSSCs. Use of LSPR is also demonstrated in the absorption enhancement of iron(III) oxide ultra-thin films for water oxidation.

P2-B04 - SYNTHESIS AND CHARACTERIZATION OF SILICON QUANTUM DOTS AS NOVEL MATERIALS FOR GENERATION III SOLAR CELLS

[CASP] Brian J. Simonds¹, Jeremy D. Fields¹, and P. Craig Taylor¹

¹Colorado School of Mines

The CASP team at Colorado School of Mines has established a procedure for growing and functionalizing Si quantum dots with dimensions down to approximately 5 nm. These dots are grown at relatively low temperatures using plasma-enhanced chemical vapor deposition (PECVD) techniques. Some of these dots are currently being supplied to the group at National Renewable Energy Laboratory for experiments on multiexciton generation. We have characterized these dots using electron paramagnetic resonance, photoluminescence and optical absorption measured using a calorimetric technique. The results on these dots can be compared with a model system of 6 x 20 nm Si dots embedded into a hydrogenated amorphous Si matrix, for which considerable characterization results are available. These comparisons elucidate the role of surface states in determining the optical and electronic properties, including defects at surfaces and interfaces, increased absorption at surfaces and interfaces, and the role of hydrogen in passivating quantum dots. Preliminary results on reducing the size-distribution of the quantum dots using field flow fractionation techniques, and on microwave contact-free measurements of carrier lifetimes will also be presented.

P2-B05 - SIZE- AND COMPOSITION-DEPENDENT CARRIER MULTIPLICATION STUDIES ON PbSe, PbS AND PbSSE QDs

[CASP] Jayson T. Stewart¹, Aaron G. Midgett², Lazaro A. Padilha³, Danielle K. Smith¹, Jeffrey M. Pietryga², Joseph M. Luther¹, Matthew C. Beard², Arthur J. Nozik², and Victor I. Klimov²

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We present the results of recent CASP efforts in which we compare Auger-recombination lifetimes and carrier multiplication (CM) yields for strongly confined PbSe, PbS and PbSSe nanocrystal quantum dots (QDs). QDs made of PbX are attractive candidates for third-generation solar cells because of their narrow band gaps, large Bohr exciton radii, and good natural abundance. In this work, we study a large collection of samples using two different experimental techniques (photoluminescence up-conversion and transient absorption) spread over two different institutions. We observe that the biexciton Auger lifetimes are similar for PbSe and PbS QDs with matching band gap energies (E_g), indicating similar strengths of Coulomb interactions. Given other parallels between the materials, one would predict similar CM efficiencies; however, we find that these two types of the QDs exhibit strikingly different CM trends. Specifically, we observe that for all PbSe QDs studied, the quantum yield (QY) of photon-to-exciton conversion increases with increasing the ratio of the photon energy ($h\nu$) to E_g , while for both PbS and PbSSe QDs following an initial increase, the QY drops above a certain values of $h\nu/E_g$. We analyze these results in the context of known trends for phonon emission rates in bulk PbSe and PbS as well as CM rates expected based on the measured Auger recombination lifetimes.

P2-B06 - CHARGE TRANSPORT STUDIES IN PbSe AND PbS NANOCRYSTAL FILMS

[CASP] Matt Law¹, Yao Liu¹, Markelle Gibbs¹, Jason Tolentino¹, and Rachele Ihly¹

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At CASP, we are investigating lead chalcogenide (PbX, X = S, Se, Te) nanocrystal (NC) thin-films for application in high efficiency solar cells. However, inherently metastable PbX films are prone to oxidative and photothermal degradation owing to their large surface-to-volume ratios, high surface energies and chemically active surfaces. The fabrication of

practical electronic devices based on NC solids hinges on preventing oxidation, surface diffusion, sintering, photobleaching and other unwanted physicochemical changes that can plague these materials. Here we use low-temperature atomic layer deposition (ALD) to infill conductive PbSe NC solids with metal oxides and sulfides to produce inorganic nanocomposites in which the NCs are locked in place, protected against oxidative and photothermal damage, and yet retain their quantum-confined NC properties. Infilling NC field-effect transistors and solar cells yields devices that operate with enhanced performance stable for at least months in air. Furthermore, ALD infilling with small bandgap oxides and sulfides lowers the height of the inter-NC tunnel barriers and passivates the surface trap states, yielding NC films with carrier mobilities enhanced by 1-2 orders of magnitude. Our ALD technique is a versatile means to fabricate robust NC solids for optoelectronic devices.

P2-B07 - GERMANIUM AND SILICON NANOCRYSTAL THIN-FILM FIELD EFFECT TRANSISTORS PROCESSED FROM SOLUTIONS [CASP] Zachary Holman¹, Chin-Yi Liu¹, and Uwe Kortshagen¹

¹University of Minnesota

Despite their global availability and non-toxicity, germanium and silicon have lagged behind more popular II-VI and IV-VI semiconductor materials in the emerging field of semiconductor nanocrystal photovoltaic devices. At CASP, we seek to establish the true potential of germanium and silicon thin films prepared from colloidal nanocrystal solutions by exploring their optical and electronic properties. Here, we study the electrical properties of nanocrystal films by testing them in field-effect transistors. Germanium and silicon nanocrystals were synthesized in a gas-discharge plasma, transferred into solution, and cast into thin films. Integrated into transistor structures, germanium nanocrystal films showed n-type, ambipolar, or p-type behavior depending on annealing temperature with electron and hole mobilities as large as 0.02 and 0.006 cm²/Vs, respectively. Silicon devices exhibited n-type behavior without any post-deposition heat treatment, but are plagued by poor film morphology, which may be responsible for their poor electrical properties.

P2-B08 - NANOPATTERNING FOR ADVANCED NANOWIRE PHOTOVOLTAIC DEVICES

[CEN] Anuj R. Madaria¹, Maoqing Yao¹, ChunYung Chi¹, Ruijuan Li¹, Chenxi Lin¹, Ningfeng Hunag¹, P. Daniel Dapkus¹, Michelle Povinelli¹, and Chongwu Zhou¹

¹University of Southern California

Here we report a scalable method of fabricating vertical III-V semiconducting nanowires using selected area metalorganic chemical vapor deposition (SA-MOCVD) which can find application in various optoelectronic devices. We use both nanosphere lithography (NSL) and diblock copolymer nanopatterning techniques to obtain highly ordered pattern for SA-MOCVD and demonstrate wafer-scale fabrication of GaAs nanowires on both GaAs (111)B and Si (111) substrates. A comparison between nanowires grown by NSL and nanowires grown by using ebeam patterned substrates, which is a more conventional but expensive and slow techniques, was done. A comparative study between the simulated results and experimental results was done and effect of defects in the pattern on optical properties is discussed. Reflection values of less than 5% were obtained by using nanowires arrays with length of only 100nm which is order of magnitude less than planar substrates. In case of nanosphere lithography technique, the packing density and the dimensions of these nanowires can be easily tuned by changing the diameter of the nanospheres and the etching times and in case of diblock copolymer, it can be changed by the type of copolymer used. Fabrication of low-cost, high throughput and high efficiency photovoltaic devices are proposed by application of these nanowires.

P2-B09 - UNDERSTANDING AND EXPLOITING STOICHIOMETRY ASYMMETRY TO CREATE ENHANCED P-TYPE OXIDE SPINELS

[CID] Andriy Zakutayev¹, Tula Paudel¹, John Perkins¹, Nicola Perry², Thomas Mason², Joanna Bettinger³, Yezhou Shi³, Michael Toney³, Stephan Lany¹, David Ginley¹, and Alex Zunger¹

¹NREL; ²Northwestern University and ³SLAC National Accelerator Laboratory

P-type transparent conducting oxides (TCOs) are highly desirable for thin film photovoltaics but, to date, have been hard to achieve. Here, we use the strategy of Inverse Design, which closely integrates theory and experiments, to purposefully address the fundamental barriers to making better p-TCO materials. In particular, while holes can be readily doped into small-gap semiconductors, such as GaAs, p-type doping in wide-gap oxide materials has proven difficult. By combining theoretical design principles with systematic experiments on the prototype material Co₂ZnO₄, we formulate three practical Design Rules for p-type doping wide-gap ternary oxide spinels. First is the use of extrinsic metal dopants where, through Mg doping, we demonstrate a 20-fold increase in the hole density for Co₂ZnO₄. Second is the enhancement of antisite disorder and for Co₂ZnO₄ we show that the intentional non-equilibrium growth of Zn-rich Co₂ZnO₄ enhances both the conductivity and optical transparency. Finally, third is the conversion, through alloying, of normal spinels, such as Co₂ZnO₄, into related inverse spinels, such as Co₂NiO₄ for which the maximum conductivity is ~ 200 S/cm, roughly 104 times higher than that for intrinsic Co₂ZnO₄. The Design Rules presented here are generalizable beyond just spinels to the

broader class of multi-cation oxides. Further, the overall approach of Inverse Design successfully applied here can be applied to most any desired materials development challenge.

P2-B10 - CONFORMAL COATING OF SIZE-CONTROLLED LEAD SULFIDE QUANTUM DOTS BY ATOMIC LAYER DEPOSITION AND IRRADIATION

[CNEEC] Hee Joon Jung¹, Neil P. Dasgupta¹, Orlando Trejo¹, Matthew T. McDowell¹, Aaron Hryciw¹, Robert Sinclair¹, and Fritz B. Prinz¹

¹Stanford University

The capability to tune the bandgap of semiconductors using quantum confinement structures (size control of nano-meter scale) enables the fabrication of next-generation solar cells. Lead Sulfide (PbS), which has a low bandgap (0.41 eV), is a strong candidate for a quantum confining medium in the photovoltaics field. Our previous study demonstrated a thickness-dependence of the bandgap of PbS thin films fabricated by atomic layer deposition (ALD); the bandgap of PbS can be tuned up to almost 2.0 eV. Our group has been studying deposition of PbS QDs below 20 nm size for high-efficiency solar cells. Here we show a new technique for deposition of QDs during the initial nucleation cycles of atomic layer deposition (ALD), as well as e-beam irradiation annealing and coalescence of smaller dots into larger, isolated dots during *in-situ* transmission electron microscope (TEM) observations. In particular, coalescence of QDs based on surface grain movement and morphology evolution of QDs from a flat island to a dome shape and sublimation with an increasing exposure time provide the new method of size and shape control of QDs. To demonstrate this ability, SiNWs were conformally coated with monolayer films of PbS QDs and observed them by TEM. Photoluminescence (PL) measurements on these QD-coated SiNWs showed a clear blue shift with a decreasing number of ALD cycles, suggesting the ability to create novel optoelectronic devices that take advantage of the unique properties of nanowires.

P2-B11 - QUANTUM DOTS: FROM INTERFACES TO INTERMEDIATE BAND ABSORPTION

[CSTEC] Simon Huang¹, Divine P. Kumah¹, Jia-Hung Wu¹, Naji S. Hussein¹, Andrey V. Semichaevsky², Harley T. Johnson², Roy Clarke², and Rachel S. Goldman²

¹University of Michigan and ²University of Illinois

The Stranski–Krastanow growth mode has produced self-assembled quantum dots (QDs) with a wide range of potential applications. In particular, QD superlattices (SLs) have the potential to enhance photocurrent and efficiency of solar cells by providing intermediate energy bands to allow sub-bandgap photon absorption. Using a unique combination of experiments and theory, we have revealed new insights into the formation, interface structure, and absorption properties of QDs. Coherent Bragg rod analysis x-ray mapping and cross-sectional scanning tunneling microscopy (XSTM) of self-assembled InAs QDs reveal bowing of atomic layers throughout the QDs, with a half-layer stacking shift that may provide electronic decoupling of the QDs from the substrate. The wetting layer (WL) appears to be consumed entirely by the QDs; thus, the light-absorbing surface is zero-dimensional, and therefore a high electronic density of states is expected. Using a finite-element Schrödinger-Poisson model that considers QD and WL shapes, sizes, and spacings from XSTM and atomic force microscopy data, we have examined the influence of the QD size dispersion on the external quantum efficiency (EQE) of QD solar cells. A comparison between experiments and computations reveals that the sub-bandgap EQE is dominated by the spectral response from the largest QDs in the SL. This unique combination of experiment and theory provides new insight for designing QD SLs for intermediate band solar cells.

P2-B12 - TRANSFORMATION OPTICS FOR PHOTOVOLTAICS

[LMI] Christopher Gladden¹, Majid Gharghi¹, Ze'ev Abrams¹, and Avi Niv¹

¹UC Berkeley

One of the challenges in harvesting optical energy is to control the propagation of light. Transformation optics (TO) is a design principle that offers the ability to manipulate light in sophisticated ways within geometrically simple structures. Low-loss TO devices have been limited to infrared wavelengths due to material and fabrication constraints. To extend these devices into the visible will require a fundamental shift in materials and synthesis procedure. We report on the implementation of TO device for visible light. As a first demonstration, we present the design, fabrication, and operation of a carpet cloak device, which is capable of making an object undetectable throughout the visible spectrum. The device is fabricated in a silicon nitride waveguide on a specially developed nano-porous silicon oxide substrate with very low refractive index. The spatial index variation is realized by etching variable radius holes in the nitride layer at deep subwavelength scale, creating a local index variation. The fabricated device demonstrates wideband invisibility throughout the visible spectrum with low loss. This silicon nitride on low index substrate material system opens the door for more sophisticated transformations that can potentially demonstrate broadband, wide angle concentration of solar light. These types of concentrators could enable flat plate solar cells with much lower filling fractions of expensive high quality semiconductor materials.

P2-B13 - NOVEL LIGHT TRAPPING SCHEMES FOR SOLAR CELL APPLICATIONS

[LMI] Emily Kosten¹, Emily Warren¹, and Harry Atwater¹¹*California Institute of Technology*

Silicon nanowire and microwire arrays have attracted significant interest as an alternative to traditional wafer-based technologies for solar cell applications. In addition to the device physics advantages of a radial junction, such arrays have been found to exhibit significant light trapping and absorption properties, and some recent experimental results suggest that these structures could exceed the ergodic light trapping limit. In an attempt to understand this strong light trapping, we have developed a ray optics model of silicon microwire arrays. For an array on a Lambertian back reflector, this model shows asymptotic increase in the light trapping factor for low areal filling fractions. This asymptotic increase exceeds the ergodic limit for light trapping within the wires, as the back reflector acts like a concentrator with a large acceptance angle. Comparing the ray optics model to experimental data, we find that it shows reasonable agreement with large (4 μm radius) wires, but underpredicts the absorption in smaller (1 μm radius) wires. This indicates that in smaller wires, which show the strongest light trapping effects, wave optics effects are significant. Thus, in addition to the ray optics results, we will present preliminary work on a hybrid model that accounts for wave optics effects by combining a ray tracing multiple scattering model with cross sections derived from exact solutions to Maxwell's equations.

P2-B14 - LIGHT-MATTER INTERACTIONS IN PERIODIC 3D PHOTONIC STRUCTURES

[LMI] Hailong Ning¹, Augstin Mihi¹, Erik Nelson¹, John Rogers¹, and Paul Braun¹¹*UIUC*

The continuous demand for increasing the efficiency of photovoltaic devices has led to advanced concepts for enhancing light-matter interactions. Within the seeming diversity of schemes to enhance light-matter interaction, almost all can be characterized by a common feature - the existence of resonance. This resonance is more pronounced in 3D photonic structures compared to 1D and 2D cases, because photons can be fully confined and manipulated in those structures; this is particularly important for a broadband light source such as the sun. Here we study the spontaneous emission from the light emitters which are sandwiched in the middle of inverse opal photonic crystals. Two systems that are involved with different fabrication methods (GaAs MOCVD, Si CVD) and excitation schemes (electrical and optical) are showed. The novel fabrication techniques enable us to invert the templates with high refractive index materials and finely engineer the photonic band structures. Our experimental results demonstrate that both the spectral distribution and the emission lifetime of the emitters can be strongly modified in these periodic 3D photonic structures. Photonic crystals with high refractive index contrast and tunable photonic properties as well as localized emitting media provide a basis to strongly control light.

P2-B15 - SI NANOPHOTONICS: EXTREME LIGHT LOCALIZATION FOR THERMAL AND SOLAR ENERGY CONVERSION

[LMI] Jeffrey T Hill¹, Alexander G Krause¹, Amir Safavi-Naeini¹, and Oskar Painter¹¹*California Institute of Technology*

Thermoelectric materials allow for the sustainable, generation of electricity from heat that may help satisfy our increasing global demand for clean energy. The figure of merit for thermoelectric materials is $zT = S^2pT/k$. To be a competitive solution, a thermoelectric device needs a figure of merit $zT > 3$. Currently most bulk materials have $zT < 1$ due to the interdependence of the thermal (k) and electrical (p) conductivities. The ability to independently modify (decrease) the thermal conductivity while not significantly modifying the electrical conductivity provides a path to increase zT . By creating a phononic crystal pattern in silicon, reductions in the thermal conductivity can be achieved while not affecting the electrical transport properties. Recent experimental results have demonstrated high zT thermoelectric parameters in silicon by periodic patterning. Further, complete phononic bandgaps have been studied, designed and demonstrated in thin film silicon. The techniques developed to create and analyze phononic crystals can be applied to the study, design and fabrication thermoelectric materials. This implementation is fully CMOS compatible suggesting a practical and affordable route towards creating high zT thermoelectric materials for sustainable energy generation. Additionally we study the fundamental processes which allow micron-scale superlattices to modify the thermal phonon spectrum.

P2-B16 - MECHANISMS OF NANOSTRUCTURE FORMATION AND INSTABILITY IN Bi_2Te_3 [S3TEC] Chuang Deng¹, Samuel Humphry-Baker¹, Weishu Liu¹, and Christopher Schuh¹¹*MIT*

Bulk nanocrystalline thermoelectric materials manufactured via mechanical alloying (MA) have great advantages due to their high figure-of-merit and low cost. In this study, we have pursued efforts to understand the underlying mechanism of nanostructure formation during MA in Bi_2Te_3 , and the instability of the nanostructure due to grain growth during subsequent heat treatment or exposure to elevated use temperatures. Experimentally, we have gained a good understanding of the mechanisms of MA in these materials by studying the structural evolution and phase morphology by

x-ray diffraction, calorimetry and electron microscopy. We found that the reaction occurred by a series of local combustion events at the early stage of the MA, which was followed by subsequent grain size refinement. Theoretically, we have developed a new atomistic simulation technique that can reproduce grain boundary velocities in the experimental range and extract grain boundary mobility at homologous temperatures as low as 0.2. Our methodological development opens the door to fundamental screening studies to reveal the effect of dopant atoms on the grain boundary mobility of Bi_2Te_3 . Our preliminary work on this topic suggests that atoms with a high cohesive energy can significantly reduce the grain boundary mobility.

P2-B17 - SOLAR THERMOELECTRIC POWER CONVERSION

[S3TEC] Daniel Kraemer¹, Kenneth McEnaney¹, Bed Poudel², Hsien-Ping Feng¹, J. Christopher Caylor², Bo Yu³, Xiao Yan³, Yi Ma³, Xiaowei Wang³, Dezhi Wang³, Andrew Muto¹, Matteo Chiesa⁴, Zhifeng Ren³, and Gang Chen¹
¹MIT; ²GMZ Energy; ³Boston College and ⁴Masdar Institute of Science and Technology

The conversion of sunlight into electricity has been dominated by photovoltaic and solar thermal power generation. Photovoltaic cells are mostly deployed as flat panels on rooftops or solar farms, while solar-thermal electricity generation technology relying on optical concentrators and mechanical heat engines is used in large-scale power plants. We demonstrate a promising flat-panel solar-thermal electricity conversion technology based on the Seebeck effect and large thermal concentration, enabling rooftop applications. The developed solar thermoelectric generators (STEGs) based on bulk thermoelectric Bi_2Te_3 compounds achieved a peak efficiency of 4.6% under AM1.5G (1 kWm^{-2}) conditions and 5.2% at a solar intensity of 1.5 kWm^{-2} with solar absorber operation temperatures below $200 \text{ }^\circ\text{C}$. The efficiency is 7 times higher than the previously-reported best value for a flat-panel STEG without optical concentration, and is enabled by the use of high-performance nanostructured thermoelectric materials and spectrally-selective solar absorbers in an innovative design that exploits large thermal concentration and an evacuated environment. Our work opens up a promising new approach that has the potential to achieve cost-effective conversion of solar energy into electricity.

P2-B18 - DESIGN AND GLOBAL OPTIMIZATION OF HIGH-PERFORMANCE SOLAR THERMOPHOTOVOLTAIC SYSTEMS

[S3TEC] Peter Bermel¹, Michael Ghebrebrhan¹, Yi Xiang Yeng¹, Youngsuk Nam¹, Evelyn Wang¹, John Joannopoulos¹, Ivan Celanovic¹, and Marin Soljacic¹
¹MIT

Solar thermophotovoltaic (TPV) systems can in principle exhibit extremely efficiency conversion of sunlight into electricity. In practice, most previous experimental solar TPV systems have exhibited much lower efficiencies of a few percent, caused in large part by infrared thermal radiation losses. This problem can be addressed by introducing photonic crystals (PhCs), which offer an unprecedented ability to control the emission and flow of light. First, introducing 1D PhCs to selective solar absorbers can improve spectrally absorptivity up to 98% while holding spectrally averaged emissivity down to 4%. Second, 2D periodic PhCs can be used to enhance thermal radiation for wavelengths shorter than the cutoff of the corresponding TPV diode, while suppressing emission of longer wavelength photons. Third, 1D PhC filters can help recycle the vast majority of the remaining long-wavelength photons. Combining all these PhC elements and operating at 1000 degrees celsius can potentially result in up to 45% efficient conversion of sunlight to electricity, well above the Shockley-Queisser limit for single-junction photovoltaic cells.

P2-B19 - 2D METALLIC PHOTONIC CRYSTALS AS SELECTIVE EMITTERS FOR SOLAR THERMOPHOTOVOLTAIC ENERGY CONVERSION

[S3TEC] Yi Xiang Yeng¹, Michael Ghebrebrhan¹, Peter Bermel¹, Walker Chan¹, John Joannopoulos¹, Marin Soljacic¹, and Ivan Celanovic¹
¹MIT

In this investigation, we present theory, design, fabrication, and optical characterization of 2D metallic photonic crystals as selective thermal emitters for solar thermophotovoltaic applications. They exhibit almost ideal emissivity characteristics, with nearly blackbody emissivity for shorter wavelengths, as well as dramatically lower emissivity for long wavelengths, with a sharp cutoff between the two regimes. This combination of properties is achieved by starting with a highly reflective metal, such as tungsten, and then introducing a 2D array of holes which give rise to resonant absorption peaks, which can be tuned as one's application dictates. Detailed experimental results at both room and operating temperatures are presented that demonstrate excellent agreement with simulation. The structures are fabricated using standard nanofabrication techniques that are easily scalable, making it potentially viable for widespread adoption as selective infrared emitters in large scale solar thermophotovoltaic energy conversion systems.

P2-B20 - NANO STRUCTURED THERMOELECTRIC MATERIALS $(\text{Bi,Sb})_2(\text{Te,Se,S})_3$
 [S3TEC] Weishu Liu¹, Qian Zhang¹, Qing Jie¹, Yucheng Lan¹, Kevin Lucas¹, Cyril Opeil¹, Zhifeng Ren¹, Shuo Chen²,
 Chris Carlton², Yang Shao Horn², Mildred Dresselhaus², and Gang Chen²
¹Boston College and ²MIT

We have found that a small amount of Cu added to $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ can drastically improve the process repeatability of the thermoelectric properties of $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. Preliminary evidence shows that Cu is at the interstitial site between the Te layers, which probably prevents the escaping of Te and improve the repeatability. Further study of replacing Te by S finds that $\text{Bi}_2\text{Te}_2\text{S}$ is very stable even at 400 °C, which will probably be very useful for applications with the hot side temperature at 400 °C. Further reduction of grain size of the p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ by either adding a separate phase or by melt spinning followed by ball milling and hot pressing has not resulted in any further improvement in ZT due to the reduction in power factor even though the grain size is indeed smaller in the case of adding a separate phase. Microstructure study by transmission electron microscope provided some useful information of nanostructures. More detailed studies will be carried out in the coming year hoping to further improve ZT.

P2-B21 - TOWARDS LIGHT HARVESTING POLYMERS PREPARED BY LIVING POLYMERIZATION FEATURING PENDANT IONIC TRANSITION METAL COMPLEXES (ITMCs)
 [UNC] Yali Sun¹, Egle Puodziukynaite¹, John R. Reynolds¹, and Kirk S. Schanze¹
¹University of Florida

A polystyrene assembly featuring pendant ruthenium(II) polypyridyl complexes is being developed with an effort to investigate the polymer-assisted charge and exciton transport processes between the excited states of transition metals over long distance. The reversible addition-fragmentation chain transfer (RAFT) method is employed to construct the polystyrene backbone with controlled molecular weight and narrow polydispersity (PDI). Typically we are working with polymers with $M_n = 3300$, corresponding to ~ 20 repeat units. 1,3-Dipolar "click" cycloaddition chemistry between the azide functionality on the polystyrene units and an alkyne group on the metal complex was used to attach the Ru(II) chromophores to the polymer. The resulting polymers were characterized by NMR, Uv-visible absorption, emission, quantum yield, lifetime and electrochemistry. The results of Stern-Volmer quenching studies of the polymer chromophores in homogenous solution using steady-state photoluminescence spectroscopy exhibit an amplified quenching compared to the model monomeric Ru(II) complex. This amplified quenching effect is proposed to arise due to energy transfer among Ru(II) chromophores along the polymer backbone. In addition, the effect of polymer repeat unit on the lifetime and amplified quenching effect will be studied.

P2-B22 - ENERGY TRANSFER IN RUTHENIUM AND OSMIUM FUNCTIONALIZED COILED-COIL PEPTIDES
 [UNC] Stephanie Bettis¹, Dale Wilger¹, Christopher Materese¹, Maria Minakova¹, Garegin Papoian¹, John M. Papanikolas¹, and Marcey L. Waters¹
¹University of North Carolina at Chapel Hill

A growing amount of research has focused on the development of synthetic molecular light-harvesting structures for solar cells designed to mimic the light-harvesting antenna in photosynthesis. A highly structured peptide scaffold has been designed for studying the distance dependence of energy transfer processes between polypyridal Ru(II) and Os(II) complexes using ultrafast time-resolved emission spectroscopy. The peptide coiled-coil dimers were functionalized with single Ru(II) and Os(II) chromophores on opposing coils placed at various distances from one another. Evidence for distance dependent energy transfer from Ru(II) to Os(II) was found with the quenching of the Ru(II) excited state emission, and molecular modeling has confirmed the relative distances. This study has enabled for a better understanding of energy transfer between chromophore pairs with a defined distance and orientation. Future experiments will expand to the characterization of energy transport between multiple chromophores along a single peptide coil attached to a titanium dioxide surface.

P2-C01 - GROUP 6 DINITROGEN COMPLEXES SUPPORTED BY DIPHOSPHINE LIGANDS CONTAINING PROTON RELAYS: TOWARD THE REDUCTION OF DINITROGEN TO AMMONIA
 [CME] Michael T. Mock¹, Amy Groves¹, Charles J. Weiss¹, Shentan Chen¹, Roger Rousseau¹, Daniel L. DuBois¹, and R. Morris Bullock¹
 Pacific Northwest National Laboratory

The reduction of dinitrogen to ammonia from N_2 and H_2 is currently carried out by the Haber-Bosch process, an energy intensive process that requires high pressures and high temperatures and accounts for the production of millions of tons of ammonia per year. The development of a catalytic, energy-efficient process for N_2 reduction is of great interest and remains a formidable challenge. In our approach, we are developing "Chatt-type" $((\text{P-P})_2\text{M}(\text{N}_2)_2$, P-P = diphosphine ligand) molecular electrocatalysts of the Group 6 metals (Cr, Mo, W), supported by diphosphine ligands containing non-

coordinating pendant amines (e.g., PNP, $(R_2PCH_2)_2N(R')$ and $PR_2NR'_2$, substituted 1,5-diaza-3,7-diphosphacyclooctanes) to serve as proton relays. These studies are aimed at answering fundamental questions regarding the role of proton relays in the second coordination sphere in their ability to facilitate proton movement from an external acid to metal-bound dinitrogen ligands in the challenging multi-proton/electron reduction of N_2 to ammonia.

P2-C02 - MULTI-FUNCTIONAL, BIOMIMETIC POROUS CHALCOGENIDE FRAMEWORKS: ELECTRO- AND PHOTOCATALYSTS FOR SOLAR FUELS

[ANSER] Benjamin D. Yuhas¹, Amanda L. Smeigh¹, Amanda P. S. Samuel¹, Yurina Shim¹, Michael R. Wasielewski¹, and Mercuri G Kanatzidis¹

¹Northwestern University

Biological systems capable of capturing and storing solar energy are highly rich in a variety of chemical functionalities, incorporating light harvesting components, electron transfer cofactors and redox-active catalysts all into one supramolecular structure. Any artificial mimic of such systems designed for solar fuels production will necessarily require the integration of complex subunits into a larger architecture. Here, we present porous chalcogenide frameworks that are capable of containing both immobilized redox-active Fe_4S_4 clusters and light-harvesting photoredox dye molecules in close proximity. These multi-functional gels are shown to electrocatalytically reduce protons and carbon disulfide. In addition, incorporation of a photoredox agent into the chalcogels is shown to photochemically produce hydrogen. The gels have a high degree of synthetic flexibility which should allow for a wide range of light-driven processes relevant to the production of solar fuels.

P2-C03 - CATALYTIC TRANSFORMATION OF BIOMASS POLYSACCHARIDES

[C3Bio] Nate Mosier¹, Eurick Kim¹, Joshua Abbott², Craig Barnes², and Mahdi Abu-Omar¹

¹Purdue University and ²University of Tennessee

Effective direct catalytic conversion of biomass to biofuels requires catalysts that can depolymerize polysaccharides and convert the resulting sugars to fuel molecules. In C³Bio, we developed biomimicking, aqueous phase catalysts and heterogeneous catalysts for tandem hydrolysis and conversion of plant cell wall polysaccharides to biofuels. We demonstrated that maleic acid, a dicarboxylic acid, is an effective catalyst for fractionating hemicellulose from biomass (switchgrass, poplar, and pine) into the aqueous phase. The same catalyst, at a higher temperature, then dehydrates the aqueous pentoses to furfural, a platform chemical for biofuel production. The yield of furfural from biomass was nearly 70% in the best case. A family of heterogeneous catalysts involving atomically dispersed high valent metals in silica has been synthesized and tested for activity in hydrolyzing and dehydrating the cellulose model, cellobiose. High activity has been observed in cases where silyl chloride groups on the surface hydrolyze to produce HCl. Work is currently focused on developing tandem tethered phenyl sulfonic acid groups in silica matrices for biomass hydrolysis.

P2-C04 - METABOLIC FLUX ANALYSIS OF OIL PRODUCTION IN DEVELOPING SEEDS OF CAMELINA

[CABS] Lisa Carey¹

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Camelina sativa is an oilseed well suited for use as a biofuel because of its fast growth, tolerance to drought, and its lack of use in the food industry. To understand the accumulation of storage products to shed light on the metabolism of these embryos we use a ¹³C labeling strategy and analyze oil, protein and starch via GCMS or ¹H NMR. The effect of light on developing *Camelina* embryos has also been addressed and has impacts on biomass composition, growth rate, and label distribution. These differences can be analyzed best with computer-aided flux mapping techniques. Here we present the flux map of the normal condition *Camelina* embryo including separate labeling experiments using either U-¹³C Alanine, U-¹³C Glutamine, or 80%1,2-¹³C Glucose and 20%U-¹³C Glucose. Also illustrated are select labeling differences between light levels analyzed by GCMS.

P2-C06 - BIOMIMETIC CATALYSTS FOR HYDROGEN EVOLUTION

[ANSER] Thomas Rauchfuss¹, Wenguang Wang¹, Raja Angamuthu¹, Amanda Samuel², and Michael Wasielewski²

¹University of Illinois and ²Northwestern University

Catalysts for producing hydrogen can be constructed using nature's designs and modern organometallic chemistry. The poster will summarize synthetic methods and catalytic modalities developed within the ANSER program with an emphasis on catalysts featuring two iron centers. Photochemical hydrogen production entails both sensitized and direct photoreduction of protons with these catalysts. Critical is control of the redox potentials of the catalysts. In our concept, protonation of catalysts enables photoactivation by lowering reduction potentials. For the sensitized work, we will present our designs of sensitizer-catalyst hybrids. A recurring issue is the stability of the catalysts to photolytic conditions, and we will present strategies for meeting this challenge. Also to be described are new catalysts containing pairs of chelating

ligands to stabilize the catalyst both thermally and photochemically. Thermal and in principle photochemical hydrogen production by biomimetic catalysts depends on the amine cofactors that facilitate proton transport to the catalytic centers. We will describe a new synthetic route to such proton-relays.

P2-C07 - STRUCTURAL CHARACTERIZATION OF WATER OXIDATION CATALYSTS COVALENTLY BOUND TO TiO₂ SURFACES
[ANSER] Julio L. Palma¹, Laura J. Allen¹, Rebecca L. Milot¹, Karin Brumback¹, Gary W. Brudvig¹, Charles A. Schmuttenmaer¹, Robert H. Crabtree¹, and Victor S. Batista¹
¹Yale University

We characterize the electronic rectification properties of molecular linkers that covalently bind Mn catalysts to TiO₂ surfaces. We focus on Mn-complexes with phenylterpyridine ligands attached to 3-phenyl-acetylacetonate anchors via amide bonds. We find that a suitable choice of the amide linkage yields directionality of interfacial electron transfer, essential to suppress recombination. Our findings are supported by calculations of current-voltage (I-V) characteristics at metallic atomic junctions, based on first-principles methods that combine non-equilibrium Green's function techniques with density functional theory. Our computational results are consistent with EPR measurements, confirming an asymmetry of electron transfer rates for linkers with significant rectification. The reported studies are particularly relevant for the development of photovoltaic, or photocatalytic, devices based on functionalized TiO₂ thin-films where the overall performance is affected by recombination processes competing with interfacial electron injection.

P2-C08 - METAL CATALYZED OXIDATION OF BIOREFINERY LIGNIN
[C3Bio] Diana Cedeno¹ and Joseph J. Bozell¹
¹University of Tennessee

Lignin comprises as much as 25% of terrestrial biomass, but remains one of the most underused carbon sources in the biosphere. The main obstacle in utilizing lignin is its irregular, heterogeneous structure. Developing processes that convert lignin into a single material in high yield would greatly increase its value and utility within the biorefinery. To solve this problem, we are focusing on the single unifying structural feature of lignin - its network of aromatic rings - and examining processes that cause selective oxidation of this aromatic network. This conversion process occurs by using an environmentally benign material, such as oxygen, and activating it for this transformation by means of a family of metal catalysts. Our program has targeted p-quinones (essential building blocks for dyes, antibiotics, compounds with biological, pharmacological and antitumor activity and critical components of the respiration process of almost all living organisms) as initial targets from application of our technology to both lignin and lignin models. Our results show that by proper choice of reaction conditions, we are able to convert a number of lignin models, representing most of the primary structural units in lignin, into p-quinones with high efficiency. Moreover, we have adapted our system to transform lignin itself and induce structural modifications that we believe will lay the foundation for significantly expanded utility of lignin as a source of high-value renewable carbon.

P2-C09 - TRANSITION METAL BASED CATALYST DEVELOPMENT AND CATALYTIC DECONSTRUCTION OF NATIVE AND ENGINEERED BIOMASS
[C3Bio] Hui Wei¹, Haibing Yang², Joe Cox², Bryon S. Donohoe¹, Peter N. Ciesielski¹, Michael E. Himmel¹, Angus Murphy², Wendy Peer², Maureen McCann², Melvin P. Tucker¹, and Mahdi M. Abu-Omar²
¹National Renewable Energy Laboratory and ²Purdue University

A crucial factor for successful cellulosic biofuels development is reducing the cost of deconstructing complex biomass polymers into simple intermediates for conversion to fuels and other bio-based products. To reduce biomass recalcitrance and the high costs associated with deconstruction, we are developing transition metal based catalysts that will be genetically engineered into biomass energy crops for expression into the cell walls during plant growth. We are studying conversion processes using iron as a catalyst for the hydrolysis of biomass and model substrates. Increased solubilization and enzymatic digestion of both cellulose and xylan to glucose and xylose, respectively, was found in comparison to control pretreatments. Control pretreatments were conducted without iron, when iron was used as a catalyst alone (ferric), or as a co-catalyst in dilute acid (ferrous). Analyses by TEM, SEM, EDS, as well as FT-Raman spectroscopy were used to characterize the metal-biomass interactions that contribute to the enhanced biomass pretreatment and enzymatic saccharification observed. A parallel research effort has led to the development of transgenic *Arabidopsis* and biomass energy crops expressing metal-binding proteins into plant cell walls to enhance biomass deconstruction.

P2-C10 - BIOCHEMICAL MECHANISMS OF CELLULOSE BIOSYNTHESIS

[C3Bio] Anna T. Olek¹, Lake Paul¹, Catherine Rayon¹, Subhangi Ghosh¹, and Nicholas C. Carpita¹
¹*Purdue University*

Cellulose is the most abundant biopolymer on Earth and the principal source of biomass for conversion to biofuels, but we have a hazy understanding of its biological synthesis. Cellulose is described as a para-crystalline array of about two to three dozen linearly arranged glucan chains synthesized at the plasma membrane by very large six-membered "particle rosettes". The special linkage of cellulose and other related polysaccharides gives a linear structure in which one sugar is inverted nearly 180 degrees with respect to each neighboring sugar. How the synthesis mechanism accounts for this 3-D steric problem inherent in this structure is completely unknown. We expressed fusion proteins containing only the catalytic domain of a rice cellulose synthase and observed by size-exclusion chromatography and analytical centrifugation that dimers of the catalytic domains form spontaneously but are converted to monomeric forms by thiol-reducing agents. Dimers reform when the thiol-reducing agents are diluted. The dimerization of catalytic domains solves the three basic problems of synthesis: (1) coordinate synthesis and attachment of cellobiose units instead of monomers preserves the integrity of the site of attachment and solves the steric problem (2) a channel of 16 membrane-spanning domains is consistent with sugar transporters and (3) the interaction produces two Zn-finger domains for recruitment of the catalytic dimer into rosette particles.

P2-C11 - CATALYTIC TRANSFORMATIONS OF LIGNIN STUDIED BY USING A NOVEL MASS SPECTROMETRIC APPROACH

[C3Bio] Trenton H. Parsell¹, Laura J. Haupt¹, Lucas M. Amundson¹, Benjamin C. Owen¹, Christopher L. Marcum¹, Tiffany M. Jarrell¹, Christopher J. Pulliam¹, Padmaja Narra¹, Mohammad Sabir Aqueel¹, Nelson R. Vinueza¹, Joseph J. Bozell¹, Hilikka I. Kenttamaa¹, and Mahdi M. Abu-Omar¹
¹*Purdue University*

The development of chemical methods for the direct catalytic conversion of biomass to high value organic molecules is an area of increasing interest. The plant matter component known as lignin is a polymer consisting of aromatic rings that could provide a means of obtaining aromatic materials currently derived solely from petroleum. The results shown here were obtained by using a catalytic system that can selectively deoxygenate several monomeric lignin surrogates and also successfully cleave the beta-O-4 linkages found in dimeric lignin model complexes in good yield, while leaving the valuable aromaticity of the products intact. The effects of this system on organosolv oak lignin have also been probed. As gas chromatography/mass spectrometry is only able to provide information on the low molecular weight products, a tandem mass spectrometric method was developed for the determination and structural elucidation of the products of catalytic degradation of lignin. These experiments were performed using high-pressure liquid chromatography coupled to a linear quadrupole ion trap mass spectrometer equipped with an electrospray ionization source using negative ion mode. Hydroxide ions were doped into the analyte solutions to encourage negative ion formation. This method ionizes all the mixture components to only yield one ion/analyte with no fragmentation. Structural information is then obtained by isolating each ion and subjecting it to collision-activated dissociation.

P2-C12 - DIRECT PRODUCTION OF MOLECULES IN THE FUEL RANGE BY SELECTIVE TAILORING OF BIOMASS FAST-PYROLYSIS

[C3Bio] Piotr Gawecki¹, Andrew D. Smeltz¹, Matthew R. Hurt¹, David J. Borton II¹, Nelson R. Vinueza¹, Nicholas J. Nugent¹, Rakesh Agrawal¹, W. Nicholas Delgass¹, Hilikka I. Kenttamaa¹, William E. Anderson¹, and Fabio H. Ribeiro¹
¹*Purdue University*

A novel methodology using mass spectrometry has been developed for the direct analysis of fast-pyrolysis vapors allowing real-time quantification during pyrolysis. A sub-milligram sample is heated at up to 20,000 K s⁻¹ and the products quenched and analyzed with a linear quadrupole ion trap (LQIT) mass spectrometer. Using cellulose as a model biomass feedstock, we were able to identify the primary product of fast-pyrolysis as the dehydrated glucose building block. We have also shown that the primary product can be re-polymerized in the gas phase and that by adjusting the temperature and reaction time, the product distribution can be directed to the range C12 - C18, useful for fuels. The results obtained from the model studies have been verified in a novel millisecond residence time reactor generating products a rate of 10 grams per minute.

P2-C13 - CAPTURING GENETIC DIVERSITY FOR ADVANCED BIOFUELS IN CAMELINA

[CABS] Jillian Collins-Silva¹, Rebecca Cahoon¹, and Edgar Cahoon¹
¹*University of Nebraska*

The rising cost of petroleum-based fuels and limiting supplies justify the need for alternative sources of energy. However, early generation biofuels are not an economically feasible replacement to petroleum-based fuels. *Camelina sativa* is a non-food oilseed crop that can accumulate up to 40% oil in seeds, and while its oil does have some limitations as a desirable biofuel, genetic transformation of camelina is possible. Several plant species, including some in the genus

Cuphea, accumulate high levels of short- and medium-chain fatty acids in seed oil. These fatty acids are similar in structure to the hydrocarbon compounds found in jet fuel and thus could be used as a renewable source of jet fuel. Consequently, we aim to engineer short- and medium-chain fatty acid biosynthesis in camelina. To date, several homozygous transgenic *camelina* lines expressing different C8, C10, C12, and C14 fatty acid synthesis and triacylglycerol biosynthetic specific genes from *Cuphea* and other plant species have been generated. The transgenic lines show diverse fatty acid profiles. To augment our transgenic approach, next generation in-depth 454 sequencing was done on developing seed from two different *Cuphea* species. Several new candidate genes have been identified and are being expressed in *camelina* to screen for optimal fatty acid phenotypes and oil properties.

P2-C14 - ENHANCING PHOTOSYNTHETIC EFFICIENCY OF CHLAMYDOMONAS REINHARDTII

[CABS] Shayani Pieris¹

¹Donald Danforth Plant Science Center

Photosynthesis occurs via light and dark reactions in the chloroplast thylakoid membranes and stroma respectively. Under saturating light and CO₂ conditions, there is an excess capacity for the electron transfer reactions of the light reactions whereas the carbon metabolism of the dark reactions have been found to be limiting. The enzyme rubisco, in which a great nitrogen investment is made, has the limitations of a slow turnover number, a high K_m for CO₂ and has an active site where oxygen can also bind to allow photorespiration and the ultimate loss of fixed carbon. Green algae have a built-in system of increasing the CO₂ concentration to facilitate the function of rubisco by the use of bicarbonate pumps as well as carbonic anhydrases. We have made transformant lines to further increase the bicarbonate concentration within the chloroplast as well as increase the carbonic anhydrase activities in the stroma of the chloroplast to improve rubisco function and thereby increase photosynthetic efficiency. Results of these transformant lines will be presented in this poster

P2-C15 - ANALYZING THE INDUCTION OF OIL PRODUCTION IN CHLAMYDOMONAS

[CABS] Rahul Deshpande¹ and Yair Shachar-Hill¹

¹Michigan State University

Metabolic flux analysis (MFA) is a powerful methodology for the determination of intracellular flows of material and energy through metabolic networks to study cellular physiology. The advantage of MFA is that it provides a quantitative snapshot of the physiological state of the cell. In this work we will determine metabolic fluxes in *Chlamydomonas* for furthering metabolic engineering strategies to improve oil production. The cells are grown in stable isotope labeled substrates (¹³C Acetate) and the external fluxes are determined as well as the isotope label distribution in the monomeric units of polymeric biomass components. A metabolic network and corresponding carbon mapping description for interpreting labeling data has been constructed of all major pathways. Qualitative flux information has also been obtained for cells grown in nitrogen replete compared with cells grown under nitrogen depleted (oil producing) condition. The labeling data suggests that the transition of the cells from normal to oil producing is accompanied by very fast regulatory changes. Fluxes obtained for a starch-less mutant of *Chlamydomonas reinhardtii* (sta 6) are compared with the parental strain. Both of the above reveal important insights into the regulation of metabolism for oil production in *Chlamydomonas reinhardtii*. A collaborative multiomic (transcriptome, proteome, metabolome, fluxome) analysis of the transition to oil synthesis is underway with other CABS groups.

P2-C16 - PRODUCTION OF HYDROCARBONS IN OILSEED AND ALGAE

[CABS] Yasuhiro Higashi¹, Xiaohong Feng¹, and Toni M Kutchan¹

¹Danforth Plant Science Center

Terpenes are natural products primarily derived from plants. Cyclic volatile monoterpene and sesquiterpene hydrocarbons could serve as chemical precursors to produce jet fuel aromatics. We are attempting to biosynthesize and accumulate monoterpenes and sesquiterpenes in an oilseed *Camelina sativa* and in a green alga *Chlamydomonas reinhardtii*. Two monoterpene biosynthesis genes, peppermint geranyl diphosphate synthase and peppermint limonene synthase, or two sesquiterpene biosynthesis genes, Arabidopsis farnesyl diphosphate synthase and tobacco epi-aristolochene synthase, were introduced into *Camelina*. Biosynthesis of limonene and epi-aristolochene were directed to the cytosol and to the plastid by either eliminating plastidial transit peptides or by adding a RuBisCO signal peptide. Gene expressions were regulated by seed-specific oleosin and napin promoters. The transgenic plants were screened using Discosoma red fluorescent protein as a selection marker. *Camelina* seed extracts were analyzed by gas chromatography-mass spectrometry. The transgenic *Camelina* plants which express the monoterpene biosynthesis genes in plastid accumulated volatile monoterpene hydrocarbons containing 10 carbon atoms. Limonene is 97% in quantity of monoterpenes extracted from the transgenic *Camelina* seeds. A single locus of T-DNA insertion was estimated from the segregation ratio of transgenic to non-transgenic T2 seeds. The T3 homozygous transgenic seeds accumulated limonene up to 3 mg/g seed.

P2-C17 - ARTIFICIAL HYDROGENASES: PROPERTIES OF [Ni-RU(ARENE)] COMPLEXES IN A PEPTIDE FRAMEWORK

[BISfuel] Arnab Dutta¹ and Anne K. Jones¹¹Arizona State University

[NiFe]-hydrogenases catalyze the reversible oxidation of hydrogen to protons and electrons at rates that rival precious metal catalysts. However, unraveling the mechanistic details of this remarkable reactivity has proven difficult. Enzymological studies are complicated by the biological roles of the proteins, and small structural mimics of the organometallic active site usually have very limited activity. There is a need to construct structural and functional models of [NiFe]-hydrogenases coordinated by peptides or easily modifiable small proteins to elucidate the roles played by protein in modulating metalcenter reactivity to achieve this exquisite redox catalysis. In this project, we utilized a seven amino acid peptide (ACDLPCG), SODA, known to bind nickel in a square planar N₂S₂ environment, as a scaffold for construction of peptide coordinated heterobimetallic complexes related to the [NiFe] active site. We demonstrate that the preformed Ni-SODA complex can be reacted with a variety of organometallic fragments to create sulfur bridged metalcenters. In particular, Ru(arene) complexes, related to small models able to heterolytically cleave hydrogen, have been prepared, and their interactions with hydride/hydrogen explored.

P2-C18 - PREPARATION OF HIGHLY POROUS TRANSPARENT ANTIMONY-DOPED TIN OXIDE (ATO) ELECTRODES FOR SOLAR FUEL PRODUCTION

[BISfuel] Alex M. Volosin¹, Dominik S. Schmitt², and Dong-Kyun Seo¹¹Arizona State University and ²Johannes Gutenberg University

Artificial solar fuel production requires a high-surface electrode material that is transparent to sunlight and relays photo-generated electrons among various photoelectrochemical components. Transparent conducting oxides (TCOs) are among the excellent candidates for this application and yet their structures should be nanoengineered to have desirable high surface areas and pore morphologies without sacrificing their transparency and electrical conductivity. We report a new facile synthetic method for producing highly porous transparent conducting antimony-doped tin oxide (ATO) materials and films. Solutions of metal salt sol-gel precursors are combined with polymerizable organic template precursors in a one-pot process based on the sequential formation of interpenetrating solid networks. By manipulating the organic template concentration, the average pore size can be controlled between 8 and 14 nm. After calcination, BET surface areas as high as 100 m²/g (equivalent to ~700 m² per 1 cm³ solid volume) and porosities up to 69 % can be achieved. The electrical conductivity of a pressed pellet from the materials was up to 0.14 S/cm. The potential functionality of the materials was demonstrated by absorbing protein molecules, such as cytochrome c and azurin, and showing their photochemical activities through cyclic voltammetric and UV-VIS studies.

P2-C19 - PROTON-COUPLED ELECTRON TRANSFER IN ARTIFICIAL PHOTOSYNTHETIC MODELS FOR LIGHT-DRIVEN WATER OXIDATION

[BISfuel] Jackson D. Megiatto, Jr.¹, Benjamin D. Sherman¹, Antaeres' Antoniuk-Pablant¹, Gerdenis Kodis¹, Ana L.Moore¹, Thomas A. Moore¹, and Devens Gust¹¹Arizona State University

Bio-inspired artificial photosynthetic reaction centers able to undergo proton-coupled electron transfer processes have been synthesized and their photophysical and electrochemical properties investigated. One such model consists of three covalently linked subunits (triad), with a high-potential photo-active fluorinated-porphyrin (which acts as an antenna and primary electron donor) bearing a cyanated-porphyrin moiety (the primary electron acceptor) and a benzoimidazole-phenol pair (the secondary electron donor). We have specifically designed the benzoimidazole-phenol pair to share a hydrogen bond between the phenolic oxygen and the nitrogen lone pair of the benzimidazole residue such that it mimics the tyrosine-histidine pair in PS II. Electrochemical investigation has revealed that the triad can undergo cascade electron transfer reactions upon irradiation, ultimately yielding a charge separated state consisting of a phenoxyl radical and a reduced cyanated-porphyrin; the former is thermodynamically poised for oxidizing water. Further molecular engineering has allowed the introduction of specific functionalities on the benzimidazole-phenol pair in the triad structure that are able to bind metal oxide nanoparticles that can function as water oxidation catalysts. The triad-capped nanoparticles will be used to prepare the photoanode component of photo-driven water-oxidizing devices.

P2-C20 - DESIGN AND ASSEMBLY OF AN ARTIFICIAL OXYGEN-EVOLVING COMPLEX IN DNA NANOSTRUCTURES

[BISfuel] Kimberly Rendek¹, Chad Simmons¹, Justin Flory¹, Sudipta Biswas¹, Xixi Wei¹, Chenxiang Lin¹, Sandip Shinde¹, Ingo Grotjohann¹, Raimund Fromme¹, Giovanna Ghirlanda¹, Hao Yan¹, Yan Liu¹, and Petra Fromme¹¹Arizona State University

The need for a renewable and sustainable energy source is apparent. A bio-inspired approach based on the water splitting mechanism in photosynthesis is an attractive yet challenging strategy. In this work, a stable framework consisting of a three-dimensional DNA tetrahedron has been used for the design of a mimic of the oxygen-evolving complex (OEC)

found in natural Photosystem II (PSII). In nature, one of PSII core proteins, D1, is degraded every half hour in bright sunlight. The sensitivity of D1 to photodamage resides in chlorophyll P680⁺, the primary donor of PSII. Our project aims to build the heart of the OEC, including the Mn₄CaCl metal cluster and its protein environment, in DNA nanocages, which then can be connected to a photostable artificial reaction center that performs light-induced charge separation. The peptide sequences responsible for coordinating the Mn₄CaCl cluster have been identified through X-ray analysis of PSII. Truncated regions of the peptide sequences that contain Mn₄CaCl ligation sites are implemented in the design of the artificial OEC and are covalently attached to specific sites within the DNA tetrahedron. Crystals of the DNA tetrahedron have been obtained, and X-ray crystallography has been investigated as the method of characterization. Once the entire structure has been assembled, X-ray crystallography, EPR, and electrochemistry will be used to test the activity of the artificial OEC in its stable three-dimensional DNA framework.

P2-C21 - MOLTEN METAL ANODES FOR DIRECT CARBON FUEL CELLS
[CCEI] Abhimanyu Jayakumar¹, John Vohs¹, and Raymond Gorte¹
¹*University of Pennsylvania*

The electrochemical oxidation of solid carbonaceous fuels into electrical energy could significantly affect our energy future. In principle, Direct Carbon Fuel Cells (DCFC) are possible in fuel cells with solid-oxide electrolytes, such as yttria-stabilized zirconia (YSZ). The challenge in making these practical lies in the fabrication of low impedance anodes for facile oxygen transfer from the electrolyte to the fuel. One promising approach involves the use of a molten metal anode. In this study, a number of molten metals were tested for this application, including Sn, In, Pb, and Sb. For each of the molten metals, the open-circuit voltage (OCV) was found to be close to the theoretical Nernst potential associated with oxidation of the metals. However, for metals with oxides that have high melting temperatures (e.g. Sn and In), the impedance was found to increase dramatically after drawing current through the cell due to formation of an oxide layer at the electrolyte interface. Although this also occurs with Pb below 1161 K, the melting temperature of PbO, the cell characteristics improve dramatically at higher temperatures. The impedance of cells with molten Sb anodes are found to be excellent at 973 K due to the low melting temperature of Sb₂O₃ (929 K). Because Sb₂O₃ is easily reduced by solid carbons, cells with molten Sb anodes are shown to be capable of direct utilization of solid carbonaceous fuels.

P2-C22 - CATALYSIS FOR BIOMASS REFORMING
[CCEI] Michael Salciccioli¹, Weiting Yu¹, Mark Barteau¹, Jingguang Chen¹, and Dion Vlachos¹
¹*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, as the simplest representative of biomass-derived polyols, was studied via density functional theory (DFT) calculations to identify the differences in reaction pathways between Pt and the more active Ni/Pt bimetallic catalyst. Temperature programmed desorption (TPD) experiments were conducted with deuterated ethylene glycols for comparison with DFT results. These experiments confirmed that decomposition of ethylene glycol on Pt proceeds via initial O-H bond cleavage, followed by C-H and the second O-H bond cleavage, whereas on the Ni/Pt surface, both O-H bonds are cleaved initially. Finally, a semi-empirical based microkinetic model was developed to probe for active and selective catalysts for ethylene glycol decomposition to synthesis gas.

P2-C23 - CATALYTIC STUDIES OF REFORMING OF OXYGENATES
[CCEI] Sarah Tupy¹, Tushar Vispute², George Huber², Jingguang Chen¹, and Dionisios Vlachos¹
¹*University of Delaware* and ²*UMass-Amherst*

Aqueous phase catalytic reforming is a promising technology for the production of hydrogen from biomass feedstocks. Challenges arise from intrinsic properties of biomass processes such as low thermal stability of reactants and support stability. To rationally design catalysts for biomass conversion to fuels and chemicals, a fundamental understanding of surface processes must be linked to reactor scale performance. Previous studies under ultrahigh vacuum conditions have found that the reforming activity was higher for Ni/Pt than either monometallic Pt or Ni. The objective of this work is to correlate these findings with supported catalysts under aqueous phase reforming conditions. Using ethylene glycol as a model biomass compound, the aqueous phase reforming of ethylene glycol was studied on Pt/?-Al₂O₃, Ni/?-Al₂O₃, and NiPt /?-Al₂O₃ in a packed bed reactor. Under the experimental conditions used, the Ni catalyst deactivates quickly. The bimetallic catalyst NiPt /?-Al₂O₃ exhibited higher activity than the monometallic Pt catalyst, which is in agreement with literature. The catalysts have been characterized using chemisorption, transmission electron microscopy (TEM), and extended X-ray absorption fine structure spectroscopy (EXAFS).

P2-C24 - CORRELATING SURFACE SCIENCE WITH FIRST-PRINCIPLES STUDIES OF BIOMASS DERIVATIVES

[CCEI] Weiting Yu¹, Mark Barteau¹, and Jingguang Chen¹¹University of Delaware

Biomass derived molecules are a promising class of alternative energy to fossil fuels with the advantages of being widely available, renewable, and potentially carbon-neutral. In this work we investigated the decomposition of glycolaldehyde, with both -OH and -CH=O functionalities similar to biomass derived molecules, to produce syngas. Glycolaldehyde was studied on Ni/Pt(111) bimetallic surfaces using density functional theory (DFT) calculations, temperature programmed desorption (TPD) experiments and high resolution electron energy loss spectroscopy (HREELS). As established in previous studies of alcohols and polyols, enhanced catalytic conversion of these molecules on the bimetallic surfaces was correlated to the binding energies and the surface d-band center with respect to the Fermi level. The binding energy of glycolaldehyde was found to increase as the surface d-band center approached the Fermi level, with the NiPtPt(111) surface exhibiting the highest binding energy and thus predicted to present the highest activity. Experimentally, the NiPtPt(111) surface showed the highest activity, consistent with the DFT prediction. Moreover, one monolayer Ni modified WC (1ML NiWC) surface was proposed as an alternative to NiPtPt(111) structure. Similar glycolaldehyde activity was observed on the 1ML NiWC surface after performing parallel DFT calculation and TPD experiments, suggesting the 1ML NiWC surface could be used to replace NiPtPt(111) for higher stability and lower cost.

P2-C25 - RENEWABLE GASOLINE RANGE AROMATICS FROM CATALYTIC FAST PYROLYSIS OF WOODY BIOMASS

[CCEI] Yu-Ting Cheng¹ and George W. Huber¹¹UMass-Amherst

Catalytic fast pyrolysis (CFP) is a technology being developed in the CCEI to economically convert woody biomass into gasoline range aromatics and renewable petrochemicals in a single reactor using zeolite catalysts. Biomass first thermally decomposes into oxygenated vapors. These vapors then enter the zeolite pores where they are converted into aromatics, olefins, CO, CO₂, H₂O and coke. The CCEI is improving CFP by: (1) studying the pyrolysis of biomass, (2) studying the catalytic chemistry of CFP, (3) using *in-situ* spectroscopy to identify reaction intermediates, (4) performing first principle calculations and (5) designing new generations of zeolite catalysts. We have studied the conversion of furan (a biomass model compound) over ZSM-5 to understand the catalytic chemistry. The products include C2 - C6 olefins, benzene, toluene, and xylenes in high carbon yields (40%). Benzofuran and allene were identified as key reaction intermediates. Temperature-programmed studies show that furan first oligomerizes inside ZSM-5. Temperatures above 450°C are required to form aromatics and olefins. Important reactions involved in furan conversion include: Diels-Alder condensation, decarbonylation, oligomerization, and alkylation. Using fundamental knowledge of the catalytic chemistry we have been able to modify the catalytic properties to improve catalyst performance (e.g. increase in benzene selectivity of 50% and increase in aromatic selectivity of 30%).

P2-C26 - SOOT FORMATION IN FUEL COMBUSTION - THE ROLE OF AROMATIC DIRADICALS

[CEFR] Enoch Dames¹ and Hai Wang¹¹University of Southern California

A generally undesired product of fossil fuel combustion, soot is a prevalent anthropogenic aerosol, affecting atmospheric visibility, climate, and human health. Soot formation is a highly reversible process driven, in part, by enthalpy release from chemical bond formation and entropy increase due to release of gas phase species accompanying particle formation. The initial growth of PAHs (e.g., naphthalene) is essentially captured by the hydrogen-abstraction carbon-addition (HACA) mechanism. However, an entropic resistance to PAH dimerization at high temperatures rules out the self-binding thermodynamically driven growth of PAH stacks and clusters. Additional observations conflict with our current understanding of soot formation: nascent soot can be rich in aliphatics and soot mass growth can occur without the presence of H atoms. In light of these findings, other avenues to soot formation must be explored. A strong possibility involves the role of aromatic diradicals in sustaining soot growth. Quantum chemical studies show that polyacenes of increasing length exhibit a vanishing HOMO-LUMO gap. In fact, those with more than six rings are open-shell singlet diradicals. Some graphenes also have open-shell singlet ground states. The characteristics of such pi radicals makes them obvious candidates for explaining significantly enhanced binding in PAH clusters. Radical effects originating from localized electrons are discussed, as are their implications in facilitating soot growth.

P2-C27 - COMBUSTION KINETICS STUDY OF T-BUTANOL AND ITS PRINCIPAL INTERMEDIATES, I-BUTENE, ACETONE, AND METHANE [CEFRC] Joseph Lefkowitz¹, Joshua Heyne¹, Sang Hee Won¹, Stephen Dooley¹, Hwanho Kim¹, Francis Haas¹, Saeed Jahangirian¹, Frederick Dryer¹, and Yiguang Ju¹
¹Princeton

The combustion chemistry of tertiary-butanol was studied experimentally in a Variable Pressure Flow Reactor and in counterflow diffusion flames. It was found that t-butanol does not exhibit low temperature chemistry, and thus has no negative temperature coefficient behavior. The onset of gas phase chemistry at high pressure occurs at ~780 K. In the temperature range of 780-1000 K the primary decomposition pathway of t-butanol was suggested to be hydrogen abstraction/alkyl radical beta-scission to form a methyl radical and propen-2-ol, which undergoes tautomerization to form acetone. In the counterflow configuration, the extinction strain rate of t-butanol and its primary intermediates, acetone and iso-butene, have been measured experimentally. It was found that t-butanol exhibits earlier extinction than either of its primary intermediates, signifying that the initial decomposition route is of paramount importance in the kinetic processes leading to extinction. Sampling studies on the diffusion flame using gas chromatography were conducted. It was found that the primary high temperature consumption routes of t-butanol lead to iso-butene and acetone, with the former existing in larger quantities. Numerical simulation has also been performed and the analysis revealed that the extinction limits are dominantly affected by the iso-butene and acetone sub-mechanisms. Finally, it was concluded that the current understanding of iso-butene chemistry needs to be improved.

P2-C28 - TURBULENT COMBUSTION OF FUTURE TRANSPORTATION FUELS [CEFRC] Stephen Pope¹, Jacqueline Chen², Haifeng Wang¹, Chun Sang Yoo², and Gaurav Bansal²
¹Cornell University and ²Sandia National Lab

Future transportation fuels have different combustion characteristics than current fuels. We are developing predictive computer simulation methodologies to investigate the combustion of such fuels under the turbulent flow conditions encountered in engines and other combustion applications. A major challenge is that, compared to the length scales of the device, turbulent combustion contains very small scales. The first of the two approaches we are pursuing is Direct Numerical Simulation (DNS) in which all scales are resolved. This approach can make excellent use of exa-scale computations and is yielding valuable insights into the small-scale interactions between turbulence and the fuel chemistry. Recently we have applied DNS to understand the stabilization mechanism in lifted turbulent ethylene-air jet flames in a hot co-flow. The second approach we are pursuing is based on large-eddy simulation (LES) in which only the largest scales are explicitly represented, whereas the influence of the smaller scales is modeled. Compared to DNS, the computational requirements of LES are substantially reduced, so that it is a practicable engineering design tool. The challenge of modeling the small, unresolved scales is met by representing the temperature and compositions through their joint probability density function (PDF). We have applied the LES/PDF approach to a lifted flame in a hot co-flow, and observe excellent agreement between the LES/PDF simulations and experimental data.

P2-C29 - BIOCHEMICAL CHARACTERIZATION OF *GLUCONACETOBACTER HANSENI* CELLULOSE SYNTHESIS [CLSF] Prashanti R. Iyer¹, Jeffrey M. Catchmark¹, Nicole R. Brown¹, and Ming Tien¹
¹The Pennsylvania State University

The Gram negative bacterium, *Gluconacetobacter hansenii* is considered the model organism for investigation and elucidation of cellulose synthesis. The proteins encoded by the bacterial cellulose synthase (acs) operon contribute to the process of cellulose synthesis and extrusion. In order to gain insights into the biochemistry and mechanism of cellulose production, we have used several biochemical techniques including chromatography, cross-linking, Western blotting, native gel electrophoresis, in vitro assays and zymogram. Our major contribution to the field of bacterial cellulose synthesis is the sequencing of the *Gluconacetobacter hansenii* ATCC 23769 genome. This has paved way for the identification of all the known and unknown proteins that constitute the cellulose synthase complex, by Mass spectrometry. We have also expressed all the proteins encoded by the cellulose synthase operon and have biochemically and structurally characterized one of the proteins, AcsD. We are presently trying to determine the molar concentrations of the Acs proteins in the bacterial cell and calculate their stoichiometry.

P2-C30 - DOES XYLOGLUCAN REALLY TETHER CELLULOSE IN PRIMARY CELL WALLS? EVIDENCE FOR A MINOR, STRUCTURAL FORM OF XYLOGLUCAN

[CLSF] Yong Bum Park¹ and Daniel J. Cosgrove¹

¹*The Pennsylvania State University*

The primary cell wall is a key determinant in plant cell growth and morphogenesis. Architectural models of plant cell walls implicate potential molecular mechanisms of cell wall enlargement. Currently the most popular wall model proposes that cellulose microfibrils are directly tethered to one another by xyloglucans (XyGs) that stick to cellulose surfaces or become entrapped during microfibril formation. This model was supported by experiments in which digestion by Cel12A, a glycosyl hydrolase family 12 endo-(1,4)- β -glucanase, caused wall extension (creep). We have now found that XEG, another family-12 endoglucanase that is XyG-specific, does not induce cell wall creep. From assays of wall mechanics in concert with HPAEC-PAD analysis of xyloglucan oligosaccharides released by XEG and Cel12A, we see evidence for a protected form of XyG that controls cell wall mechanics. We conclude that XEG-susceptible XyG does not tether cellulose fibrils into a load-bearing network, but cellulose is somehow linked by a protected form of XyG.

P2-C31 - SIZE EFFECT OF CELLULOSE MICROFIBRIL AND ITS INTERACTION WITH HEMICELLULOSE

[CLSF] Zhen Zhao¹, Linghao Zhong¹, and James D. Kubicki¹

¹*The Pennsylvania State University*

Various cellulose microfibril models were built based on cellulose crystal I-beta structure. All-atom molecular dynamics (MD) simulations with explicit solvent were utilized to study structural stability and conformational dynamics of cellulose microfibrils. In these models, glucan chains form in-register parallel hydrogen-bonded sheets. Different topologies were explored for fiber cross section size, cross section shape, and fiber length. In our simulations, all models developed a right-hand twist, and the twisted microfibrils remained stable for the rest of the simulated time. It was found that cellulose microfibrils with smaller cross section sizes twisted to a greater extent than ones with larger cross section sizes. The degree of twist is found to be independent of microfibril length. Further analysis suggested that the twisting is related to the asymmetric interactions of a glucan chain with its nearest neighboring chains. Recently, we started our investigation on the cellulose-hemicellulose interactions by computer modeling. Our initial study on the cellulose-xylan binding indicated that xylan binds to various faces of cellulose microfibril. While a xylan chain prefers binding parallel to cellulose glucan chains, some xylan chains bind perpendicularly to the glucan chains. Xylan aggregation was also observed in our simulations.

P2-C32 - HEMICELLULOSE AND PECTIN INTERACTIONS WITH CELLULOSE

[CLSF] Joshua D. Kittle¹, Xiaosong Du¹, Xiao Zhang¹, Chen Qian¹, Maeve Budi¹, Alan R. Esker¹, Feng Jiang¹, Maren Roman¹, Jing Gu², and Jeffrey M. Catchmark²

¹*Virginia Tech and Pennsylvania State University*

Hemicelluloses and pectins can alter cellulose pellicles formed in bacterial expression systems. In this work, quartz crystal microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR) studies explore hemicellulose and pectin adsorption onto cellulose films. Cellulose regenerated in the gas phase by HCl vapor from spincoated trimethylsilylcellulose and spincoated nanocrystalline cellulose samples with and without sulfate groups are the main film systems. The nanocrystalline cellulose films are highly crystalline and porous, while the regenerated cellulose films are mostly amorphous and non-porous. Trends for hemicellulose and pectin adsorption onto the cellulose films strongly correlate with pellicle morphology changes. The sulfate-free cellulose films are particularly attractive for preparing model cell wall composites.

P2-C33 - AB-INITIO STRUCTURE PREDICTION OF A CELLULOSE SYNTHASE PROTEIN

[CLSF] Latsavongsakda Sethaphong¹, Abhishek Singh¹, and Yaroslava G. Yingling¹

¹*North Carolina State University*

Cellulose, a crystallized polymer comprised of β -1,4 linked glucose residues, is the earth's major biopolymer of enormous global economic importance. Cellulose synthase (CesA) integral membrane proteins are responsible for its synthesis in plants, algae, some bacteria, and animals such as sponges. In a broader context, CesA's are in the family of glycosyltransferases which are a diverse set of enzymes dedicated to catalyzing monosaccharide subunits into larger glycosyl acceptors such as carbohydrates and polysaccharides. Obtaining a complete structure of this vital protein would aid in an understanding of the mechanisms responsible for cellulose synthesis. This remains difficult to attain by traditional experimental means. In order to bridge this knowledge gap, we used *ab-initio* structure prediction following by refinement by molecular dynamics simulations of the CesA protein of *Gossypium hirsutum* and CesA's of *Arabidopsis*. The resulting macromolecular structures possess similarities with the other UDP-glucose glycosyltransferases and explain the positions

and functions of known mutations. This work is supported by the US Department of Energy, Office of Basic Energy Sciences as part of The Center for LignoCellulose Structure and Formation, an Energy Frontier Research Center.

P2-C34 - THE USE OF INTERDIGITATED ARRAY (IDA) ELECTRODES TO INVESTIGATE ELECTROCATALYTIC REACTIONS

[CME] Fei Liu, Yongxin Li¹, John A. Roberts¹, Dan Dubois², Morris Bullock², and Bruce A. Parkinson¹

¹University of Wyoming and ²Pacific Northwest National Laboratory

The efficient production of solar fuels requires electrocatalysts that can perform multielectron transfer reactions. We are investigating new inorganic complexes as electrocatalysts that do not contain rare or precious metals. Although a practical solar fuel-generating electrode would most likely employ surface-bound electrocatalysts, the rates and mechanisms of these electrocatalytic reactions are more easily investigated in solution. Reaction intermediates and chemical steps following electron transfer are traditionally investigated using rotating ring-disk electrodes (RRDE), however this technique uses large amounts of catalyst and is bulky and difficult to do in a glove box. Therefore we have been developing interdigitated array (IDA) electrodes, which are compact and have no moving parts, as an alternative to RRDEs for investigating new electrocatalysts for solar fuel producing reactions. We have obtained IDA electrodes with 70 electrode pairs with electrode widths and spacings of between 1.0 and 1.5 μm , with one of the electrode pairs used as the generator electrode and the other as the collector, with collection efficiencies of over 90%. The small spacing allows for the measurement of fast following chemical steps. We have been testing these IDA electrodes on hydrogen evolving nickel phosphine complexes synthesized at PNNL. The mechanism involving the various oxidation states of the nickel and the rates of reaction with various proton sources was investigated.

P2-C35 - NMR STUDIES ON THE ROLE OF PROTON RELAYS IN NICKEL CATALYSTS FOR OXIDATION OR PRODUCTION OF HYDROGEN

[CME] O'Hagan, Molly¹, Shaw, Wendy¹, Yang, Jenny Y. ¹, Appel, Aaron M. ¹, Rakowski DuBois, M. ¹, DuBois, Daniel L. ¹, and Bullock, R. Morris¹

¹Pacific Northwest National Laboratory

In the family of bio-inspired hydrogen production/oxidation catalysts, $[\text{Ni}(\text{PR}_2\text{NR}'_2)_2]^{2+}$, the ligand design includes pendant amines, similar to those found in the active site of the FeFe hydrogenase. The pendant amines function as proton relays, greatly increasing catalytic rates. ³¹P lineshape analysis and 2D EXSY NMR experiments were used to characterize proton exchange between pendant amines in the hydrogen oxidation catalyst, $[\text{Ni}(\text{PCy}_2\text{NBn}_2\text{H})_2]^{2+}$. In this system, three doubly protonated isomers are observed which differ by the orientation of the N-H bonds with respect to the metal center: endo-endo, endo-exo, or exo-exo. Rapid intramolecular proton exchange is observed for the endo-endo and endo-exo isomers with a measured free energy of activation of 11-12 kcal/mol. Intermolecular proton exchange is only observed under conditions similar to those used in catalysis, where base and/or water are present. Rapid intermolecular exchange is observed for the same two isomers. The exo-exo isomer has each proton "pinched" between two pendant amines, exo to the metal center. This isomer exchanges on a much slower timescale (hours to days); therefore, the protons are essentially locked away from the metal center for the duration of catalysis, which has a timescale of seconds. These NMR studies guide more efficient catalyst design by providing mechanistic insight into how the proton relays function during catalysis.

P2-C36 - MOLECULAR TRANSITION METAL COMPLEXES FOR DIOXYGEN ACTIVATION AND REDUCTION

[CME] Tristan Tronic¹, Colin Carver¹, Johanna Blacquiere¹, Benjamin Matson¹, Werner Kaminsky¹, Tianbiao Lui², Mary Rakowski-DuBois², and James Mayer¹

¹University of Washington and ²Pacific Northwest National Lab

Molecular complexes of iron and ruthenium have been explored as catalysts for the oxygen reduction reaction (ORR). The complexes studied have basic sites in the second coordination sphere of the metal that may act as proton relays. Tetra-ortho-carboxy-phenylporphyrinato Fe(III)Cl, has been prepared and the efficacy of this complex as an electro-catalyst for the ORR is being investigated. Cyclic voltammetric studies of the catalyst indicate that oxygen reduction is rapid in acetonitrile with added acid, and rotating ring disk voltammetry indicates that the desired 4-electron reduction of oxygen to water predominates under these conditions. Control experiments with the tetra-para-carboxyphenylporphyrinato derivative indicate that the position of the proton relays is critical to the reduction kinetics. Cp*Ru(II)Cl(diphosphine) complexes have been synthesized with 1,5-diaza-3,7-diphosphacyclooctane ligands ($\text{PR}_2\text{NR}'_2$). Chloride abstraction in aerobic solvent gives stable, cationic species with O₂ bound in a side-on fashion. In the presence of acid, a non-coordinating amine is protonated. X-ray crystallographic characterization of one derivative shows that the added proton forms a hydrogen bond to the O₂ ligand, lengthening the O-O bond by 0.054(3) Å This model study shows that proton relays can be effective in activating a dioxygen-derived ligand. The effects of the relays and acid on chemical and electrochemical reductions of the Cp*Ru($\text{PR}_2\text{NR}'_2$)O₂⁺ are currently being examined.

P2-C37 - PLASMONS AND RUST FOR SOLAR ENERGY CONVERSION

[CNEEC] Isabell Thomann¹, Blaise Pinaud¹, Zhebo Chen¹, Bruce M. Clemens¹, Thomas F. Jaramillo¹, and Mark. L. Brongersma¹
¹Stanford

I will present progress towards the use of plasmonic metal nanostructures to enhance the efficiency of solar fuel generation. Future generations of photoelectrodes must employ cheap, earth-abundant absorber materials in order to provide a large-scale source of clean energy. These materials tend to have poor electrical transport properties and exhibit carrier diffusion lengths which are significantly shorter than the absorption depth of light. As a result, many photo-excited carriers are generated too far from a reactive surface, and recombine instead of participating in solar-to-fuel-conversion. We demonstrate that plasmonic resonances in metallic nanostructures and multi-layer interference effects can be engineered to strongly concentrate sunlight close to the electrode/liquid interface, precisely where the relevant reactions take place. By comparing spectral features in the enhanced photocurrent spectra to full-field electromagnetic simulations, the contribution of surface plasmon excitations is verified. These results open the door to the optimization of a wide variety of photochemical processes by leveraging the rapid advances in the field of plasmonics.

P2-C38 - A STUDY OF OER ON TRANSITION METAL OXIDES

[CNEEC] Monica Garcia Mota¹, Aleksandra Vojvodic², Horia Metiu³, Isabela C. Man⁴, Jan Rossmeisl⁴, and Jens K. Norskov²
¹Stanford University, ²SUNCAT Center for Interface Science and Catalysis SLAC National Accelerator Laboratory; ³University of California, Santa Barbara and ⁴Technical University of Denmark

Electrochemical water splitting or oxygen evolution reaction, OER, is of huge interest as key process in hydrogen production from sunlight and other sources of electricity.[1] Unfortunately, acidic electrochemical water splitting is associated with substantial energy loss, mainly due to the high overpotential at the oxygen-evolving anode. It is therefore important to find the optimal oxygen-evolving electro-catalyst in order to minimize the energy loss. The oxygen evolution reaction (OER) on rutile M-Ti₁₅O₃₂(110) (M=V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Ir, Ni) surfaces is investigated using density functional theory (DFT) calculations. The scaling relationship between the binding energy of OER intermediates (OOH* vs OH*) is found to follow the same trend as for undoped oxides.[2] The activity of doped TiO₂ is considerably enhanced compared to that on TiO₂. Given that TiO₂ is extremely cheap, some of the systems considered here may serve as candidates for cheap alternatives to expensive RuO₂ catalyst. [3] [1] Bockris, J.O. Int J Hydrogen Energy 33, 2129 (2008). [2] I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Norskov, and J. Rossmeisl, Universality in Oxygen Evolution Electro-Catalysis on Oxide Surfaces, Chem.Cat.Chem, doi: 10.1002/cctc.201000397, 2011. [3] M. Garcia-Mota, A. Vojvodic, H. Metiu, I. C. Man, J. Rossmeisl, and J. K. Norskov, In preparation (2011).

P2-C39 - HYDROGEN PRODUCTION ON NANOSTRUCTURED MoS₂ BY ELECTROCATALYSIS AND SOLAR PHOTOELECTROCHEMISTRY

[CNEEC] Zhebo Chen¹, Hee Joon Jung¹, Robert Sinclair¹, and Thomas F. Jaramillo¹
¹Stanford University

We develop nanoparticles of MoS₂ for photoelectrochemical water splitting. Bulk MoS₂ possesses a band gap of 1.0-1.2 eV, which is too small to drive the water splitting reaction requiring 1.23 eV. Furthermore, its band edges are misaligned relative to the hydrogen evolution and oxygen evolution potentials. However, nanostructured MoS₂ has previously been shown to exhibit quantum confinement of its band gap and high activity for the hydrogen evolution reaction. We leverage these properties for the purposes of tuning the band gap and band edge alignment of MoS₂ to affect water splitting. Using a reverse micelle encapsulation method and a highly scalable synthetic procedure that is entirely conducted at room temperature, we produce MoS₂ nanoparticles in controlled sizes with mean diameters ranging from 2.4 to 8.3 nm, as determined by transmission electron microscopy (TEM). The molybdenum and sulfur content is further confirmed using energy filtered TEM. UV-Vis measurements confirm a blueshift in absorption onset with smaller size, and the smallest nanoparticles exhibit a band gap of ~1.8 eV. The nanoparticles are supported onto conductive fluorine-doped tin oxide substrates utilizing a facile spray coating deposition and produce photocurrent when characterized in a 3-electrode photoelectrochemical cell. Lastly, band diagrams are presented using the flat band potentials of the nanoparticles as determined using illuminated cyclic voltammetry measurements.

P2-C40 - PROTON-COUPLED ELECTRON TRANSFER AT FLUID-SOLID INTERFACES: MECHANISTIC PATHWAYS FOR ELECTROCATALYTIC AND PHOTOCATALYTIC REACTIONS

[FIRST] Daniela M. Anjos¹, Glen Alliger¹, Alexander I. Kolesnikov¹, Yu Cai², Matthew Neurock², Zili Wu¹, John McDonough³, Yury Gogotsi³, Gilbert M. Brown¹, and Steven H. Overbury¹

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Proton-coupled electron transfer (PCET) reactions play an essential role in a broad range of energy conversion processes. Elucidating the mechanism of PCET reactions at a fluid-solid interface is at the heart of advances in important applications dependent upon oxygen reduction (energy conversion), carbon dioxide reduction (carbon capture) or water splitting (solar fuels). Our approach is to probe how model redox reactions occur by combining vibrational, computational and electrochemical methods to probe adsorbed quinone on carbon surfaces. This redox model is chosen for PCET investigations due to its functionality and stability over a wide pH range. The impact of the interaction and orientation of adsorbed quinone on carbon onions was investigated by ATR, Raman and INS (inelastic neutron scattering). Very low frequency modes related to torsion and deformation modes in the INS spectrum produced clear indications of the effect of bonding to the carbon surface. The results combined with computational calculations will be used to determine the orientation and bonding of the molecule on carbon surfaces. The coverage, reversibility, reduction potential, and stability of quinone on carbon were determined by cyclic voltammetry and the redox kinetics has been investigated by high speed chronoamperometry and kinetic isotope effects. Finally, the application of PCET for improvement of photocatalysis for water splitting has been investigated by photoelectrochemistry of modified TiO₂.

P2-C41 - THE DECOMPOSITION OF FORMIC ACID AND BUTYL FORMATE FOR THE CONVERSION OF BIOMASS TO BIOFUELS

[IACT] Brandon O'Neill¹, Elif Gurbuz¹, and James Dumesic¹

¹University of Wisconsin-Madison

The use of biomass to replace petroleum has been proposed as a way to promote national security, stimulate economic development, and ensure environmental conservation. Hydrogen generation from biomass is an active area of study as hydrogen is necessary for the generation of sustainable electricity from fuel cells and for the transformation of raw biomass into fuels and chemicals. Formic acid is a common hydrogen carrier for fuel cells, and carboxylic acids, especially formic acid, may be important hydrogen sources in future biorefineries as both hydrolysis and pyrolysis produce carboxylic acid rich streams. Our group developed a liquid phase process utilizing carboxylic acids to produce fuels. A similar strategy utilizing esters rather than acids provides processing benefits including moderate pH, lower reactivity, and increased hydrophobicity. To economically leverage these advantages ester decomposition must be achieved with rates and selectivities comparable to those of the acids. Kinetic studies using formic acid and butyl formate as probe molecules have been undertaken, to understand how the rate, primary decomposition pathway, and overall selectivity of ester decomposition compares to the acid. The results indicate formic acid can provide high yields of hydrogen in liquid phase biomass processing. Also, despite lower rates and a different primary decomposition pathway, the ester can provide a sufficient rate and selectivity via the proper process conditions.

P2-C42 - AN NMR STUDY OF THE MECHANISM OF THE DEHYDRATION OF D-FRUCTOSE USING ¹³C LABELING

[IACT] Jing Zhang¹ and Eric Weitz¹

¹Northwestern University

Substantial efforts have been focused on converting biomass into 5-hydroxymethylfurfural (HMF), due to HMF's versatility as a starting material for biofuel production and/or its precursors. A convenient method for the preparation of HMF is acid-catalyzed dehydration of fructose. However, the dehydration of fructose and rehydration of HMF to levulinic acid is a complex multistep process. Understanding the mechanisms for the above processes are fundamental to improvements in biomass conversions and the development of tailored catalysts. It is not clear that the mechanism for conversion of fructose into HMF has been completely delineated, nor is it clear that the same mechanism is dominant with different catalysts. We report on the dehydration of fructose in different solvents (water or DMSO) with different catalysts (PO₄³⁻/niobic acid or Amberlyst 70 catalysts) by monitoring the ¹H and ¹³C NMR spectra. Using ¹³C-labeled fructose we have identified two key intermediates in the formation of HMF, and we have investigated the mechanism of HMF formation utilizing ¹³C-labeled precursors. Results with ¹³C fructose indicate that the 1-C or 6-C carbon of fructose is the origin of the 1-C or 6-C carbon of HMF. Results with ¹³C HMF indicate that 1-C or 6-C carbon of fructose is the origin of the 1-C or 5-C carbon of formic acid and levulinic acid respectively. Work supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center.

P2-C43 - HYDROGEN PRODUCTION FROM GLYCEROL: REACTION MECHANISM ANALYSIS VIA KINETICS AND OPERANDO SPECTROSCOPY

[IACT] Paul Dietrich¹, Rodrigo Lobo², Neng Guo², Tianpin Wu², Bradley Fingland², Fabio Ribeiro¹, Nicholas Delgass¹, Jeffrey Miller², and James Dumesic³

¹Purdue University; ²Argonne National Lab and ³University of Wisconsin-Madison

Hydrogen is an important component for biomass conversion reactions, particularly those involving the removal of oxygen. Current hydrogen generation is predominantly from non-renewable resources such as natural gas, and thus a renewable source of hydrogen is paramount in developing renewable processes. We are working to develop better catalysts for the reforming of biomass derived molecules. We investigate the conversion of glycerol to hydrogen over two catalysts: Pt and PtMo supported on carbon. Kinetic experiments were carried out to determine reaction parameters as well as major intermediate products. X-ray absorption spectroscopy (XAS) was performed under reaction conditions to determine oxidation state, local coordination, and catalyst particle size and identify surface intermediates, all under reaction conditions. Catalyst characterization via XAS spectroscopy reveals the presence of Pt and PtMo nanoparticles (2-2.5nm), with extended x-ray absorption fine structure results indicating the formation of a Pt rich PtMo alloy. Analysis of the x-ray absorption near edge spectra indicates a fully reduced Pt phase, as well as the presence of CO, H₂, and H₂O species on the catalyst surface. Kinetic experiments reveal that the rate of hydrogen production is five times higher over PtMo/C than over Pt/C, but analysis of reaction intermediates indicates that the reaction mechanism is the same over both catalysts. We conclude that new active sites are created by the addition of Mo.

P2-C44 - CATALYSTS PREPARED BY ATOMIC LAYER DEPOSITION FOR CONVERSION OF BIOMASS TO CHEMICALS

[IACT] Yomaira J. Pagan-Torres¹, Jean Marcel R. Gallo¹, Dong Wang¹, Hien N. Pham¹, Joseph A. Libera¹, Christopher L. Marshall², Jeffrey W. Elam², Abhaya K. Datye³, and James A. Dumesic¹

¹University of Wisconsin-Madison; ²Argonne National Laboratory and ³University of New Mexico

Transformation of biomass-derived carbohydrates to fuels and chemicals is of significant interest based on growing concerns of global climate change and diminishing fossil resources. A challenge encountered in these processes is the synthesis of heterogeneous catalysts that can withstand liquid water at high temperatures. Here we present the synthesis of a mesoporous niobia-based catalysts using atomic layer deposition (ALD), to achieve conformal and uniform deposition of Nb₂O₅ within the well-defined pores of a mesoporous silica scaffold (SBA-15). The materials synthesized combine the highly porous structure of SBA-15 with the surface properties of niobia and demonstrate remarkable hydrothermal stability in liquid water at elevated temperatures and pressures. Furthermore, to explore the potential of these materials as solid acid catalyst suitable for biomass processing, Pd nanoparticles were supported on mesoporous niobia to create bifunctional catalysts. These catalysts exhibited better catalytic stability versus time on stream compared to conventional catalyst Pd supported on niobic acid (HY-340) in the transformation of δ^3 -valerolactone (GVL) to pentanoic acid.

P2-C45 - LIGHT-HARVESTING PIGMENT DISTRIBUTION IN ALGAE AND CYANOBACTERIA DETERMINED BY HYPERSPECTRAL CONFOCAL FLUORESCENCE MICROSCOPY

[PARC] Aaron M. Collins¹, Michelle Liberton², Sangeeta Negi³, Howland D.T. Jones¹, Omar F. Garcia¹, Michael B. Sinclair¹, Himadri B. Pakrasi², Richard T. Sayre³, and Jerilyn A. Timlin¹

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Photosynthetic organisms possess diverse light-harvesting antennas to use various colors and qualities of light. For example, green algae are very efficient at utilizing most of the visible light spectrum with the exception of the so-called "green gap" (500-600 nm). On the other hand, cyanobacteria are often found in nature, living beneath green algae and have evolved unique photosynthetic antennae called phycobilisomes, which absorb the light that filters through the algal layer above. Understanding the global distribution of natural photosynthetic pigments from various organisms can provide the framework for the next-generation of energy conversion systems. To quantify, locate and identify pigments in wild-type and selected mutants of the green alga *Chlamydomonas reinhardtii* and the cyanobacterium, *Synechocystis* sp. PCC 6803 we employ hyperspectral confocal fluorescence microscopy (HCFM) and multivariate analysis. HCFM records the entire emission spectrum (500-850 nm) at each spatial voxel of an image. The added informational content over a traditional multi-channel microscope requires robust analysis tools, such as multivariate curve resolution (MCR), which can mathematically and reliably separate highly over-lapping spectral components from a hyperspectral dataset. We demonstrate how such analyses can be used to determine spatial location and relative quantity of pigments in living photosynthetic organisms.

P2-C46 - PARC COMMUNICATION STRATEGIES: STREAMING, ONLINE, AND VIRTUAL

[PARC] [Elizabeth Dorland](#)¹¹*Washington University in St. Louis*

Our goal at PARC is to facilitate the use of 21st Century online communication tools for our researchers worldwide. This poster describes our communication and networking strategies. The Photosynthetic Antenna Research Center, based at Washington University in St. Louis, has 10 partner sites including four US and two UK universities, three US government labs, and a plant sciences center. Our extended network includes 17 PIs, several affiliate research scientists and many grad students and post-docs. Our efforts towards facilitating communication and collaboration include: 1) Live streaming seminars by local and visiting scientists to all PARC sites with video archives. 2) A private Ning online network for professional communications among individuals and groups within PARC. 3) A poster session in the virtual world of Second Life to include short presentations following the EFRC Summit in Washington DC and targeted to EFRC scientists and students who were not able to attend the main event. The poster will summarize communication efforts and results to date as well as future plans.

P2-C47 - WINNING THE FUTURE: ENERGY EDUCATION FOR THE NEXT GENERATION

[PARC] [Rachel Ruggirello](#)¹¹*Washington University in St. Louis*

The integration of research with education and outreach is an essential aspect of PARC's mission. The energy solutions of the future will depend on the identification, training, and support of our next generation of scientists. By offering education and outreach programs at the K-12, undergraduate, and graduate level, PARC provides the community with a forum to access expert knowledge. Specifically, PARC has a three-prong focus: energy education for teachers, energy experiences through project-based curriculum for K-12 students and interdisciplinary studies in bioenergy and the environment for undergraduate students. For teachers, PARC partners with Science Outreach to offer a series of "hot topics" workshops. This workshop series is focused on energy and sustainability for grades 6-12 teachers. Teachers are provided with content knowledge and access to materials to integrate these concepts into their curriculum. For K-12 students, PARC has designed a series of activities and investigations to expose students to real-world applications of renewable energy sources and solutions. Students come to campus or PARC personnel travel to schools to work with students as they learn that energy has a source and can be transferred and transformed. Finally, the certificate of accomplishment for undergraduate students provides an organized channel for students to pursue interdisciplinary, co-curricular bioenergy and environmental studies in addition to their major.

P2-C48 - ENERGY TRANSFER IN PHOTOSYNTHETIC LIGHT-HARVESTING COMPLEXES FOR BIO-HYBRID SOLAR UTILIZATION

[PARC] [William Bricker](#)¹ and [Cynthia Lo](#)¹¹*Washington University in St. Louis*

Photosynthetic light-harvesting complexes (LHC) have evolved over many millions of years to become extremely efficient at funneling excitation energy into their respective reaction centers. If these funneling processes are better understood, we can apply this knowledge to building an efficient bio-solar photovoltaic cell. Peridinin-chlorophyll-protein (PCP) complex is a LHC containing twenty-four peridinin and six chlorophyll-a pigment molecules, as shown by its x-ray crystallography structure. We are studying the excitation energy transfer rates throughout the PCP complex using time-dependent density functional theory (TD-DFT) to calculate the pigment excited states, and Förster theory to calculate the transfer rates between pigment excited states. Since Förster theory does not take into account delocalized excitation states, we will extend our study to other quantum dynamics theories that allow delocalization. The excitation transfer pathway in PCP has been shown experimentally to go from the S₂ to S₁ state in peridinin, and from the S₁ state in peridinin to the Q_y state in chlorophyll-a. Researchers have also been successful in reconstituting different species of chlorophyll molecules into the PCP complex array to tune the transfer efficiencies. Our goal is to validate the transfer efficiencies of these known complexes using the computational methods outlined above and to extend these methods to study unknown LHC systems.

P2-C49 - CHROMOPHORE-CATALYST SELF-ASSEMBLED BILAYERS FOR LIGHT DRIVEN CATALYSIS

[UNC] [Christopher R. K. Glasson](#)¹, [Javier J. Concepcion](#)¹, [Michael R. Norris](#)¹, [Dennis L. Ashford](#)¹, [Wenjing Song](#)¹, [Kenneth Hanson](#)¹, [Aaron K. Vannucci](#)¹, [Patrick L. Holland](#)¹, and [Thomas J. Meyer](#)¹¹*UNC*

The Meyer group is interested in the development of dye-sensitized photoelectrosynthesis cells (DSPEC) to generate solar fuels. Briefly, our strategy relies on the oxidation of water at a photoanode which provides reductive equivalents for fuel (e.g. methanol or hydrogen) production at the cathode. These systems rely on the efficiency of water oxidation; a process thermodynamically easier at neutral to high pH (1.23 V at pH 0 vs 0.82 V at pH 7). To obtain surface binding

stability at titanium dioxide coated electrodes in aqueous conditions we typically use phosphonic acid derivatives. However, in buffered solutions above \sim pH 6 these species readily desorb. As a result, we have been examining several approaches to counteract this deleterious behavior. An initial study found that treatment with perfluorinated silanes in hexanes of ITO slides, that were pre-loaded with $[\text{Ru}(\text{P}_2\text{bpy})_2(\text{bpy})]^{2+}$ (as a chromophore redox mediator (CRM)), resulted in vast improvements in terms of surface stability in phosphate buffered solutions at neutral pH. An extension on this approach was to use a bi-functional surface protecting species that consisted of a water oxidation catalyst (WOC) tethered to the surface via long alkyl chains with terminal phosphonic acid groups. This presentation will report on results relating to this study and compare between this modular self-assembled bilayer (SAB) approach to surface bound CRM / WOC assemblies and prefabricated covalently bridged CRM / WOC assemblies.

P2-C50 - THE DEVELOPMENT OF CATALYSTS FOR ELECTROCHEMICAL AND PHOTOCHEMICAL CO_2 REDUCTION

[UNC] David R. Weinberg¹, Zuofeng Chen¹, Peng Kang¹, Javier Concepcion¹, Chuncheng Chen¹, Aaron Vannucci¹, David Stewart¹, Marsha Massey¹, Maurice Brookhart¹, Cynthia Schauer¹, Shubin Liu¹, and Thomas J. Meyer¹

¹The University of North Carolina at Chapel Hill

Within the EFRC centered at UNC, metal-centered catalysts, organic/ligand-centered catalysts, and surface-immobilized catalysts are being used to achieve, optimize, and gain insight into carbon dioxide reduction electrocatalysis. In metal-centered catalysis, ligand/metal based reduction is used to create strongly reducing metal complex or metal-hydride intermediates which reduce carbon dioxide. The organic/ligand-centered carbon dioxide reduction catalysts utilize organic species that can transfer both electrons and protons to carbon dioxide. This includes organic molecules and acceptor ligands in transition metal complexes. Both metal-centered catalysts and organic/ligand-centered catalysts can be bound to electrode or semiconductor surfaces for interfacial reduction of carbon dioxide. Molecular catalysts can be covalently linked to the electrode surface, or they can be deposited by precipitation, sometimes involving polymerization. These studies on electrocatalytic carbon dioxide reduction are being actively supported by theory including calculations associated with reaction pathways, intermediates, and electronic structure.

P2-C51 - CATALYTIC MECHANISM FOR SINGLE-SITE WATER OXIDATION PROCESS: A THEORETICAL STUDY

[UNC] Xiangqian Hu¹

¹Duke University

Water oxidation catalyzed by single-site ruthenium complexes has generated enormous interests related to solar fuels. Combining several theoretical tools, we studied the entire catalytic cycle of water oxidation for a single site catalyst starting with $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{tpy})(\text{bpm})]^{2+}$ (i.e. $[\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$) as a representative example of a new class of single site catalysts. The electronic spin states of ruthenium intermediates during the catalytic cycle are identified as well as the corresponding optimal geometries. Results about each individual step will be presented in this talk. Our theoretical studies with atomistic details shed light on the reaction mechanisms of several pivotal reaction steps during the entire catalytic cycle and should be helpful in the design new catalysts for solar fuels.

P2-D01 - HIGH POWER NANOSTRUCTURED ANODES, CATHODES AND THERMAL PROTECTANT FOR LI-ION BATTERIES: FABRICATION BY NOVEL BIO-INSPIRED, KINETICALLY CONTROLLED, LOW-TEMPERATURE CATALYSIS

[CEEM] Daniel E. Morse¹ and Hong-Li Zhang¹

¹University of California, Santa Barbara

We report a new low cost method for kinetically controlled catalytic synthesis of nanostructured components for high-performance Li ion batteries. Anodes are Sn or Si nanoparticles grown *in situ*, uniformly dispersed in compliant and conductive graphite or commercial carbon nanotubes (CNTs). They exhibit exceptionally high power, electrochemical capacity and cyclability. Our Sn-in-graphite nanocomposite exhibits 30% greater specific electrochemical capacity (50% greater volumetric capacity) than commercial graphite anodes, retains 90% of initial electrochemical capacity at 10C and ca. 50% after discharge at 50C, with complete recovery to 100%. Our Si-in-CNTs nanocomposite anodes exhibit exceptionally high energy density and stable cyclability. Cathodes catalytically synthesized as nanocomposites of nanocrystalline metal oxides in highly conductive CNT matrices exhibit high voltage, high power and high energy. BaTiO_3 and BaSrTiO_3 nanocrystals made by this method, when doped and sintered, yield fine-grained nanocrystalline ceramics with strong positive thermal coefficients of resistivity with sharp 10,000-fold increase of resistance when heated above the Tc (tunable between 50 and 150 °C by doping with Sm), useful as an internal protectant against thermal runaway. Catalytic syntheses of the anodes, cathodes, and PTCR protectant are affordably scalable. We formed LifeCel Technology LLC to commercialize these technologies.

P2-D02 - CHARACTERIZATION OF ENGINEERED GRAPHENES FOR HIGH CAPACITY ELECTRODES

[CEES] Cary M. Hayner¹ and Sudeshna Chattopadhyay¹

¹Northwestern University

There is a pressing need for rechargeable batteries with high energy and power densities to meet the performance demand of advanced portable electronics and electric vehicles. Graphene has shown potential to address unsatisfactory rate capability, limited cycling performance and abrupt failure of conventional electrical energy storage devices. Here, we demonstrate that graphitization of SiC significantly enhances the lithiation of SiC, a material previously considered electrochemically inactive. Direct observations show that lithium penetrates into SiC after lithiation of the epitaxial graphene/SiC interface, but not bare SiC. Additionally, we demonstrate that the introduction of high density, in-plane, carbon vacancies into graphene sheets markedly enhances power capabilities by facilitating ion diffusion through the basal planes. Enhanced ion diffusion through basal planes is supported by *ab initio* studies for multiple defect types. Porous graphene composites containing ~65wt% Si nanoparticles achieved a reversible capacity of ~3200 mAh/g when cycled at 1 A/g and ~1100 mAh/g at 8 A/g, a rate comparable to those of supercapacitors. These experimental studies are complemented with both computational investigation and material characterization, including *in situ* measurements, which generate a fundamental understanding of the nature of graphene and how it facilitates charge storage in order to harness its full potential as a component of an energy storage material.

P2-D03 - THEORETICAL STUDIES OF SURFACES, INTERFACES AND NOVEL MATERIALS IN ELECTRICAL ENERGY STORAGE SYSTEMS

[CEES] Maria Chan¹, Scott Kirklín², Hakim Iddir¹, Kah Chun Lau¹, Jishnu Bhattacharya², David Snyder², Jeff Greeley¹, Chris Wolverton², and Larry Curtiss¹

¹Argonne National Laboratory and ²Northwestern University

Which combinations of elements form materials suitable for use in lithium-ion batteries? What are the arrangements of atoms in the electrodes and electrode-electrolyte interfaces of these batteries? How do these atomic arrangements affect Li ion migration and electronic conduction? At the Center for Electrical Energy Storage (CEES), we use atomistic first principles computation to answer these questions. Our goals are to understand fundamental surface and interfacial processes in Li-ion batteries, and to search for novel materials for use as anodes and electrode coatings. In silicon anodes, we reveal atomistic details of the lithiation processes and discover thermodynamic and kinetic bases for the dependence of electrochemical properties on crystal orientation and doping. For lithium carbonate films in the solid-electrolyte interphase, we find their vibrational signatures and demonstrate fast Li transport. From a high-throughput combinatorial search of alloys for high-capacity anode materials, we find several promising candidates for synthesis and further investigations. For two types of transition metal oxides, olivines and spinels, we uncover design rules for protective coating materials on cathodes. In simulating a novel synthesis method of carbon spheres, we find an intriguing combination of graphite-like and diamond-like bonding. These computational investigations are closely informed by, and aid in the understanding of, experimental efforts in CEES.

P2-D04 - FUNDAMENTAL STUDIES OF SILICON LITHIATION FOR BATTERY ANODES

[CEES] Tim Fister¹, Maria Chan¹, Paul Fenter¹, Jeff Greeley¹, Jason Goldman², Brandon Long², Michael Cason², Ralph Nuzzo², and Andy Gewirth²

¹Argonne National Laboratory and ²University of Illinois Urbana Champaign

Silicon has the highest known gravimetric capacity for lithium--nearly ten times greater than graphite, the most commonly used anode in today's lithium ion batteries. However, the volume of silicon increases by 400% when fully lithiated ($\text{Li}_{4.4}\text{Si}$), typically amorphizing crystalline electrodes and leading to rapid degradation over repeated cycling. To better understand these processes, we have studied changes in crystalline and amorphous silicon electrodes using several *in situ* approaches that are compatible with traditional electrochemical methods. Using x-ray reflectivity, we observe the substantial volume and density changes of silicon thin film electrodes during lithiation. *In situ* Raman spectroscopy indicates that kinetics for lithiation are strongly influenced by dopants and crystalline orientation. First principle computational studies reproduce these findings and point to thermodynamic and kinetic routes for each effect. To take advantage of silicon's anisotropic lithiation, we have etched (111) silicon wafers to form complex three-dimensional microstructures with (110)-oriented crystal planes that expand laterally during lithiation. Reducing the separation between (110)-planes can strain-limit lithiation in the silicon electrode; design rules based on variably-spaced microstructures has led to anodes that optimally balance capacity with stability. This coordinated, high-level study provides new insights into the limitations and opportunities of silicon as an anode material in lithium ion batteries.

P2-D05 - MICRO/NANO-PHASE CARBON ANODES FOR LITHIUM-ION BATTERIES

[CEES] [Vilas G. Pol](#)¹, [Laila Jaber-Ansari](#)², Mark C. Hersam², and Michael M. Thackeray¹
¹Argonne National Laboratory and ²Northwestern University

A solvent-less, single step autogenic process has been developed for the fabrication of carbon- and carbon-coated electrode materials from organic- and organometallic precursors, respectively, for lithium-ion battery applications. Micron sized TiO₂-carbon particles, prepared from a titanium alkoxide precursor, consist of 30-40 nm sized TiO₂ nanoparticles that are uniformly coated and interconnected by a 2-3 nm carbon layer. The decomposition of a single polymer or organic precursor in the autogenic reactor results in amorphous carbon spheres, approximately 3 microns in diameter, which retain their shape after heat treatment at higher temperature (2400°C/Ar) and have improved graphitic character. The electrochemical properties of these anode materials are reported. Due to their high surface area, high conductivity, chemical stability, and mechanical resilience, single-walled carbon nanotubes (SWCNT) are also promising candidates for lithium ion battery anodes. We employed density gradient ultracentrifugation (DGU) to sort metallic and semiconducting SWCNTs based on their electronic structure. Surfactants are generally used for dispersing SWCNTs in aqueous solutions for DGU. Our study shows that biocompatible block copolymers such as pluronics and tetronics can be used as an alternative to the commonly used ionic surfactants, such as sodium cholate and sodium dodecyl sulfate, to improve the reversible lithium insertion-deinsertion capacity.

P2-D06 - DESIGN OF ELECTROLYTES AND MEMBRANES FOR DEHYDROGENATION FUEL CELL SYSTEMS

[CETM] [Kyle Clark](#)¹, [Zulima Martin](#)¹, [Tobias Brecht](#)¹, [Peter Driscoll](#)¹, [Xioabing Zhu](#)¹, [Ravi Potrekar](#)¹, [John B. Kerr](#)¹, and [Gary Yeager](#)²
¹LBNL and ²GE Global Research

The use of liquid fuels with a polymer electrolyte membrane (PEM) fuel cell platform provides significantly larger challenges than exist for hydrogen fueled PEM fuel cells. The membrane still has to facilitate proton conduction while preventing diffusion of the fuel or the oxidant (oxygen) across the membrane. Since water is produced at the cathode it is also desired to prevent diffusion of water across the membrane. To provide such selectivity is no small task. The approach described here is to use polyelectrolyte materials which are much less dependent upon the presence of liquid water to provide the solvation for proton conduction and to incorporate these materials into a nanoporous support material that can withstand the plasticization of the polymer structure by the liquid fuel. Polyelectrolyte materials that conduct protons without the need for added water include heterocyclic bases, phosphoric and phosphonic acids. To provide the most selectivity it is desired to immobilize these solvent molecules on the polymer architecture so that only protons move across the membrane. To do this efficiently enough to be useful requires considerable polymer organization and structure. This poster will describe the approaches that are being considered to achieve these goals as well as many of the types of measurements and techniques that will be used to develop the deep understanding required to provide the desired membrane properties.

P2-D07 - HOMOGENEOUS REDOX CATALYSIS OF DEHYDROGENATION REACTIONS

[CETM] [Leah Rubin](#)¹, [John Arnold](#)¹, [John B. Kerr](#)¹, [Peter Driscoll](#)¹, [Dan Kellenberger](#)¹, [Oana R. Luca](#)², [Robert H. Crabtree](#)², and [Guillermo Zappi](#)³
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Catalysis of electrochemical reactions by homogeneous catalysts can occur via outer-sphere electron transfer mechanisms or by inner-sphere mechanisms where a transient bond is formed between catalyst and reactant to facilitate charge transfer. For dehydrogenation reactions the mechanism can involve the exchange of a hydride ion between substrate and catalyst (a common process in biological systems) or the stepwise loss of electrons and protons. In general electron transfer steps are fast while deprotonation and hydride transfer steps depend upon the acid-base chemistry of the medium and hence the exact pathway that is followed depends on the conditions. For an energy application that requires very high chemical efficiency (>99.9%) and very high catalyst turnover frequencies (> 1/s), detailed understanding of the mechanisms and kinetics is critical. This poster described measurements used to perform mechanistic diagnosis and kinetic rate determination as well as product distribution measurements that are used to understand sources of inefficiency. The inherent advantage of energy storage in a liquid fuel over a solid electrode (e.g. Lithium ion batteries) is illustrated by these measurements which demonstrate how very much easier it is to understand and correct the sources of inefficiency.

P2-D08 - APPLICATIONS OF HIGH POTENTIAL QUINONES AND Pincer COMPLEXES FOR VIRTUAL HYDROGEN STORAGE

[CETM] Oana R. Luca¹, Steven J. Konezny¹, Jeremy M. Praetorius¹, Kurt M. Luthy¹, Ting Wang¹, Grigori L. Soloveichik², Mark D. Doherty², Davide L. Simone², Victor S. Batista³ and Robert H. Crabtree³
¹Yale University; ²GE Global Research and ³Yale University

The current work focuses on the development of electrocatalysts for the efficient storage of hydrogen equivalents in liquid heterocyclic compounds. We find that dichlorodicyanoquinone (DDQ) a known dehydrogenation reagent can be electrochemically regenerated and used in the dehydrogenation of a model fuel [1]. Nickel pincer complexes are also promising; they are proton reduction catalysts and they are being studied for heterocycle reductions in aqueous acidic conditions. [1]. Oana R. Luca Ting Wang Steven J. Konezny Victor S. Batista and Robert H. Crabtree New J. Chem. 2011 in press DOI:10.1039/C0NJ01011A.

P2-D09 - USE OF LIQUID FUEL CELL FOR EVALUATION OF SYSTEM COMPONENTS

[CETM] Tracy Huang¹, Lakshmi Krishnan¹, Davide Simone¹, Mark D. Doherty¹, Grigori L. Soloveichik¹, Guillermo D. Zappi¹, Matthew Rainka¹, Oltea Siclovan¹, Thomas Miebach¹, John Kerr², and Judith Stein¹
¹GE Global Research and ²LBNL

Organic liquid regenerative fuel cells have the potential advantages of high energy density zero CO₂ production and low fuel crossover. To evaluate the organic fuels and optimize a fuel-electrocatalyst combination we benchmarked and modeled the half-cell oxidative dehydrogenation reaction. In this study cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry were used to study electrooxidation of organic fuels at a Pt disk and commercial Pt/C catalyst coated on a graphite disk using a Nafion containing catalyst ink. Three carbocyclic organic fuels (tetralin decalin and cyclohexane) and three nitrogen containing heterocyclic fuels (tetrahydroquinoline, tetrahydroisoquinoline, and indoline) were investigated. Among the carbocyclic fuels tetralin was oxidized at the lowest potentials (1.5 V vs. SCE). The slow reaction rate of these hydrocarbons and possible passivation of the electrode surface prevented reaching a mass transport controlled regime. Contrarily the N-containing heterocyclic fuels exhibited typical diffusion controlled RDE behavior suggesting that the nitrogen atom facilitates the oxidation process of these fuels. The location of the N-atom also affects the oxidation rate due to changing of the resonance effect. Fast degradation of the fuel oxidation peak observed for the supported Pt/C catalyst ink indicates a strong adsorption effect by the organic fuels or oxidized products at the electrode surface.

P2-D10 - INVESTIGATING THE HYSTERESIS OF THE FEF₃/LI NANOSCALE ELECTRODE REACTION

[CNEEC] John Vajo¹, Jun Liu¹, Wen Li¹, John Wang¹, and Ping liu¹
¹HRL

FeF₃ has been studied extensively as a high capacity cathode material for lithium batteries. During lithiation, FeF₃ goes through a series of structural changes that eventually leads to the formation of LiF+Fe. This reaction, similar to other conversion reactions, suffers from very large hysteresis during lithiation and lithium removal. This hysteresis has been argued to be intrinsic (or thermodynamic), ie, it persists even when current polarization is very small. This argument was supported by the profiles measured at C/200. Later, theoretical arguments were provided to explain the hysteresis. In order to further clarify whether the observed hysteresis is still a result of extraordinarily slow reaction kinetics or indeed thermodynamic in nature, we employ the galvanostatic intermittent coulomb titration (GITT) method to measure the open circuit voltage as a function of state of discharge. Preliminary results indicate that the results obtained at C/200 are far from equilibrium and the observed hysteresis might not be intrinsic.

P2-D11 - KINETICS OF Li⁺ DIFFUSION IN OLIVINE PHOSPHATES

[CST] Gopi Krishna Phani Dathar¹, Daniel Sheppard¹, Nicholas Delone¹, Jing Wu¹, Keith J. Stevenson¹, and Graeme Henkelman¹
¹University of Texas at Austin

Relevant kinetic pathways of Li ion diffusion in olivine phosphates are calculated from density functional theory (DFT). Previously reported theoretical diffusion rates for Li ions and vacancies in FePO₄ and LiFePO₄ are about six orders of magnitude faster than experimentally measured values. However, the Li ion diffusion rate consists of different components including diffusion in the bulk, on the surface, in the presence of defects, and in varying local environments. Using DFT and DFT+U, we quantify each of these effects and find that while bulk diffusion is affected by strain and Li concentration, these can not explain the slow diffusion observed unless antisite defects are present. We find the Li ions near the antisite defects bind stronger than Li ions in corresponding defect-free channels. Concerted motion of Li ions across the channel around the antisite defect is facile in FePO₄. The mechanism switches to single vacancy hopping with a higher barrier for cross-channel diffusion in LiFePO₄, giving rise to distinct diffusion coefficients in the two materials. The diffusion barriers for surface diffusion are calculated to be high, which would contribute to slow kinetics in nanostructured

olivine phosphates. Raman spectroscopy is used to characterize FePO_4 and LiFePO_4 and partially lithiated phases during cycling. Vibrational modes are calculated using DFT and compared against the experiments to identify changes in the Raman modes due to cycling Li ions.

P2-D12 - PdCo@Pd/C CORE-SHELL NANOPARTICLES AND Pt-DECORATED PdCo@Pd/C FOR OXYGEN REDUCTION

[EMC2] Deli Wang¹, Huolin Xin¹, David Muller¹, Francis DiSalvo¹, and Hector Abruña¹

¹Cornell University

We describe a simple method for the preparation of Pd-rich PdCo alloy nanoparticles supported on carbon (PdCo@Pd/C), which has been developed using an adsorbate-induced surface segregation effect. The electronic properties of Pd were modulated by alloying with different amounts of Co, which affects the oxygen reduction reaction (ORR) activity. The stability and electrocatalytic activity of the PdCo@Pd/C nanoparticles for the ORR were enhanced by spontaneous deposition a nominal monolayer of Pt. The experimentally measured ORR activities for the different catalysts could be correlated with the oxygen adsorption energy and the d-band center of the surface elements, as calculated by density functional theory, in agreement with previous theoretical studies. The facile method described herein is suitable for large-scale production significantly lowering the Pt loading and thus, cost. These materials are promising cathode catalysts for fuel cell applications.

P2-D13 - FUEL CELL ELECTROCATALYST DEVELOPMENT AND CHARACTERIZATION

[EMC2] Eric Rus¹, Hongsen Wang¹, Anna Legard¹, Michele Tague¹, Bruce van Dover¹, and Hector Abruña¹

¹Cornell University

To study mechanistic details of electrochemical reactions relevant to fuel cell anode catalysis, we employ *in situ* spectroscopic methods. Differential electrochemical mass spectroscopy (DEMS) is used to detect volatile solution species, while as a complement, *in situ* FTIR can detect electrode-adsorbed species. We have used these techniques to investigate the electrooxidation of small organic molecules (SOMs), and the CO tolerance of fuel cell anode materials. In recent work, we have developed a scanning DEMS, in which a membrane-covered probe serves as the interface between the electrochemical cell and the mass spectrometer vacuum chamber. The probe can be rastered over the surface of an electrode, yielding spatial resolution of product formation. This instrument is employed to screen combinatorial libraries of catalyst compositions, produced by magnetron sputtering, for activity towards the electrooxidation of SOMs.

P2-D14 - SOLVENT PROCESSABLE TETRAALKYLAMMONIUM-FUNCTIONALIZED POLYETHYLENE FOR USE AS AN ALKALINE ANION EXCHANGE MEMBRANE

[EMC2] Henry Kostalik, IV¹, Timothy Clark¹, Nicholas Robertson¹, and Geoffrey Coates¹

¹Cornell University

Fuel cells are energy conversion devices that have the potential to serve as alternative power generators for both mobile and stationary applications. The vast majority of fuel cell membranes operate under acidic conditions, and are therefore proton conducting with Nafion being the industry standard. However, proton conducting membrane fuel cells rely heavily on expensive noble metal catalysts, predominantly platinum. As a result, there is considerable current interest in the synthesis and implementation of hydroxide conducting membranes for use under alkaline conditions. This interest has arisen primarily due to the favorable reaction kinetics at high pH that may allow for the use of non-noble metal catalysts (e.g. Ni). In this poster, I will present a new synthetic route to alkaline anion exchange membranes (AAEMs) that yields stable and robust hydroxide conducting thin films for fuel cell applications.

P2-D15 - BATTERY MATERIALS AND ARCHITECTURES

[EMC2] Michael Lowe¹, Zichao Yang¹, Jayaprakash Navaneethakrishnan¹, Jennifer Nugent¹, Jie Gao¹, Hector Abruña¹, Lynden Archer¹, and Stephen Burkhardt¹

¹Cornell University

Research efforts in the Energy Materials Center at Cornell are pursuing new materials and architectures for the cathodes, anodes, and electrolytes of high energy-density lithium-based batteries. In this poster, results will be presented for several systems, including organic and elemental sulfur cathodes and metal-oxide anodes. Significant improvements in energy density and rate capability will be demonstrated upon modification with appropriate carbon coatings. *In-situ* x-ray investigations will also be discussed as an example of the techniques available for characterizing the reaction mechanisms of electrode materials within operational batteries. Finally, initial results will be shown for a nanoscale organic-inorganic hybrid electrolyte for lithium battery applications that exhibits a 6V electrochemical window.

P2-D16 - HIGH THROUGHPUT METHODS FOR ELECTROCATALYST DISCOVERY

[EMC2] Eva Smith¹, Michele Tague¹, John Gregoire¹, Darren Dale¹, Anna Legard¹, Bruce van Dover¹, Frank DiSalvo¹, Richard Hennig¹, and Hector Abruna¹

¹Cornell University

The space of potential catalysts for PEM fuel cell cathode and anode catalysts is of such size and diversity that it behooves the materials engineer to develop methods for quick and efficient candidate synthesis and characterization. We review the high-throughput methodology employed at the Energy Materials Center at Cornell, including sputter deposition of continuous composition spreads, parallel screening of catalytic activity, and automated X-ray diffractometry and fluorescence. We present results for anode catalyst activity in the large family of Pt-M (M= transition or main group metal) phases. We also discuss methods for the tuning of electronic structure in intermetallic phases with intercalation of carbon and nitrogen atoms.

P2-D17 - CARBON ONIONS FOR IMPROVED ELECTRICAL ENERGY STORAGE

[FIRST] J. McDonough¹, P. Ganesh², P. Fulvio², V. Mochalin¹, V. Presser¹, S. Dai², P.R.C. Kent², and Y. Gogotsi¹

¹Drexel University and ²Oak Ridge National Laboratory

Carbon onions, or onion-like carbons (OLC), are spherical 5-10 nm nanoparticles consisting of concentric shells of graphitic carbon that can be considered as multishell fullerenes. Recently, OLC has attracted attention as a material for supercapacitor electrodes for high scan rate, high power applications. To better understand the parameters of OLC governing electrochemical applications, we performed a comprehensive study on the influence of annealing temperature on structure and electrochemical performance by employing Raman spectroscopy, X-ray diffraction, gas sorption, electron microscopy, cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy. Experimental work on carbon onion synthesis and structural changes was correlated with molecular dynamics simulations utilizing the ReaxFF. Carbon onions were tested as a raw material, as a thin film mixed with polymeric binder, and as an additive to templated mesoporous carbon. In particular, OLC was evaluated as a replacement for the commonly used carbon black. The high capacitance compared to carbon black and high rate performance of OLC was found to be beneficial for both carbon onion electrodes and carbon onion additions to carbon supercapacitor electrodes.

P2-D18 - NANOSTRUCTURED MnO_x FOR SUPERCAPACITORS

[HeteroFoaM] Min-Kyu Song¹, Shuang Cheng¹, Feng Liu², and Meilin Liu¹

¹Georgia Institute of Technology and ²University of Utah

Electrochemical capacitors or pseudocapacitors represent a promising option for many applications, from portable electronics to hybrid electric vehicles, as they have the potential to exhibit both features of capacitors and batteries. To date, however, the existing pseudocapacitors often suffer from poor cycling stability and rate capability and their energy density is still significantly lower than those of batteries. Creation of nanostructured electrodes represents one of the most attractive strategies to dramatically enhance the performance, including capacity, rate capability, and cycling life. Here, we report a mixed valent oxide electrode for pseudocapacitors with enhanced energy density while maintaining high rate capabilities and cycling performance. We used highly porous carbon substrates as both current collector and backbone for thin and conformal coating of MnO_x . Due to the efficient ion diffusion between porous carbon fibers, improved electrical contacts between manganese oxides and current collectors (without any insulating binders), and nanostructured MnO_x having enhanced pseudocapacitive behavior, electrochemical capacitors constructed from novel electrodes showed dramatically improved specific capacitance, better rate capability, enhanced cycling ability.

P2-D19 - THE ROLE OF MATERIAL STRUCTURE AND COMPOSITION IN NANOSTRUCTURED TRANSITION METAL OXIDE ELECTROCHEMICAL CAPACITORS

[MEEM] Veronica Augustyn¹, Zheng Chen¹, Jong Woung Kim¹, Thomas Quicke¹, Sarah Tolbert¹, Yunfeng Lu¹, and Bruce Dunn¹

¹University of California, Los Angeles

To increase the energy and power densities of electrochemical capacitors, new materials and architectures for capacitive charge storage are needed. With this in mind, we have investigated nanostructured Nb_2O_5 , a promising material that can deliver more than 300 F/g within seconds. We have also developed a method for forming nanocomposites of V_2O_5 and carbon nanotubes (CNTs) into thick electrodes which provide significantly higher rate capabilities than V_2O_5 nanowires alone. Orthorhombic Nb_2O_5 synthesized through sol-gel routes into particles or mesoporous films shows very high specific capacitance when using non-aqueous lithium electrolytes. Through a combination of experiments and analysis of the kinetic behavior, we find that an overwhelming amount of charge storage is due to pseudocapacitive processes. Moreover, the capacitive storage properties are dependent on crystal phase, suggesting that the mechanism involves rapid lithium ion penetration into the Nb_2O_5 lattice. Transition metal oxides can offer very high capacitance, but they are

usually poor electronic conductors. Through the *in-situ* synthesis of V_2O_5 /CNT nanowire nanocomposites, we have developed a method to effectively "wire" the highly capacitive V_2O_5 for high rate capability. The CNTs act as electron highways, leading to improved charge transfer to the V_2O_5 nanowires. For a charging time of 100 seconds, a 120 μm -thick nanocomposite electrode can deliver 350 F/g.

P2-D20 - CONTINUUM-LEVEL SIMULATION OF CONVERSION REACTIONS: FROM A LI-CU-TIS₂ SYSTEM TO A LI-FE-F SYSTEM [NECCES] Hui-Chia Yu¹, Tapiwa Mushove¹, Jishnu Bhattacharya¹, Chen Ling¹, Anton Van der Ven¹, Katsuyo Thornton¹, Glenn G. Amatucci², and Nathalie Pereira²

¹University of Michigan and ²Rutgers University

The Energy Frontier Research Center funding is enabling close collaboration between experimentalists and theorists to elucidate the science needed for discovering novel materials for battery cathodes. Recent research and development of lithium-ion battery cathode materials have mainly focused on intercalation compounds. However, scientists are beginning to examine alternative materials that undergo conversion reactions. Such systems have potential to achieve higher capacity than currently possible. As part of the Northeastern Center for Chemical Energy Storage (NECCES), we explore the conversion reaction in a Li-Fe-F system with nanoscale morphologies. Our starting point is a model system of spinel $\text{Cu-Ti}_2\text{S}_4$ in which Cu is extruded during Li insertion. Using the free energy landscape and diffusion coefficients calculated by kinetic Monte Carlo simulations, the kinetics and the accompanying morphological evolution during charge and discharge of electrode particles are simulated at the continuum level. We investigated the effects of parameters such as reaction rate constants, current and electrostatic potential loadings, and particle morphologies. Building upon this model, we developed possible models that would describe the experimental results for the Li-Fe-F system. This work provides a framework for developing understanding of kinetics and hysteresis observed in conversion-reaction electrodes, which may be applicable to other systems including anode materials.

P2-D21 - CHARACTERIZATION OF LI-ION BATTERY MATERIALS AND PROCESSES USING MAGNETIC STUDIES

[NECCES] Natasha A. Chernova¹, Fredrick Omenya¹, Ruigang Zhang¹, M. Stanley Whittingham¹, Feng Wang², Jason Graetz², Glenn Amatucci³, Nathalie Pereira³, Thomas McGilvray⁴, and Y. Shirley Meng⁴

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A variety of characterization techniques are being used and developed in the Northeastern Center for the Electrochemical Energy Storage (NECEES) with the goal to reveal the atomic-scale structural details and reaction mechanisms of Li-ion battery electrode materials. This presentation will highlight the application of magnetic properties, which are sensitive to the oxidation state, structural disorder, and phase composition, often beyond the sensitivity of x-ray diffraction. Magnetic studies have been used to characterize several systems investigated throughout NECESS. Magnetic properties have proved sensitive in differentiating between a true substitution of, for example, vanadium in LiFePO_4 from impurity phase formation. In the former case, a change in antiferromagnetic ordering transition was found, while in the latter case, additional magnetic transitions were observed. The magnetic properties were also successfully applied to investigate the reaction mechanism of the FeF_2 -C cathode and SnCo-C anode. We were able to determine the amount and particle size of Fe and Co displaced upon lithiation of FeF_2 and SnCo, respectively. Combined with the results of other characterization techniques, this has led to clearer understanding of conversion mechanism. This research is supported as part of the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award Number DE-SC0001294.

P2-D22 - AMORPHOUS SNCO-CARBON ANODE: UNDERSTANDING THE REACTION MECHANISM

[NECCES] Shailesh Upreti¹, Ruigang Zhang¹, Natasha Chernova¹, Feng Wang², Lin-Shu Du³, Jaroslaw Syzdek⁴, ⁵Faisal Alamgir, Christian Burger³, Jun Wang², Cole Petersburg⁵, Elaine Lin⁵, Jason Graetz², Robert Kostecki⁴, Clare P. Grey³, and M.S. Whittingham

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Amorphous tin-cobalt based anode, which demonstrates its ability to possess much better electrochemistry than traditionally used graphite, has attracted considerable interest since it was first introduced by SONY in 2005. Combination of intercalation and conversion reactions appear to offer a great potential for increasing its gravimetric and volumetric capacities. However, a rational elucidation of fundamental mechanisms is required to build a roadmap for developing future crossover materials. In this work, nanostructured SnCo embedded in carbon matrix is considered as a model system, where both intercalation reaction forming Li_xSnCo and conversion reaction with $\text{Li}_x\text{Sn} + \text{Co}$ products could occur. We investigate how the nano-SnCo alloy reacts with lithium in the electrochemical cell by ⁷Li MAS NMR, STEM, *in-situ* X-ray absorption, Raman spectroscopy, *in-situ* small-angle x-ray scattering (SAXS), and magnetic studies. Co displacement upon Li insertion is confirmed by magnetic properties, SAXS and STEM. Since the corresponding Li NMR spectra

revealed only small shifts, indicating diamagnetic Li environment, we are further investigating the existence of Li_xSnCo using *in-situ* and *ex-situ* pair distribution function analysis. This research is supported as part of the NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Basic Energy Sciences under Award Number DE-SC0001294, and at Georgia Institute of Technology - by the Creating Energy Options program.

P2-D23 - USING SYNCHROTRON BASED X-RAY DIFFRACTION AND ABSORPTION TO UNDERSTAND LiFePO_4 AND FeF_2 AS CATHODE MATERIALS FOR LITHIUM BATTERIES

[NECCES] Xiao-Jian Wang¹, Kyung-Wan Nam¹, Xiao-Qing Yang¹, Nathalie Pereira², and Glenn G. Amatucci²
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In this study, synchrotron radiation techniques including *in-situ* X-ray diffraction (XRD), *in-situ* X-ray absorption spectroscopy (XAS) and *ex-situ* soft XAS provide a detailed picture of the whole extraction process. A delay, not only for crystal structure, but also electronic structure, can be observed: *in-situ* XRD experiment shows that the appearance of crystallized FePO_4 is almost at $x=0.35$; *In-situ* XAS experiment also indicates that the electronic structure in $\text{Li}_{1-x}\text{FePO}_4$ almost close to a linear with the electrochemical data. By further soft XAS analysis of Fe L-edge XAS data, we attribute the observed phase transition delay during lithium extraction to the slow Li ion diffusion in the bulk part of $\text{LiFePO}_4/\text{FePO}_4$ system. On the second part, we find that it is a two phase transition behavior during 1st discharge and charge.

P2-D24 - FUNDAMENTAL INSIGHTS INTO PERFORMANCE LIMITATIONS OF OXOANION CATHODE MATERIALS

[NECCES] Yuri Janssen¹, Shouhang Bo¹, Lin-Shu Du¹, Derek Middlemiss¹, Peter Khalifah¹, and Clare P. Grey¹
¹Stony Brook University

The development of LiFePO_4 as a high-capacity high-rate material has opened a new frontier for battery electrode materials by demonstrating that compounds with poor ionic and electronic conductivity can still effectively serve as high capacity cathodes. The NECCES EFRC aims to understand the detailed mechanisms by which the conductivity limitations of LiFePO_4 are surmounted in functioning batteries, and to apply this knowledge to the design and development of next generation cathode materials. Large single-crystal samples of LiFePO_4 , LiMnPO_4 , and Li(Fe/Mn)PO_4 with very low defect concentrations ($>0.2\%$) have been prepared using newly-developed flux growth methods, and are serving as a platform for fundamental studies into this class of olivine compounds. Work has begun on improving the cycling performance of next-generation oxoanion systems such as LiFeBO_3 which have a substantially improved capacity (220mA/g vs. 170 mAh/g for LiFePO_4) but still suffer from serious performance limitations. The full range of experimental and theoretical methods available to the EFRC are being applied to understanding and overcoming the performance limitations of this alternative class of oxoanion cathode materials. This research is supported as part of the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award Number DE-SC0001294.

P2-D25 - NANO-ELECTRODE NETWORKS: CHEMISTRY AND MECHANICS AT NANOSTRUCTURED INTERFACES

[NEES] Hongwei Liao¹, Alexandra H. Brozena¹, Khim Karki¹, Yin Zhang¹, John Cumings¹, and YuHuang Wang¹
¹The University of Maryland, College Park

Carbon nanotube (CNT) @amorphous Si ($\hat{\text{I}}_{\pm}\text{-Si}$) core-shell structures are a promising anode material for lithium ion batteries because this heterogeneous structure combines the optimal properties of two materials: $\hat{\text{I}}_{\pm}\text{-Si}$ maximizes Li^+ storage capacity while the CNT core enhances structural stability and electrical conductivity. We have developed a synthetic approach for fabricating CNT@ $\hat{\text{I}}_{\pm}\text{-Si}$ co-axial nanostructures that are suspended over the edge of a cleaved Si substrate. The surface chemistry of CNTs plays a vital role for $\hat{\text{I}}_{\pm}\text{-Si}$ coating on CNTs. With plasma enhanced chemical vapor deposition, $\hat{\text{I}}_{\pm}\text{-Si}$ forms a conformal coating on carboxylic acid functionalized CNTs while discontinuous coating occurs on non-functionalized CNTs. The interfacial mechanical properties of these heterogeneous structures were studied with SEM and *in situ* TEM. We found that the $\hat{\text{I}}_{\pm}\text{-Si}$ shell ruptured at the Si substrate anchoring point when a force applied on the free end of these cantilever-like structures increased. The broken $\hat{\text{I}}_{\pm}\text{-Si}$ shell could be pulled off like pulling a sheath from a sword, leaving the CNT core typically intact. These observations illustrate a striking difference in the mechanical properties between $\hat{\text{I}}_{\pm}\text{-Si}$ and CNTs and the relatively weak interfacial bonding between the two materials.

P2-D26 - NANOSCALE ENGINEERING FOR SI-BASED HIGH PERFORMANCE LI ION BATTERIES

[NEES] Jeong-Hyun Cho¹, Xianglong Li¹, Xiao Hua Liu², Jian Yu Huang², and S. Thomas Picraux¹
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Silicon nanowire anodes are one-dimensional structures with great promise for significant enhancement in the energy capacity of lithium ion batteries. However, the growth of high density arrays of silicon nanowires (SiNWs) on metal current collectors is challenging due to wetting of the nanowire growth catalyst which leads to formation of micro-scale Si clumps as well as to competing metal silicide formation during the Si nanowire growth process. The Si clump and silicide

formation reduces overall capacity and leads to capacity fade during cycling. Moreover, limited areal loading density and high fabrication costs must be solved for commercialization. Here, we demonstrate high density, electrically contacted Si nanowire growth on stainless steel substrates (metal current collectors) with minimal unwanted substrate-silicide and Si clump formation for high Li ion battery performance. The charging behavior of individual Si nanowires was revealed by *in-situ* transmission electron microscopy, which showed a highly anisotropic volume expansion, leading to crack formation in the lithiated nanowires. It is also found that the lithiated phase is crystalline $\text{Li}_{15}\text{Si}_4$ under fast charging condition. Furthermore, we are going to show a method which boosts the growth of SiNWs on stainless steel substrates and reduces fabrication cost. Specific energy capacity and Li ion cycling results with SiNW half-cell batteries will be presented to illustrate the beneficial effects of our new approach.

P2-D27 - HETEROGENEOUS NANOTUBES AND NANOWIRES: FABRICATION, MECHANISM, AND ELECTROCHEMICAL CHARACTERIZATION FOR SUPERCAPACITORS

[NEES] [Jonathon Duay](#)¹, [Stefanie A Sherrill](#)¹, [Sung Kyoung Kim](#)¹, and [Sang Bok Lee](#)¹

¹*University of Maryland*

Supercapacitors have gained attention due to the demand for rapid power delivery in applications such as the electric grid and transportation sector owing to their ability to provide moderate energy densities at high power demands. Our research is focused on the fabrication, mechanism and electrochemical characterization of heterogeneous nanostructured materials in order to enhance their electrochemical energy storage properties. We combined the deposition techniques of atomic layer deposition and electrochemical deposition (ECD) within the anodic aluminum oxide (AAO) template to integrate multiple materials with favorable energy storage properties. We report the energy storage enhancement of MnO_2 nanowires by exploiting the electrochemistry of MnO_2 to produce MnO_2 nanoparticles on the surface of each nanowire. We created coaxial $\text{MnO}_2/\text{PEDOT}$ nanowires, by a one-step ECD technique, which maintain high energy density even at high current densities due to the conductive polymer shell. Other metal/metal oxide nanotubes (Ni, NiO, Co, NiFe, NiFeCo) were synthesized to elucidate the mechanism which results in the ECD of metal nanotubes in the AAO template. The unusual properties of these hollow structures in the nanometer scale were examined and controlled by adjusting the nanotube's composition and size (e.g., wall thickness), which enhances their applicability to the development of ultrafast sensors, highly efficient catalysts, and high power energy storage devices.

P2-D28 - NANOARCHITECTURED 3D ELECTRODES FOR LI-ION MICROBATTERIES

[NEES] [Ekaterina Pomerantseva](#)¹, [Konstantinos Gerasopoulos](#)¹, [Xinyi Chen](#)¹, [Gary Rubloff](#)¹, [James Culver](#)¹, [Chunsheng Wang](#)¹, and [Reza Ghodssi](#)¹

¹*University of Maryland, College Park*

We report a new approach combining biotemplating/nanostructuring and three-dimensional (3D) microfabrication methods for the preparation of hierarchically structured lithium-ion microbattery electrodes (TiO_2 anodes and V_2O_5 cathodes) with advanced electrochemical characteristics. The nanostructuring is achieved using self-assembly of Tobacco mosaic virus (TMV) templates containing cysteine (Cys) residues within the virus coat protein. The Cys-modified TMV molecules demonstrate enhanced binding to the Au-coated surfaces through the thiol groups, resulting in ordered virus patterns. Using electroless plating, TMV particles are covered with Ni followed by electrochemically active battery materials coating using Atomic Layer Deposition (ALD). ALD is applicable for the production of uniform thin nanolayers of materials thus maintaining the high surface area established by the self-assembled TMV scaffolds. 3D microfabricated substrates for electrodes preparation consist of electroplated gold micropillars on silicon wafers. To make hierarchically structured electrodes, the micropillars were coated with the metalized TMV template followed by active battery material coating. The novel micro/nano patterning approach results in higher electrochemically active material loading without increasing areal footprint, enabling higher energy density. The use of nanostructured materials creates larger electrode/electrolyte interface and reduces ion diffusion paths, improving the power density.

P2-D29 - ELECTRON TRANSPORT IN CHARGE-SEPARATED NANOPARTICLE FILMS DRIVEN BY EXTERNAL FIELDS: A NON-EQUILIBRIUM APPROACH

[NERC] [Anthony Costa](#)¹, [Jason Green](#)¹, and [Igal Szleifer](#)¹

¹*Northwestern University*

Although the treatment of non-equilibrium lacks the set of unifying principles enjoyed by equilibrium problems, the tools of molecular simulation are ideally suited to address the fundamental theory of these processes and its application to important problems in the field of energy research. The focus of the current work is the central idea of dissipation. We begin by considering the Hamiltonian dynamics of a simple model fluid system in which a subset of particles may self-assemble (and disassemble) depending on their time-varying interactions. No dissipation is integrated out of the dynamics by the inclusion of a fictitious bath. That is, the dissipation of kinetic energy during assembly processes is explicitly

retained in explicit bath particles. Averaging over many trajectories between an initial unassembled and final assembled state, a course-grained dynamical picture begins to emerge. The application of these types of methods to physical systems is a fledgling field. The current system of interest is a film of functionalized nanoparticles with non-ohmic conductance properties when subjected to periodic applications of an external electric field. A multiscale approach is adopted, including monte-carlo structural landscape searches and *ab initio* density functional and perturbation theory. Finally, atomistic Newtonian trajectories are propagated in an approximate forcefield and the relationship of the results to the model self-assembly system is discussed.

P2-D30 - ACCESSING TETRATHIAFULVALENE RADICAL DIMERS AND NON-EQUILIBRIUM STATES IN MECHANICALLY INTERLOCKED MOLECULES

[NERC] Gokhan Barin¹, Ali Coskun¹, Jason M. Spruell¹, and J. Fraser Stoddart¹

¹Northwestern University

Two donor-acceptor [3]catenanes(1,2)-composed of a tetracationic molecular square, cyclobis(paraquat-4,4'-biphenylene), as the pi-electron deficient ring and either (i) two tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) containing macrocycles or (ii) two TTF-butadiyne-containing macrocycles as the pi-electron rich components-have been investigated in order to investigate their propensity to form TTF radical dimers. The mechanical stabilization of the TTF radical dimers in these [3]catenanes under ambient conditions has been demonstrated by UV-Vis-NIR and EPR spectroscopies, cyclic voltammetry, and X-ray diffraction analysis. The mechanically interlocked nature of the [3]catenanes has allowed us to study the intermolecular interactions between the TTF radical dimers in a molecule at room temperature in air. The results could contribute in the fullness of time to the development of molecular electronic devices based on tetrathiafulvalene units. Another piece of research is focused on a new approach to manipulating the dynamic behavior associated with mechanically interlocked molecules (MIMs) with a higher degree of control. The approach could allow us to access non-equilibrium states by using a dynamic barrier which limits the movement of components in a [3]rotaxane. Design principles and progress towards the preparation of these MIMs have been demonstrated. [1] Spruell, J. M. et al. Nature Chem. 2010, 2, 870-879. [2] Coskun, A. et al. J. Am. Chem. Soc. 2011, 133, 4538-4547.

P2-E01 - DEVELOPMENT OF SOLID OXIDE CELLS FOR ENERGY CONVERSION AND STORAGE

[HeteroFoaM] Chenghao Yang¹, Chao Jin¹, and Fanglin (Frank) Chen¹

¹University of South Carolina

Conventional LSM-YSZ/YSZ/Ni-YSZ solid oxide cells (SOCs) have been fabricated and evaluated, but their performance has found to be limited in either fuel cell (SOFCs) or electrolysis cell (SOECs) mode. The cell performance has been significantly improved by employing an infiltrated LSM-YSZ electrode, due to dramatically decreased polarization resistance. However, mass transport limitation has been observed, particularly in electrolysis mode. By utilizing micro-tubular SOC with novel hydrogen electrode produced via a phase inversion method, the mass transport limitation has been mitigated. Finally, mass transport limitation has been further improved by using cells electrodes fabricated with a freeze-drying tape-casting method.

P2-E02 - APPLICATION OF PULSED ELECTRIC CURRENT SINTERING ON NEW THERMOELECTRIC OXIDES

[RMSSEC] Chang Liu¹ and Donald T. Morelli¹

¹Michigan State University

In the past decade, great effort has been made to enhance the efficiency of thermoelectric materials for waste heat recovery and solid-state cooling/heating. More recently, after the discovery of large thermopower in single crystal sodium cobaltite, oxide-based compounds have received increased attention. Compared to traditional TE materials, oxides have better thermal stability, less toxicity and lower production cost. The adoption of advanced consolidation techniques assisted the production of highly condensed poly-crystalline samples and further boosts the investigation into this promising material category. In this research, pulsed electric current sintering (PECS) has been applied to the preparation of three p-type complex oxides for prospective thermoelectric applications: delafossite-type copper aluminum oxide with magnesium doping to reduce electrical resistivity and improve power factor; Na-rich sodium cobaltite for low-temperature Peltier cooling; partially rare-earth element doped calcium cobaltite for high-temperature power generation. Starting from solid-state reaction and powder processing, highly densified samples (above 95% of theoretical density) were achieved in all of the three materials systems after PECS treatment. Structural analysis and transport coefficient measurement were performed to study the thermoelectric properties. Systems such as these can offer potential low cost, manufacturable materials for power generation from waste heat.

P2-E03 - WAVELENGTH DOWNCONVERSION MATERIALS FOR SOLID-STATE LIGHTING

[SSLS] James E. Martin¹, Lauren Rohwer¹, and May Nyman¹¹Sandia National Laboratories

The current generation of white LEDs is largely based on blue-emitting InGaN LEDs that excite yellow-emitting YAG:Ce phosphors. The cold white emission from such devices can be made warm by adding a red component. Sandia is developing two types of red emitters: doped tantalates and II-VI quantum dots. Both of these materials can generate reasonably narrow bandwidth red emission under blue excitation. We will present our recent progress on these materials.

P2-E04 - NANOWIRE AND NANOPARTICLE COMPOSITES FOR EFFICIENT THERMOELECTRICS

[CEEM] Benjamin Curtin¹, Hong Lu¹, Jacqueline Hall¹, Chris Palmstrøm¹, Arthur Gossard¹, and John Bowers¹¹University of California - Santa Barbara

Nanostructured materials offer enhanced thermoelectric figure of merit, ZT, through the ability to decouple electrical and thermal properties during material optimization. Thermal conductivity is reduced with nanoparticles and nanowires by additional phonon scattering, while embedded Er-V nanostructures can enhance electrical conductivity of their III-V matrix due to their semi-metallic behavior. At the Center for Energy Efficient Materials, we have studied different methods to fabricate and embed nanostructures for improved thermoelectric material and device performance. One approach was to pattern and etch sub-100 nm Si nanowires into optimally doped Si wafers. Large area nanowire arrays with nanowire areal fill-factors of 15% were fabricated and embedded in spin-on glass, resulting in a thin-film composite material useful for characterization and power generation devices. Additionally, semi-metallic nanoparticles and nanowires were grown within a III-V host matrix using molecular beam epitaxy (MBE). Through a co-deposition MBE growth process and by varying the Er concentration, a variety of ErSb nanostructures were formed within a GaSb matrix. Other rare earths, such as scandium, have also been investigated. Sc-V nanoparticles are expected to be significantly smaller and effectively scatter different wavelength phonons than Er-V. Sc and Er have been used simultaneously during MBE growth of InGaAs and the thermoelectric properties of this material are presented.

P2-E05 - COMBUSTION AT HIGH PRESSURE

[CEFRC] Jeffrey S. Santner¹, Michael P. Burke¹, Frederick L. Dryer¹, and Yiguang Ju¹, Swetaprovo Chaudhuri¹, Peng Zhang¹, Fujia Wu¹, and Chung K. Law¹, David F. Davidson² and Ronald K. Hanson², Bryan W. Weber³, Mruthunjaya Uddi³, Apurba Das³, and Chih-Jen Sung³, Fokion N. Egolfopoulos⁴, and Stephen J. Klippenstein⁵¹Princeton University; ²Stanford University; ³University of Connecticut; ⁴University of Southern California and ⁵Argonne National Laboratory

Current chemical models for combustion consist of kinetic data for thousands of reactions. These models are validated through detailed comparisons with wide ranging experimental observations of flame properties. Unfortunately, much of the validation data is for low pressures (e.g., 1 bar), whereas combustion devices are generally operating at much higher pressures (e.g., 100 bar for many advanced engine concepts). Recent studies have demonstrated great shortcomings for even the best chemical models at high pressure. The CEFRC is addressing these shortcomings through the generation of wide-ranging validation data at significantly higher pressures and the use of this data in the development of improved chemical models. In particular, we are developing and applying methods for studying ignition, propagation, and extinction in stagnation and spherically expanding flame configurations, flame properties for turbulent flames, ignition delays and multi-species time histories in both rapid compression machines and shock tubes, and elementary rate coefficients in shock tubes. All of these measurements are being performed for pressures ranging up to 20 to 40 bar, with an initial focus on butanol combustion as a key prototypical biofuel. The combination of modeling and theoretical reaction kinetics is being used to improve the chemical model for butanol combustion through careful theoretical studies of the key chemical reactions as indicated by the modeling.

P2-E06 - MATERIALS AND SYNTHESIS OF KNOWN SUPERCONDUCTORS

[CES] Jian-Min Zuo¹, Hefei Hu¹, Ivan Bozovic², Cedomir Petrovic², Genda Gu², Lei Fang³, Wai-Kwon Kwok³, Mercouri Kanatzidis³, and Jim Eckstein¹¹University of Illinois; ²Brookhaven National Lab and ³Argonne National Lab

Superconductivity is observed in certain materials when cooled below a characteristic temperature, T_c , the electrical resistance becomes exactly zero. In superconducting metals, the T_c is well below the liquid nitrogen temperature (90K). The discovery of high T_c superconductors has opened up the possibility to bring a fundamental change to electric power technologies, including the electrical grids that have been the foundation for the nation's technological progress of the past century. To help overcome key barriers leading to the viable application of high temperature/high current superconductivity, we need to understand the fundamental mechanisms of high-temperature and high-current superconductivity, which will allow directed discovery of new or improved families of materials with higher critical

temperatures and currents. Along this direction, the CES has assembled a team of materials scientist and physicist to synthesize single crystals and thin-films of known superconductors. The highlights include: 1) synthesis of high quality $K_xFe_{2-y}Se_2$ crystals, 2) single crystals grown across most of the compositional range of the superconducting system $Fe_{1+y}Te_{1-x}Se_x$, and 3) superconducting $La_{2-x}Sr_xCuO_4$ (LSCO) films grown on a-axis cut $SrLaAlO_4$ substrates. The materials efforts have allowed the discovery of semiconducting spin glass ground state in isostructural $K_xFe_{2-y}Se_2$ crystals, the transport resistance anisotropy in LSCO and ongoing electrical, thermal and magnetic study.

P2-E07 - SUPERCONDUCTORS AS AN ENERGY CARRIER

[CES] Qiang Li¹, Peter Johnson¹, Vycheslav Solovyov¹, Wai-Kwong Kwok², George Crabtree², Ulrich Welp², Vitalii Vlasko-Vlaskov², Alexei Koshelev², Venkat Selvamanackam³, and Alexis Malozemoff⁴
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Superconductors are capable of carrying electrical current without loss, and hence offer powerful opportunities for increasing capacity, reliability, and efficiency of the electrical grid. Superconducting coils can provide a lower cost alternative to the rare-earth permanent magnet or geared systems for high power (> 6MW) direct-drive wind turbines. The mismatch between variation of renewable energy resources and electricity demand makes it necessary to capture electricity for later use. Developing affordable, large-scale energy storage systems would be a game changing advance for the grid. Superconducting magnet energy storage systems use magnetic fields in superconducting coils to store energy with near zero energy loss, and have instantaneous dynamic response. The performance of superconductors as an energy carrier depends crucially on the critical current density. Our research aims at understanding the fundamental limits of critical current density in superconductors and exploring methods of increasing that. A diverse suite of experimental techniques was assembled to investigate the correlation between the superconducting properties and defects. Both individual defect structure and defect landscape are tuned in order to provide the most effective pinning of vortices that maximizes critical current density. Close interaction with leading superconductor manufacturers provides a means for us to respond rapidly and aggressively to new developments.

P2-E08 - PROBING THE HIGH T_C-SUPERCONDUCTING ORDER PARAMETER WITH PHOTOEMISSION AND POLARIZED X-RAYS.

[CES] Peter Johnson¹, Peter Abbamonte², Juan Carlos Campuzano³, John Hill¹, James Lee², and Mike Norman³
¹Brookhaven National Laboratory; ²University of Illinois and ³Argonne National Laboratory

The Center for Emergent Superconductivity carries out studies of the physical properties of the high T_c superconductors, both cuprates and the more recently discovered iron base superconductors, using photon sources covering a range of different wavelengths. The latter range from the longer wavelengths associated with laser based sources through to the shorter wavelengths associated with synchrotron radiation in the soft X-ray and X-ray ranges. Amongst other things these studies seek to identify the correct nature of the Fermi surface in the normal state as a function of carrier concentration. In the cuprates such studies extend from the Mott insulating state associated with low doping through to the more metallic like state associated with higher levels of doping. In the Fe based superconductors the low doping levels are associated with a more metallic state. It is important to identify the correct Fermi surface because it is from this surface that the superconductivity ultimately emerges. Studies at low temperatures enable the identification of the superconducting gap function which provides insights into the superconducting order parameter. Soft X-ray and polarized X-rays are used in studies aimed at identifying competing ground states associated with the different degrees of freedom, including spin, charge and orbital ordering, that might compete with the superconductivity, and to identify the collective excitations associated with these degrees of freedom.

P2-E09 - THE BEHAVIOR OF IRON-BASED SUPERCONDUCTORS

[CES] George W. Crabtree¹, Seamus J. C. Davis², Russell Giannetta³, Laura Greene³, Wai-Kwong Kwok¹, Cedomir Petrovic¹, Ulrich Welp³, Hamood Z. Arham², Lei Fang³, Cassi R. Hunt¹, Wan Kyu Park³, and Alexei E. Koshelev¹
¹Argonne National Laboratory; ²Brookhaven National Laboratory and ³University of Illinois at Urbana-Champaign

The discovery of iron-based high temperature superconductors in 2008 launched an intense international research effort to explore the unique properties of these multi-band superconductors. Iron is an unexpected component of a superconducting material since magnetism is typically anathema to superconductivity, yet several types of iron-based superconducting materials with wide-ranging characteristics have been discovered thus far. The Center for Emerging Superconductors has studied these new materials using its formidable tools for characterizing microscopic and bulk behavior, uncovering intriguing behavior in their fundamental dynamic and thermodynamic properties. Discoveries include the (i) ability of these materials to sustain superconductivity at very high magnetic fields while maintaining low anisotropy, (ii) changes in the critical temperature, vortex pinning behavior and Fermi surface with doping, (iii) an intriguing strongly correlated ground state above the transition temperature, (iv) a new electron-orbital ordered regime in the normal state and (v) nodal behavior in the energy gap in some materials. These multi-band superconductors are highly tunable with

elemental doping, demonstrating their potential for probing how novel superconducting behavior might be engineered. These superconductors may hold the key to meeting the grand challenge of designing an isotropic high temperature superconductor, an important step toward technological implementation.

P2-E10 - UNDERSTANDING PAST FAILURE OF EARTH ABUNDANT MATERIALS SUCH AS FeS_2 TO BE GOOD SOLAR ABSORBERS - PROBLEMS AND CURE

[CID] Douglas Keszler¹, John Wager¹, Vorrannuch Jieratum¹, Ram Ravichandran¹, Brian Pelatt, Emmeline Altschul¹, Robert Kykyneshi¹, and Liping Yu^{1,2}
¹Oregon State University and ²NREL

Inorganic materials exhibiting band gaps > 1 eV and high absorption coefficients ($\hat{\Gamma} > 105 \text{ cm}^{-1}$) can enable new pathways to highly efficient photovoltaic (PV) technologies. With elements amongst the most abundant in the Earth's crust, iron pyrite (FeS_2) has long been considered to be an example of such a material. Yet, research over the past two decades has not yielded operational PV devices based on FeS_2 , or even agreement in the community on the origin of its failure mechanism. From our experimental and first-principles computational investigations, we have found that the co-existence of energetically favorable metallic Fe-S phases with FeS_2 has detrimental effects on its electrical and optical properties. To evade issues present in such multi-phase systems, we present new design rules for identifying transition metal-chalcogenide based PV absorbers that exhibit high absorption above the band gap. In accord with these design rules, we identify Fe_2MS_4 ($M = \text{Si, Ge}$) as a class of highly stable semiconductors with band gaps near 1.5 eV. Furthermore, calculated high formation energies of native point defects provide the potential to achieve favorable open circuit voltages in Fe_2MS_4 thin-film PV devices.

P2-E11 - NANOSTRUCTURED CERIA-BASED ANODES FOR LOW TEMPERATURE SOLID OXIDE FUEL CELLS

[HeteroFoam] James Wright¹, Meilin Liu², and Anil Virkar¹
¹University of Utah and ²GeorgiaTech

The objective of this work is to investigate the ceria-based anode for low temperature solid oxide fuel cells. Samaria-doped cerium oxide powders were synthesized by combustion synthesis. The resulting powders were nanosize as determined by X-ray diffraction. Powder compacts were sintered and their electrical conductivity was measured over a temperature range from 200 to 800 degrees centigrade and over a wide range of oxygen partial pressures. The oxygen partial pressure was varied by using gas mixtures from pure hydrogen to pure oxygen. Powders were also synthesized with rhenium added as a dopant. Microstructures of the sintered samples were investigated by scanning electron microscopy. Chemical analysis was conducted by EDX. Both conductivity and polarization resistance are functions of morphology of porous electrodes. It is shown that while broad necks and large particles are preferred for high conductivity, board necks and small particles are preferred to achieve low polarization resistance. This work thus shows that in Heterogeneous Functional Materials (HeteroFoams), interaction of the external species (atmosphere) and microstructure/morphology determine functionality. Thus, directionality is an important aspect of heterogeneous functional materials.

P2-E12 - NEW ANODE MATERIALS WITH ENHANCED TOLERANCE TO SULFUR AND COKING

[HeteroFoam] Lei Yang¹, Yongman Choi², and Meilin Liu¹
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The existing Ni-YSZ (yttria-stabilized zirconia) anodes in solid oxide fuel cells (SOFCs) perform poorly in carbon-containing fuels due to carbon buildup and deactivation at desired operating temperatures. Here we report a new anode with nanostructured interfaces for low-cost SOFCs, demonstrating high power density and stability in C_3H_8 , CO, and gasified carbon fuels at 750 °C. Synchrotron-based X-ray analyses and microscopy reveal that nano-sized oxide islands grow on the Ni surface, creating numerous nanostructured oxide/Ni interfaces. It is these interfaces that readily adsorb water and facilitate water-mediated carbon removal reactions, thus enhancing fuel cell power output and tolerance to coking at lower temperatures. Density functional theory (DFT) calculations predict that the dissociated OH from H_2O on the oxide particles reacts with C on Ni near the oxide/Ni interface to produce CO and H species, which are then electrochemically oxidized at the triple-phase boundaries of the anode. This anode offers potential for ushering in a new generation of SOFCs for efficient conversion of readily available fuels to electricity with minimal emissions.

P2-E13 - NOVEL PROTON CONDUCTORS WITH ENHANCED CHEMICAL STABILITY
 [HeteroFoaM] Siwei Wang¹, Fei Zhao¹, Fanglin Chen¹, and Kyle Brinkman²
¹University of South Carolina and ²Savannah River National Laboratory

A series of complex perovskites $Ba_3Ca_{1.18}Nb_{1.82-x}Y_xO_9$ ($x=0, 0.1, 0.2, 0.3, \text{ and } 0.5$) were systematically investigated as potential intermediate temperature proton conductors. The solubility limit of yttrium was found to be between 0.3 and 0.5. All the samples showed impressive chemical stability in water and CO_2 . After treatments in boiling water for 24 h or in pure CO_2 for 4 h, the pure perovskite structure of all the samples was unchanged and no impurities were observed. The total conductivity increased quickly with increasing yttrium concentration, reaching a maximum at $x=0.3$ with a value of $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 600°C in wet air. Open circuit voltage (OCV) tests under wet H_2 /air gradient showed that $Ba_3Ca_{1.18}Nb_{1.52}Y_{0.3}O_9$ behaved as an almost pure ionic conductor below 550°C . Overall $Ba_3Ca_{1.18}Nb_{1.52}Y_{0.3}O_9$ turned out to be a promising intermediate temperature proton conductor that possessed both high chemical stability and conductivity.

P2-E14 - SINGLE MOLECULE PHOTODRIVEN MACHINES FOR TRANSDUCING PHOTON ENERGY INTO MECHANICAL ENERGY
 [NERC] Ignacio Franco¹, Martin McCullagh¹, Mark A. Ratner¹, and George C. Schatz¹
¹Northwestern University

We theoretically investigate the use of light to drive molecular motors in a single-molecule force spectroscopy setup. The advantage of this class of motors with respect to most other reported examples of molecular motors is that the AFM acts as an interface with the outside world that permits extracting any generated work. As a specific example we consider an azobenzene-capped DNA hairpin coupled to an AFM. The photoinduced trans to cis isomerization of azobenzene is used to reversibly change the elastic properties of the hairpin structure. These changes in elasticity are used to extract net mechanical work by performing a single-molecule analog of a Stirling thermodynamic cycle. The work that can be extracted from such a cycle is estimated using a combination of molecular dynamics simulations and free energy reconstruction techniques. The disruption of the hairpin structure gives a maximum of 3.4 kcal/mol of extractable work per cycle with an estimated maximum efficiency of 2.4%. Structure-function insights into the operation of this motor are provided, and the effect of the cantilever stiffness on the extractable work is characterized.

P2-E15 - NON-EQUILIBRIUM CHIRAL ASSEMBLY
 [NERC] Thomas Hermans¹ and Bartosz Grzybowski¹
¹NERC

Improving energy efficiency is expected to reduce greenhouse gas emissions by two-thirds in 2030 (International Energy Agency, 2006). Energy reductions in the chemical industry, a large (~25%) contributor to industrial energy consumption, are of key importance to meet these expectations. Not only optimization of established procedures, but also development of new technologies is necessary to this end. Our efforts are geared toward the separation of chiral compounds, especially important in pharmaceutical processes, using chiral liquid vortices. We show that chiral millimeter-sized objects, floating on an air-liquid interface, behave differently when placed in a clockwise versus a counter-clockwise vortex. The magnitude and direction of the shear forces that are present in the vortex are well controlled using a cylindrical Couette cell. The in-plane chiral lift forces acting on the objects (i.e. fluid-object interactions) and their assembly (i.e. object-object interactions) are described. Translated down to the molecular (nanometer) scale this technology might lead to new tools for performing efficient chiral separations.

P2-E16 - UNUSUAL THERMOELECTRIC PROPERTIES OF VANADIUM BASED ORGANIC COMPOUNDS
 [RMSSEC] A. M. Chamoire¹, C.M. Jaworski¹, C.-Y.Kao¹, A.J.Epstein¹, and J.P.Heremans¹
¹The Ohio State University

Thermoelectric material are characterized by the dimensionless figure of merit $ZT=S^2pT/k$, where S is thermopower, T the absolute temperature, and p and k are the electrical and thermal conductivities respectively, and consists of interrelated factors that are difficult to optimize simultaneously. Organic conductors are usually known to have low p due to their disordered structures, and fairly low S ($100\mu\text{V/K}$). Even if some can have high p, they are not known to be efficient thermoelectric materials. $V\text{-TCNE}_x$ or $V\text{-(C}_2\text{(CN)}_4)_x$ is here revealed to have an exceptionally large thermopower, and may be the first of the new class of hybrid organic/inorganic material that do so. Thermopower measurements have been performed from 220 to 300K on thin films of $V\text{-TCNE}_x$ deposited by molecular layer deposition on glass. At room temperature $S > 1\text{mV/K}$ and increases with decreasing temperature. The dependence of S and ρ upon temperature as well as conductivity measurement will be shown. This value of S is possibly related to the valence band that shows a very high density of states (DOS) over a very narrow energy range, ascribed to $3d(t2g)$ orbitals of vanadium[1] and may be a good illustration of what Mahan and Sofo theoretically calculated to be the "best thermoelectric material"[2]. Work

supported by DOE-EFRC - RMSSEC 61-32128 (through MSU). [1] Y-J Yoo et al., Nat. Mat. 9 (2010)638 [2] G.D Mahan and J.O. Sofo, Proc. Natl. Acad. Sci. USA, 93 (1996) 74367

P2-E17 - THERMOELECTRIC PROPERTIES OF SKUTTERUDITE-BASED NANOCOMPOSITES

[RMSSEC] Chen Zhou¹, Jeffery Sakamoto¹, and Donald Morelli¹

¹Michigan State University

Thermoelectric semiconductors are a unique class of solids that are capable of converting heat to electricity. Bulk thermoelectric nanocomposite materials are significantly easier to synthesize compared to sophisticated structures such as superlattices and nanowires that, due to their reduced dimensionality, have displayed very unusual and potentially useful thermoelectric properties. In bulk nanocomposites, nanoparticles imbedded in a matrix material can preserve part of the benefits from the reduced dimensionality, thus offering unconventional thermoelectric transport properties in a potentially low-cost, easily manufacturable platform. One class of very interesting thermoelectric materials are the skutterudite compounds. Iron diantimonide (FeSb₂) is a naturally occurring impurity phase found in p-type skutterudites. Early research in "unfilled" skutterudite nanocomposite Co_{0.9}Fe_{0.1+x}Sb_{3+2x} has demonstrated that FeSb₂ particles of sizes from 20-200nm can be synthesized *in-situ* via a well controlled starting stoichiometry and rapid solidification process. The thermoelectric figure of merit in the best performing nanocomposite is increased by 100% compared to the matrix material. In this study, we extend our work of making nanocomposites to an optimized p-type "filled" skutterudite matrix Yb_{0.6}Co₂Fe₂Sb_{12/x}FeSb₂. Once again, we demonstrate enhanced thermoelectric performance in nanocomposites due to effects from the presence of nanoparticles.

P2-E18 - BORON SEGREGATION AT GRAIN BOUNDARIES IN CO-SI ALLOYS

[RMSSEC] Edgar Lara-Curzio¹, Melanie J. Kirkham¹, Harry M. Meyer III¹, Shengyon Qin¹, An-Ping Li¹, Hui Sun², and Don Morelli²

¹ORNL and ²Michigan State University

The role of boron addition on the microstructure, chemical composition and electrical resistivity of CoSi alloys was investigated. Contrary to previous reports, we demonstrate that boron does not enter the lattice on the silicon site, but rather segregates to the grain boundaries in these alloys. Through a combination of x-ray diffraction, scanning electron microscopy, and scanning Auger electron spectroscopy techniques, we present clear evidence of the formation of a CoB phase at the grain boundaries. The bulk electrical resistivity of CoSi was found to exhibit a non-monotonic dependence on boron concentration: for concentrations up to 2.0 at% the resistivity decreased with boron concentration, while it increased for concentrations between 2 at% and 10 at%. Results from 4-pt nanoprobe resistivity measurements inside CoSi grains and across grain boundaries are also presented. The effect of microstructure and composition on the electrical resistivity of these materials is discussed.

P2-E19 - CONTROLLING THE LIGHT AND HEAVY HOLE BANDS OF P-TYPE PbTe WITH K AND NA CO-DOPING

[RMSSEC] John Androulakis¹, Iliya Todorov², Duck-Young Chung², Guoyu Wang³, Ctirad Uher^{1,3} and Mercuri Kanatzidis²

¹Northwestern University; ²Argonne National Laboratory and ³University of Michigan

We discuss the effect of K-Na co-substitution for Pb atoms in the rocksalt lattice of PbTe. Simultaneous doping with K⁺ that has a larger ionic radius compared to Pb²⁺ and Na⁺ that has a smaller ionic radius can control the lattice parameter of PbTe and subsequently the energy difference and temperature dependence of the maxima of the L and $\bar{\Gamma}$ valence subbands in PbTe. The enhanced interband interaction with rising temperature was found to contribute to unusual electronic effects such as the appearance of a Lorenz number as high as two times the Sommerfeld value for metals. Despite a dramatic increase in the total thermal conductivity a significant rise in the thermoelectric figure of merit was recorded, purely on account of power factor enhancements, suggesting that a heavy effective mass is important in designing high efficiency thermoelectric systems.

P2-E20 - NANOSTRUCTURED MATERIALS BASED ON PbTe/Bi₂Te₃ FOR THERMOELECTRIC APPLICATIONS

[RMSSEC] Shreyashi Ganguly¹, Kevin Zhou², Donald Morelli², Jeff Sakamoto², Ctirad Uher², and Stephanie L. Brock¹

¹Wayne State University and ²Michigan State University

With the rising demand for energy and concern over global climate change, there is a clear need for clean renewable energy technologies. Thermoelectric energy conversion, which converts thermal energy into electrical energy or vice versa, has received considerable attention because of its ability to convert waste energy (heat) into useful energy (electricity). However, low efficiency and high material costs preclude large scale and widespread use of thermoelectric, underscoring a need for better performing materials. The efficiency of a thermoelectric device is given by figure of merit, ZT where $ZT = (S^2 \rho) T / k$; S = Seebeck coefficient, ρ = electrical conductivity, k = thermal conductivity. Recently, it has

been shown that inclusion of nanoscale features within a bulk matrix can dramatically reduce the thermal conductivity and augment the thermopower (S), thereby increasing the overall ZT of the system. Herein, we report a systematic study on the preparation of heterostructured nanocomposites based on incorporation of PbTe nanoparticles in a bulk Bi₂Te₃ matrix using an incipient wetness approach. The effect of PbTe nanoparticle concentration within the bulk matrix and the doped state of the matrix (n vs p type) on the resultant thermoelectric properties will be presented and discussed in terms of the current understanding of how nanostructuring effects electronic and thermal transport.

P2-E21 - IMPACT OF CRYSTALLINE DEFECTS ON THE EFFICIENCY OF BLUE LIGHT EMITTING DIODES FOR SOLID-STATE LIGHTING

[SSLS] Tania A. Henry¹, Andrew M. Armstrong¹, Mary H. Crawford¹, and Dan D. Koleske¹

¹*Sandia National Laboratories*

Solid-state lighting (SSL) is poised to become the next generation in energy efficient lighting. InGaN/GaN semiconductor light emitting diodes (LEDs) are the light engine for SSL technology. However, crystalline defects adversely impact the performance of InGaN/GaN LEDs. Realizing the full potential of SSL requires mitigating the influence of these defects by optimizing material growth conditions and device design. To enable systematic optimization, we developed new methodologies capable of quantitatively studying the electrical and optical properties of defects within active regions of InGaN/GaN LEDs. We use deep level optical spectroscopy (DLOS) to quantify the energy level of defect states in InGaN/GaN LEDs by measuring the time-resolved, differential photocapacitance response due to sub-bandgap optical excitation. We are able to discriminate between defects in the nanoscopic, optically active multi-quantum well region of the LED and defects in the surrounding electrical injection layers by controlling the spatial extent of the p-n junction. The defect density is obtained from lighted capacitance-voltage measurements, which measure the change in space-charge of the p-n junction due to defect level photoemission. We will present the evolution of defect incorporation in InGaN/GaN LEDs as a function of growth nucleation parameters and indium mole fraction in the LED quantum wells. The variation of defect type and density will be directly correlated with LED performance.

P2-E22 - LASERS FOR SOLID-STATE LIGHTING

[SSLS] A. Neumann¹, J.J. Wierer², W. Davis³, Y. Ohno³, S.R.J. Brueck¹, and J.Y. Tsao²

¹UNM; ²SNL and ³NIST

Solid-state lighting based on light-emitting diodes (LEDs) and phosphors is now the most efficient source of white light for general illumination. Solid-state lighting based on lasers would offer significant potential advantages including ultra-high efficiency at high input current densities and facile spatial controllability. Light emitted from lasers, however, has a much narrower spectral linewidth than light emitted from LEDs or phosphors. Therefore it is a common belief that white light produced by a set of lasers of different colors cannot provide white light of high enough quality for general illumination. We tested this belief experimentally, by constructing a four-color laser white illuminant and asking human subjects to compare it to high-quality reference illuminants. No strong preference between the laser and reference illuminants was found. This result paves the way for serious consideration of the use of lasers in solid-state lighting.

P2-E24 - LASING FROM OPTICALLY PUMPED GALLIUM NITRIDE NANORODS

[SSLS] Jeremy Wright¹, Qiming Li¹, Igal Brener¹, Willie Luk¹, George Wang¹, and Luke Lester²

¹*Sandia National Laboratories* and ²*University of New Mexico*

The use of laser emission is a promising strategy for solid-state lighting due to high quantum efficiency. Nanowire lasers are potentially more advantageous over traditional semiconductor lasers because they offer higher crystallinity, and a path for reduced strain and hence a greater range of alloy compositions and emission wavelengths. Furthermore, the periodicity of nanowire assemblies might allow for enhanced absorption, light extraction and/or emission directivity. We study lasing in top-down fabricated gallium-nitride nanowires and strategies for reducing laser threshold. Top-down nanowires are potentially better suited for larger scale processing over bottom-up nanowires due to their periodic spacing, constant cross section, and uniform length. Our experiments were performed by optically pumping individual nanowires (4-6½µm long, 100-300nm diameter) at 266nm and at room-temperature. For the smallest diameter nanowires we measure lasing thresholds of 250kw/cm². For different diameter nanowires, we observe single mode emission at threshold with linewidths of less than 1nm. Above threshold, the mode structure becomes richer with multiple lasing modes. 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.

P2-F01 - STRUCTURE AND DYNAMICS OF CO₂-BEARING FLUIDS AT NANOSCALE INTERFACES[NCGC] David Cole¹, Gernot Rother², Lukas Vlcek², Mirek Gruskiewicz², and Larry Anovitz²¹Ohio State University and ²Oak Ridge National Laboratory

Injection of CO₂ into geologic formations has been identified as a key strategy for mitigating the impact of anthropogenic emissions of CO₂. A key aspect of this process is the prevention of leakage from the host formation by an effective cap or seal rock which has low porosity and permeability characteristics. Shales comprise the majority of cap rocks encountered in subsurface injection sites with pore sizes typically less than 100 nm and surface chemistries dominated by quartz (SiO₂) and clays. We still lack a fundamental understanding of the structural and dynamic behavior of CO₂ (and CO₂-bearing aqueous fluids) in cap rock environments dominated by nanoporosity for state conditions encountered in injection systems. Even for a simple fluid such as CO₂ we have not adequately explored interfacial phenomena such the wetting and adsorption for variable pore sizes, pore geometries and pore wall chemistry at conditions approaching and crossing into the supercritical regime. Using a combination of electron microscopy, neutron scattering and molecular dynamics we have addressed: (i) the nature of nanoporosity in shales, (ii) key experimental results on CO₂-matrix interactions relevant to sequestration, (iii) a MD assessment of adsorption behavior of gaseous and supercritical CO₂ interacting with a SiO₂ substrate, (iv) MD modeling of the microscopic behavior of CO₂-H₂O at SiO₂ surfaces and (v) a new MD description of CO₂ in slit pores (muscovite).

P2-F02 - CO₂ FROM BENCHTOP TO OUTCROP: MULTIPHASE REACTIVE TRANSPORT AND A NATURAL ANALOGUE FOR LEAKAGE[CFSES] Hongkyu Yoon¹, Matt Balhoff², Steve Bryant², Peter Eichhubl², Tom Dewers¹, Yashar Mehmani², and Tie Sun²¹Sandia National Laboratories and ²University of Texas at Austin

Development and mitigation of leakage pathways from subsurface CO₂ storage reservoirs may well depend on coupled thermal, mechanical, hydrological, and chemical interactions. We link laboratory micro-scale and rock core-scale experimental and modeling efforts to examine the fate of supercritical carbon dioxide (scCO₂) in subsurface saline formations from the perspective of multiphase flow, reactive transport, and rock deformation. Pore-scale experiments on micromodel calcite precipitation, scCO₂-brine flows in mm-size rock cores in a high pressure stage, and crack-growth experiments on a microscope loading frame are being used as a basis for understanding coupled physics of systems perturbed by scCO₂ injection. Pore scale models, including lattice Boltzmann methods as well as network models, describe these physics, and in the case of calcite precipitation and dissolution, capture observations quite adequately. Progress on novel methods for upscaling pore-scale models for reactive transport and multiphase flow are discussed, and are being applied to core-scale measurements on scCO₂ breakthrough and wettability. The model allows for prediction of the formation of preferential pathways for CO₂ transport in porous media. All of these results bear on the transport and disposition of CO₂ and associated mineral precipitation patterns observed in outcrop samples from the Crystal Geysers, near Green River, Utah, a natural analog for subsurface CO₂ leakage.

P2-F03 - MULTIPHYSICS MODELS OF CAPROCK FRACTURING DURING CO₂ INJECTION[CFSES] Mario Martinez¹, Joe Bishop¹, Panio Newell¹, Sean McKenna¹, Sanjay Srinivasan², Peter Eichhubl², Tom Dewers², and Alex Reinhart¹¹Sandia National Laboratories and ²University of Texas at Austin

Worldwide energy consumption, mainly through the use of fossil fuels, has contributed to a significant increase in atmospheric levels of carbon dioxide (CO₂), a so-called greenhouse gas. Long term sequestration of anthropogenic CO₂ by injection into deep saline formations has been espoused as a viable option for reducing atmospheric levels of CO₂ and thereby extending the use of fossil fuels until cleaner power sources can be developed. The objective of our research is the development of coupled multi-scale multi-physics simulation tools for modeling both the short term and long term geologic effects of injected CO₂. Geologic trapping of CO₂ by a low permeability caprock layer is the primary mechanism for initial sequestration. Therefore, it is critically important to understand the processes that could cause caprock breaching. This work presents studies of several critical coupled processes encountered during CO₂ injection and demonstrates their impact on the feasibility of long-term sequestration in deep saline formations.

P2-F04 - ALTERATIONS IN MECHANICAL PROPERTIES OF ROCKS DUE TO CO₂ INJECTION -- IMPLICATIONS FOR FIELD SCALE MONITORING OF SEQUESTRATION PROCESSES[CFSES] Mrinal Sen¹, Sean McKenna², Ranjana Ghosh¹, Hongkyu Yoon², Son Phan¹, Sanjay Srinivasan¹, and Rui Zhang¹¹University of Texas at Austin and ²Sandia National Laboratories

The effects of CO₂ injection both in carbonate and sandstone reservoirs are being studied using a combination of laboratory experiments and numerical models. The primary focus here is to relate the changes in elastic properties of the host formation observed at the laboratory scale to larger field or seismic scale changes. This upscaling process has

important bearing on the development of seismic techniques for monitoring the progress of the CO₂ plume post-injection. Towards this goal, we have carried out three primary tasks: (1) laboratory measurements of elastic stiffness of cores from the Cranfield CO₂ injection site, (2) development of an effective medium model for modeling the unusual behavior of rocks observed in the laboratory and to mapping those properties to the field scale, and (3) development of advanced seismic inversion techniques to improve resolution of subsurface images. The laboratory measurements show that compressional and shear wave velocities decrease as a function of CO₂ saturation caused by chemical changes in the rock matrix and porosity. This unusual behavior can be modeled very well using our new effective medium model that can incorporate changes in the rock matrix (containing fractures and pores) and patchy and uniform saturation of CO₂. Further, since our model is frequency dependent, we are able to predict changes in wave velocities at seismic frequencies (field scale). New stochastic and deterministic high resolution seismic inversion methods have been applied to two seismic datasets, for the Cranfield and Dickman sequestration sites. Our results show marked improvement over those derived by the existing seismic inversion tools.

P2-F05 - INSIGHTS INTO MECHANISMS FOR CO₂ SEEPAGE BASED ON FIELD OBSERVATIONS AT CRYSTAL GEYSER NATURAL ANALOG

[CFSES] Peter Eichhubl¹, Matt Balhoff¹, Steve Bryant¹, Tom Dewers², Larry Lake¹, Sanjay Srinivasan¹, Young Kim¹, and Alex Urquhart²

¹University of Texas at Austin and ²Sandia National Laboratories

The Little Grand Wash normal fault in Green River, Utah, hosts 10-15 naturally occurring active and inactive CO₂ seeps. We studied the association of fault structure with CO₂-related chemical rock alteration around an inactive seep as an analogue for the long-term (103- to 104-year) effects of carbon leakage through reservoir faults. We combined 1:700-scale field mapping of fault structure and alteration with laboratory analyses of mineralogical, isotopic, and textural changes in an effort to characterize and model sealing mechanisms of leaking faults in CO₂ systems. CO₂ seepage is focused along fault segment intersections within the 200-meter-wide fault zone. CO₂ visibly reacted with the host sandstone over a distance of 10-20 m away from the flow conduits. In thin section, intergranular and fracture porosity near the CO₂ flow conduits is extensively or completely occluded by calcite cement. Cementation reduces permeability by up to two orders of magnitude, to about 1-10 md, compared to sandstone away from the CO₂ flow conduits. The observed reduction in porosity and permeability would restrict the upward flow of CO₂-charged water through fault conduits over time. Field structural observations and available radiometric dates on travertine suggest, however, that CO₂ seep activity shifted over time along the fault zone illustrating that cementation can be effective on the pore scale and in sealing single conduits but ineffective in limiting flow along complex fault system.

P2-F06 - TAKING FUNDAMENTALLY NEW MATERIALS FOR CO₂ CAPTURE TOWARD APPLICATION: AN EFRC/NETL COLLABORATION

[CGS] David Luebke¹, Hunaid Nulwala¹, Erik Albenze², Damodaran Krishnan Achary³, Lang Sui¹, and Wei Shi²

¹NETL; ²URS and ³University of Pittsburgh

Understanding that scientific advancement is often frustrated by segregation of researchers within areas of capability such as molecular modeling, device fabrication, or systems analysis, NETL pursues resolution of energy-related scientific challenges through a vertically integrated technology development approach. Within the context of this approach, scientists and engineers with a variety of expertise are asked to work closely with one another on a team focused on development of a single technology. As a team moves its technology from inception through proof-of-concept into development and finally to technology transfer and commercialization, it may make use of a huge variety of facilities and research disciplines. The process is greatly enhanced when basic disciplines like those found within the Center for Gas Separations Relevant to Clean Energy Technologies work closely with the applied disciplines tied to technology development. In a collaborative effort, new technology and greater understanding are being created through a combination of advanced computational techniques, soft x-ray analysis, targeted synthetic methods, novel fabrication approaches, high throughput performance screening and economic analysis.

P2-F07 - MODEL DEVELOPMENT FOR RAPID SCREENING OF ADSORBENT MATERIALS USING IDEAL ADSORBED SOLUTION THEORY AND MOLECULAR SIMULATION

[CGS] Joseph Swisher¹ and Berend Smit^{1,2}

¹UC Berkeley and ²LBNL

Microporous materials have the potential to provide a more energy efficient alternative to amine scrubbing processes for the removal of carbon dioxide from gas streams by reducing regeneration costs. Decades of research on zeolites and recent advances in synthesis of metal-organic frameworks have provided us with a large catalogue of potential adsorbents, many of which are available in convenient databases. However, the data required to select a material and

design a separation process is not available for most of these materials. Simulation methods such as grand canonical Monte Carlo (GCMC) can provide most of the data, would require an infeasible amount of CPU time to compare a large number of materials over a wide range of design parameters. We have developed a simplified model for screening databases of porous materials. We generate infinite dilution data using NVT simulations for a set of materials and extrapolate to higher pressures using the Langmuir isotherm model. Mixture behavior is modeled using ideal adsorbed solution theory. Using this approach, it is possible to estimate the adsorption data for a mixture of gases over a wide pressure range in minutes, rather than the hours required for GCMC calculations. This approach has been tested on a set of zeolites. Compared to the full mixture GCMC calculation, the simplified model predicts selectivities within a factor of 2 for almost all structures for both carbon dioxide/nitrogen and carbon dioxide/methane mixtures.

P2-F08 - FIRST-PRINCIPLES CALCULATIONS OF THE INTERACTION BETWEEN CO₂ AND METAL-ORGANIC FRAMEWORKS [CGS] Roberta Poloni^{1,2}, Allison Dzubak³, Jeffrey B. Neaton², Laura Gagliardi³, Giulia Galli⁴, and Berend Smit¹
¹University of California, Berkeley; ²LBNL; ³University of Minnesota and ⁴University of California, Davis

Significant experimental efforts are focusing on the design of the optimal metal-organic frameworks (MOFs) to capture CO₂ from flue gas streams [1]. Due to the nearly infinite array of structures that can be prepared together with the time-consuming process of synthesis, characterization, data collection, computer simulations, which allow us to predict the adsorption properties of these materials, would be highly desirable. A prerequisite for these simulations is to have a fundamental understanding of the CO₂-MOF interactions. We are developing a multi-scale theoretical approach in which we combine various quantum mechanical methods to describe these challenging systems. We employ Density Functional Theory with the inclusion of van der Waals forces to explore the interactions between the CO₂ molecule and different MOF sites. This study provides insight into the CO₂-MOF binding in the presence of different metal atoms within the MOF (Ca, Mg, Sr, Fe, and Cu) and extraframework cations (H, Li, N, K). Wave-function based quantum chemical calculations are performed on the MOF fragments to analyze the nature of the various interactions, and develop first principle force-fields for these systems for subsequent classical simulation [2]. [1] D. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.* 49,6058 (2010). [2] O. Engkvist, P. O. Astrand and G. Karlstrom, *Chem. Rev.* 100, 4087(2000).

P2-F09 - METAL-ORGANIC FRAMEWORKS AS MATERIALS FOR CARBON DIOXIDE CAPTURE [CGS] Eric Bloch¹, Zoey Herm¹, Kenji Sumida¹, Thomas McDonald¹, Jarad Mason¹, Hye Jin Choi¹, Joseph Swisher¹, Berend Smit¹, Rajamani Krishna², and Jeffrey R. Long¹
¹UC Berkeley and ²University of Amsterdam

Metal-organic frameworks are porous, crystalline materials composed of inorganic building blocks linked by organic ligands. They have been shown to selectively adsorb gases relevant to carbon dioxide capture in three distinct scenarios: post-combustion capture (CO₂/N₂ separations), pre-combustion capture (CO₂/H₂ separation), and oxyfuel combustion (O₂/N₂ separation). The pore surfaces of these materials can be modified post-synthetically to achieve selectivities for CO₂ over N₂ well over 10. The working capacity and selectivities for metal-organic frameworks for CO₂ in the presence of H₂ at high pressures relevant to CO₂/H₂ separations render them more attractive than other porous materials. Coordinatively unsaturated redox-active metal centers decorating the pore surface of metal-organic frameworks can undergo selective electron-transfer reactions with O₂ that cannot be achieved with N₂, resulting in strong candidates for oxygen separation for air. A summary of our results towards these approaches will be presented.

P2-F10 - UNDERSTANDING GAS ADSORPTION IN ZEOLITIC IMIDAZOLATE FRAMEWORKS: MOLECULAR MODELING [MEEM] Keith Ray¹, David Olmsted¹, Ning He², Jessica Burton¹, Yao Houndonoubo³, Brian Laird², and Mark Asta¹
¹UC Berkeley; ²University of Kansas and ³Eastern Washington University

Zeolitic Imidazolate Frameworks (ZIFs) are excellent candidate carbon capture materials owing to their high surface area, selectivity, and stability. To guide the optimization of these materials we are undertaking molecular-scale modeling aimed at understanding the roles of chemical functionality and structural topology in CO₂ adsorption and diffusion. A combined experimental and simulation effort [1] has focused on a set of five ZIFs exhibiting the same topology, but different functionality. Calculations have reproduced the dependence of the equilibrium adsorption on functionalization and suggest that polarizability and symmetry are key factors to high CO₂ uptake. Diffusion studies were performed, revealing multiple strong binding sites with high escape activation energy. We have worked to establish a procedure to predict a framework's CO₂ adsorption from first principles calculations. Since van der Waals (vdW) forces create much of the CO₂ binding, we are exploring different density functional theory (DFT) + vdW methods, including vdW-DFT [2]. We use these methods to refit Lennard-Jones potentials which are then employed in Monte Carlo adsorption simulations and compared with experiment. [1] W. Morris, B. Leung, H. Furukawa, O. K. Yaghi, N. He, H. Hayashi, Y. Houndonoubo, M. Asta, B. B. Laird, and O. M. Yaghi, *J. AM. CHEM. SOC.* 132, 11006-11008 (2010) [2] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* 92, 246401 (2004)

P2-F11 - UNDERSTANDING GAS ADSORPTION IN ZEOLITIC IMIDAZOLATE FRAMEWORKS: EXPERIMENTAL SYNTHESIS AND CHARACTERIZATION

[MEEM] William Morris¹
¹*UCLA*

Zeolitic Imidazolate Frameworks (ZIFs) are porous extended frameworks that are comprised of imidazolate and tetrahedral metal ions. These frameworks with high surface area up to 2000 m²/g have shown promise in the uptake and separation of carbon containing gases CO₂, CO, and CH₄. It is important to understand the factors that affect the gas uptake in these materials, to further enhance their carbon capture abilities. The main variables that can be changed in ZIF materials include the topology, the functionalization of the imidazolate, and the metal ion. Firstly, a group of five ZIFs with varying functionalities but the same topology RHO and containing the metal ion Zn²⁺ were studied. These frameworks showed that certain functionalities played an important role in CO₂ uptake. Secondly, new results on the affect of topology and gas uptake will be presented. Joint experimental computational results will be presented that offer understanding of these factors.

P2-F12 - UPSCALING PORE SCALE CARBONATE PRECIPITATION RATES TO THE CONTINUUM SCALE

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An integrated approach combining experimental reactive flow columns and continuum-scale reactive transport modeling has been used to compare microscopic and bulk rates of carbonate mineral precipitation. The experiments consisted of the injection of supersaturated, carbonate-rich solutions into calcite packs. Bulk rates of precipitation based on the change in chemistry over the length of the column were compared with spatially resolved determinations of carbonate precipitation using X-ray synchrotron imaging at the micron scale. These data are supplemented by well-stirred reactor experiments to evaluate the rate of precipitation as a function of solution supersaturation in the absence of transport effects. Results indicate good agreement between rates determined with fluid chemistry and with microtomography. Precipitation is greatest on Iceland spar seeds, with crystal morphology of the new precipitates suggesting growth via a 2D heterogeneous nucleation mechanism. Using the rates of precipitation as a function of supersaturation determined in the well-stirred flowthrough reactors, it is possible to match the spatially-resolved microtomographic data with a continuum reactive transport model if the generation of new reactive surface area is accounted for. The experimentally-determined value of 0.90 m²/g for the specific surface area of the neoformed calcite, added to the initial calcite surface area of 0.012 m²/g, results in good agreement with the continuum model.

P2-F13 - AGING IN DISSOLUTION AND PRECIPITATION RATES FOR MINERALS RELEVANT TO CO₂ SEQUESTRATION

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It has been observed that rates of dissolution and precipitation at mineral-fluid interfaces evolve with time. Specifically, observational evidence suggests that the effective rate constants decay like the inverse of the time over which the reactions occur. We have explored several physical mechanisms and associated models that can explain the observed aging. One mechanism involves the slow approach to equilibrium of a system that exhibits nonlinear reaction kinetics. We demonstrate how observed time dependent weathering rates of deep sea sediments can be described with such a model. Another aging mechanism appeals to disordered kinetics. In this model, the reaction is characterized by a distribution of (possibly evolving) kinetic rates. A large class of initial distributions yields an inverse age scaling. The individual rates could correspond to, for example, various reactivities at the mineral-fluid interface or different grain sizes with an appropriate model for size-dependence. An understanding of this apparent age-dependence is necessary for predicting the rate at which CO₂ is converted to minerals or dissolved in aqueous solution, both in the context of long-term mineralization of CO₂ and short-term modification of the subsurface porosity and conductivity.

P2-F14 - CARBON DIOXIDE - WATER INTERFACIAL TENSION UNDER GEOLOGIC CO₂ STORAGE CONDITIONS: A MOLECULAR DYNAMICS SIMULATION STUDY[NCGC] Laura Nielsen¹ and Ian Bourg²¹University of California, Berkeley and ²Lawrence Berkeley National Laboratory

Carbon dioxide storage in subsurface geologic formations, principally saline aquifers, is currently under development as a major approach for abating anthropogenic CO₂ emissions. To ensure the long-term viability of geologic carbon storage, buoyancy-driven escape of reservoir CO₂ must be inhibited by an overlying cap rock of very low permeability. A major impediment to predicting cap rock sealing performance is insufficient knowledge of the capillary force that acts to prevent the entry of supercritical CO₂ into the cap rock pore space. This force, which depends on closely related properties such as brine-CO₂ interfacial tension (IFT), remains poorly characterized in conditions relevant to CO₂ sequestration. In the present study, we tested the ability of molecular dynamics (MD) simulations to predict the properties of CO₂-water (and eventually CO₂-brine-caprock) systems that control the capillary force. Our results showed that MD simulations using carefully chosen interatomic potential parameters can predict the best available CO₂-water IFT data. Our results also showed that IFT is most sensitive to the short-range portion of the CO₂-H₂O interaction, thus indicating a future means for improving model parameters. Finally, our results confirmed that pressure—especially below the critical CO₂ pressure of 7 MPa—exerts the dominant control on IFT and, therefore, on the CO₂ storage capacity and sealing integrity of a subsurface reservoir.

P2-F15 - IN SITU KINETIC ANALYSIS OF CALCIUM CARBONATE NANOPARTICLE FORMATION USING GRAZING INCIDENCE SMALL ANGLE X-RAY SCATTERING

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To better control the fate and transport of CO₂, which are affected by changes in fluid chemistry and porosity-permeability during geologic CO₂ sequestration (GCS), we need to advance our mechanistic and kinetic understanding of the nucleation and growth of carbonate minerals in subsurface environments. This experimental work used *in situ* SAXS/GISAXS to simultaneously measure both homogeneous nucleation and growth in solution, as well as heterogeneous nucleation and growth on a representative mineral surface (quartz). After the measurements, the mineral surfaces were also probed with atomic force microscopy. Salinity and Ca²⁺ concentrations similar to those encountered in subsurface reservoir conditions were used. The solutions' ionic strengths ranged from 10 mM to 1M NaCl. CaCO₃ nucleation experiments on quartz (100) substrates showed a decrease of the nucleation rate with increasing salinity, as expected from the reduced activity of Ca²⁺ and CO₃²⁻ at high ionic strength. The GISAXS data from CaCO₃ particles nucleated on quartz show a characteristic q⁻² slope corresponding to the formation of discoid particles. The SAXS/GISAXS results also show preferential formation of CaCO₃ particles on the quartz (100) substrate. These *in situ* and ex situ observations can yield important quantitative parameters and qualitative information – such as nucleation and growth rates and potentially interfacial energies – usable in reactive transport models of nucleation at the reservoir scale.