Science for our Nation's Energy Future

Energy Frontier Research Centers Summit & Forum

May 25–27, 2011
Washington, D.C.

Renaissance Penn
Quarter Hotel

Agenda

Wednesday, May 25, 2011
8:30 AM – 7:00 PM

7:30 AM	**Registration**
8:30 AM	Welcome and Introduction of Keynote Address Steve Koonin, *DOE Under Secretary for Science*
8:35 AM	Keynote Address Steven Chu, *DOE Secretary of Energy*
9:00 AM	Congressional Keynote Speakers Senator Jeff Bingaman (D-NM), Congresswoman Judy Biggert (R-IL) (invited), Congressman Daniel Lipinski (D-IL), Congresswoman Zoe Lofgren (D-CA)
10:00 AM	**Break**
10:30 AM –12:15 PM	**Leading Perspectives in Energy Research**
10:30 AM	Introduction of Session Bill Brinkman, *DOE Director of the Office of Science*
10:45 AM	John Hennessy, *President of Stanford University*
11:15 AM	Mark Little, *Senior Vice President and Director of GE Global Research*
11:45 AM	Eric Isaacs, *Director of Argonne National Laboratory*
12:15–1:30 PM	**Lunch Provided**
12:30–1:00 PM	Disruptive Innovations in Computing Tilak Agerwala, *Vice President, Systems at IBM T. J. Watson Research Center*
1:30 PM	Fuels from Sunlight Energy Innovation Hub Nate Lewis, *Director of JCAP*
2:00 PM	**EFRCs: A Response to Five Challenges for Science and the Imagination**
	Moderator: Paul Alivisatos, *Director of Lawrence Berkeley National Laboratory*
	George Crabtree, *Distinguished Fellow at Argonne National Laboratory*
	Mildred Dresselhaus, *Institute Professor at the Massachusetts Institute of Technology*
	Mark Ratner, *Professor at Northwestern University*

2:45 PM **Science for Energy Technology: The Industry Perspective**

Moderator: Jeffrey Wadsworth, *President and CEO of Battelle Memorial Institute*

David E. Carlson, *Chief Scientist of BP Solar*

Yet-Ming Chiang, *Professor at the Massachusetts Institute of Technology and founder of A123 Systems*

Catherine T. Hunt, *R&D Director of Innovation Sourcing and Sustainable Technologies at The Dow Chemical Company*

3:30 PM **Break**

4:00 PM **EFRCs: A View from Senior EFRC Representatives**

Moderator: Persis Drell, *Director at SLAC National Accelerator Laboratory*

Neal Armstrong, *Director of the Center for Interface Science: Solar Electric Materials led by the University of Arizona*

Emily Carter, *Co-Director of the Combustion Energy Frontier Research Center led by Princeton University and Team Leader of the Heterogeneous Functional Materials Center led by the University of South Carolina*

Don DePaolo, *Director of the Center for Nanoscale Control of Geologic CO_2 led by Lawrence Berkeley National Laboratory*

Brent Gunnoe, *Director of the Center for Catalytic Hydrocarbon Functionalization led by the University of Virginia*

5:00 PM **Award Ceremony: *Life at the Frontiers of Energy Research* Video Competition**

Ivan Amato, *Senior communications officer in the Pew Health Group of the Pew Charitable Trusts*

Paula Apsell, *Senior Executive Producer, NOVA and Director of the WGBH Science Unit*

William Phillips, *Physicist, Joint Quantum Institute at the National Institute of Standards and Technology and the University of Maryland, and recipient of the 1997 Nobel Prize in Physics*

5:30 PM–7:00 PM **Poster Session and Reception**

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Thursday, May 26, 2011
8:00 AM – 7:30 PM

8:00–10:00 AM	**Global Perspectives on Frontiers in Energy Research**
8:00 AM	Facing Our Energy Challenges in a New Era of Science Patricia Dehmer, *Deputy Director for Science Programs at DOE*
8:30 AM	Kazunari Domen, *Professor at the University of Tokyo, Japan*
9:00 AM	Robin Grimes, *Professor at Imperial College, United Kingdom*
9:30 AM	Jean-Marie Tarascon, *Professor at the University de Picardie Jules Verne, France*
10:00 AM	**Break**
10:15 AM	Parallel Scientific Sessions I
A.	Organic photovoltaics, *Grand Ballroom*
C.	Solar fuels and biomass, *Mount Vernon Square*
D.	Energy storage and transmission, *Congressional Hall A & B*
E.	Energy conservation, *Renaissance Ballroom East*
G.	Materials in extreme environments, *Renaissance Ballroom West A*
H.	Effective and sustainable materials design: integration of computation, theory and experiment, *Renaissance Ballroom West B*
12:15–1:45 PM	**Lunch on Your Own**
12:35–1:35 PM	Optional Bring Your Own Lunch Sessions (3)
	Career Opportunities in Energy Sciences and Technology, *Renaissance Ballroom East*
	Michelle Buchanan, *Associate Laboratory Director in Physical Sciences at Oak Ridge National Laboratory*
	Marc Kastner, *Dean of the School of Science at the Massachusetts Institute of Technology*
	Joseph F. Mercurio, *Manager New Business Development, Global Research and Development at General Motors*
	Translating Basic Research to Energy Technology, *Congressional Hall A & B*
	Karina Edmonds, *Technology Transfer Coordinator at DOE*
	Celia Merzbacher, *Vice President of Innovative Partnerships at the Semiconductor Research Corporation*
	Science Policy, the Budget Battles of the 112th Congress, and the EFRCs, *Mount Vernon Square*
	Benjamin L. Brown, *Senior Science and Technology Advisor in the Office of Science*

1:45 PM	Parallel Scientific Sessions II
A.	Organic photovoltaics, *Grand Ballroom South*
B.	Inorganic photovoltaics, *Grand Ballroom Central*
C.	Solar fuels and biomass, *Grand Ballroom North*
D.	Energy storage and transmission, *Congressional Hall A & B*
E.	Energy conservation, *Renaissance Ballroom East*
G.	Materials in extreme environments, *Renaissance Ballroom West A*
H.	Effective and sustainable materials design: integration of computation, theory and experiment, *Renaissance Ballroom West B*
3:45 PM	**Break**
4:00 PM	Parallel Scientific Sessions III
A.	Organic photovoltaics, *Grand Ballroom South*
B.	Inorganic photovoltaics, *Grand Ballroom Central*
C.	Solar fuels and biomass, *Grand Ballroom North*
D.	Energy storage and transmission, *Congressional Hall A & B*
E.	Energy conservation, *Renaissance Ballroom East*
F.	Carbon capture and sequestration, *Renaissance Ballroom West A*
I.	New tools and methods for materials synthesis and characterization, *Renaissance Ballroom West B*
6:00 PM	EFRC and DOE Research and Networking Poster Reception
7:30 PM	**Adjourn**

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Friday, May 27, 2011
8:00 AM – 12:30 PM

8:00 AM		Parallel Scientific Sessions IV
	A.	Organic photovoltaics, *Grand Ballroom South*
	B.	Inorganic photovoltaics, *Grand Ballroom Central*
	C.	Solar fuels and biomass, *Grand Ballroom North*
	F.	Carbon capture and sequestration, *Renaissance Ballroom West A*
	I.	New tools and methods for materials synthesis and characterization, *Renaissance Ballroom West B*
8:00 AM		Scientific Sessions Close-Out Panel
	H.	Effective and sustainable materials design: integration of computation, theory and experiment, *Renaissance Ballroom East*
9:00 AM		Scientific Sessions Close-Out Panels
	G.	Materials in extreme environments, *Renaissance Ballroom East*
	I.	New tools and methods for materials synthesis and characterization, *Renaissance Ballroom West B*
10:00 AM		Poster Session #2
11:30 AM		Scientific Sessions Close-out Panels
	A.	Organic photovoltaics, *Grand Ballroom South*
	B.	Inorganic photovoltaics, *Grand Ballroom Central*
	C.	Solar fuels and biomass, *Grand Ballroom North*
	D.	Energy storage and transmission, *Congressional Hall A & B*
	E.	Energy conservation, *Renaissance Ballroom East*
	F.	Carbon capture and sequestration, *Renaissance Ballroom West A*
12:30 PM		**Adjourn**

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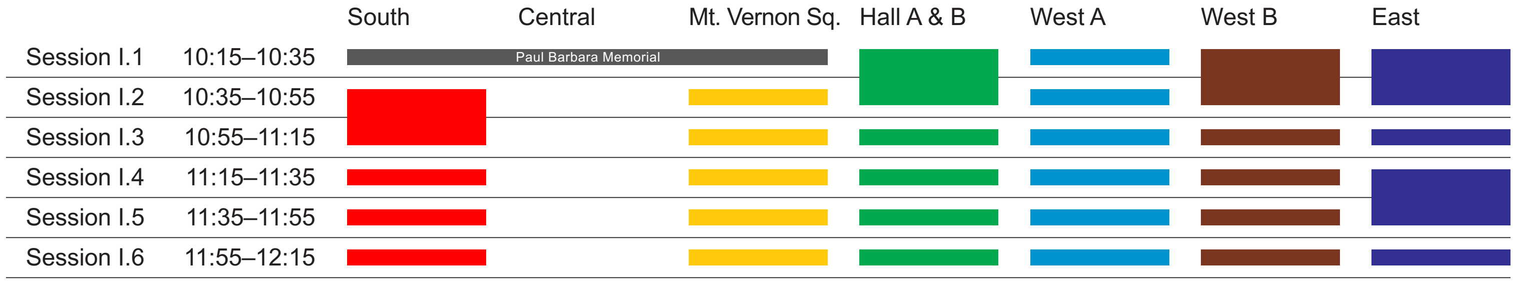
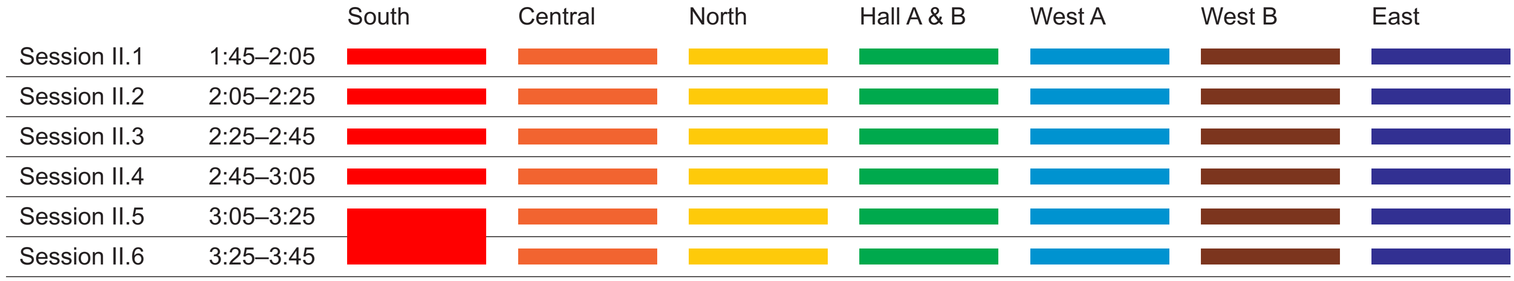


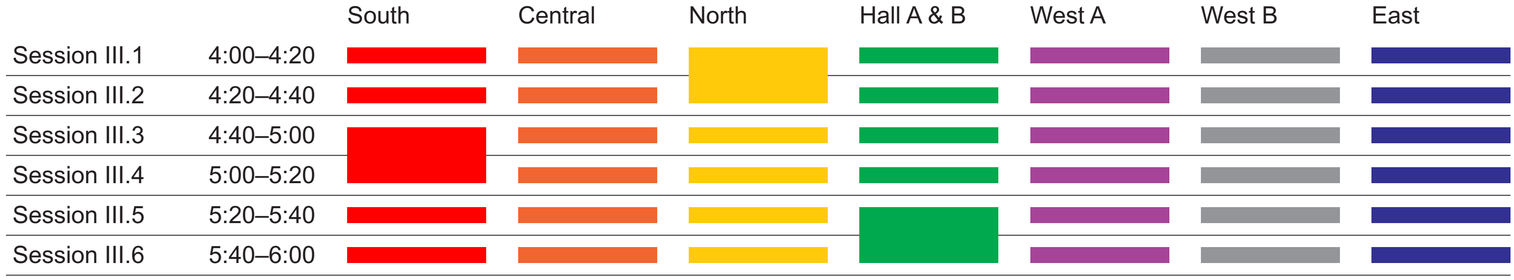
		South	Central	Mt. Vernon Sq.	Hall A & B	West A	West B	East
Session I.1	10:15–10:35	⬛ Paul Barbara Memorial			🟩	🟦	🟫	🟦
Session I.2	10:35–10:55	🟥		🟨		🟦		
Session I.3	10:55–11:15			🟨	🟩	🟦	🟫	🟦
Session I.4	11:15–11:35	🟥		🟨	🟩	🟦	🟫	🟦
Session I.5	11:35–11:55	🟥		🟨	🟩	🟦	🟫	
Session I.6	11:55–12:15	🟥		🟨	🟩	🟦	🟫	🟦

12:35–1:35 **Lunch (Optional Lunch Sessions from 12:35–1:35)**



		South	Central	North	Hall A & B	West A	West B	East
Session II.1	1:45–2:05	🟥	🟧	🟨	🟩	🟦	🟫	🟦
Session II.2	2:05–2:25	🟥	🟧	🟨	🟩	🟦	🟫	🟦
Session II.3	2:25–2:45	🟥	🟧	🟨	🟩	🟦	🟫	🟦
Session II.4	2:45–3:05	🟥	🟧	🟨	🟩	🟦	🟫	🟦
Session II.5	3:05–3:25	🟥	🟧	🟨	🟩	🟦	🟫	🟦
Session II.6	3:25–3:45		🟧	🟨	🟩	🟦	🟫	🟦

3:45–4:00 **Break**



		South	Central	North	Hall A & B	West A	West B	East
Session III.1	4:00–4:20	🟥	🟧	🟨	🟩	🟪	⬜	🟦
Session III.2	4:20–4:40	🟥	🟧		🟩	🟪	⬜	🟦
Session III.3	4:40–5:00	🟥	🟧	🟨	🟩	🟪	⬜	🟦
Session III.4	5:00–5:20		🟧	🟨	🟩	🟪	⬜	🟦
Session III.5	5:20–5:40	🟥	🟧	🟨	🟩	🟪	⬜	🟦
Session III.6	5:40–6:00	🟥	🟧	🟨		🟪	⬜	🟦

6:00–7:30 **EFRC and DOE Research and Networking Poster Reception I**

Key:
- A. Organic photovoltaics
- B. Inorganic photovoltaics
- C. Solar fuels and biomass
- D. Energy storage and transmission
- E. Energy conservation and efficiency
- F. Carbon capture and sequestration
- G. Materials in extreme environments
- H. Effective and sustainable materials design: integration of computation, theory and experiment
- I. New tools and methods for materials synthesis and characterization

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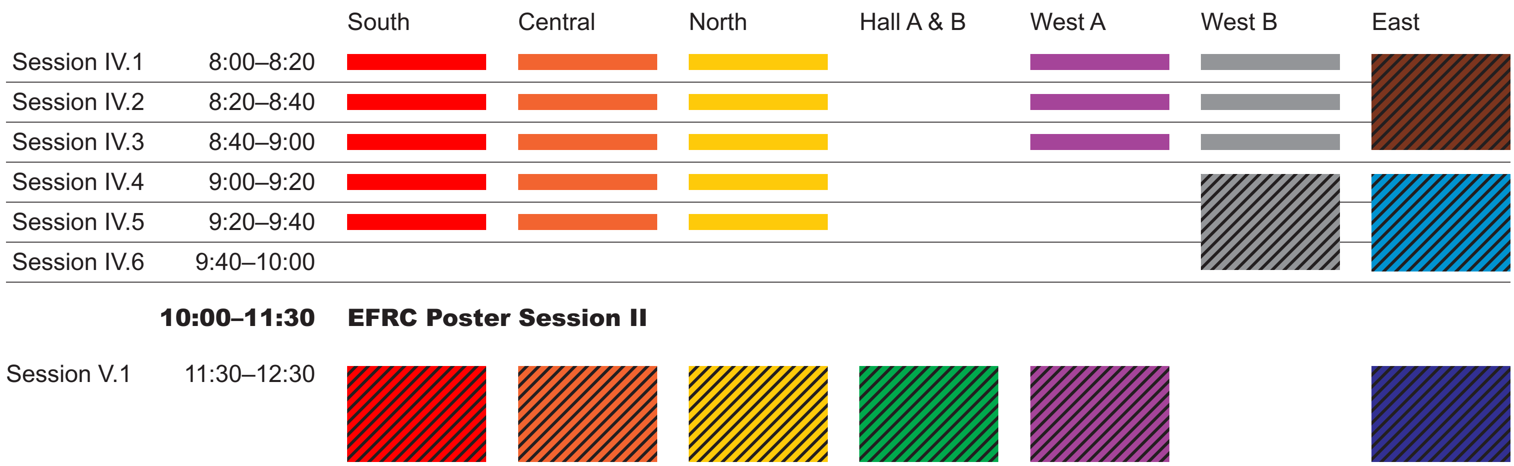


		South	Central	North	Hall A & B	West A	West B	East
Session IV.1	8:00–8:20	🟥	🟧	🟨		🟪	⬜	▨ 🟫
Session IV.2	8:20–8:40	🟥	🟧	🟨		🟪	⬜	
Session IV.3	8:40–9:00	🟥	🟧	🟨		🟪	⬜	
Session IV.4	9:00–9:20	🟥	🟧	🟨			▨ ⬜	▨ 🟦
Session IV.5	9:20–9:40	🟥	🟧	🟨				
Session IV.6	9:40–10:00							
	10:00–11:30	**EFRC Poster Session II**						
Session V.1	11:30–12:30	▨ 🟥	▨ 🟧	▨ 🟨	▨ 🟩	▨ 🟪		▨ 🟦

Key:
A. Organic photovoltaics
B. Inorganic photovoltaics
C. Solar fuels and biomass
D. Energy storage and transmission
E. Energy conservation and efficiency
F. Carbon capture and sequestration
G. Materials in extreme environments
H. Effective and sustainable materials design: integration of computation, theory and experiment
I. New tools and methods for materials synthesis and characterization
Slashed sessions are close-out panels

A lifelong Illinois resident, **Congresswoman Judy Biggert** combines a wealth of experience as a legislator, lawyer, community leader, and small business owner to serve the suburban Chicago residents of Illinois' 13th District in the US House of Representatives.

Since her first election to Congress in 1998, Judy has spearheaded efforts to advance U.S. competitiveness in areas ranging from supercomputing to alternative energy technologies. She also has authored legislation to advance science and math training, and to provide greater educational opportunities for homeless children. Having taken on several ranking positions within the Financial Services Committee, Judy also consistently works to incorporate fiscal responsibility and sound economic principles in the government's response to weaknesses in the U.S. financial marketplace. Voted by her peers as one of the ten most bi-partisan Republican members of the House, Judy has led the Congressional Women's Caucus in areas like domestic violence and health research; and promoted judicial and legislative cooperation through the Congressional Judicial Caucus.

In the 112th Congress, Judy is a member of three committees -- Financial Services, Education and the Workforce, Science, Space and Technology – and of six subcommittees. She serves as Chairman of the House Financial Services Subcommittee on Insurance, Housing and Community Opportunity

Cited by Glamour as one of the "New Female Power Players" and by Fortune as one of "The Picks of Congress' New Litter," Judy met and matched expectations. During her first term in office, two of her initiatives became law: the Cybertipline legislation made it easier to report and track down computer-based sex crimes against children, and another initiative that increased penalties for traffickers of club drugs such as Ecstasy.

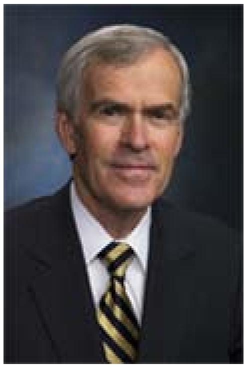
Judy has maintained her strong legislative track-record under the Congressional majorities of both parties. During the 110th Congress, she successfully secured bipartisan passage and enactment of several top legislative priorities, including the Genetic Information Nondiscrimination Act, which prohibits health insurers and employers from discriminating on the basis of a person's genetic information. The President also signed into law her Energy Tech Transfer Act, which will help move breakthrough energy technologies out of the laboratory and into the marketplace, helping individuals and businesses dramatically reduce their energy usage. Finally, through her work as Co-Chair of the Missing and Exploited Children's Caucus, she secured enactment of legislation to help find and protect missing and runaway youth.

Judy began her legislative career in 1992, when she was elected to the Illinois House of Representatives to serve the newly created 81st District.

A lifetime of community service prepared Judy for the challenges of public office. She served as President of the Board of Education of Hinsdale Township High School District 86 and Chairman of the Village of Hinsdale Plan Commission. She has also served as Chairman or President of the Hinsdale Assembly of the Hinsdale Hospital, the Hinsdale Antiques Show, the Visiting Nurses Association of Chicago, the Junior League of Chicago, the Traveler's Aid Society and the Salt Creek Ballet. She also has served as a Sunday School teacher, an Assistant Soccer Coach in the American Youth Soccer Organization, and as President of the Oak School PTA.

A graduate of Stanford University and Northwestern University School of Law, Judy began her legal career as clerk to the Honorable Luther M. Swygert, U.S. Court of Appeals for the 7th Circuit. While raising her four children, Judy ran a home-based private law practice specializing in real estate, estate planning and probate law. She is a member of the American Bar Association, the Illinois State Bar Association, the DuPage Bar Association, and the DuPage Association of Women Lawyers.

Judy was born in Chicago on August 15, 1937 and attended New Trier High School in Winnetka, Illinois. She and her husband Rody are the parents of four children and the grandparents of nine grandchildren.



Senator Jeff Bingaman was born on October 3, 1943. He grew up in the southwestern New Mexico community of Silver City, in a family with deep small town roots. His father was a science professor at Western New Mexico University, and his mother taught in the public schools.

After graduating from Western (now Silver) High School in 1961, Jeff attended Harvard University and earned a Bachelor of Arts degree in government in 1965. He then entered the Stanford University School of Law, where he met, and later married, fellow law student, Anne Kovacovich.

Upon earning his law degree from Stanford in 1968, Jeff and Anne returned to New Mexico and had their son, John. Jeff served in the Army Reserves from 1968 to 1974.

After one year as New Mexico Assistant Attorney General and eight years in private law practice, Jeff was elected Attorney General of New Mexico in 1978. In 1982, he won election to the United States Senate. He was re-elected to a fifth Senate term in 2006, becoming the third longest-serving U.S. Senator in New Mexico history.

Jeff is one of the most senior Democrats in the United States Senate. His seniority, along with his leadership positions on key committees, has allowed him to champion issues important to New Mexican families and communities.

Congressman Daniel Lipinski is a proud native and Representative of Illinois' Third Congressional District. The district includes large parts of south and southwest Chicago, as well as several suburban communities in west and southwest Cook County. All of these neighborhoods and the families who call them home make the Third District one of the most diverse and vibrant areas in the entire country.

As a skilled legislator, Congressman Lipinski has fought tirelessly for the residents of the district, as well as all Americans, by leading the way in improving our nation's schools, making the healthcare system more accessible and transparent, strengthening Social Security and Medicare, protecting the American worker, improving our nation's transportation and infrastructure, and ensuring our families' safety and security.

To advance the interests of the Third District, Congressman Lipinski is a member of two House Committees: Transportation and Infrastructure and Science and Technology. The most-senior Chicago-area member of the House Committee on Transportation and Infrastructure, Congressman Lipinski serves on the Subcommittee on Aviation and the Subcommittee on Railroads, Pipelines, and Hazardous Materials. In the Committee on Science and Technology, Congressman Lipinski is Ranking Member of the Subcommittee on Research and Science Education and sits on the Subcommittee on Technology and Innovation.

Prior to his election to the House of Representatives, Congressman Lipinski taught Political Science at the University of Tennessee and at the University of Notre Dame. He served on the staff of former Minority Leader Richard Gephardt and on the staffs of four Illinois Congressmen. He also served on the staffs of the House Administration Committee and the House Democratic Policy Committee and worked for the U.S. Department of Labor and the Illinois General Assembly's Commission on Intergovernmental Cooperation.

Congressman Lipinski earned a Bachelor's Degree in Mechanical Engineering from Northwestern University, a Master's Degree in Engineering-Economic Systems from Stanford University, and a PhD in Political Science from Duke University.

Congressman Lipinski and his wife, Judy, currently reside in Western Springs, IL.

Congresswoman Zoe Lofgren

Personal Information

- Born on December 21, 1947 in San Mateo, California
- Married to John Marshall Collins
- Mother of two children, Sheila and John Collins

Education

- K-12 public schools, Palo Alto, California
- B.A., Political Science, Stanford University, 1970
- J.D., cum laude, University of Santa Clara School of Law, 1975

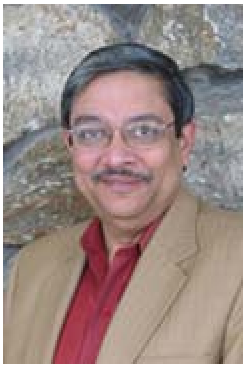
Professional Career

- Served as Staff Assistant to her predecessor, Congressman Don Edwards, 1970-1978; Worked on impeachment proceedings, the Equal Rights Amendment, and creation of the Don Edwards National Wildlife Refuge in the South San Francisco Bay
- Practiced immigration law as a partner in the firm of Webber & Lofgren, 1978-1980

- Taught immigration law at University of Santa Clara School of Law, 1977-1980
- Served on Santa Clara County Board of Supervisors, 1981-1994

U.S. Congress

- Elected in 1994 as only freshman Democrat from west of the Rocky Mountains
- Serves as Chair of the 34 Member California Democratic Congressional Delegation



Dr. Tilak Agerwala is vice president, Systems at IBM Research. He is responsible for developing the next-generation technologies for IBM's systems, from microprocessors to commercial systems and supercomputers, as well as novel supercomputing algorithms and applications. Dr. Agerwala joined IBM at the T.J. Watson Research Center and has held executive positions at IBM in research, advanced development, development, marketing and business development. His research interests are in the area of high performance computer architectures and systems. Dr. Agerwala received the W. Wallace McDowell Award from the IEEE in 1998 for "outstanding contributions to the development of high performance computers." He is a founding member of the IBM Academy of Technology. He is a Fellow of the Institute of Electrical and Electronics Engineers. He received his B.Tech. in electrical engineering from the Indian Institute of Technology, Kanpur, India and his Ph.D. in electrical engineering from the Johns Hopkins University, Baltimore, Maryland.

Dr. Paul Alivisatos serves as Director of the Lawrence Berkeley National Laboratory. Additionally, he is Professor of Chemistry and Materials Science, and the Larry and Diane Bock Professor of Nanotechnology at the University of California, Berkeley. He attended the University of Chicago, receiving a Bachelor's degree in Chemistry with Honors and a Ph. D at the University of California, Berkeley. Dr. Alivisatos is a member of the US National Academy of Sciences and of the American Academy of Arts and Sciences, and is the Editor of the American Chemical Society Journal Nanoletters.

Dr. Alivisatos is a leader in the study of the optical, electrical, and structural properties of colloidal nanocrystals, and their applications in biological imaging and renewable energy technologies.

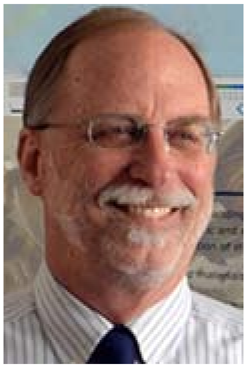
Ivan Amato has been a science writer, editor, and communicator since the mid-1980s. For much of that time he worked independently as a freelancer and has written for many publications, among them *Time, Fortune, Wired, Technology Review,* and the *Washington Post*. He has covered science for National Public Radio and has written for Discovery's Science Channel. Amato also has written several books, including *Stuff: The Materials the World is Made of*, which was chosen as a New York Times Notable Book, and the coffee table book, *Super Vision; A New View of Nature,* which is a celebration of science imagery. He also has worked on the staffs of magazines, including *Science News* and *Science*. In addition to continuing his freelance work, he now is a senior communications officer with the Pew Health Group. Additionally, he recently organized the DC Science Café, which offers DC residents and visitors engaging discussions each month about the science and technology of our times.

Paula S. Apsell got her start in broadcasting at WGBH Boston, where she was hired fresh out of Brandeis University to type the public broadcaster's daily television program logs—a job that Apsell notes is now, mercifully, automated. Within a year, she found her way to WGBH Radio, where she developed the award-winning children's drama series, *The Spider's Web,* and later became a radio news producer. In 1975, she joined WGBH's NOVA, a science documentary series that has set the standard for science programming on television.

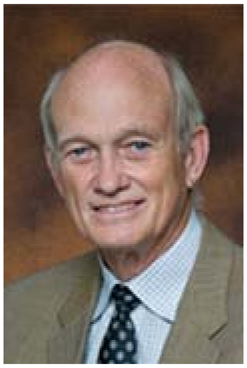
In 1985, she was asked to take over the reins at NOVA where she is now Senior Executive Producer and Director of the WGBH Science Unit. As well as overseeing the production of NOVA documentaries and miniseries for television, she has directed the series' diversification into other media—most notably online, where NOVA is the most visited site on PBS.org. NOVA can also be found in classrooms nationwide, where it is the most widely used television series among high school teachers.

In January 2005, Apsell introduced a NOVA spinoff in *NOVA scienceNOW,* a critically acclaimed science newsmagazine hosted by Dr. Neil deGrasse Tyson. Other recent signature NOVA and Science Unit productions include *The Elegant Universe, Origins, Einstein's Big Idea, Forgotten Genius* and the large format feature *Shackleton's Antarctic Adventure*.

Apsell has been recognized with numerous individual awards for her work, including the Bradford Washburn Award from the Museum of Science, Boston; the Carl Sagan Award given by the Council of Scientific Society Presidents; the American Institute of Physics Andrew Gemant Award; the Planetary Society's Cosmos Award; the International Documentary Association's Pioneer Award; the National Space Club of Huntsville Media Award; and the New York Hall of Science Distinguished Service Award for Public Understanding of Science.

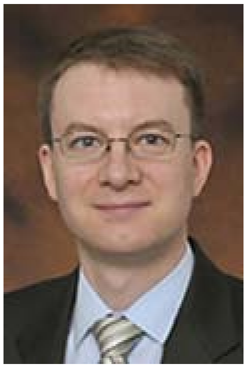


Dr. Neal R. Armstrong is Professor of Chemistry & Biochemistry and Optical Sciences at the University of Arizona (UA), where he has been located since 1978. He is a recipient of an Alexander von Humboldt Senior Research Prize at Technische Universität Dresden and the Max Planck Institute für Polymer Forschung – Mainz (2002), a Galileo Circle Fellow for the College of Science at UA (2011), and a UA Leading Edge Researcher Innovation Day Award (2011). Professor Armstrong is the Director of the Center for Interface Science: Solar Electric Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0001084. His research interests include the characterization of critical interfaces in emerging energy conversion, light emitting, and sensor technologies, using photoemission spectroscopies, scanning probe microscopies, and electrochemistry, and the development and characterization of new molecular electronic and energy conversion materials.

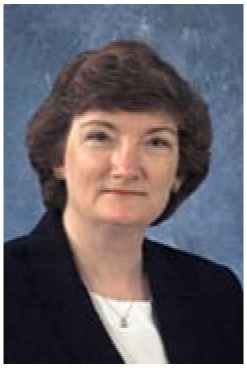


Dr. William F. Brinkman was confirmed by the Senate on June 19, 2009 and sworn in on June 30, 2009 as the Director of the Office of Science in the U.S. Department of Energy. Dr. Brinkman brings decades of experience in managing scientific research in government, academia, and the private sector to the post. Prior to joining DOE, he was a Senior Research Physicist in the Physics Department at Princeton University where he played an important role in organizing and guiding the physics department's condensed matter group for the proceeding eight years.

He joined Bell Laboratories in 1966 and after a brief sojourn as the Vice President of Research at DOE's Sandia National Laboratories, where he oversaw the expansion of its computer science efforts, Dr. Brinkman returned to Bell Laboratories in 1987 to become the executive director of its physics research division. He advanced to the Vice President of Research in Bell Laboratories in 2000, where he directed research to enable the advancement of the technology underlying Lucent Technologies' products. Brinkman led a research organization that developed many of the components and systems used in communications today, including advanced optical and wireless technologies.

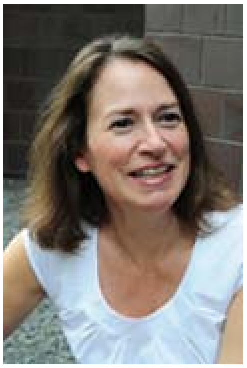


Dr. Benjamin L. Brown joined the Office of the Deputy Director for Science Programs as Senior Science and Technology Advisor in September 2008. His responsibilities include advising the Deputy Director on science program management and policy issues, and providing coordination and analysis of budget, scientific, technical, programmatic, and operational issues regarding the SC Program Offices and national laboratories. Ben also currently serves as a primary liaison to the Office of Basic Energy Sciences, the Office of Fusion Energy Sciences, and the Office of Project Assessment. During the twelve months prior to his joining DOE Ben worked on energy and climate policy as an AAAS Congressional Fellow in the office of U.S. Senator Ken Salazar. Ben is an experimental atomic, molecular, and optical physicist who received his Ph.D. in Optics from the University of Rochester and his A.B. in physics *magna cum laude* from Harvard University. His doctoral research was carried out at the University of Oxford, where he was in residence for three years following the move of his thesis advisor from Rochester to Oxford. After graduating in 2005 he spent two years at the National Institute of Standards and Technology in Gaithersburg, Maryland as a National Research Council postdoctoral research associate working in the Laser Cooling and Trapping Group. Ben's postdoctoral and doctoral research focused on the use of lasers to control quantum systems.



Dr. Michelle Buchanan is the Associate Laboratory Director (ALD) for Physical Sciences at Oak Ridge National Laboratory (ORNL). In this role she is responsible for the Chemical Sciences, Materials Science and Technology, Physics, and the Center for Nanophase Materials Sciences research divisions. She is also the Program Manager for the Basic Energy Sciences Program at ORNL. Prior to assuming the role of ALD, she served as the Director of the Chemical Sciences Division, Associate Director of the Life Sciences Division and Group Leader for Organic and Biological Mass Spectrometry at ORNL. She is also an adjunct professor in the Department of Chemistry at the University of Tennessee. She has over 150 scientific publications and reports, holds two patents, and was editor of a book on Fourier transform mass spectrometry. She has held positions in the Analytical Chemistry Division of the American Chemical Society and the American Society for Mass Spectrometry. She was recently named a Fellow by the American Chemical Society. She has served as North American Editor of *Biological Mass Spectrometry* and as a member on the editorial boards of *Analytical Chemistry, Organic Mass Spectrometry, Journal of Mass Spectrometry, Biological and Environmental Mass Spectrometry,* and *Frensenius' Journal of Analytical Chemistry.* She has also served on numerous advisory boards for Universities and for major research centers; current board memberships include Vanderbilt University, the University of North Carolina, Cornell University, Boston University, and the University of Tennessee. Over the past decade, she has worked at the national level helping to define basic research needs in a number of key energy-related areas.

Dr. David Carlson invented the ion depletion process in inorganic glasses in 1971 and the amorphous silicon solar cell in 1974 both while working at RCA Laboratories. He has received numerous awards including the Ross Coffin Purdy Award (American Ceramic Society), the Morris N. Liebmann Award (IEEE), the Walton Clark Medal (Franklin Institute), the William R. Cherry Award (IEEE) and the Karl W. Boer Medal (International Solar Energy Society and the University of Delaware). Dr. Carlson became the Vice President of the Thin Film Division of Solarex (an Amoco subsidiary) in 1988, and he became the Chief Scientist of BP Solar in 1994. He is a fellow of the IEEE and a member of the American Physical Society, the American Vacuum Society, and Sigma Xi. He has published more than 150 technical papers and has been issued 26 U.S. patents.



Dr. Emily Carter is the Founding Director of the Andlinger Center for Energy and the Environment at Princeton University, the Gerhard R. Andlinger Professor in Energy and the Environment, and Professor of Mechanical and Aerospace Engineering and Applied and Computational Mathematics. She earned her B.S. (Chemistry) from UC Berkeley in 1982 and a Ph.D. (Chemistry) from Caltech in 1987, spent a brief postdoc at CU Boulder, and then was on the UCLA faculty for 16 years in Chemistry and later also Materials Science and Engineering. She moved to Princeton in 2004, where she is also associated with Chemistry, Chemical Engineering, and three interdisciplinary institutes. The author of over 240 publications, she has delivered over 400 invited lectures worldwide. Her scholarly work has been recognized by numerous honors, including election in 2008 to both the American Academy of Arts and Sciences and the National Academy of Sciences, and in 2009 to the International Academy of Quantum Molecular Science. Her current research is focused entirely on enabling discovery and design of materials for sustainable energy, including converting sunlight to electricity and fuels, providing clean electricity from solid oxide fuel cells, clean and efficient combustion of biofuels, and optimizing lightweight metal alloys for fuel-efficient vehicles.

Dr. Yet-Ming Chiang is Kyocera Professor in the Department of Materials Science and Engineering at Massachusetts Institute of Technology (MIT). He holds S.B. and Sc.D. degrees from MIT, where he has been a faculty member since 1984. His work focuses on advanced materials and their role in clean energy technologies, medical devices, "smart" structures, and micro/nano electronics. He is a member of the U.S. National Academy of Engineering, and a Fellow of the American Ceramic Society and the Materials Research Society. He is a recipient of the American Ceramic Society's Ross Coffin Purdy, R. M. Fulrath, and F. H. Norton awards, has published about 200 scholarly articles and a textbook on ceramic materials, and holds about 25 issued patents (excluding substantially identical foreign filings). Chiang is a co-founder of four companies: American Superconductor Corporation (NASDAQ: AMSC), A123 Systems (NASDAQ: AMSC), Entra Pharmaceuticals, and 24M Technologies. He serves or has served on numerous study panels including the U.S. Department of Energy's Energy Efficiency and Renewable Energy Advisory Committee (ERAC) and Basic Energy Sciences Advisory Committee (BESAC), and the National Materials and Manufacturing Board (NMMB), and the National Nanotechnology Initiative (NNI) Working Group of the President's Council of Advisors in Science and Technology (PCAST).

As United States Secretary of Energy, **Dr. Steven Chu** is charged with helping implement President Obama's ambitious agenda to invest in clean energy, reduce our dependence on foreign oil, address the global climate crisis, and create millions of new jobs.

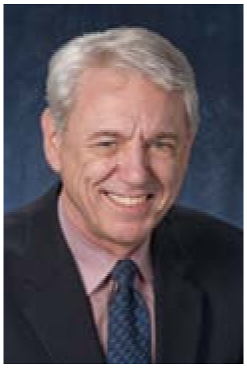
Dr. Chu is a distinguished scientist and co-winner of the Nobel Prize for Physics (1997). He has devoted his recent scientific career to the search for new solutions to our energy challenges and stopping global climate change - a mission he continues with even greater urgency as Secretary of Energy.

Prior to his appointment, Dr. Chu was the Director of the Department of Energy's Lawrence Berkeley National Lab, where he led the lab in pursuit of alternative and renewable energy technologies. He also taught at the University of California as a Professor of Physics and Professor of Molecular and Cell Biology. Previously, he held positions at Stanford University and AT&T Bell Laboratories.

Dr. Chu's research in atomic physics, quantum electronics, polymer and biophysics includes tests of fundamental theories in physics, the development of methods to laser cool and trap atoms, atom interferometry, the development of the first atomic fountain, and the manipulation and study of polymers and biological systems at the single molecule level. While at Stanford, he helped start Bio-X, a multi-disciplinary initiative that brings together the physical and biological sciences with engineering and medicine.

The holder of 10 patents, Dr. Chu has published nearly 250 scientific and technical papers. He remains active with his research group and has recently published work on general relativity and single molecule biology and biophysics that includes sub-nanometer molecular imaging with optical microscopy, cadherin adhesion, neural vesicle fusion, and nerve growth factor transport. About 30 alumni of his research group have gone on to become professors in their own right and have been recognized by dozens of prizes and awards.

Dr. Chu is a member of the National Academy of Sciences, the American Philosophical Society, the Chinese Academy of Sciences, Academia Sinica, the Korean Academy of Sciences and Technology and numerous other civic and professional organizations. He received an A.B. degree in mathematics, a B.S. degree in physics from the University of Rochester, and a Ph.D. in physics from the University of California, Berkeley as well as honorary degrees from 15 universities.

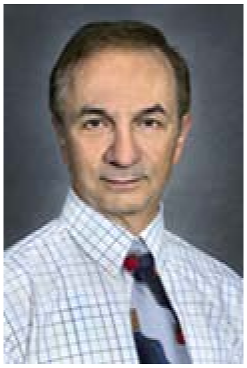


Dr. George Crabtree is Senior Scientist and Distinguished Fellow in the Materials Science Division at Argonne National Laboratory and Distinguished Professor of Physics, Electrical, and Mechanical Engineering at University of Illinois-Chicago. He has published more than 400 papers in leading scientific journals and has given over 100 invited talks at national and international scientific conferences. His research interests include materials science, sustainable energy, nanoscale superconductors and magnets, vortex matter in superconductors, and highly correlated electrons in metals. He has led workshops for the Department of Energy on hydrogen, solar energy, superconductivity, materials under extreme environments, basic science supporting energy technology, and computational materials and chemistry for economic competitiveness, and he has co-chaired the Undersecretary of Energy's assessment of DOE's Applied Energy Programs. He is a member of the National Academy of Sciences and has testified before the U.S. Congress on the hydrogen economy and on meeting sustainable energy challenges.

Dr. Patricia M. Dehmer is the Deputy Director for Science Programs in the Office of Science at the U.S. Department of Energy (DOE). In this capacity, Dr. Dehmer is the senior career science official in the Office of Science, which is third largest Federal sponsor of basic research in the United States, the primary supporter of the physical sciences in the U.S., and one of the premier science organizations in the world.

From 1995 to 2007, Dr. Dehmer served as the Director of the Office of Basic Energy Sciences (BES) in the Office of Science. Under her leadership, the BES budget more than doubled in size to $1.2B annually. She built a world-leading portfolio of work in condensed matter and materials physics, chemistry, and biosciences. A five-year effort to relate fundamental research in these disciplines to real-world problems in energy - including problems in fossil energy and carbon dioxide sequestration, nuclear energy, renewable energy, energy efficiency, energy transmission and storage, and the mitigation of environmental impacts of energy use - facilitated greater integration of basic and applied research across DOE. During this period, Dr. Dehmer also was responsible for the planning, design, and construction phases of more than a dozen major construction projects totaling $3 billion.

Before joining DOE, Dr. Dehmer spent 21 years as a research scientist at Argonne National Laboratory, achieving the rank of Argonne Distinguished Fellow in 1992. She is the author of more than 125 peer-reviewed scientific papers and is a Fellow of the American Physical Society and the American Association for the Advancement of Science.



The University Of California Board Of Regents appointed **Dr. Donald Depaolo** Associate Laboratory Director for Energy and Environmental Sciences of Lawrence Berkeley Lab on April 1, 2011, a position that he served in an acting capacity since June 1, 2010. As Associate Lab Director of Energy and Environmental Sciences, DePaolo oversees the Chemical Sciences, Environmental Energy Technologies, Materials Sciences, and Earth Sciences Divisions.

Don DePaolo began his term in Berkeley in 1988 as a UC Berkeley Professor of Geochemistry in the Department of Earth and Planetary Science, with a joint appointment in the Earth Sciences Division at Berkeley Lab. DePaolo was officially announced as the Earth Sciences Division Director in 2007, a position he still holds. DePaolo established and is the director of the Center for Isotope Geochemistry, a joint research facility between Berkeley Lab and UC Berkeley. In Spring of 2009, DePaolo became the Director of the Center for Nanoscale Control of Geologic CO2 (EFRC). DePaolo is also the Class of 1951 Professor of Geochemistry in UC Berkeley's Department of Earth and Planetary Science. He is a member of the National Academy of Sciences and the American Academy of Arts and Sciences.

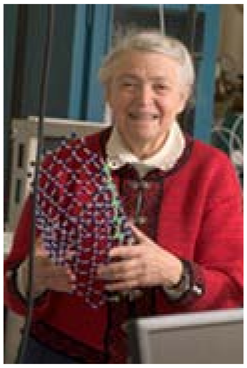
DePaolo attended SUNY Binghamton and received a Bachelor of Science degree with Honors in 1973. He received a PhD in Geology from the California Institute of Technology in 1978.

Dr. Kazunari Domen received B.S.c. (1976), M.S.c. (1979), and Ph.D. (1982) honors in chemistry from the University of Tokyo. Dr. Domen joined Chemical Resources Laboratory, Tokyo Institute of Technology in 1982 as Assistant Professor and was subsequently promoted to Associate Professor in 1990 and Professor in 1996. Moving to the University of Tokyo as Professor in 2004.

Domen has been working on overall water splitting reaction on heterogeneous photocatalysts to generate clean and recyclable hydrogen. In 1980, he reported NiO-SrTiO3 photocatalyst for overall water splitting reaction, which was one of the earliest examples achieving stoichiometric H2 and O2 evolution on a particulate system. In 2005, he has succeeded in overall water splitting under visible light (400 nm<λ<500nm) on GaN:ZnO solid solution photocatalyst.

His research interests now include heterogeneous catalysis and materials chemistry, with particular focus on surface chemical reaction dynamics, photocatalysis, solid acid catalysis, and mesoporous materials.

Dr. Persis S. Drell is Professor and Director at SLAC. She received her B.A. in mathematics and physics from Wellesley College in 1977, and her Ph.D. in atomic physics from the University of California, Berkeley, in 1983. She then switched to high-energy experimental physics and worked as a postdoctoral scientist with Lawrence Berkeley National Laboratory. She joined the faculty of the Physics Department at Cornell University in 1988. In 2000, she became head of the Cornell high-energy group; in 2001, she was named deputy director of Cornell's Laboratory of Nuclear Studies. In 2002, Dr. Drell accepted a position as Professor and Director of Research at SLAC. Her current research activities are in particle astrophysics. In 2007 she was named Director at SLAC. Dr. Drell is a fellow of the American Physical Society, a member of the American Academy of Arts and Sciences, and a member of the National Academy of Sciences.



Dr. Mildred Dresselhaus is an Institute Professor of Electrical Engineering and Physics at MIT. She is the recipient of the National Medal of Science and 28 honorary degrees worldwide. She has served as President of the American Association for the Advancement of Science, Treasurer of the National Academy of Sciences, President of the American Physical Society, and Chair of the Governing Board of the American Institute of Physics. She is also a member of the National Academy of Engineering, the American Philosophical Society, and a Fellow of the American Academy of Arts and Sciences. She served as the Director of the Office of Science at the U.S. Department of Energy. Professor Dresselhaus' research over the years has covered a wide range of topics in Condensed Matter and Materials Physics. She is best known for her work on carbon science and carbon nanostructures, as well as nanoscience and nanotechnology more generally. She is also one of the researchers responsible for the resurgence of the Thermoelectrics research field through her early work on low dimensional thermoelectricity in the early 1990's.

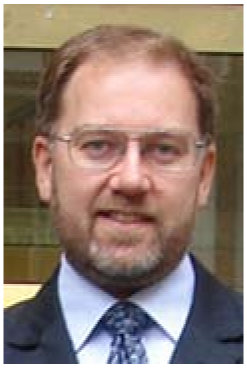
Dr. Karina Edmonds was appointed Technology Transfer Coordinator for the U.S. Department of Energy (DOE) in April 2010 by Secretary of Energy Dr. Steven Chu. Created by the Energy Policy Board Act of 2005, this is the first time that the Department has appointed a full-time person to fill this role. Dr. Edmonds is responsible for working with the Department's National Laboratories to accelerate the process of moving discoveries from the laboratory to the private sector, ensuring that America's scientific leadership translate into new, high-paying jobs for America's families.

Dr. Edmonds joined the DOE after working at the Jet Propulsion Laboratory (JPL) at California Institute of Technology where she served as Director of JPL Technology Transfer. While at JPL, Dr. Edmonds also held positions in the Strategic Intellectual Assets Management Office as Senior Technology Transfer Specialist and in the Strategic University Research Partnership Office as Manager before finally becoming the Director of JPL Technology Transfer. In that position, her job duties included licensing technologies developed at both JPL and Caltech to industry and start-ups, managing the JPL patent portfolio, assisting Caltech start-ups, and managing prosecution of

Caltech's patent filings. Dr. Edmonds is a registered patent agent with the U.S. Patent and Trademark Office.

Prior to her work at JPL, she worked as Principal Investigator at TRW, Inc. for internal research and development efforts. During her tenure there, she co-authored two patent applications in the area of noise reduction for the automotive environment.

Dr. Edmonds received a bachelor's degree in mechanical engineering from the University of Rhode Island. She holds master's and doctorate degrees in aeronautics with a minor in material science from the California Institute of Technology in Pasadena, California.



Dr. Robin Grimes is Professor of Materials Physics in the Materials Department at Imperial College, Director of the Imperial College Centre for Nuclear Engineering and Director of the Rolls Royce University Technology Centre in Nuclear Engineering. In 2000 he spent a year at Los Alamos National Laboratory as Bernd T. Matthias Scholar. His primary research interest is the application and development of computer simulation techniques to predict structural and dynamic properties of nuclear materials including mechanisms of radiation damage, nuclear fuel performance and waste form behavior. He is the Principle Investigator of the UK Research Councils multi-university nuclear research coordination initiative, a member of the Royal Society Working Group on Nuclear non-proliferation and the Specialist Advisor to the House of Lords review of Nuclear Research Requirements for the UK (2011). He has authored over 200 peer-reviewed publications and is on the editorial board of the Journal of Nuclear Materials.

Dr. Brent Gunnoe received a B.A. in chemistry from West Virginia University, where he performed research focused on early transition metal chemistry under the direction of Professor Jeffrey Petersen. In 1997, he received a Ph. D. in inorganic chemistry from the University of North Carolina at Chapel Hill working with Professor Joseph Templeton on application of chiral group VI complexes toward stereoselective ligand transformations. After postdoctoral work at the University of Virginia with Professor W. Dean Harman, Dr. Gunnoe began as an Assistant Professor at North Carolina State University in 1999, where he was the recipient of a National Science Foundation CAREER Award, the Sigma Xi Faculty Research Award and an Alfred P. Sloan Research Fellowship. In 2008, he returned to the University of Virginia as full professor, where he is serving as director of the Center for Catalytic Hydrocarbon Functionalization and associate editor for the journal *ACS Catalysis*. In addition to research, he has received recognition for his efforts in teaching and advising including serving as a Beckman mentor and receiving the Park Scholar Outstanding Mentor Award and the LeRoy and Elva Martin Award for Teaching Excellence.

Dr. John Hennessy joined Stanford's faculty in 1977 as an assistant professor of electrical engineering. He was named the inaugural Willard R. and Inez Kerr Bell Professor of Electrical Engineering and Computer Science in 1987. He served as director of the Computer Systems Laboratory, chair of computer science, dean of the School of Engineering, and provost prior to being inaugurated as Stanford University's 10th president in 2000. In 2005, he became the inaugural holder of the Bing Presidential Professorship.

Dr. Hennessy is a recipient of the 2000 IEEE John von Neumann Medal, the 2000 ASEE Benjamin Garver Lamme Award, the 2001 ACM Eckert-Mauchly Award, the 2001 Seymour Cray Computer Engineering Award, a 2004 NEC C&C Prize for lifetime achievement in computer science and engineering, and a 2005 Founders Award from the American Academy of Arts and Sciences. He is a member of the National Academy of Engineering and the National Academy of Sciences, and is a fellow of the American Academy of Arts and Sciences, the Association for Computing Machinery, and the Institute of Electrical and Electronics Engineers.

He has lectured and published widely and is the co-author of two internationally used undergraduate and graduate textbooks on computer architecture design. Dr. Hennessy earned his bachelor's degree in electrical engineering from Villanova University and his master's and doctoral degrees in computer science from the State University of New York at Stony Brook.

Dr. Catherine T. "Katie" Hunt is R&D Director in Innovation Sourcing & Sustainable Technologies at The Dow Chemical Company. Dr. Hunt is actively building collaboration teams across Dow with universities, companies, national labs and government agencies (esp., DOE and DOD) focused on accelerating the pace of innovation. Katie began her career as a senior scientist in analytical research at Rohm and Haas in 1984 after completing an NIH Postdoctoral Fellowship at Yale University. During her 25 years at Rohm and Haas, Katie held positions of increasing responsibility, from research scientist to process chemist to plant laboratory manager to Director of their worldwide Analytical and Computational Competency Network (better known as ACNET) and ultimately, Corporate Sustainability Director and Leader for Technology Partnerships.

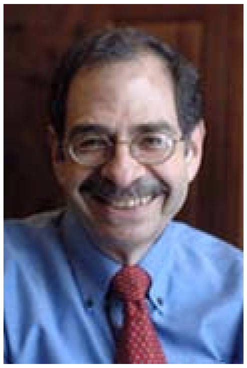
She is especially proud of the **RetroFIT Philly** "Coolest Block" Contest project with the City of Philadelphia, the Energy Coordinating Agency of Philadelphia, The Dow Chemical Company and The Dow Foundation. For details visit: www.retrofitphilly.com.

Dr. Eric D. Isaacs is President of UChicago Argonne, LLC, and Director of Argonne National Laboratory.

Before becoming Argonne Director, Isaacs served as Argonne's deputy laboratory director for programs, with responsibility for leading the laboratory's strategic planning process and overseeing the laboratory-directed research and development program as well as its educational programs.

Earlier he distinguished himself both as director of the Center for Nanoscale Materials at Argonne and as professor of physics in the University of Chicago's James Franck Institute. During his 13-year tenure at Bell Laboratories, he was a member of the technical staff, director of the Materials Physics Research Department and director of the Semiconductor Physics Department.

He received a Ph.D. degree from the Massachusetts Institute of Technology in 1988 in the area of magnetic semiconductors and was a postdoctoral fellow at Bell Laboratories (1988-1990) studying magnetism and correlated electronic systems, mostly with synchrotron-based X-ray techniques.



Dr. Marc Kastner received his SB in Chemistry and his PhD in Physics, both from the University of Chicago. After one year as a Harvard Research Fellow, he joined the Department of Physics at MIT 1973 where he became the Donner Professor of Physics in 1989. In 1993, he was appointed director of the Center for Materials Science and Engineering at MIT, which became the largest of the NSF Materials Research Science and Engineering Centers. He left that position to become Head of the Department of Physics in 1998, and he became Dean of the School of Science in 2007.

Kastner's early research focused on the electronic and optical properties of amorphous semiconductors, especially chalcogenide glasses. Although the atoms in these materials are not arrayed on a crystal lattice, they are still useful for electronic and optical memories. He invented a model that relates the electronic properties of these materials to their chemical bonding. He has also studied the physics of high temperature superconductors, especially the relationship of their magnetic properties to their electron transport. In 1990 Kastner's group fabricated the first semiconductor single-electron transistor. His group continues to use these devices as tools to study the quantum mechanical behavior of electrons confined to nanometer dimensions. In particular, his group discovered the Kondo effect in these nano-structures, a state in which electrons inside and outside the transistor are quantum mechanically entangled. The single-electron transistor allowed the study of the Kondo effect out of equilibrium, which was not possible in other Kondo systems. Kastner has served as Chair of the Solid State Sciences Committee and as Chair of the Board on Physics and Astronomy of the National Research Council.

Dr. Steven Koonin serves as the Undersecretary for Science in the U.S. Department of Energy, a post he has held since May, 2009. He brings to the post a distinguished career as a university professor and administrator at the California Institute of Technology (Caltech) as well as experience in industry.

Undersecretary Koonin received his B.S. in Physics from Caltech in 1972, and received his Ph.D. in Theoretical Physics from Massachusetts Institute of Technology (MIT) in 1975. Dr. Koonin joined the Caltech faculty in 1975 and served the seventh provost of Caltech from 1995 to 2004.

As the Chief Scientist at BP between 2004 and early 2009, Dr. Koonin developed the company's long-range technology strategy for alternative and renewable energy sources and played a central role in establishing the Energy Biosciences Institute.

He is a member of the Council on Foreign Relations and the Trilateral Commission and a fellow of the American Physical Society, the American Association for the Advancement of Science, and the American Academy of Arts and Sciences. He was elected to membership in the National Academy of Sciences in 2010.

Dr. Koonin has been involved in scientific computing throughout his career and is a strong advocate for research into renewable energies and alternate fuel sources.

Dr. Nathan Lewis, George L. Argyros Professor of Chemistry, has been on the faculty at the California Institute of Technology since 1988 and has served as Professor since 1991. He has also served as the Principal Investigator of the Beckman Institute Molecular Materials Resource Center at Caltech since 1992, and is the Principal Investigator of the Joint Center for Artificial Photosynthesis, the DOE's $122 MM Energy Innovation Hub in Fuels from Sunlight. He was on the faculty at Stanford, as an assistant professor from 1981 to 1985, and as a tenured Associate Professor from 1986 to 1988. Dr. Lewis received his Ph.D. in Chemistry from the Massachusetts Institute of Technology.

Dr. Lewis has been an Alfred P. Sloan Fellow, a Camille and Henry Dreyfus Teacher-Scholar, and a Presidential Young Investigator. He received the Fresenius Award in 1990, the ACS Award in Pure Chemistry in 1991, the Orton Memorial Lecture award in 2003, the Princeton Environmental Award in 2003 and the Michael Faraday Medal of the Royal Society of Electrochemistry in 2008. He is currently the Editor-in-Chief of Energy & Environmental Science. He has published over 300 papers and has supervised approximately 60 graduate students and postdoctoral associates.

His research interests include artificial photosynthesis and electronic noses.

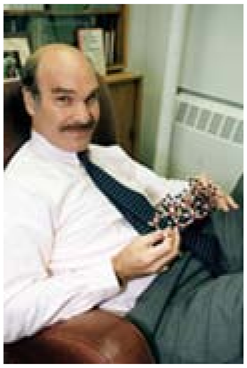
Dr. Mark M. Little was named Senior Vice President and Director of GE Global Research in October 2005, becoming the ninth director in the organization's 105 year history. Mark is responsible for leading one of the World's largest and most diversified industrial research and technology organizations.

At Global Research, some 2,500 people from virtually every major scientific and engineering discipline focus on the company's long-range technology needs. The organization has research facilities in the United States, India, China and Germany, working in collaboration with GE businesses around the world. Prior to becoming Research Director, Little was Vice President of GE Energy's power generation segment headquartered in Schenectady, New York. GE Energy is a world leading supplier of power generation equipment including gas, steam, wind and hydro turbine-generators, turnkey power plant services, gasification technologies and IGCC (integrated gasification combined cycle).

Mark joined GE in 1978, starting out in the Company's Turbine Business. After holding several management positions in engineering, he was named Product General Manager for generators in 1989. In 1991, he became General Manager – Business Development for GE Energy, responsible for strategic planning and joint venture development. In 1992, he was appointed Product General Manager for gas turbines and in 1994 was named Vice President, Power Generation Engineering. In 1997, Mark became Vice President GE Power Generation, responsible for the turbine, generator, and power plants business. In 2004, the hydro and wind turbine businesses were added to his portfolio.

Dr. Celia Merzbacher is Vice President for Innovative Partnerships at the Semiconductor Research Corporation (SRC), a nonprofit industry consortium that invests in university research. She is responsible for developing new areas of business and partnerships with stakeholders in government and the private sector. Currently, she is involved with growing SRC's Energy Research Initiative, which was launched in 2010. Prior to joining SRC, Dr. Merzbacher was Assistant Director for Technology R&D in the White House Office of Science and Technology Policy (OSTP), where she coordinated and advised on a range of issues, including nanotechnology, technology transfer, technical standards, and intellectual property. She also served as Executive Director of the President's Council of Advisors on Science and Technology (PCAST). Previously, Dr. Merzbacher was on the staff of the Naval Research Laboratory in Washington D.C. where she held positions as a research scientist and technology licensing executive. Dr. Merzbacher currently represents SRC on the National Academies Government-University-Industry Research Roundtable and the Alliance for Science and Technology Research in American. She served on the Board of Directors of the American National Standards Institute and led the U.S. delegation to the OECD Working Party on Nanotechnology.

Dr. William D. Phillips is a physicist at the National Institute of Standards and Technology in Gaithersburg, MD, where he leads the Laser Cooling and Trapping Group in the Atomic Physics Division of NIST's Physics Laboratory. The group is part of the Joint Quantum Institute, a cooperative research enterprise of NIST and the University of Maryland. In 1997 Phillips shared the Nobel Prize in Physics "for development of methods to cool and trap atoms with laser light."



Dr. Mark Ratner is Dumas University Professor at NU. Ratner is interested in structure and function at the nanoscale, and theory of fundamental chemical processes. He tries to bring together structure and function in molecular nanostructures, based on theoretical notions, on exemplary calculations, and (very importantly) on collaborations with experimentalists and other theorists, in the US and around the world. Areas of interest include molecular electronics, electron transfer, self-assembly, nanoscience and technology, energy systems and processes, and theories of quantum dynamics. He spends as much time trout fishing as possible.

Ratner is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, the International Academy of Quantum Molecular Sciences and the Royal Danish Academy of Sciences. He received the Langmuir Award and the Feynman Award. He has honorary doctorates from the University of Copenhagen and from the Hebrew University of Jerusalem. He has chaired the Department at Northwestern, has been on the Faculty Teaching Honor Roll at Northwestern eleven times, and taught roughly five thousand students in General Chemistry in the last dozen years.

He received his BA and PhD from Harvard and NU, respectively.

Dr. Jean-Marie Tarascon (1953) is presently professor at the University of Picardie (Amiens), but most of his career was done in the USA, first at Cornell University (1980), then at Bell Laboratories and finally at Bellcore until 1994 where he developed the plastic Li-ion technology. He is the creator of the European network of excellence ALISTORE-ERI who is headed till 2010 prior to take over the directorship of the new LABEX "STORE-EX" and become in charge of the recently created French network on electrochemical energy storage energy (RS2E). His research deals with new electrode materials, obtained via eco-efficient processes for the development of sustainable and "greener" Li-ion batteries.

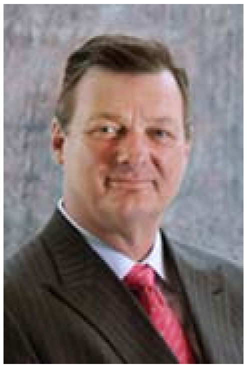
He is Author of about 70 patents and more than 520 publications, recipient of many awards, the last in line being his nomination at the college de France in 2010 to hold the chair on Sustainable energy and the recipient of the 2011 ENI "Protection of the Environment" Prize.

Dr. Alan Taub is Vice President, Global Research & Development, for General Motors Company. In this post, he leads GM's global R&D organization, advanced technical work (ATW) activity, and global science offices.

Dr. Taub received his bachelor's degree in materials engineering from Brown University and master's and Ph.D. degrees in applied physics from Harvard University. He spent 15 years in research and development at General Electric, where he earned 26 patents, authored more than 60 papers, and ultimately managed the GE materials properties and processes laboratory. He also worked at Ford Motor Company for eight years, where he was manager of the materials science department, manager of North American vehicle crash safety, and manager of vehicle engineering for the Lincoln brand. He joined GM R&D as executive director in 2001 and was appointed to his current post in July, 2009.

Dr. Taub was elected to membership in the National Academy of Engineering in 2006. He serves on the Operating Council for the United States Council for Automotive Research (USCAR) and the Executive Steering Committee for the FreedomCAR Partnership. He also is Vice Chair for the Visiting Committee on Advanced Technology (VCAT) advisory board for the National Institute of Standards and Technology (NIST). In addition, Taub serves on advisory boards for the University of Michigan, Massachusetts Institute of Technology, Northwestern University, and the University of California, Berkeley.

Dr. Taub has been selected to receive the 2011 Acta Materialia Materials & Society Award. He was awarded the Charles S. Barrett Medal from ASM International's Rocky Mountain Chapter in 2010. He received the Materials Research Society's Special Recognition Award in 2004 and Woody White Service Award in 2002. He also received the Brown University Engineering Alumni Medal in 2002. He was a member of the USCAR Automotive Composites Consortium from 1993 to 1997 and served with the PNGV Materials Tech Team from 1995 to 1997. He was recognized with the ASM Alfred H. Geisler Award for Young Metallurgist in 1987. He was elected to Tau Beta Pi and Sigma Xi in 1976 and received the AIME Morris Cohen Award for Materials Science Undergraduate in 1975.



Dr. Jeff Wadsworth has been President and CEO of Battelle Memorial Institute since January 2009. Battelle is the world's largest nonprofit research and development organization, executing about $6B of work annually and employing about 21,000 people. Formed in 1925 as a charitable trust and headquartered in Columbus, Ohio, Battelle counts among its successes the development of the Xerox machine, pioneering work on the compact disc, and a number of innovations in medical technology, telecommunications, environmental waste treatment, homeland security, and transportation. Battelle has spun off new ventures and companies in fiber optics, pharmaceuticals, energy, electronics, and informatics. Its principal businesses today are fee-for-service contract research, laboratory operations, and commercial ventures, executing more than 5,000 projects for some 1,500 industrial and government clients throughout the world.

Jeff formerly led Battelle's Global Laboratory Operations business, where he oversaw the management or co-management of six national laboratories of the U.S. Department of Energy, representing more than

$3B in annual business (Pacific Northwest National Laboratory, Brookhaven National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory, Idaho National Laboratory, and Lawrence Livermore National Laboratory), and the Department of Homeland Security's National Biodefense Analysis and Countermeasures Center. He also led the development of partnerships with the private sector in Kuala Lumpur, Malaysia, and the expansion of Battelle's operations into Japan, Korea, and India. In March 2009, a consortium including Battelle was awarded a contract to manage the National Nuclear Laboratory of the United Kingdom's Department of Energy and Climate Change.

Jeff was educated at Sheffield University in England, where he studied metallurgy, earning a bachelor's degree in 1972 and a Ph.D. in 1975. He was awarded a Doctor of Metallurgy degree in 1991 for his published work and received the highest recognition conferred by the university, an honorary Doctor of Engineering degree, in July 2004.

Jeff came to the United States in 1976 and has worked at Stanford University, Lockheed Missiles and Space Company, and Lawrence Livermore National Laboratory. In 2002, he joined Battelle and served as a member of the White House Transition Planning Office for the U.S. Department of Homeland Security. From 2003 to June 2007, Jeff was director of Oak Ridge National Laboratory, the Department of Energy's largest multipurpose science laboratory.

Session A – Organic Photovoltaics - Grand Ballroom South

Parallel Scientific Session I - May 26, 2011
Grand Ballroom South

10:15 - 10:35
T-A01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA
[CST] Xiaoyang Zhu and Jennifer Lyon
University of Texas at Austin

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

10:35 - 11:15
T-A02 - CHARGE SEPARATION AND TRANSFER AT ORGANIC SEMICONDUCTOR INTERFACES: FROM SINGLE MOLECULES TO SINGLE CRYSTALS
[CST] Xiaoyang Zhu, Peter J. Rossky, Loren Kaake, Adam Willard, Michael Bedard-Hearn, and Raluca Gearba
University of Texas at Austin

We highlight recent successes in our coordinated experimental and theoretical efforts to understand fundamental charge separation and transfer (CST) mechanisms at model organic photovoltaic (OPV) interfaces. Experimentally, we have developed a femtosecond electric field meter based on nonlinear optical spectroscopy to probe charge separation dynamics at organic donor/acceptor interfaces. In contrast to traditional approaches such as transient absorption where signals from interfacial CST processes are often overwhelmed from processes in the bulk donor or acceptor phase our technique is most sensitive to charge separation at the interface and thus allows us to probe key charge separation mechanisms e.g. the dependences of charge separation rates on relative molecular orientation at the interface or the amount of excess energy from optical excitation. We are applying our theoretical developments in a mixed quantum-classical nonadiabatic molecular dynamics simulation to directly simulate the coupled nuclear and excitonic dynamics of model OPV molecular systems allowing a priori observation of dynamical electronic events. Thus we can study the same processes as measured experimentally without imposing an assumed model for molecular-scale structure or active kinetic processes. Examples of results from simulation that visualize the nanoscale electronic excited state dynamics of oligomers of PPV and thiophene as well as their interfaces with C_{60} will be described.

11:15 - 11:35
T-A03 - PLASTIC SOLAR CELLS: SELF-ASSEMBLY OF BULK HETEROJUNCTION NANO-MATERIALS BY SPONTANEOUS PHASE SEPARATION
[CEEM] Alan Heeger
University of California, Santa Barbara

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

11:35 - 11:55
T-A04 - UNDERSTANDING THE MORPHOLOGY OF ORGANIC PHOTOVOLTAICS
[PHaSE] Thomas Russell
University of Massachusetts Amherst

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

11:55 - 12:15

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

[ANSER] Tobin Marks[1], Lin Chen[2], Luping Yu[3], Mark Ratner[4], and Robert Chang[4]
[1]*Northwestern U.;* [2]*Argonne National Lab.;* [3]*U. of Chicago;* [4]*Northwestern U.*

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

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

1:45 - 2:05

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

[CISSEM] Neal Armstrong[1], Erin Ratcliff[1], Brian Zacher[1], Gordon MacDonald[1], Laura Schirra[1], Oliver Monti[1], Xerxes Steirer[1], Dana Olson[2], Jens Meyer[3], Antoine Kahn[3], Hyeunseok Cheun[4], and Bernard Kippelen[4]
[1]*University of Arizona;* [2]*National Renewable Energy Laboratory;* [3]*Princeton University;* [4]*Georgia Institute of Technology*

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

2:05 - 2:25

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

[PHaSE] Dhandapani Venkataraman
University of Massachusetts Amherst

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

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

2:25 - 2:45

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

[CISSEM] Bernard Kippelen, Yinhua Zhou, Hyeunseok Cheun, William Potscavage Jr., Canek Fuentes-Hernandez, Seth Marder, Jens Meyer, and Antoine Kahn
Georgia Institute of Technology

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

2:45 - 3:05

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

[MEEM] Benjamin Schwartz, Sarah Tolbert, Yves Rubin, Daniel Neuhauser, Nikos Kopidakis, Alex Ayzner, Stephanie Doan, Chris Tassone, Bertrand Tremolet de Villers, Krastina Petrova, and Daniel Kilbride
University of California, Los Angeles

Although tradition polymer/fullerene solar cells make use of spin-coated blends of the two materials, producing a so-called bulk-heterojunction, we find that a sequential solution-deposition method, first spin-coating the polymer and then the fullerene, can produce reproducible, high-efficiency polymer-based solar cells. Part of the reason that the sequential deposition method works so well is that it leaves the polymer in a highly crystalline state, opening a long-range energy transfer mechanism that helps separate excitations on the polymer into charge carriers on the different organic components. In light of this new mechanism, we have reexamined the exciton diffusion length in polymeric materials like P3HT using both modified TiO_2 and fullerenes as quenchers, and found that when the polymer is highly crystalline, excitons can easily be quenched as distances of over ~30 nm. This is several times longer than the canonical numbers for the exciton diffusion length in the literature, and suggests several new routes for both developing new materials and optimizing device architecture to produce efficient, inexpensive, polymer-based solar cells.

3:05 - 3:45

T-A10 - MATERIALS AND DEVICES FOR ORGANIC PHOTOVOLTAIC DEVICES

[RPEMSC] Colin Nuckolls, Theanne Schiros, and Ioannis Kymissis
Columbia University

We are developing new organic semiconductor materials that are explicitly designed to give controlled nanoscale structure at the interface in heterostructure photovoltaic device configurations. One such concept is the development of a shape-complementary interface between curved donor (doubly concave contorted hexabenzocoronene) and acceptor (C_{60}) molecules. Devices based on this concept have achieved relatively high open circuit voltages within 10% of the theoretical limit. X-ray measurements indicate an extended "ball-and-socket" structure and fast charge transfer between molecular partners in intimate electronic contact at the donor-acceptor interface in bilayer device structures. The data suggests that the improved functional device performance results from an improved donor-acceptor interface that enhances exciton dissociation. A second concept involved development of materials that undergo a heat-induced self-assembly process to form pi-stacked, columnar superstructures that merge into a 3-D network of cables. The 3-D network functions as a scaffold for the molecular recognition and directed assembly of C_{60}, thereby forming a nanostructured p-n bulk heterojunction. When incorporated into a solar cell, this reticulated heterojunction provides a significant increase in the power conversion efficiency over the parent compound.

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

4:00 - 4:20
T-A11 - Excitonic Antennas for Solar Cells
[CE] Marc Baldo, Troy Van Voorhis, Jiye Lee, Priya Jadhav, Carmel Rotschild, and Phil Reusswig
MIT

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

4:20 - 4:40
T-A12 - Exciton Management in Organic Photovoltaics
[CEN] Mark Thompson[1], Barry C. Thompson[1], Stephen Bradforth[1], Sean Roberts[1], Matthew Whited[1], Robert McAnally[1], Beate Burkhart[1], Stephen Forrest[2], and Jeramy Zimmerman[2]
[1]University of Southern California; [2] University of Michigan

We have explored the use of both polymeric and molecular materials for extending the active wavelengths for photovoltaic devices into the near infrared. I will discuss the use of these materials as donor materials in both lamellar and bulk heterojunction OPVs, illustrating how these materials can be used to enhance both the efficiency and Voc.The exciton is a critical part of each of these processes, and being able to control the location, lifetime and energy of the exciton is essential to achieving high efficiency. We have investigated methods for tuning exciton energies and controlling their migration paths, both intramolecularly and within a thin film. I will discuss our most recent work with porphyrinic materials for OPVs. This involves a careful materials design study that leads to both low energy absorption (into the nearIR) and the use of substituted porphyrins to efficiently harvest photons through the entire visible spectrum. Both long wavelength and broad absorption are achieved with high extinction ($> 105\ cm^{-1}$). Moreover, we have measured the intra- and intermolecular exciton dynamics for both singlet and triplet excitons in these materials.

4:40 - 5:20
T-A13 - Dye-Sensitized Photoelectrosynthesis Cells: From Synthesis to Assembly
[UNC] Javier Concepcion, Rene Lopez, and Kenneth Hanson
UNC

The efficiencies of dye-sensitized solar cells (DSSCs) and dye-sensitized photoelectrosynthesis cells (DSPECs) are dictated by the interfacial structure, semiconductor, and intra-assembly dynamics. A UNC EFRC goal is to use a modular approach to DSPECs for water splitting and reduction of CO_2. In this approach, individual components for light absorption, intramolecular and interfacial electron and proton transfer, and catalysis are investigated and integrated in molecular assemblies on the surfaces of high band gap oxide semiconductors. Performance of the resulting device configurations is evaluated by transient laser, photocurrent, and product measurements. In this presentation we will summarize recent progress towards this goal including 1) synthesis and characterization of interfacial catalysts for water oxidation and CO_2 reduction, 2) development of vertically structured arrays of TiO_2, Nb_2O_5 and $SrTiO_3$ electrode materials fabricated by pulsed laser deposition, 3) strategies for assembly and stabilization of chromophores and catalysts on metal-oxide surfaces, and 4) quantitative evaluation of the resulting structures by laser spectroscopic and photocurrent measurements.

5:20 - 5:40

T-A14 - COMPUTATIONAL MOLECULAR ELECTROCATALYSIS: THE ROLE OF PROTON RELAYS IN H_2 OXIDATION AND EVOLUTION CATALYSTS

[CME] Michel Dupuis[1], Simone Raugei[1], Roger Rousseau, Shentan Chen, M.H. Ho, R. Morris Bullock, Daniel L. DuBois, Jenny Y. Yang, Sharon Hammes-Schiffer[2], Alexander V. Soudackov[2], Samantha Horvath[2], and Laura E. Fernandez[2]
[1]Pacific Northwest National Laboratory; [2]Pennsylvania State University

The rational design of improved molecular electrocatalysts for small molecule activation (for example H_2, O_2, N_2, H_2O) requires a detailed molecular level understanding of the energetic and mechanistic factors controlling the movement of protons and electrons during the catalytic cycle. $Ni(P_2N_2)_2^{2+}$ complexes are a family of mononuclear nickel complexes with cyclic diphosphine ligands that incorporate amine bases as a mimic of enzyme functionalities. The presence and positioning of the amine bases near the metal center is the critical structural feature for the activity[1-2] and the efficiency of these catalysts, as these bases facilitate the heterolytic cleavage or formation of the H-H bond while acting as proton relays in the management of the proton and electron movement during the catalytic cycle. We will highlight novel first-principles studies of the catalytic cycles of the $Ni(P_2N_2)_2^{2+}$ catalysts. Complexes with N-H and Ni-H bonds ("Proton-hydride" species) are key intermediates. H_2 oxidation and evolution proceed via heterolytic bond cleavage or formation of the H-H bond. We will discuss what we have learned about these catalysts, the importance of the proton relays, their number, their active and inactive states, the role of solvent and water molecules in giving rise to fast turnover rates, and aspects of proton coupled electron transfers in the electrocatalytic steps. The concept of proton relays is being extended to O_2 and N_2 reduction reactions. REFERENCES: [1] DuBois D. L. and Bullock R. M., Eur. J. Inorg. Chem. 2011, 1017; \r\n[2] Yang, J. Y.; Chen, S.; Dougherty, W. G.; Kassel, W. S.; Bullock, R. M.; DuBois, D. L.; Raugei, S.; Rousseau, R.; Dupuis, M.; Rakowski DuBois, M. Chem. Comm. 2010, 46, 8618.

5:40 - 6:00

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

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

The objective of this research is to design an artificial leaf that combines selected features of photosynthesis with dye-sensitized photovoltaic technology to achieve solar-to-fuel efficiencies that surpass those of photosynthesis or single-junction PV-driven electrolysis of water. Features from photosynthesis include pigments and catalysts inspired by those used in water-oxidizing photosystem II (PSII) and in bacterial photosynthesis. The combination of these two pigment systems in an artificial construct will harvest approximately twice the photon flux of natural photosynthesis, thereby providing a much improved match of the solar spectrum to the chemical work of driving water oxidation and proton reduction. Features and principles taken from technology include the use of DSSC-type photoelectrodes sensitized by these pigments and assembled in a tandem, two-junction system architecture. Excited dyes on the photoanode will inject electrons into semiconductors such as SnO_2, leaving an oxidized high-potential sensitizer to drive the catalyst. The second photosystem will be sensitized by low-potential naphthalocyanines/phthalocyanines which are functional mimics of bacteriochlorophyll and absorb light in the near IR. These dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to drive the reduction of protons to hydrogen. A redox relay will connect the output of the photoanode to the input of the low-potential photoelectrode.

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

8:00 - 8:20

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

[PHaSE] Todd Emrick
UMass-Amherst

This lecture will describe progress in the synthesis of novel conjugated polymers and nanocomposites with the ultimate objective of producing plastic solar cells with higher efficiency and at lower cost than can be done today. Two primary lines of research will be highlighted: 1) the synthesis of hybrid materials, in which semiconductor particles, such as quantum dots, are surface-functionalized with conjugated polymers, such as poly(phenylene vinylene) and poly(3-hexylthiophene), and 2) the fabrication of robust cross-linked assemblies and materials from functionalized polythiophene based diblock and triblock copolymers. Particularly noteworthy is the ability to stabilize crystalline forms of these conjugated polymers through cross-linking chemistry performed in solution and/or in the solid state. In addition to key synthetic elements, the structural and photophysical characterization of these materials will be presented, including UV-Vis absorption, photoluminescence, and transmission electron microscopy data that provides insight into polymer assembly in the solid state.

8:20 - 8:40

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

[CISSEM] David Ginger[1], Bradley Macleod[1], Andreas Tillack[1], Matthew Gliboff[1], Kristina Knesting[1], Hong Li[2], Jean-Luc Bredas[2], Sergio Paniagua[2], Seth Marder[2], Matthew Schalnat[3], Jeanne Pemberton[3], and Mariola Macech[3]
[1]University of Washington ; [2]Georgia Institute of Technology; [3]University of Arizona

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

8:40 - 9:00

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

[CSTEC] Theodore Goodson III
University of Michigan

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

9:00 - 9:20

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

[CE] Keith A Nelson
MIT

Direct measurements of exciton dynamics and transport are critical in order to reach a fundamental understanding and how exciton properties and interactions are mediated by factors that might be engineered, including chromophore electronic structure, multichromophore complexation and aggregation, and material morphology. We have developed a versatile method for conducting multidimensional coherent optical spectroscopy of excitons, multiexcitons, and exciton-polaritons in inorganic, organic, and hybrid systems. The measurements have revealed coherent multiexciton energetics and dynamics, correlations among multiple exciton-polaritons, and organic J-aggregate exciton correlation lengths and inhomogeneities. In a typical experiment, multiple optical fields in different beams interact with the sample in succession to generate exciton coherences, biexciton coherences, and perhaps triexciton and even higher-order coherences; a time period passes during which coherent exciton or multiexciton oscillations take place and additional optical fields reduce the multiexciton coherence to a single-exciton coherence that finally radiates the signal that is measured as a function of the time period, revealing the coherent oscillations, the multiexciton energetics and dephasing, and the extent of high-order multiexciton correlation that is possible. The entire measurement is controlled through reconfigurable beam shaping and femtosecond pulse shaping, with no interferometers or moving parts.

9:20 - 9:40
T-A20 - MEG TO MORPHOLOGY: THEORY APPLIED TO PHOTOVOLTAIC CONCEPTS
[RPEMSC] David Reichman, Ashraf Alam, and Mark Hybertsen
Columbia University; Purdue University and Brookhaven National Laboratories

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

Session B – Inorganic Photovoltaics - Grand Ballroom Central

Parallel Scientific Session I – May 26, 2011
Grand Ballroom

10:15 - 10:35 (Joint with Session A)
T-B01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA
[CST] Xiaoyang Zhu and Jennifer Lyon
University of Texas at Austin

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

1:45 - 2:05
T-B02 - EXCITONICS IN NANOCRYSTAL QUANTUM DOTS
[CE] Moungi Bawendi
MIT

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

2:05 - 2:25
T-B03 - NANOSTRUCTURED COMPOUND SEMICONDUCTORS FOR SOLAR ENERGY CONVERSION: FROM INTERFACES TO INTERMEDIATE BAND ABSORPTION
[CSTEC] Rachel Goldman, Roy Clarke, Steve Forrest, Harley Johnson, Peicheng Ku, Cagliyan Kurdak, Joanna Millunchick, Xiaoqing Pan, Jamie Phillips, Vanessa Sih, Katsuyo Thornton, and Ctirad Uher
University of Michigan

Currently, the highest efficiency solar cells are based upon compound semiconductor thin films. Further efficiency increases will require decreases in intrinsic loss mechanisms. Specifically, thermalization and transparency losses are linked as the bandgap energy cannot be simultaneously increased and reduced. Therefore, we are exploring new compound semiconductor materials architectures with outstanding electronic transport properties that can also absorb a greater portion of the solar spectrum. Within the inorganic photovoltaics thrust of CSTEC, we examine interface structure, carrier transport, and absorption in nanostructured compound semiconductors, including site-controlled nanostructures, type II bandoffset materials, and highly mismatched alloys. Our coupled experimental-computational approach has enabled several achievements including the discovery of bowing of the atomic layers within quantum dots (QDs), with a half-layer stacking shift that may provide electronic decoupling of the QDs from the substrate, the development of a phase-field crystal model to examine QD/cap interfaces, the development of a transmission electron microscopy method for real-time studies of photo-induced transformations of the structure and electrical properties, the achievement of luminescent site-controlled QDs, and new insights into the role of the wetting layer and QD size variations on the sub-bandgap external quantum efficiency of QD intermediate-band solar cells.

2:25 - 2:45

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

[CEN] Chenxi Lin, Ningfeng Huang, and Michelle L. Povinelli
University of Southern California

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

2:45 - 3:05

T-B05 - NANOPHOTONICS FOR OPTIMAL SOLAR THERMOPHOTOVOLTAIC SYSTEMS

[S3TEC] Marin Soljacic
MIT

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

3:05 - 3:25

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

[CASP] Victor I. Klimov
Los Alamos National Laboratory

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

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

4:00 - 4:20

T-B07 - WHAT WENT WRONG WITH PAST EFFORTS TO USE EARTH ABUNDANT ABSORBERS SUCH AS FES2: THE DESIGN OF A MATERIAL FIX.

[CID] Douglas Keszler[1], John Wager[1], and Liping Yu[2]
[1]*Oregon State University* [2]*NREL*

Realizing new, efficient solar absorbers containing earth-abundant materials represents a critical element for expanding the reach of photovoltaic (PV) technologies, meeting growing energy needs, and ameliorating atmospheric CO_2 concentrations. Among all of the elements, Fe is ranked fourth in terms of abundance in the earth's crust, and it is the least expensive metallic element to extract from Nature. The use of Fe in PV was proposed more than 25 years ago in the form of FeS_2 pyrite. Unfortunately, the material has been plagued by performance problems that to this day are both persistently present and not well understood. In this contribution, we report a concerted and integrated theoretical and experimental study that provides new insight into the problem of FeS_2. Computational results on FeS_2 reveal high formation energies for bulk point defects and small formation energies for S vacancies near the surface. These findings are consistent with the formation of metallic S-deficient binary Fe-S phases at low temperatures that affect the electrical and optical properties of thin films. We have used this new understanding to propose and implement design rules for identifying new Fe-containing materials – Fe_2SiS_4 and Fe_2GeS_4 – that may circumvent the limitations of pyrite. These ternary p-type materials have band gaps near 1.5 eV and absorption coefficients that exceed 105 cm^{-1} at E_g + 0.5 eV.

4:20 - 4:40

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

[ANSER] Joseph Hupp
Northwestern University

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

4:40 - 5:00

T-B09 - LIGHT TRAPPING AND ABSORPTION BEYOND CLASSICAL LIMITS

[LMI] Harry Atwater
California Institute of Technology

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

5:00 - 5:20

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

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

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

5:20 - 5:40

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

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

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

5:40 - 6:00

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

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

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

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

8:00 - 8:20
T-B13 - ADVANCED IN CHARGE MANIPULATION IN QUANTUM DOT ARRAYS AND ARCHITECTURES FOR 3RD GENERATION SOLAR CELLS

[CASP] Arthur J.Nozik
National Renewable Energy Laboratory

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

8:20 - 8:40
T-B14 - LIGHT CAPTURE IN SILICON MICROCELL PHOTOVOLTAICS

[LMI] John Rogers
UIUC

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

8:40 - 9:00
T-B15 - LIGHT HARVESTING WITH FRAMEWORK MATERIALS

[UNC] Wenbin Lin[1], Spiros Skourtis[2], Caleb A Kent[1], Demin Liu[1], Cheng Wang[1], Andre van Rynbach[2], Xiangqian Hu[2], Brian Mehl[1], Thomas Meyer[1], John Papanikolas[1], and David Beratan[2]
[1]University of North Carolina at Chapel Hill; [2]Duke University

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

9:00 - 9:20
T-B16 - DEVELOPMENT OF NOVEL NANOMATERIALS AS THE BUILDING BLOCKS FOR NEXT-GENERATION SOLAR CELLS
[CASP] Jeffrey M. Pietryga
Los Alamos National Laboratory

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

9:20 - 9:40
T-B17 - UNDERSTANDING CARRIER DOPING AND ELECTRICAL CONDUCTIVITY OF WIDE GAP OXIDES AS TRANSPARENT CONDUCTORS FOR SOLAR PHOTO CONVERSION.
[CID] Stephan Lany[1], Andriy Zakutayev[1], Thomas Mason[2], John Wager[3], Kenneth Poeppelmeier[2], John Perkins[1], Joseph Berry[1], David Ginley[1], and Alex Zunger [1]
[1]NREL; [2]Northwestern University ; [3]Oregon State University

Functional oxides in optoelectronic applications are today most commonly employed in the thin-film form, e.g. in photovoltaic energy conversion technologies. The materials and device design is, however, still guided by models for defect mechanisms that were developed half a century ago for bulk materials. The conductivity of transparent conducting oxides, for example, has been described by extrinsic dopants like Sn-on-In in In_2O_3, intrinsic defects like O-vacancies, or unintentional impurities like hydrogen. Such models, however, cannot account for the observation of very high conductivities above 1000 S/cm in pure In_2O_3 thin films. By a comparison of electronic structure theory predictions with transport measurements we show here that the traditional point defect mechanism of O-vacancy formation consistently describes the behavior of pure In_2O_3 in the bulk, but that such bulk concepts are insufficient and fail for thin-films. Instead, we find that the thin-film conductivity is dominated by surface donors having particularly low formation energies. This finding implies that oxides which are non-conductive or even non-dopable as bulk materials can nevertheless become highly conductive as thin films.

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

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

10:15 - 10:35 (Joint with Session A in the Grand Ballroom)
T-C01 - BOUNDLESS ENERGY: THE LIFE AND SCIENCE OF PAUL F. BARBARA
[CST] Xiaoyang Zhu and Jennifer Lyon
University of Texas at Austin
A memorial tribute to Paul F. Barbara (1953-2010), world-renowned laser spectroscopist, Professor of Chemistry at the University of Texas at Austin, member of the National Academy of Sciences and founding Director of the DOE Energy Frontier Research Center on Understanding Charge Separation at Interfaces in Energy Materials (EFRC:CST). Here we celebrate Paul's "lifetime in the excited state," including his numerous scientific achievements, academic developments and, above all, his tireless enthusiasm for the pursuit of fundamental scientific knowledge.

10:35 - 10:55

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

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

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

10:55 - 11:15

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

[ANSER] Michael R. Wasielewski
Northwestern University

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

11:15 - 11:35

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

[CME] R. Morris Bullock[1], Daniel L. DuBois[1], Michel Dupuis[1], James M. Mayer[2], Sharon Hammes-Schiffer[3], Bruce A. Parkinson[4], Jenny Y. Yang[1], Michael T. Mock[1], John A. S. Roberts[1], Simone Raugei[1], and Roger Rousseau[1]
[1]Pacific Northwest National Laboratory; Pacific Northwest National Laboratory; Pacific Northwest National Laboratory; [2]University of Washington; [3]Pennsylvania State University; [4]University of Wyoming

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

11:35 - 11:55

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

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

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

11:55 - 12:15

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

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

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

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

1:45 - 2:05

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

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

This paper will cover current research activities at the Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, with a focus on the theme of controlling catalysis at the nano-scale. The overarching goal is to understand catalysis for energy conversion reactions at the molecular level, and then to use that insight in developing materials and processes with increased performance. To accomplish this goal, we are combining theory and experiment to understand chemical and physical processes on surfaces, nano-structured materials, and biological systems. Results will be presented in the following areas: (1) Bandgap engineering of MoS_2 through quantum confinement effects, with relevance to solar fuel synthesis, (2) Development of active and stable hydrogen evolution catalysts based on nano-structured MoS_2, (3) Development of oxygen reduction catalysts and water oxidation catalysts based on manganese oxides, combining Density Functional Theory (DFT) calculations with experimental electrochemical surface science in order to tailor surface chemistry through nano-structure, (4) DFT studies of the influence of carbon supports onto the electronic and geometric structure of metal nanocatalysts, and (5) Investigation of photosynthetic membrane proteins by *in-situ* atomic force microscopy (AFM).

2:05 - 2:25

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

[PARC] Robert E. Blankenship and Himadri B. Pakrasi
Washington University in St. Louis

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

2:25 - 2:45

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

[PARC] Dewey Holten and C Neil Hunter
Washington University in St. Louis and University of Sheffield

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

2:45 - 3:05

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

[CABS] Edgar Cahoon
University of Nebraska

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

3:05 - 3:25

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

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

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

3:25 - 3:45

T-C12 - INTERACTIONS OF CELLULOSE WITH MATRIX POLYSACCHARIDES

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

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

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

4:00 - 4:40

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

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

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

4:40 - 5:00

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

[CLSF] Candace H. Haigler[1], Rami Alkhatib[1], Mark J. Grimson[2], James D. Kubicki[3], Le Li[1], Antonin Marek[1], Mohamed Naseer[3] Ali Mohamed[3], Tuyen Nguyen[1], Latsavongsakda Sethaphong[1], Abhishek Singh[1], Alex I. Smirnov[1], Maxim A. Voinov[1], and Yaroslava G. Yingling[1]
[1]North Carolina State University, North Carolina State University; [2]Texas Tech University; [3]The Pennsylvania State University

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

5:00 - 5:20

T-C15 - SELECTIVE TRANSFORMATION OF BIOMASS DERIVATIVES

[CCEI] Dion G. Vlachos
University of Delaware

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

5:20 - 5:40

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

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

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

5:40 - 6:00
T-C17 - CATALYSIS FOR BIOMASS REFORMING
[CCEI] Michael Salciccioli, Weiting Yu, Mark Barteau, Jingguang Chen, and Dion Vlachos
University of Delaware

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

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

8:00 - 8:20
T-C18 - COMPUTATIONAL AND ENABLING TECHNOLOGIES IN THE CENTER FOR ADVANCED BIOFUELS (CABS)
[CABS] Lisa Carey[1], Rahul Deshpande[1], David Gang[2] , Mahmoud Gargouri[2], Jeong-Jin Park[2], Leslie Hicks[3], Yair Shachar-Hill[1], Hongxia Wang[3], and Baichen Zhang[3]
[1]Michigan State University; [2]Washington State University [3]Donald Danforth Plant Science Center

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

8:20 - 8:40
T-C19 - PYROPROBE/TANDEM MASS SPECTROMETRY PROVIDES INSIGHTS INTO FAST PYROLYSIS OF BIOMASS
[C3Bio] Piotr Gawecki, Andrew D. Smeltz, Matthew R. Hurt, David J. Borton II, Nelson R. Vinueza, Nicholas J. Nugent, Rakesh Agrawal, W. Nicholas Delgass, Hilkka I. Kenttamaa, William E. Anderson, and Fabio H. Ribeiro
Purdue University

Fast pyrolysis appears to be a relatively simple and scalable process to transform biomass into fuels. However, the low quality and instability of the resulting bio-oil limit its utility. Since pyrolysis lasts from seconds to minutes at temperatures high enough to sustain multiple reactions, the resulting bio-oil is a very complex mixture of primary, secondary, and later products. C^3Bio has developed a novel technique utilizing a pyroprobe coupled with a tandem mass spectrometer to identify the primary reaction products of fast pyrolysis. In these experiments, sub-milligram samples were heated to 600 C at a rate of 1,000 C s^{-1}, with the reactions quenched instantly or after a specified time delay, and the products analyzed with a linear quadrupole ion trap mass spectrometer via chloride attachment atmospheric pressure chemical ionization. These experiments revealed that the major product of fast pyrolysis of cellulose is an isomer of levoglucosan, which re-polymerizes in the gas phase to predominantly yield either dimers, trimers or tetramers of this structure, depending on conditions. Similar results were obtained for intact (dried and crushed) sorghum biomass. Finally, a novel millisecond residence time "rocket" reactor capable of pyrolysing biomass at a rate of 10 grams per minute was used to determine the mass balance and demonstrate the feasibility of obtaining simple product distributions in laboratory-scale experiments.

8:40 - 9:00
T-C20 - MULTISCALE KINETIC KNOWLEDGE PROPAGATION - COMBUSTION CHEMISTRY OF SMALL HYDROCARBONS
[CEFRC] Hai Wang
University of Southern California

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

9:00 - 9:20
T-C21 - IDENTIFICATION OF NEW REGULATORY NETWORKS FOR INCREASING PLANT OIL ACCUMULATION
[CABS] Geliang Wang[1], Maoyin Li[1], Amanda Tawfall[1], Carlotta Peters[1], Brian Fanella[2] , and Xuemin (Sam) Wang[1]
[1]Donald Danforth Plant Science Center; [2]University of Missouri

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

9:20 - 9:40
T-C22 - DESIGN, ENGINEERING, AND PHOTOPHYSICAL CHARACTERIZATION OF ARTIFICIAL LIGHT-HARVESTING COMPLEXES USING SYNTHETIC CHLORINS AND MAQUETTES
[PARC] Goutham Kodali[1], Joseph W. Springer[2], Olga Mass[3], Lee A. Solomon[1], Tammer A. Farid[1], David F. Bocian[4], Christine Kirmaier[2], Jonathan S. Lindsey[3], Dewey Holten[2], Christopher C. Moser[1], and P. Leslie Dutton[1]
[1]University of Pennsylvania; [2]Washington University in St. Louis; [3]North Carolina State University; [4]University of California, Riverside

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

D – Energy Storage and Transmission - Congressional Hall A&B

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

10:15 - 10:55
T-D01 - ELECTRODE REACTIONS IN LITHIUM ION BATTERIES - FUNDAMENTAL RESEARCH AT NECCES
[NECCES] Clare P. Grey[1], Anton Van Der Ven[2], Hui-Chia Yu[2], and Katsuyo Thornton[2]
[1]Stony Brook University; [2]University of Michigan

NECCES' goals are to identify the key fundamental mechanisms by which electrode materials for rechargeable batteries operate and the factors that control the rate and the reversibility of these processes. This is done by investigating a series of systems (Thrusts 1 and 2, intercalation and conversion materials) and by developing novel methodologies and theoretical approaches (Thrusts 3 and 4, diagnostics and theory). This talk will provide a general overview of the activities of the center and specific examples of activities from the intercalation, diagnostics and theory thrusts. The Intercalation thrust, working closely with the theory and characterization thrusts, is focused on the elucidation of the ultimate limits of intercalation reactions for chemical energy storage, what factors prevent the limits from being reached, and how to overcome these barriers. We investigate pure intercalation systems, such as the olivine $LiFePO_4$, and materials that may exhibit intercalation and conversion chemistry, as well as intercalation chemistry combined with extrusion. The talk will illustrate how, by using a combination of theory -- from the atomistic level through to the continuum level -- in close concert with appropriate experiments, we can achieve a fundamental understanding of the electrochemical performance of these materials. A strong emphasis of NECCES is on the development of *in situ* and ex situ methods and multi-functional probes to investigate the mechanisms of electrode reactions under conditions that closely mimic those in operating batteries. Examples include the development of new *in situ* NMR and MRI approaches, the use of synchrotron sources to image electrodes by using a variety of different techniques, and approaches involving the investigation of single particles - from nanoparticles to large single crystals.

10:55 - 11:15
T-D02 - COLLABORATIVE ENERGY FRONTIER RESEARCH: CONTROLLED SILICON NANOSTRUCTURES FOR LITHIUM STORAGE
[NEES] John Cumings[1] and S. T. Picraux[2]
[1]Unversity of Maryland and [2]Los Alamos National Lab

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

11:15 - 11:35
T-D03 - UNDERSTANDING AND DESIGNING SURFACES AND INTERFACES IN LI-ION BATTERIES FROM FIRST PRINCIPLES
[CEES] Maria Chan[1], Scott Kirklin[2], Hakim Iddir[1], Kah Chun Lau[1], Jishnu Bhattacharya[2], David Snydacker[2], Jeff Greeley[1], Chris Wolverton[2], and Larry Curtiss[1]
[1]Argonne National Laboratory; [2]Northwestern University

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

11:35 - 11:55

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

[NECCES] Glenn Amatucci
Rutgers University

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

11:55 - 12:15

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

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

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

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

1:45 - 2:05

T-D06 - ELECTROCATALYTIC APPROACHES TO VIRTUAL HYDROGEN STORAGE

[CETM] Oana R. Luca[1], Steven J. Konezny[1], Jeremy Praetorius[1], Gary Yeager[2], Guillermo D. Zappi[2], David Simone[2], Grigorii L. Soloveichik[2], John B. Kerr[2], Judith Stein[3], Thomas Miebach[2], Chris E.D. Chidsey[4], Victor S. Batista[5], and Robert H. Crabtree[5]
[1]*Yale University;* [2]*GE Global Research;* [3]*LBNL;* [4]*Stanford University;* [5]*Yale University*

Energy storage is a vital part of any alternative energy economy, and more efficient methods are eagerly sought. Our proposed regenerative fuel cell [1,2] relies on reversible electrochemical hydrogenation/dehydrogenation of an organic liquid carrier or 'fuel' (L/LH_2) with Eq. 1 being the energy release step and Eq. 2 the storage step. $LH_{2n} + n/2\ O_2 \Rightarrow L + n\ H_2O$ (1) $L + n\ H_2O \Rightarrow LH_{2n} + n/2\ O_2$ (2) The main challenges are the choice of a suitable fuel, LH_n, and development of suitable electrocatalysts, ideally ones that can catalyze both steps: Eq 1 and 2. Each of these components must also be stable and active under the fuel cell conditions. We have computational and experimental data that incorporating N atoms into a carbocyclic framework results in suitable fuel thermodynamics. Electrocatalysts for Eq. 1-2 are entirely unknown so we have been looking at organocatalysts such as quinones, transition metal catalysts such as NNN pincer complexes and also outer sphere electron transfer catalysts. The problem will be finding the right selectivity pattern so as to avoid overoxidation and tuning the redox potentials of catalyst and fuel so they can work in harmony. The whole team has been in close contact during the work, with regular meetings, both physical and electronic, as well as exchange of materials for testing. [1]. R. H. Crabtree, Energy & Environmental Science, 1, (2008), 134-138. [2] G. L. Soloveichik, J.-C. Zhao, US Patent Application 2008/0248345 (2008).

2:05 - 2:25
T-D07 - THERMODYNAMIC AND ELECTROCHEMICAL STUDIES ON ORGANIC FUELS
[CETM] Davide L. Simone[1], Thomas Miebach[1], Matthew Rainka[1], Robert H. Crabtree2, and Grigorii L. Soloveichik[1]
[1]GE Global Research; [2]Yale University

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

2:25 - 2:45
T-D08 - NANOSCALE CONTROL OF THERMODYNAMIC POTENTIALS
[CNEEC] Bruce Clemens[1], Fritz Prinz[1], David Goldhaber-Gordon[1], Robert Sinclair[1], John Vajo[2], Ping Liu[2], Sung Chul Lee[1], Chia-Jung Chung[1], James Donough[1], Jang Wook Choi[1], Men Young Lee[1], James Williams[1] , Phil Van Stockum[1], James Mack[1], Jun Liu[2], Adam Gross[2], Elena Sherman[2], and Sky Mahoney[2]
[1]Stanford University; [2]HRL Laboratories

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

2:45 - 3:05
T-D09 - EMC^2: OVERVIEW AND FUTURE PROJECTIONS
[EMC2] Hector Abruna
Cornell University

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

3:05 - 3:25
T-D10 - Nano-Structured Surfaces and Interfaces for Efficient Energy Storage and Conversion
[HeteroFoaM] Matt Lynch[1], Min Kyu Song[1], Kevin Blinn[1], Lei Yang[1], Mostafa El-Sayed[1], Feng Liu[2], Andreas Heyden[3], Anil Virkar[2], Ken Reifsnider[3], and Meilin Liu[1]
Ga Tech; [2]University of Utah; [3]USC; University of Utah

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

3:25 - 3:45
T-D11 - Fuel Cells and Battery Materials: Challenges and Progress
[EMC2] Frank Disalvo and Michael Lowe
Cornell University

The EMC^2 thrust in fuel cells and battery materials involves a broad search for improved performance and durability in cathode and anode materials as well as new polymeric ionic conductors for electrode separators. We will briefly outline the synthetic and processing methods and strategies utilized in this search and the methods of characterizing such materials. Fuel cell activities include a combinatorial search for catalysts with enhanced activity, development of new methods for synthesizing complex catalysts as nanoparticles, and durable catalyst support systems that can replace carbon black. In addition, we discuss new separator materials that can enable the development of fuel cells that operate under alkaline conditions. Research on battery materials also is a broad-based investigation of cathode, anode, and electrolyte materials. Significant efforts are devoted to developing and characterizing new electrode architectures for active materials, including carbons for improved lithium-sulfur cathodes, carbon-metal oxide composites for lithium-based battery anodes, and redox-active macromolecules for supercapacitor and lithium-ion battery anodes. Concurrent development of nanoscale organic-inorganic hybrid materials is moving towards a single-ion conducting electrolyte with a large operational voltage window.

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

4:00 - 4:20
T-D12 - Pincer metal complexes as electrocatalysts
[CETM] Grigorii L. Soloveichik[1], Mark D. Doherty[1], Oltea Siclovan[1], Kenneth P. Zarnoch[1], Alex Usyatinsky[1], Guillermo D. Zappi[1], Oana R. Luca$_2$, Steven J. Konezny[2], Victor S. Batista[2], and Robert H. Crabtree[2]
[1]GE Global Research; [2]Yale University

In the proposed novel regenerative fuel cell [1,2] a hydrogenated organic liquid carrier ($L*nH_2$) is electrochemically dehydrogenated at the anode of a PEM fuel cell (cell discharge), while hydrogenation of the spent organic hydride L (reverse reaction) occurs during charge (Eq. 1). $L*nH_2$ + n/2 O2 -> L + n H_2O (1) Development of electrocatalysts for dehydrogenation and hydrogenation of organic hydrides, which are compatible with a low humidity proton exchange membrane, is critical for operation of the projected fuel cell. We have synthesized a series of cobalt, rhodium and iridium complexes with PCP and NNN pincer ligands as potential electrooxidation catalysts and studied those using standard electrochemical methods in different solvents. Cobalt NNN complexes demonstrate a reversible oxidation (Co^{2+}/Co^{3+}). An effect of different substituents (donor and acceptor) in the imino (pyridine) ligand on EÂ½ was analyzed. Electrochemical characteristics of rhodium and iridium pincer complexes have been evaluated. Measured redox potentials were compared with computational results based on the density functional theory calculations of free energy using the thermodynamic cycle formalism in conjunction with a continuum solvation model. Electrocatalytic properties of metal pincer complexes in the oxidation of hydrocarbons will be discussed. 1. R. H. Crabtree, Energy & Environmental Science, 1, (2008), 134-138. 2. G. L. Soloveichik, J.-C. Zhao, US Patent Application 2008/0248345 (2008).

4:20 - 4:40
T-D13 - CAPACITIVE ENERGY STORAGE
[MEEM] Bruce Dunn, Yunfeng Lu, Laurent Pilon, Sarah Tolbert, and Vidvuds Ozolins
UCLA

Our research on capacitive energy storage, one of three IRGs in the MEEM program, combines experimental and computational components to achieve fundamental understanding of charge storage processes in redox-based materials. These materials offer much higher energy densities than traditional double-layer capacitors, however, there are few reports of redox-active materials achieving specific capacitances comparable to their theoretical values. In this presentation, we will briefly describe our progress in three different areas. Electrochemical studies of Nb_2O_5 nanoparticles and mesoporous films indicate that this material is a very promising one for electrochemical capacitive storage. The material, when in the appropriate crystal phase, exhibits fast redox kinetics and our analysis shows that nearly all charge storage arises from pseudocapacitive processes. The second topic involves the fabrication of electrode architectures comprised of V_2O_5 nanowires and carbon nanotubes. The CNT network enhances charge transfer to the V_2O_5 nanowires so that the nanocomposite exhibits high levels of charge storage at high discharge rates for some 10,000 cycles. The third research area concerns our work on the charge storage properties of MOFs. Our initial results indicate that redox-active MOFs exhibit capacitive charge storage well above that attained by just the framework and the linker.

4:40 - 5:00
T-D14 - LITHOGRAPHICALLY PATTERNED MNO_2 NANOWIRE ARRAYS
[NEES] Reginald Penner and Yan Wenbo
University of California, Irvine

Linear arrays of delta-phase MnO_2 nanowires have been fabricated on glass. The performance of these arrays as Li^+ cathodes in aqueous solution has been evaluated and we report these results and our interpretation of them in this talk. Nanowire arrays (NWAs) were prepared using the Lithographically Patterned Nanowire Electrodeposition (LPNE) method. The nanowires within these arrays are millimeters in length and have a rectangular cross-section with adjustable heights and widths in the 20-60nm x 50-500nm range, respectively. The specific capacity of MnO_2 NWAs was measured by cyclic voltammetry as a function of the potential scan rate from 1 mV/s to 500 mV/s. The sp. capacity across this entire scan rate range increased with diminishing wire size and a diffusion-limited capacity was observed over this entire scan rate range for nanowires of all sizes. Accurate total mass estimates for the MnO_2 nanowires were obtained by calibrating the electrodeposition efficiency using quartz crystal microbalance gravimetry. The highest capacities observed were for the smallest nanowires - 20 nm in height x 200-300 nm in width - where 1300-1400F/g was measured at 1 mV/s and 200-400F/g was measured at 100 mV/s.

5:00 - 5:20
T-D15 - ELECTRICAL ENERGY STORAGE: USE-INSPIRED BASIC RESEARCH
[CEES] Michael Thackeray
Argonne National Laboratory

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

5:20 - 6:00
T-D16 - CONTACT ELECTRIFICATION: SEARCHING FOR ANSWERS TO THE MILLENIA-OLD QUESTION
[NERC] H. T. Baytekin[1], A. I. Patashinski[1], M. Branicki[2], B. Baytekin[1], and B. A. Grzybowski[1]
[1]*Northwestern University;* [2]*NYU*

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

E – Energy Conservation and Efficiency - Renaissance Ballroom East

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

10:15 - 10:55
T-E01 - HIGH PERFORMANCE NANOSTRUCTURED THERMOELECTRIC MATERIALS (NTHEM)
[RMSSEC] Mercouri Kanatzidis[1], Vidvuds Ozolins[2], David Seiman[1], Chris Wolverton[1], and Sergey Barabash[2]
[1]*Northwestern University;* [2]*UCLA*

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

10:55 - 11:15
T-E02 - NEW THERMOELECTRIC MATERIALS USING RARE EARTH NANOPARTICLE FOR INCREASED SEEBECK COEFFICIENT
[CEEM] John Bowers, Art Gossard, Chris Palmstrom, Ali Shakouri, and Shuji Nakamura
University of California, Santa Barbara

In this work, we present research on a number of novel thermoelectric materials using semimetal-semiconductor nanocomposites grown by molecular beam epitaxy (MBE). We study several different III-V semiconductors embedded with semimetallic RE-V compounds, including ErAs:InGaAs for n type and ErSb:InGaSb for p-type thermoelectric materials. Nanostructures of RE-V compounds are formed and embedded within the III-V semiconductor matrix. The thermoelectric properties have been engineered for enhanced thermoelectric device performance. Segmented thermoelectric power generator modules using 50 Î¼m thick Er-based nanocomposites have been fabricated and measured. Research on different rare earth elements for thermoelectrics is discussed. For high temperature thermoelectrics, two approaches are being pursued. We discuss fabrication and characterization of arrays of Si nanowires with sub-100 nm diameters with low thermal conductivities below 10 W/m-K. Promising measurements of InGaN/GaN based thermoelectrics up to 600C will also be presented.

11:15 - 11:55

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

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

This talk will start with a brief introduction to the solid-state solar-thermal energy conversion center (S^3TEC Center), followed by in depth discussion on phonon transport and solar thermoelectric energy conversion. The S^3TEC Center aims at advancing fundamental science and developing materials to harness and convert heat from the sun into electricity via solid-state thermoelectric and thermophotovoltaic technologies. Solar thermophotovoltaics (STPV) first use solar radiation to raise the temperature of a terresterial object, which then emits photons optimized to the bandgap of a photovoltaic cell to generate electricity. Solar thermoelectric energy conversion uses solar radiation to create a temperature difference across a solid-state material to generate electricity. For solar thermoelectric generation, the S^3TEC center aims at improving thermoelectric materials through detailed experimental and theoretical studies of electron and phonon transport in nanostructures and bulk materials. First-principle based simulations carried out at the Center show phonons contributing to heat conduction in solids have a wide range of mean free path distributions, pointing to the characteristic length scales needed to reduce phonon thermal conductivity via nanostructuring that can lead to improved thermoelectric figure of merits. Optical techniques are being developed at the Center to map out the distributions of phonon mean free path experimentally. Prototype devices developed at the Center using nanostructured thermoelectric materials points to the promising future of solar thermoelectric energy conversion.

11:55 - 12:15

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

[CSTEC] Ctirad Uher
University of Michigan

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

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

1:45 - 2:05

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

[RMSSEC] Ctirad Uher
University of Michigan

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

2:05 - 2:25

T-E06 - EFFECT OF ELECTRODE MORPHOLOGY AND MATERIALS CHEMISTRY ON POLARIZATION IN SOLID OXIDE FUEL CELLS

[HeteroFoaM] Anil Virkar[1], Wilson Chiu[2], Kenneth Reifsnider[3], Prasun Majumder[3], Fazle Rabbi[3], MD. Raihan[3], and Qianlong Liu[3]
[1]University of Utah; [2]University of Connecticut; [3]University of South Carolina

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

2:25 - 2:45

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

[SSLS] Mary Crawford[1], Weng Chow[1], Daniel Koleske[1], Normand Modine[1], Andrew Armstrong[1], Tania Henry[1], Jeffrey Tsao[1], Qi Dai[2], Jaehee Cho[2], and E. Fred Schubert[2]
[1]Sandia National Laboratories; [2]Rensselaer Polytechnic Institute

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

2:45 - 3:05

T-E08 - NANOSTRUCTURES FOR ENERGY GENERATION AND CONSERVATION

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

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

3:05 - 3:25
T-E09 - BEYOND 2D: NANOWIRES FOR SOLID-STATE LIGHTING
[SSLS] George Wang
Sandia National Laboratories

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

3:25 - 3:45
T-E10 - LIGHT-MATTER INTERACTION IN SUBWAVELENGTH PHOTONIC STRUCTURES
[SSLS] Arthur J. Fischer, Ganapathi Subramania, Ting S. Luk, Weng W. Chow, Eric A. Shaner, Daniel D. Koleske, and Igal Brener
Sandia National Labs

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

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

4:00 - 4:20
T-E11 - SUPERCONDUCTIVITY AS AN ENERGY CARRIER
[CES] George Crabtree
Argonne National Laboratory and University of Illinois at Chicago

Superconductors carrying high density currents with little or no heating offer unique solutions to fundamental grid challenges of the 21st century: high capacity power delivery in urban areas, long distance transmission of renewable electricity from remote sources to population centers, seamless interconnection of the three national power grids, and high capacity, low weight offshore wind turbines. Wide penetration of superconducting power technologies depends on raising the performance and lowering the cost of second generation high temperature superconducting coated conductors based on $YBa_2Cu_3O_7$. The Center for Emergent Superconductivity has identified two grand challenges for advancing superconducting power applications: raising the magnitude and lowering the anisotropy of the critical current of commercial superconducting wires. Working with industry partners, we show that splayed columnar defects produced by heavy ion bombardment at Argonne's ATLAS accelerator raise the lowest critical current values of commercial superconducting wire by a factor of two, and reduce the anisotropy from a factor of ~ 2 to a factor of ~ 1.2. These results provide a proof of principle that splayed columnar defects are an effective route to addressing the two grand challenges of superconducting power applications.

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

[HeteroFoaM] Emily Carter[1], Andreas Heyden[2], Hanno Zur Loye[2], Prasun Majumdar[2], Kyle Brinkman[2], and Fanglin Chen[2]
[1]Princeton University; [2]University of South Carolina

Solid oxide fuel cells (SOFCs) can directly convert the chemical energy in the fuel directly to electrical energy with very high energy conversion efficiency and fuel flexibility. Electrodes provide active sites where the electrochemical reactions taking place in SOFCs. One particular issue that arises with the use of conventional Ni-based anode in SOFCs is their dimensional instability when subjected to redox (reduction–oxidation) cycling. On the other hand, when SOFCs are operated at very high current density, O_2 partial pressure at the cathode triple phase boundary region is quite low, potentially causing partial decomposition of the conventional manganite and colbaltite-based material and thus long-term deterioration of the cell performance. In addition, if the electrode is a mixed ionic and electronic conducting material, the triple phase boundary sites can be extended beyond the physical interfaces between the electrode and the electrolyte, consequently enhancing the electrode electrochemical performance. We have recently discovered a perovskite based on $Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) which has demonstrated excellent redox stability and electrochemical performance in both reducing and oxidizing environment. SFM has been applied as both anode and cathode on $La_{0.8}Sr_{0.2}Ga_{0.87}Mg_{0.13}O_3$ (LSGM) electrolyte supported cells, achieving a peak power density of 835 $mW \times cm^{-2}$ at 900 ^oC using H_2 as fuel and ambient air as oxidant, in spite that the LSGM electrolyte has a thickness of 265 mm.

4:40 - 5:00
T-E13 - DEVELOPMENT OF KINETIC MODELS FOR METHYL-ESTER MOLECULES FOR BIODIESEL MODELING

[CEFRC] Pascal Divart[1], Stephen Dooley[1], Sang Hee Won[1], Frederick L. Dryer[1], Yiguang Ju[1], Emily A. Carter[1], Chung K. Law[1], Fokion Egolfpoulos[2], Ronald K. Hanson[3], Stephen J. Klippenstein[4], Nils Hansen[5], and Chih-Jen Sung[6]
[1]Princeton University; [2]University of Southern California; [3]Stanford University; [4]Argonne National Laboratory; [5]Sandia National Laboratories and [6]University of Connecticut

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

5:00 - 5:20
T-E14 - COMPARING IRON-BASED AND COPPER-BASED HIGH TEMPERATURE SUPERCONDUCTORS

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

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

5:20 - 5:40
T-E15 - ENERGY FRONTIER RESEARCH UNDER HIGH PRESSURES
[EFree] Ho-kwang Mao
Carnegie Institution

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

5:40 - 6:00
T-E16 - CES HIGH TEMPERATURE SUPERCONDUCTING MATERIALS RESEARCH, PRESENT AND FUTURE
[CES] Peter Abbamonte
University of Illinois at Urbana-Champaign

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

F – Carbon Capture and Sequestration - Renaissance Ballroom West A

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

4:00 - 4:20
T-F01 - COMPUTATIONAL CARBON CAPTURE
[CGS] Berend Smit[1], Joe Swisher[1], Maciej Haranczyk[2], Jeff Neaton[2], Roberta Poloni[1], Giullia Galli[3], Laura Gagliardi[4], Allison Dzubak[4], Jihan Kim[5], and Richard Martin[5]
[1]UC Berkeley [2]LBNL; [3]UC Davis; [4]U Minnesota [5]LBNL

Metal organic frameworks are a promising class of materials for carbon capture. As one can change the metal, the linker, and the structure of these frameworks there are nearly an infinite number of possible materials that can be synthesized. To support the experimental efforts in the EFRC a computational carbon capture research program focused on finding the optimal material. The aim of the computational research is to develop the methodology to predict the properties of a metal organic framework before the material has been synthesized. To achieve this we combine quantum mechanical calculations to obtain detailed insights in the interaction of CO_2 with these materials, molecular simulations to compute those thermodynamic and transport properties that are important for the separation, and finally a simple separation design to compare energy costs of various materials for a typical flue gas separation. As we need to screen many millions of different materials chemoinformatic techniques are developed to efficiently screen so many structures. In this presentation the integration of the various approaches is illustrated with some examples of adsorption studies of mixtures of CO_2 in various materials.

4:20 - 4:40

T-F02 - CARBONATE MINERAL NUCLEATION PATHWAYS

[NCGC] A. Fernandez-Martinez[1], A. Radha[2], A.G. Stack[3], L. Hedges[1], Y. Hu[4], A. Loulier[4], L. J. Banuelos[3], G. Rother[3], Y.S. Jun[4], S. Whitelam[1], D. R. Cole[5], A. Navrotsky[2], G.A. Waychunas[1], and J.J. DeYoreo[1]
[1]Lawrence Berkeley National Laboratory; [2]University of California, Davis; [3]Oak Ridge National Laboratory; [4]Washington University in St. Louis; [5]Ohio State University

A key characteristic of CO_2 storage in geological reservoirs is the presence of a porous medium that confines the geological fluid. Experimental and theoretical studies in our Center aim to understand how this confinement affects nucleation of carbonate minerals - the main expected contributors to mineral trapping of CO_2 - and the extent to which these pores are availability as nucleation sites. Neutron scattering experiments have shown that nucleation of $CaCO_3$ in model silica nano-pores is possible under mildly saturated conditions, proving that nano-confinement -and its associated solvent-structuring effects- does not prevent nucleation. Statistical mechanical models of pore nucleation reveal how pore geometries and surface characteristics control the free energy barriers to nucleation within pores as well as out into the surrounding solution. The results suggest strategies for enhancing nucleation in the experiments. In the last few decades, a new $CaCO_3$ nucleation pathway involving the initial formation of an amorphous phase (ACC) has been reported to occur in many systems. It has also been reported that the presence of Mg^{2+} ions in ACC increases its stability. In an effort to understand carbonate mineral nucleation pathways, we have studied the structural and energetic properties of ACC, confirming its thermodynamicly metastable character and its increased stability upon dehydration, and showed how variations in the Ca-to-Mg ratio help to stabilize the amorphous phase.

4:40 - 5:00

T-F03 - MOLECULAR, CHEMICAL AND PHYSICAL PROPERTIES OF CO_2-H_2O - ELECTROLYTE-MINERAL SYSTEM

[CFSES] Philip Bennett[1], Susan Altman[2], Bayani Cardenas[1], Randall Cygan[2], Eugenio Santillan[1], Matthew Kirk[2], Molly Kent[1], Kuldeep Chaudhary[1] and Wen Deng[1]
[1]University of Texas at Austin; [2]Sandia National Laboratories

Understanding the processes and risks associated with the geological storage of CO_2 requires an understanding of the properties and interactions of complex mixtures of reactive fluids that will fundamentally alter the preexisting steady state conditions of the subsurface environment. Dissolved CO_2 alters aqueous phase density and viscosity, and therefore its flow properties through porous media, while providing abundant acidity in the form of carbonic acid that will result in accelerated water-rock reactions and toxic metal mobilization, resulting in extreme geochemical disequilibrium extending across many orders of magnitude in length scale. This EFRC is investigating the physical, chemical, and biological consequences of geologic CO_2 storage from the molecular to basin scale, using experimental, field, and computational methods, with the goal of integration using numerical simulations. Our observations and simulations are providing insight into molecular-scale interactions of supercritical CO_2 with water and solutes, pore scale movement of CO_2 in brines, the reaction rates of CO_2 dissolution, physico-chemical properties of CO_2 in complex brines, changes in microbial activity caused by geological CO_2 storage, toxicity of CO_2 to subsurface microbial communities, and impact of subsurface biofilms in pore clogging. These data and interpretation are being incorporated into larger scale modeling to offer a realistic simulation of carbon dioxide sequestration in the subsurface

5:00 - 5:20

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

[NCGC] Ian Bourg
Lawrence Berkeley National Laboratory

Geological carbon sequestration (GCS) is an emerging technology that could potentially offset up to 12% of global CO_2 emissions by 2020 and up to 45% by 2050. Pilot studies have firmly established the feasibility of injecting CO_2 in geological formations in quantities of up to several megatonnes per year for durations of up to 15 years. Commercial-scale implementation of GCS will require the demonstration that much larger plumes of buoyant CO_2 (hundreds of megatonnes) can be safely stored, with negligible leakage, for durations of thousands of years, as required to achieve permanent CO_2 sequestration through naturally-occurring rock weathering reactions. A critical knowledge gap, at this point, is the long-term sealing integrity of low-permeability caprocks with respect to an underlying buoyant plume of supercritical CO_2. Here, we describe how molecular-dynamic simulations of mineral-CO_2-brine systems are contributing to reveal the molecular-scale processes (such as adsorption, diffusion, surface wetting, and capillary pressure) that determine the sealing properties of nanoporous cap-rocks.

5:20 - 5:40

T-F05 - MULTISCALE SIMULATION OF CO_2 SEQUESTRATION IN SUBSURFACE MEDIA

[CFSES] Steven Bryant[1], Matt Balhoff[1], David DiCarlo[1], Sanjay Srinivasan[1], Tom Dewers[2], Hongkyu Yoon[2], Peter Eichhubl[1], Behdad Aminizadeh-Goharrizi[1], Tie Sun[1], Yashar Mehmani[1], Matt Roberts[1], and Valentina Prigiobbe[1]
[1]University of Texas at Austin; [2]Sandia National Laboratories

The long-term security of CO_2 sequestered in geologic formations is an important pre-requisite for this form of greenhouse gas mitigation. If CO_2 escapes from its storage formation, a critical question is whether the CO_2 flux becomes focused or diffused as it approaches the Earth's surface. Several physical and chemical processes occur at small scales (individual pores 10 microns across) that govern the destiny of sequestered CO_2 at much larger scales (100 m to 100 km). These processes include the geochemical alteration of sedimentary rocks as water saturated with CO_2 migrates through them and the consequent alteration of flow paths within those rocks. We present methods that account for coupled processes at the relevant scale but uniquely allow prediction of their macroscopic consequences. The coupled phenomena are overlaid on an already heterogeneous background flow field in the subsurface. We illustrate this in a geologic fault, which is potential escape route for CO_2 or CO_2-saturated water. The implications of the influence of interfacial phenomena (surface energy at the CO_2/water meniscus) on the large-scale path of the CO_2 plume are examined at the field scale. Finally we describe experimental results that validate the small scale models, and another set of experiments that show how to prevent a focused flux of CO_2 by means of emplacing water loaded with suitably treated nanoparticles.

5:40 - 6:00

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

[CGS] Omar M. Yaghi
UCLA

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

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

8:00 - 8:20

T-F07 - BASIC SCIENCE FOUNDATIONS FOR SUBSURFACE ENERGY SECURITY

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

The Center for Frontiers of Subsurface Energy Security (CFSES) is pursuing scientific understanding of multiscale, multiphysics processes to ensure safe and economically feasible storage of carbon dioxide and other byproducts of energy production without harming the environment. We are integrating and expanding our knowledge of physical, chemical and biological processes from the molecular scale to the field scale, using both experimental and modeling approaches to better understand and quantify behavior far from equilibrium. Ultimately, we will obtain capabilities to better predict long term behavior of subsurface storage. The presentation describes foundational science activities that the Center is pursuing in order to address several questions that are critical for assessing the safety and security of subsurface disposal of energy production byproducts. How does supercritical CO_2 interact with water, brines, mineral surfaces,and bacterial growth as it flows through the subsurface? What are the relevant physics of CO_2 fate and transport in the subsurface,and how can these be synthesized,upscaled,and incorporated into more powerful continuum models? Can we engineer solutions to mitigate contaminant leakage from natural and anthropogenic leakage pathways? How can we represent the essential features of large-scale behavior (flow, transport, reaction and deformation in the Earth's subsurface) that emerge from small-scale phenomena, without resolving all small-scale features?

8:20 - 8:40

T-F08 - PROBING CO_2-RICH FLUID INTERACTIONS WITH RESERVOIR ROCKS: FROM ATOMIC TO PORE SCALES

[NCGC] Gernot Rother[1], Larry Anovitz[1], Ariel Chialvo[1], David Cole[2], Mirek Gruszkiewicz[1], Andrew Stack[1], Lukas Vlcek[1], and Garrison Sposito[3]
[1]Oak Ridge National Laboratory; [2]Ohio State University and [3]Lawrence Berkeley National Laboratory

The fate of CO_2 deposited in subsurface storage reservoirs is initially controlled by sorption and capillary trapping processes, with the possibility of formation of a buoyant plume rich in CO_2. Using a combination of experimental and simulation techniques, we study the interactions of supercritical CO_2 with reservoir and caprock materials at the nanoscale. We will discuss the properties of CO_2 in nanoporous silica materials with different nano-scale pore morphologies, which serve as proxies for natural quartz-rich rocks and sediments. Vibrating tube densimetry, excess sorption, and neutron scattering techniques are used to quantify the amount of fluid in the pore spaces and its distribution between the adsorbed and unadsorbed fluid phases, yielding a microscopic picture of pore-confined supercritical fluids. The impacts of pressure, temperature and fluid morphology will be discussed and conclusions for CO_2 storage applications drawn. Molecular-based simulations link to the experimental data and enhance our understanding of fluid-solid phenomena at the atomic level. Neutron Scattering and electron microscopy data are used to characterize the structure and pore features of natural rocks. Fractal concepts are employed to describe the multi-scale pore network. The impacts of the nano-scale pore network structure on fluid flow properties are studied by neutron tomography, addressing the mechanism of reservoir rock filling with CO_2 and migration processes of CO_2-rich plumes.

8:40 - 9:00

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

[MEEM] Omar M. Yaghi
UCLA

Zeolitic Imidazolate Frameworks (ZIFs) are an important class of materials that share many of the characteristics of zeolites, in that they are porous, crystalline and have similar atom geometries. ZIFs are comprised of tetrahedral metal centers (Zn^{2+}, Cd^{2+}, and Co^{2+}) with bridging imidazolate units. The intrinsic crystallinity and porosity of ZIF materials, combined with the many topologies that can be obtained when combining a metal tetrahedron with imidazolate, make ZIFs ideal for the study of gas adsorption. First, this talk will focus on the efficient synthesis of ZIF materials. The technique of high throughput will be highlighted as an efficient method to access a wide range of ZIF materials.Many factors, including metal center, functionality, and topology have been shown to affect gas adsorption. In our study, we chose to select ZIFs in which one aspect of the ZIF structure is altered in order to see how the gas adsorption properties change. From the wide range of ZIF frameworks that have been synthesized, we selected five ZIF materials with the same underlying topology, RHO, but with different functionalities decorating the imidazolate. The functionalities including -CHO and $-NH_2$, were shown to enhance CO_2 adsorption; the results are supported by computation. Finally, the talk will highlight the role topology can play on gas adsorption; two ZIF frameworks, ZIF-93 and -94, were selected because they possess identical components but have different functionalities.

9:00 - 9:20

T-F10 - TOWARD MOLECULARLY DEFINED POROUS MEMBRANE

[CGS] Ting Xu
University of California, Berkeley

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

G – Materials in Extreme Environments - Renaissance Ballroom West A

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

10:15 - 10:35
T-G01 - WHAT SUB-PICOSECOND X-RAY DIFFRACTION WILL TELL US ABOUT THE STRUCTURAL DYNAMICS OF DISPLACEMENT CASCADES
[CDP] Ben Larson, Jon Tischler, Roger Stoller, Yuri Osetskiy, Rad Radhakrishnan, Haixuan Xu, and Don Nicholson
Oak Ridge National Laboratory

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

10:35 - 10:55
T-G02 - THE EFRC MICROSTRUCTURAL CHARACTERIZATION OF ION IRRADIATED CeO_2
[CMSNF] Peng Xu[1], Clarissa Yablinsky[1] , Anthony Schulte[1], Todd Allen[1], Brent Heuser[2], Jian Gan[2],
In-Wook Park[3], John Moore[3], and Jianliang Lin[3]
[1]University of Wisconsin-Madison; [2]University of Illinois; [2]Idaho National Laboratory; [3]Colorado School of Mines

Microstructural development in nuclear fuels has a strong impact on fuel performance. The fundamental processes governing the fuel microstructure in a reactor involve fission gas effect, displacement damage from nuclear stopping, electronic excitation from electronic stopping, chemical effect due to fission product and transmutation, and temperature gradient effect. The first part of the presentation highlights the important microstructural features observed in the irradiated UO_2 fuels under various conditions in open literature. The second part summarizes the microstructural characterization of ion irradiated CeO_2, a commonly used surrogate for UO_2. Ion irradiation experiments with well controlled parameters allow to examine the separate effects on the microstructure. The ion irradiation studies for CeO_2 consist of large grain vs. small grains for the grain size effect on defect evolution, the high energy (>102 MeV) swift ion irradiation for fission fragment effect, Kr ion irradiation for fission gas effect, and proton irradiation for fast neutron effect. Microstructures and substructures were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The experimental work and results are important to support the modeling work on the materials science of UO_2 microstructural development.

10:55 - 11:15
T-G03 - EFREE ACTIVITY AT THE SPALLATION NEUTRON SOURCE
[EFree] Guthrie Malcolm[1], Boehler Reini[1], Karotsis Georgios[1], Tulk Chris[2], dosSantos Antonio[2], Molaison Jamie[2],
Pradhan Neelam[2], Somayazulu Maddury[3], and Strobel Tim[3]
[1]Carnegie Institution; [2]Oak Ridge National Laboratory and [3]Carnegie Institution

The mission of our Energy Frontier Research in Extreme Environments EFRC is to use extreme pressures and temperatures to fabricate, modify and understand new materials for energy science. Comprehensive understanding of atomic-level structure is fundamental in this endeavor, and neutron diffraction is a vital tool, with its unique advantages for determining the structure of light-atom and non-crystalline materials and also characterizing long-range magnetic order. Correspondingly, neutron capabilities cut through a broad swath of our research program and impact many diverse projects including studies of hydrogen rich fuels, novel superconducting and magnetocaloric materials and the structural characterization of polyamorphic transitions in metallic glasses and nanomaterials. However, the conditions of most interest - pressures and temperatures sufficient to radically alter chemical bonding - can only be applied to microscopic samples, many orders of magnitude smaller than conventional neutron sources can see. However, the intense neutron flux of the new Spallation Neutron Source at Oak Ridge National Laboratory has made these measurements feasible for the first time. The ambitious science agenda of EFree is driving a tight-knit collaboration with SNS staff, with the aim of realizing necessary breakthrough technological developments to explore these new frontiers. The latest achievements of this collaboration will be presented in terms of the impact on the science of our EFRC.

11:15 - 11:35

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

[CDP] Randolph Q. Hood[1], P. R. C. Kent[2], and Fernando A. Reboredo[3]
[1]Lawrence Livermore National Laboratory; [2]Oak Ridge National Laboratory and [3]Oak Ridge National Laboratory

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

11:35 - 11:55

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

[CMIME] Blas Uberuaga[1], Xian-Ming Bai[2], Richard Hoagland[1], Arthur Voter[2], and Mike Nastasi[2]
[1]Los Alamos National Laboratory; [2]Idaho National Laboratory

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

11:55 - 12:15

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

[CDP] George M. Pharr[1], Yanfei Gao[1], Easo P. George[1], K.S. Kumar[2], Michael J. Mills[3], B.C. Larson[4], Andrew M. Minor[5], Ian M. Robertson[6], and Eliot D. Specht[7]
[1]University of Tennessee and Oak Ridge National Laboratory; University of Tennessee and Oak Ridge National Laboratory; Oak Ridge National Laboratory and University of Tennessee ; [2]Brown University; [3]The Ohio State University; [4]Oak Ridge National Laboratory; [5]University of California Berkeley; [6]University of Illinois and [7]Oak Ridge National Laboratory

A primary goal of the Center for Defect Physics is to provide a fundamental understanding, at the level of unit events, of the defect interactions that determine the mechanical properties of structural materials. Since the strength of metals is controlled primarily by dislocations, quantification of single dislocation interactions with other defects is of paramount importance in understanding their mechanical behavior. Achieving this goal requires coordinated efforts from diverse research groups to develop new testing methodologies and verify their capabilities. Here, we report on progress toward these goals based on 3D X-ray Microscopy (3D-XM), a synchrotron-based technique that uses highly focused x-rays to quantify strength-controlling defects. Recent progress includes: preparation of simple dislocation configurations in hcp metals to serve as model specimens for initial measurements; development of nanoindentation techniques to produce controlled dislocation structures for examination in both static and dynamic experiments; proof-of-principle experiments to measure lattice rotations and stresses near dislocations; development of electron tomography techniques to characterize the 3D nature of dislocation structures; verification of dynamic defect interactions by quantitative *in-situ* TEM experiments; finite element modeling to interpret the development of slip and deformation during indentation and improvements in x-ray beam focusing to enhance spatial resolution.

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

1:45 - 2:05
T-G07 - ACTINIDE MATERIALS UNDER THE EXTREME CONDITIONS OF TEMPERATURE, PRESSURE AND INTENSE RADIATION FIELDS

[MSA] Maik Lang
University of Michigan

For the future energy needs, materials must be developed that display exceptional performance under extreme conditions. At the University of Michigan, we pursue a new experimental strategy that allows us to investigate the properties of solids simultaneously under coupled extreme conditions. This approach is based on the combination of large ion accelerator facilities, diamond-anvil cells and laser-heating experiments. We are currently developing this approach for actinide-bearing materials and have completed a systemic investigation on CeO_2. The cubic structure of this analogue for U and Pu containing compounds is very resistant to phase changes under pressure or ion irradiation. Ion-beam exposure with GeV ions at ambient conditions to a fluence of up to 8Ã—1012 cm^{-2} did not result in any evidence of amorphization, but a minor amount of radiation-induced fragmentation into nanocrystals was observed. In contrast, the application of high pressure in excess of 35 GPa leads to the formation of a cotunnite-like high-pressure phase. However, this behavior is significantly changed when irradiation is additionally applied at high pressure, and the transformation takes place at an unexpectedly low pressure (~15 GPa). This highlights the extreme conditions prevailing within tracks of energetic heavy ions. We have demonstrated in complex oxides (e.g., Gd_2TiO_5) that such projectiles trigger highly non-equilibrium collective processes, which result in multiple nanoscale phase transitions.

2:05 - 2:25
T-G08 - CHARACTERISTIC INTERFACES IN METALLIC COMPOSITES SYNTHESIZED BY SEVERE PLASTIC DEFORMATION

[CMIME] Irene Beyerlein[1], Nathan Mara[1], Jian Wang[1], Jon Ledonne[2], Tony Rollett[2], Nhon Vo[3], Pascal Bellon[3], Bob Averback[3], Ruifeng Zhang[4], and Keonwook Kang[4]
[1]Los Alamos National Laboratory [2]Carnegie Mellon University; [3]University of Illinois; [4]Los Alamos National Laboratory and Los Alamos National Laboratory

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

2:25 - 2:45
T-G09 - NUCLEAR FUEL THERMAL CONDUCTIVITY INSIGHTS FROM PHONONS IN UO2

[CMSNF] Judy Pang[1], Alexsandr Chernatynskiy[2] , Bill Buyers[3] , Mark Lumsden[4] , Bennett Larson[5] , and Simon Phillpot[2]
[1]Oak Ridge National Laboratory; [2]University of Florida ; [3]National Research Council, [4]Chalk River Laboratories, Canada

Understanding thermal transport in nuclear fuel will require accounting for a wide range of phonon scattering processes, including anharmonic as well as radiation induced phonon scattering mechanisms. Over the last five decades there have been relatively few fundamental studies of phonons in the context of thermal conductivity in uranium oxide considering its widespread use as a reactor fuel. We have made high-resolution inelastic neutron scattering measurements of phonon dispersion, lifetimes, and group velocities in single crystal uranium oxide at ambient and high temperature, 1200K. In contract to conventional expectations, the phonon lifetimes at high temperature were found to depend strongly on wavevector, and it was inferred that longitudinal optical and transverse acoustical phonons contribute as strongly as longitudinal acoustical phonons to thermal transport at high temperature. Lattice dynamics simulations of phonon lifetimes in this project predict non-monotonic, wavevector dependent lifetimes for uranium oxide at high temperature, in qualitative agreement with the neutron scattering results. However, the strong thermal conductivity inferred for the longitudinal optical and transverse acoustical modes are in stark contrast to recent first principles calculations. These measurements provide benchmarks for lattice dynamics simulations and input for Boltzmann transport equation thermal modeling.

2:45 - 3:05
T-G10 - ENABLING ATOMIC-SCALE DESIGN OF RADIATION-RESISTANT NANOCOMPOSITES BY TAILORING INTERFACES
[CMIME] Michael Demkowcz[1], Amit Misra[2], Michael Nastasi[2], and Richard Hoagland[2]
[1]*MIT; and* [2]*Los Alamos National Laboratory*

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

3:05 - 3:25
T-G11 - A NOVEL SUPERHARD SP3-BONDED NON-CRYSTALLINE CARBON ALLOTROPE
[EFree] Yu Lin, Li Zhang[1] , Ho-kwang Mao[2], Paul Chow[3], Yuming Xiao[3], Maria Baldini[3], Jinfu Shu, and Wendy L. Mao[1]
[1]*Stanford University;* [2]*Carnegie Institution of Washington;* [3]*Carnegie Institution of Washington*

Compressing glassy carbon above 40 GPa, we have observed a new carbon allotrope with a fully sp^3-bonded glassy structure and a diamond-like strength. Synchrotron x-ray Raman spectroscopy revealed a continuous pressure-induced sp^2-to-sp^3 bonding change, while x-ray diffraction confirmed the perseverance of the amorphous structure. The transition was reversible upon releasing the pressure. Used as an indentor, the glassy carbon ball demonstrated its exceptional strength by reaching 130 GPa with a confining pressure of 60 GPa. Such extremely large stress difference of >70 GPa has never been observed in any material except diamond, thus offering the exciting potential as a pressure-hardened superhard glass.

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

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

10:15 - 10:55
T-H01 - INTEGRATION OF NOVEL SYNTHESES, EXPERIMENTS AND MOLECULAR MODELING REVEALS FUNDAMENTAL PROPERTIES OF ELECTRODE/ELECTROLYTE INTERFACES
[FIRST] David J. Wesolowski[1], Sheng Dai[1], and Peter T. Cummings[2]
Oak Ridge National Laboratory and Vanderbilt University

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

10:55 - 11:15

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

[CCEI] Abhimanyu Jayakumar[1], Rainer Kangas[1], Sounak Roy[2], Ashay Javadekar[2], Douglas J. Buttrey[2], John M. Vohs[3], and Raymond J. Gorte[3]

[1]*University of Pennsylvania;* [2]*University of Delaware;* [3]*University of Pennsylvania*

It would be extremely attractive to convert solid, carbonaceous fuels directly to electrical energy using electrochemical methods, since this could be very efficient and allow for easy CO_2 capture. Although first attempts have been made in the development of Direct Carbon Fuel Cells (DCFC), the performance levels reported so far are insufficient to make this technology commercially viable. Here we demonstrate the generation of electricity at high power densities, >300 mW/cm^2 at 973 K, from solid fuel (sugar char) in a Solid Oxide Fuel Cell (SOFC) using a molten Sb anode. These power densities are comparable to state-of-the-art H_2-fuelled SOFCs. The anode design is simple and capable of operating continuously on a wide range of carbonaceous fuels, including sugar, rice starch, carbon black, and graphite.

11:15 - 11:35

T-H03 - MODELING LI^+ DIFFUSION IN BATTERY MATERIALS

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

University of Texas at Austin

During the development process of new battery materials, calculations are used to help understand what is observed in experiments. Two specific examples are given. For the layered cathode Li_2MnO_3, oxygen is seen to evolve from the material in the first charge cycle. Substitution of Ti in place of Mn is seen to reduce oxygen loss whereas Co increases it. This trend is understood with calculations of the electronic band structure in which a correlation is found between the band gap and the stability of oxygen. In a second example, potassium niobate (KNb_5O_{13}) was investigated as a possible anode material because the Li insertion potential is above that of solid-electrolyte interface formation. Experiments of charge/discharge cycling show a surprisingly large hysteresis in both the Li potential and the lattice parameters of the material. Calculations of Li intercalation show that while Li diffuses along channels in the crystal, there are additional binding sites in the framework which can be accessed from the channel. We suggest a model in which the channel is both filled first and emptied first, giving rise to the observed hysteresis.

11:35 - 11:55

T-H04 - ELECTROCATALYTIC REDUCTION OF CO_2 TO METHANOL AT CU-BASED SURFACES

[CALCD] John Flake[1], Maoming Ren[1], Ziyu Zhang[1], Minh Le[1], Phillip Sprunger[1], Richard Kurtz[1], Gregory Griffin[1], Ullie Diebold[2], Susan Sinnott[3], Aravind Asthagiri[4], and Michael Janik[5]

Louisana State University; [2]*Vienna University of Technology;* [3]*University of Florida;* [4]*Ohio State University and* [5]*Pennsylvania State University*

An efficient method to convert CO_2 to fuels using renewable energy could displace crude oil and provide high-density energy storage reservoirs similar to liquid fuels or batteries. Although photoelectrochemical conversion of CO_2 is possible, typical efficiencies are lower than the combination of conventional photovoltaics (up to 40% efficiency) and electrochemical cells (up to 80% Faradaic efficiency). In the electrochemical case, electrical energy from renewable sources may be converted to hydrocarbons or alcohols using electrocatalysts. Here, we examine the conversion of CO_2 to methanol at copper/metal oxide electrodes from a unified theoretical and experimental perspective. The objective is to leverage a fundamental understanding of electrocatalytic mechanisms to create "electrocatalysts by design". Single crystal ZnO(10-10) surfaces with Cu, CuO_x nanoclusters are considered for their potential as electrocatalysts. Electronic-structure calculations show a potential pathway for CO_2 reduction on Cu/ZnO(10-10) surfaces including a facile downhill pathway to a methoxy intermediate. *In-situ* FTIR and *ex-situ* HREELS are used to identify intermediates and support model predictions. Further work to unify experiment and simulation using empirical potentials allows larger-scale modeling of atomic scale CO_2 interactions with Cu and ZnO. Progress towards a fundamental understanding of CO_2 reduction mechanisms and selectivity as a function of electrocatalyst surfaces is discussed.

11:55 - 12:15

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

[CCHF] William Goddard[1], Robert Bergman[2], Robert Crabtree[3], Thomas Cundari[4], John Groves[5], Brent Gunnoe[6], and Thomas Meyer[7]
[1]California Institute of Technology; [2]University of California at Berkeley; [3]Yale University; [4]University of North Texas; [5]Princeton University; [6]University of Virginia and [7]University of North Carolina

As part of the DOE EFRC Center for Catalytic Hydrocarbon Functionalization we have been collaborating on several strategies for forming important molecules for energy and industry from CH_4 and other alkanes. The two key aspects are activating CH_4 at low temperature to avoid free radical processes that hinder selectivity to the desired products and the functionalization by forming new C-O and C-C bonds. The focus in this talk is achieving C-O bond formation by building catalysis with active M=O bonds. Here we are pursuing several strategies involving homogenous systems with oxo bonds, particularly porphyrin based systems and heterogonous systems with multiple types of oxo bonds. We have achieved promising results with both strategies as will be described.

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

1:45 - 2:05

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

[NERC] Kyle J.M. Bishop[1], Aaron M. Drews[1], Mikolaj Kowalik[1], and Bartosz A. Grzybowski[2]
[1]Pennsylvania State University; [2]Northwestern University

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

2:05 - 2:25

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

[MSA] Mark Asta[1], Udo Becker[2], Laura Gagliardi[3], Niels Gronbech-Jensen[4], Ed Maginn[2], and William J. Weber[5]
[1]University of California, Berkeley and [2]University of California, Davis; [3]University of Michigan; [4]University of Minnesota; [2]University of California, Davis; [5]University of Notre Dame

Computational research in the MSA-EFRC is reviewed its three focus areas. (1) Thermodynamic and kinetic properties of ThO_2 and UO_2 solid solutions. Mixing energetics with homovalent cations in these fuel materials are dominated by elastic contributions arising from cation size mismatch. Solutions with relevant transuranic elements have weakly positive mixing energies of a few kJ/mole. The addition of CeO_2 into ThO_2 decreases the oxygen vacancy formation and migration energies, leading to a minimum migration energy of 0.2 eV for 75 % Ce content. (2) Formation of nanoscale cage clusters based on uranyl ions. The U-O_2-U interaction has been considered in clusters of interest for nanoscale control of actinide chemical reactions. A covalent interaction causes the U-O_2-U dihedral angle to be bent, encouraging curvature and cluster formation. New candidate actinide groups for the formation of complex clusters are identified. (3) Pressure effects on pyrochlore compounds. Phase transitions and defect structures are investigated in pyrochlore compounds of interest as an inert matrix fuel or nuclear waste forms. Transitions to the defect-cotunnite structure are predicted at 43.6 GPa for $Gd_2Ti_2O_7$ and 13 GPa for $Gd_2Zr_2O_7$. In $Gd_2Ti_2O_7$, the dominant defect type is a cation anti-site defect, while in $Gd_2Zr_2O_7$, anion Frenkel-pair defects are favored at all pressures and the dominant defect type involving a cation is a coupled defect of a cation anti-site and an anion Frenkel pair.

2:25 - 2:45

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

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

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

2:45 - 3:05

T-H09 - ETHANOL SYNTHESIS FROM SYN-GAS: HOW SURFACE DIFFUSION OF INTERMEDIATES IMPACTS THE PRODUCT DISTRIBUTIONS PREDICTED FOR BIMETALLIC CATALYSTS

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

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

3:05 - 3:25

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

[IACT] Linda Broadbelt
Northwestern

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

3:25 - 3:45

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

[CALCD] D. Wayne Goodman[1], Li Liu[1], Zihao Zhou[1], Feng Gao[1], Lymarie Semidey-Flecha[2], Ye Xu[2], Dieh Teng[3], David Sholl[3], Philip Sprunger[4], and Ward Plummer[4]
[1]Texas A&M University; [2]Oak Ridge National Laboratory [3]Georgia Institute of Technology; Georgia Institute of Technology; [4]Louisiana State University

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

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

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

4:00 - 4:20

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

[CCHF] Roy A. Periana[1], Brian G. Hasihiguchi[1], Steven M. Bischof[1], Kapil S. Lokare[1], Claas H. Hovelmann[1], Robert J. Nielsen[2], Kenneth J. H. Young[3], and William A. Goddard, III[2]
[1]The Scripps Research Institute; [2]California Institute of Technology; [3]University of Southern California

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

4:20 - 4:40

T-I02 - SYNTHESIS OF NANOSTRUCTURED CATALYSTS FOR BIOMASS CONVERSION

[IACT] Christopher Marshall[1], Eric Stach[2], Fabio Ribeiro[3], Jeffrey Greeley[1], Justin Notestein[4], Kenneth Poeppelmeier[1], Larry Curtiss[1], Mayfair Kung[4], Peter Stair[4], Randy Winans[4], SonBinh Nguyn[4], and Jeffrey Elam[1]
[1]Argonne; [2]BNL; [3]Purdue; Argonne; [4]Northwestern

The successful transition to an energy economy based on biomass will require radical advances in catalyst science. This challenge demands a new paradigm in catalyst synthesis whereby inorganic components can be assembled at the atomic scale to yield complex, multifunctional catalysts rivaling Nature's enzymes in their specificity. To this end, we have developed a novel approach combining templated synthesis for shape-selectivity with the atomically-precise positioning of discrete functionalities. In this approach we begin with a supporting scaffold for catalyst growth upon which we chemically attach molecular templates. Next, atomic layer deposition is used to build a structure around each template in an atomically precise, layer-by-layer fashion where the thickness and composition can be tuned at each layer. Finally, the template is removed yielding a "nanobowl" defining a structured catalytic environment. The molecular template can be synthesized to contain bulky organic ligands surrounding a catalytic atom or cluster which remains anchored to the bottom of the bowl after ligand removal. Furthermore, one or more layers in the bowl wall can be selected to serve as a co-catalyst (e.g. Lewis acid group) positioned at a well-defined distance from the catalyst at the bottom of the bowl. This presentation will review our recent progress synthesizing, characterizing, modeling, and testing these unique catalytic materials.

4:40 - 5:00

T-I03 - Development of Catalysts for Selective Functionalization of Hydrocarbons

[CCHF] T. Brent Gunnoe[1], Jeremy Andreatta[1], Bradley A. McKeown[1], Victor S.-Y. Lin[2], Brian G. Trewyn[2], Hung-Ting Chen[2], and Thomas R. Cundari[3]
[1]University of Virginia; [2]Iowa State University; [3]University of North Texas

Catalysts that selectively convert hydrocarbons into value added materials are central to the chemical industry and energy sector. For example, alkyl arenes are produced and used on a multi-billion pound scale annually. Work in the CCHF seeks to exploit expertise in homogeneous catalysis, materials design/characterization and computational modeling to develop new catalysts for the production of alkyl arenes. Groups at the U. of Virginia and U. of North Texas have demonstrated that Pt(II) complexes supported by bipyridyl ligands catalyze the hydroarylation of olefins. For example, $[(tbpy)Pt(Ph)(THF)]^+$ (tbpy = 4,4'-di-tert-butyl-2,2'-bipyridyl) serves as a catalyst for using unactivated substrates (e.g., benzene, ethylene, propylene). Previous studies show that the Pt(II) catalysts operate by olefin coordination and insertion into the Pt-Ph bond followed by benzene C-H activation. Using methods for the preparation of nanomaterials developed at Iowa State U., single-site catalysts in which $(bpy)Pt(Ph)_2$ catalyst precursors are tethered to mesoporous silica nanoparticles (MSNs) have been prepared. These materials exhibit enhanced stability compared to analogous homogeneous catalysts, and the selectivity of the homogeneous catalyst is effectively transferred from the homogeneous system to the MSN-supported catalyst. The long-term goal is to tailor the MSN to control substrate selectivity for olefin hydroarylation and other hydrocarbon functionalization reactions.

5:00 - 5:20

T-I04 - Seeing Cellulose in Plant Cell Walls and Lignocellulosic Biomass -- Sum-Frequency-Generation (SFG) Vibration Spectroscopy Study

[CLSF] Seong H. Kim[1], Christopher Lee[1], Anna L. Barnette[1], Yong Bum Park[1], Daniel J. Cosgrove[1], Jin Gu[1], Jeffrey M. Catchmark[1], Sunkyu Park[1], Candace Haigler[2] and Eric Roberts[3]
1The Pennsylvania State University [2]North Carolina State University; [3]Rhode Island College

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

5:20 - 5:40

T-I05 - Dynamics of Void Growth in Irradiation

[CMSNF] Thomas Hochrainer[1], Abdel-Rahman Hassan[1], Peng Xu [2], Todd Allen[2] , and Anter El-Azab[1]
[1]Florida State University; [2]University of Wisconsin-Madison; [3]Florida State University

We are investigating the fundamental physics of void nucleation and growth in irradiated materials, by both theory and experiments. A critical step in the investigation is to understand interactions of defects with void surfaces and capture details of void growth. In oxide fuels like UO_2, defect interactions at the void surface are governed by electrochemical reactions. To develop mesoscale models of void nucleation and growth in irradiated materials, requires a detailed understanding of the defect interactions with and across the surface. We present a unified method for how defect reactions at free surfaces, which govern the growth kinetics of voids and gas filled bubbles, can be obtained from thermodynamics. This leads to requirements on transition state theoretical models of reactions at the surface which are not considered in the literature. The reaction rates at the surface define dynamic boundary conditions for the evolution of defect density fields. These equations were solved numerically as a free boundary value problem. We use these calculations to determine parameters of a phase field formulation of the same problem. The calibrated phase field simulations are used in large scale simulations of void nucleation and growth under irradiation. A key finding is that defect-surface interactions play an essential role in the growth rate of voids under irradiation. We discuss experiments currently set up to characterized the defect interations at the surface of UO_2.

5:40 - 6:00

T-I06 - NDTB-1: A SUPERTETRAHEDRAL CATIONIC FRAMEWORK MATERIAL FOR SELECTIVE TRAPPING OF RADIOISOTOPES

[MSA] Shauo Wang[1], Evgeny V. Alekseev[2], Juan Diwu[1], William H. Casey[3], Brian L. Phillips[4], Wulf Depmeier[2] and Thomas E. Albrecht-Schmitt[1]
[1]University of Notre Dame; [2]University of Kiel and University of Notre Dame; [3]University of California, Davis; [4]SUNY-Stony Brook

We have recently undertaken the study of the preparation, structure elucidation, and physico-chemical property measurements of actinide borates. During the course of these studies a highly unusual thorium borate was discovered, $[ThB_5O_6(OH)_6][BO(OH)_2] \cdot 2.5H_2O$ (Notre Dame Thorium Borate-1). The structure of NDTB-1 is a porous supertetrahedral 3D framework. Six channels form a network that pierces the whole structure, and allows facile anionic and molecular transport for exchange processes. When the single crystal X-ray data and solid-state NMR spectroscopy are taken together, we can conclude that NDTB-1 is an exceedingly rare example of a cationic framework with extraframework borate anions residing in the centers of the gates being used to maintain charge neutrality. Anion exchange experiments were conducted with a variety of common anions. These studies revealed that not only does anion exchange take place, but that the structure remains intact throughout the exchange. Exchange experiments were conducted with a variety of highly colored anions and the single crystals show the color of the transition metal anions rapidly. The critical anion exchange experiments are replacing the extraframework borate anions with TcO_4^-. These studies with NDTB-1 show rapid uptake of TcO_4^- from solution. NDTB-1 selectively removes pertechnetate from nuclear waste streams despite massive excesses of nitrate, nitrite, and chloride in these streams.

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

8:00 - 8:20

T-I07 - ELECTROCHEMICAL STRAIN MICROSCOPY: A NEW PROBE OF LI-ION DYNAMICS IN ELECTRODE MATERIALS

[FIRST] Nina Balke, Leslie Adamczyk, Nancy Dudney, and Sergei Kalinin
Oak Ridge National Laboratory

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

8:20 - 8:40

T-I08 - NANOSCALE STUDIES OF BATTERY ELECTROCHEMISTRY: IN-SITU TEM AND SPM AND ATOMISTIC MODELING

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

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

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

8:40 - 9:00
T-I09 - COMPLEX OXIDES AND COMPUTATIONAL STUDIES
[EMC2] Joel Brock, Kendra Weaver, Ravishankar Sundararaman, and Tomas Arias
Cornell University

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

EFRC and DOE Research and Networking Poster Reception

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

Department of Energy Programs

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

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

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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.enegy.gov

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

Contacts: Tien Duong, EERE, tien.duong@ee.doe.gov, 202-586-7836
Venkat Srinivasan, LBNL, vsrinivasan@lbl.gov, 510-495-2679
Website: http://berc.lbl.gov/batt/

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
Samuel Tam, Director, 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 Rochester

Contact: David D. Meyerhofer, ddm@lle.rochester.edu
Website: 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.gov
www.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 be 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

Contacts: Tim Frazier, Dirk Cairns-Gallimore, Won Yoon, and Scott Harlow
Scott.Harlow@nuclear.energy.gov
Website: http://nuclear.energy.gov/space/neSpace2a.html

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

Contact: Barbara Helland, Barbara.Helland@science.doe.gov
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
Grace Webster, cfnuser@bnl.gov
http://www.bnl.gov/cfn/

CENTER FOR INTEGRATED NANOTECHNOLOGIES
Neal Shinn, ndshinn@sandia.gov
http://www.lanl.gov/cint/

CENTER FOR NANOPHASE MATERIALS SCIENCES
Tony Haynes, cnmsuser@ornl.gov
http://cnms.ornl.gov/

CENTER FOR NANOSCALE MATERIALS
Katie Carrado Gregar, kcarrado@anl.gov
http://nano.anl.gov/

THE MOLECULAR FOUNDRY
David Bunzow, dabunzow@lbl.gov
http://foundry.lbl.gov/

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, morekl1@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, trimblejl@ornl.gov
http://neutrons.ornl.gov/facilities/SNS/

HIGH FLUX ISOTOPE REACTOR (HFIR)
Judy Trimble, User Program Manager, trimblejl@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

Contact: Ramamoorthy Ramesh, Ramamoorthy.Ramesh@EE.Doe.Gov
Website: http://www1.eere.energy.gov/solar/sunshot/

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 Akselrod[1], Elizabeth Young[1], Scott Bradley[1], and Vladimir Bulovic[1]
[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 Nakano[1], Rajiv. K. Kalia[1], and Priya Vashishta[1]
[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 MacLeod[1], Matthew Schalnat[2], Dallas Matz[2], David Ginger[1], Jeanne Pemberton[2], Sergio Paniagua[3], Seth Marder[3], Ajaya Sigdel[4], Joseph Berry[4], Mariola Macech[2], Hong Li[3], and Jean-Luc Bredas[3]
[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 Tassone[1], Alexander Ayzner[1], Robert Kennedy[1], Yves Rubin[1], Benjamin Schwartz[1], and Sarah Tolbert[1]
[1]*UCLA*

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 Chen[1], Atsuhiro Nakahara[2], Dongguang Wei[3], and Thomas P. Russell[4]
[1]*U Mass Amherst;* [2]*Kurashiki Research Center;* [3]*Carl Zeiss NTS LLC and* [4]*U 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 ^{o}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 Balazs[1], Li-Tang Yan[1], Egor Maresov[1], and Gavin A Buxton[2]
[1]*Univ of Pittsburgh and* [2]*Robert 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 erobust 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 Cossiart[1]
[1]*Columbia 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 $[(CdSe)_4Cd(OC(O)Ph)_2(H_2NR)_2]_n$ (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 Pandey[1], Liang Li[1], Bishnu P. Khanal[1], Hsinhan Tsai[1], Hsing-Lin Wang[1], Jeffrey M. Pietryga[1], and Victor I. Klimov[1]
[1]*Los 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. Semonin[1], Joseph M. Luther[1], Jianbo Gao[1], Sukgeun Choi[1], Matthew C. Beard[1], and Arthur J. Nozik[1]
[1]*National 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 MULTIJUNCTION CONCENTRATOR APPLICATION

[CEEM] Carl Neufeld[1], Samantha Cruz[1], Robert Farrell[1], Michael Iza[1], Stacia Keller[1], Shuji Nakamura[1], Steven DenBaars[1], James Speck[1], and Umesh Mishra[1]
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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

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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 Delaire[1], Karol Marty[1], Jie Ma[1], Andrew May[1], Michael McGuire[1], Mao-Hua Du[1], David Singh[1], and Brian Sales[1]
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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, Premaladha[1], Vagnini, Michael T. [1], and Wasielewski, Michael R. [1]
[1]*Northwestern 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-$Fe_2S_2(CO)_6$). 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-$Fe_2S_2(CO)_6$) 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-$Fe_2S_2(CO)_6$, 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 H_2.

P1-C02 - TAILORING THE ARCHITECTURE OF LIGNIFIED WALLS

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The toolkit of plant molecular biology allows modification of biomass composition by manipulating gene expression. In C^3Bio, 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

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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 $CuCl_2$ 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 $CuCl_2$ 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 Park[1], Mahmoud Gargouri[1], and David R. Gang[1]
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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. Simmons[1], Xixi Wei[1], Alex Volosin[1], Dominik Schmitt[1], Dong-Kyun Seo[1], Yan Liu[1], and Hao Yan[1]
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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 Koepf[1], Benjamin D. Sherman[1], Ana L. Moore[1], Devens Gust[1], and Thomas A. Moore[1]
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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 ^{1}H-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 Rajabbeigi[1] and Michael Tsapatsis[1]
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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 Alecu[1], Tao Yu[1], Jingjing Zheng[1], and Donald Truhlar[1]
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The hydrogen-atom abstraction reaction $CH_3(CH_2)_3OH + HO_2 = CH_3(CH_2)_2CHOH + HOOH$ 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-Louyeh[1], Tian Zhang[1], Yong Bum Park[1], Daniel J. Cosgrove[1], and Bernhard R. Tittmann[1]
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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. Yang[1], Uriah J. Kilgore[1], Monte Helm[1], Stuart E. Smith[1], John A, Roberts[1], Michael P. Stewart[1], Douglas P. Pool[1], Daniel L. DuBois[1], Mary Rakowski DuBois[1], and R. Morris Bullock[1]
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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 Simone[1], Chen Shentan[1], Ho Ming-Hsun[1], Rousseau Roger[1], Dupuis Michel[1], DuBois Daniel, and Bullock R. Morris[1]
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Recent advances in Ni-based bio-inspired catalysts prepared in the Center for Molecular Electrocatalysis demonstrated the possibility of cleaving H_2 or generating H_2, with high turnover frequencies. In these catalysts the transformation between H_2 and protons involves the interaction of H_2 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 H_2 oxidation and H_2 production designed at our EFRC. Results indicate that for H_2 oxidation, the loss of H_2 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 H_2 production. In the case of H_2 oxidation, once the H_2 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 H_2 production. The overall chemistry of the $Ni[P_2N_2]_2$ complexes is understood in terms of the ability of the P and N substituents to tune the pKa 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. Tang[1], Liying Zhu[1], Volker S. Urban[2], Aaron M. Collins[1], Pratim Biswas[1], and Robert E. Blankenship[1]
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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 An[1], Joseph K.H. Tang[1], Robert E. Blankenship[1], and Pratim Biswas[1]
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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 TiO_2 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 TiO_2 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 TiO_2 IN AN AQUEOUS ENVIRONMENT

[UNC] Kenneth Hanson[1], M. Kyle Brennaman[1], Hanlin Luo[1], Mike Norris[1], Christopher Glasson[1], Javier J. Concepcion[1], Wenjing Song[1], and Thomas J. Meyer[1]
[1] *UNC*

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 TiO_2 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

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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. Thackeray[1], P. Fenter[1], J. Elam[1], L. Curtiss[1], H. Kung[2], M. Hersam[2], A. Gewirth[3], and J. Moore[3]
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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. Chidsey[1], Vadim R. Ziatdinov[1], and Ali Hosseini[1]
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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] Tornoe, 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. Harris[1], Sankaran Murugesan[1], Anthony Dylla[1], Aaron M. Chockla[1], Keith J. Stevenson[1], and Brian A. Korgel [1]
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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 Zhou[1] and Vidvuds Ozolins[1]
[1]*UCLA*

We have studied the supercapacitive energy storage in hydrous RuO_2, a prototypical and high-performing supercapacitor material, with first-principles calculations. First, we have studied the surface redox reaction of RuO_2 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 RuO_2, 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 RuO_2 oxide is energetically highly unfavorable. Instead, water is predicted to agglomerate outside bulk RuO_2, supporting the picture of microscopic charge transport with nanocrystalline RuO_2 cores and structural water at the grain boundaries. The interfacial energy of RuO_2 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 Du[1], James P. Pastore[1], Clare P. Grey[1], Feng Wang[2], Yimei Zhu[2], Jason Graetz[2], Andrew Gmitter[3], Nathalie Pereira[3], Glenn G. Amatucci[3], Olaf Borkiewicz[1], Karena W. Chapman[1], and Peter J. Chupas[1]
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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, ^{19}F 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 cupper 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 Speck[1], Ravi Shivaraman[1], Elison Matioli[1], Dobri Simenov[1], Steve DenBaars[1], Shuji Nakamura[1], and Claude Weisbuch[1]
[1]*UCSB*

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 ï□—. 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 Oyeyemi[1], Ting Tan[1], Michele Pavone[1], and Emily A. Carter[1]
[1]*Princeton 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 Qi[1] and Stephen Forrest[1]
[1]*University 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 TC

[CES] Wai-Kwong Kwok[1], Ulrich Welp[1], George Crabtree[1], Mike Norman[1], Juan Atkinson[1], Dale Van Harlingen[2], Raffi Budakian[2], Gregory Polshyn[2], Peter Johnson[3], and Seamus Davis[3,4]
[1]*Argonne National Laboratory;* [2]*University of Illinois at Urbana-Champaign;* [3]*Brookhaven National Laboratory and* [4]*Cornell 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 2Ï€ 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 Tc, phase rigidity appears over macroscopic lengthscales. It is thought above Tc, 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 Kwok[1], Tony Leggett[2], Laura Greene[2], Philip Phillips[2], Cedomir Petroic[3], Ivan Bozovic[3], Peter Abbamonte[2], Mao Zheng[2], Weicheng Lee[2], Yize Li[2], James Lee[2], and Jim Eckstein[2]
[1]*Argonne National Lab;* [2]*University of Illinois, Urbana-Champaign and* [3]*Brookhaven 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 eDesign of New Superconductors Wai-xplored, 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 $A_yFe_{2-x}Te$ (A=Tl, Cs, K) and $A_2O_3Fe_2M_2$ (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 Ding[1] and Feng Liu[1]
[1]*University 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% $YO_{1.5}$, 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 Tsao[1], HD Saunders[2], JR Creighton[1], ME Coltrin[1], and JA Simmons[1]
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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 Dai[1], Qifeng Shan[1], Jaehee Cho[1], E. Fred Schubert[1], Mary H. Crawford[2], and Daniel D. Koleske [2]
[1]*Rensselaer Polytechnic Institute and* [2]*Sandia 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 Ganis[1], Gergina Pencheva[1], Mary Wheeler[1], Todd Arbogast[1], Hailong Xiao[1], Guangri Xue[1], Mojdeh Delshad[1], and Xianhui Kong[1]
[1]*University of Texas at Austin*

The challenges associated computational modeling of CO_2 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 CO_2 Trapping and Migration shows how we can incorporate a critical microscopic scale phenomena that strongly affects the behavior and distribution of CO_2 in large-scale geologic systems.

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

[CFSES] Matthew Kirk[1], Susan Altman[1], Philip Bennett[2], Bayani Cardenas[2], Thomas Dewers[1], Mojdeh Delshad[2], Eugenio Santillan[2], Wen Deng[1], Kuldeep Chaudhary[1], and Hongku Yoon[1]
[1]*Sandia National Laboratories and* [2]*University 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 CO_2 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 Yuan[1], Jinhee Park[1], Weigang Lu[1], Jian-Rong Li[1], and Hong-Cai Zhou[1]
[1] *Texas A&M University*

Flexible porous framework materials are excellent candidate for the separation for CO_2. 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 CO_2 over N_2 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 Hourani[1], Nana Zhao[1], Rob van der Weegen[2], Beverly Zhang[1], Brett A. Helms[2], and Ting Xu1,[2]
[1]University of California, Berkeley and [2]Lawrence 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 Cappuccio[1], Chun-Long Chen[1], Joanne Emerson[2], Jillian Banfield[2], Jim DeYoreo[1], Ronald Zuckermann[1], and Caroline Ajo-Franklin[1]
[1]Lawrence Berkeley National Laboratory and [2]University of California, Berkeley

Geologic CO_2 sequestration will be an essential component of global climate change mitigation. Carbonate minerals are an effective form of stable CO_2 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 CO_2 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 CO_2 rich environments and CO_2 sequestration sites. Secondly, we have explored how different environmentally prevalent bacteria affect mineralization rates. We find that many microbial surfaces bind Ca^{2+} 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 $CaCO_3$ mineralization by controlling crystal growth morphology. The $CaCO_3$ 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 Tsunekane[1] and Sharvan Kumar[1]
[1]Brown 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 $LiNbO_3$ as functions of pressure and temperature

[EFree] Ronald Cohen[1], Maimon Rose[1], Qing Peng[2], and P. Ganesh[3]
[1]Carnegie Institution of Washington; [2]RPI and [3]ORNL

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 Stocks[3], Don Nicholson[3], Roger Stoller[3], and Aurelian Rusanu[3]
[1]Pittsburgh Supercomputing Center, [2]Carnegie Mellon University and [3]Oak 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 Osetskiy[1], Andy Calder[2], and [1]Roger Stoller
[1]ORNL and [2]University 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 riches 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 Xu[1], Yury Osetsky[1], and Roger Stoller[1]
[1]Oak 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 Odbadrakh[1], Aurelian Rusanu[1], George Stocks[1], Yang Wang[2], German Samolyuk[1], and Don Nicholson[1]
[1]*ORNL and* [2]*PSC*

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 McCreary[1], Grace S. Liu[1], Martha Briceno[1], and Ian M. Robertson[1]
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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

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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. Germann[1], Ruifeng Zhang[1], Jian Wang[1], Xiang-Yang Liu[1], Shengnian Luo[1], Weizhong Han[1], Irene Beyerlein[1], and Amit Misra[1]
[1]*LANL*

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

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[1]*LANL*

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 $SrTiO_3$ AND TiO_2

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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 $SrTiO_3$ and TiO_2. Polycrystalline $SrTiO_3$ and TiO_2 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 amophization even at high radiation doses; whereas, single crystal is amorphous.

P1-G13 - ANALYTICAL PREDICTIONS OF HETEROINTERFACE INTERACTIONS WITH DEFECTS

[CMIME] Kedarnath Kolluri[1], Aurelien Vattre[1], Abishek Kashinath[1], and Michael J. Demkowicz[1]
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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 Nastasi[1], Zengfeng Di[1], Qiangmin Wei[1], Amit Misra[1], Richard Hoagland[1], Yongqiang Wang[1], Jonghan Won[1], Xian Ming Bai[1], Blas Uberuaga[1], Enrique Saez[1], Jeffery Hetherly[1], and Alfredo Caro[1]
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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 CeO_2

[CMSNF] Clarissa Yablinsky[1], Peng Xu[1], Anthony Schulte[1], David Hurley[2], Jian Gan[2], and Todd Allen[3]
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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 CeO_2, a common surrogate material for UO_2, was used in two forms: bulk CeO_2 and thin film CeO_2 on a silicon substrate. Two different grain sizes were investigated: thin film samples with ~500 nm grain size, and bulk samples with ~5um grain size. Samples were exposed to a range of energies and ions to fluences of no less than 1E10 ions/cm^2 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

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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

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Ceria films, used as a UO_2 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 CeO_2 phase with (111) or (222) preferred orientations. However, post-annealed ceria films have a hexagonal Ce_2O_3 phase with a (002) preferred orientation after RTA at 1000 deg.C for 5 min. This phase transformation, from cubic CeO_2 (111) to hexagonal Ce2O3 (002), is probably due to the Ce^{4+} to Ce^{3+} cation transformation by the formation of oxygen vacancies. X-ray photoelectron spectroscopy was performed to confirm the chemical status of Ce (e.g., Ce^{4+}, Ce^{3+}, 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 CeO_2 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 CeO_2 to Ce_2O_3. 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

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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 $[C_nMPy][Tf_2N]$ 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 $[C_nMPy][Tf_2N]$. 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 $[C_4MPy][Tf_2N]$ measured by PFG-NMR is much faster than that for rhodamine 6G. The Stokes-Einstein equation, $D=k_BT/6\pi\eta rs$ states that the diffusion coefficient is inversely proportional to the size of molecules, where rs, 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 $[C_nMPy][Tf_2N]$.

P1-G19 - Actinide Materials under Extreme Conditions: An Experimental and Computational Approach

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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 Î±-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 UO2.03 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

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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 Î¼m 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 Li[1], Yang Ding[1], Wenge Yang[1], and Ho-Kwang (Dave) Mao[1]
Geophysical Lab Carnegie Institution of Washington[1]

Heavy metal hydride is of great scientific interest as both a potential high Tc 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 LAMNO3

[EFree] Maria Baldini[1], Viktor V. Struzhkin[1], Alex F. Goncharov[1], Paolo Postorino[2], and Wendy L. Mao[3]
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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

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Karandikar[1]; Yang[1] and Boehler[1]
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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

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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 Landskron[1], Paritosh Mohanty[1], Manuel Weinberger[1], Yingwei Fei[2], Ho-Kwang Mao[2], Dong Li, Tianbo Liu[1], Neil Coombs[1], Ilke Arslan[3], Nigel Browning[4], and Volkan Ortalan[4]
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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 hydrohermal 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 Dooley[1] Michael Janik[2], Adam Mayernick[2], Rui Li[1], Matthew Krcha[2], Joseph Bridges[1], Sumana Adusumilli[1], and Weishi Kong[1]
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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 ºC in a realistic biomass/coal gasifier effluent containing water, H_2, CO, CO_2 and H_2S. Computational studies are used to help identify optimal transition metals and composition ranges. Both Mn and Fe look like good candidates with $CeO_2/La_2O_3^-$ or CeO_2/ZrO_2^- based REOs, but recent computational work on methane activation and on reduction of doped CeO_2 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 H_2S at 600-650 ºC (where the Mn-containing materials are definitely superior) and for reforming of naphthalene at similar temperatures. We found that the temperature range 600-650 ºC is the best compromise between high conversion of the naphthalene model "tar" and extended catalyst lifetime. We also found that while CO_2 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 He[1], James McAliley[1], and David Bruce[1]
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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

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This poster will report a hitherto unobserved adsorption behavior for water, which has been observed at the (001) surface of magnetite (Fe_3O_4). 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 though 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 Fe_3O_4(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: Fe_3O_4(001). Phys. Rev. Lett 94 126101 (2005).

P1-H04 - MULTI-SCALE MODELING OF CATALYSTS FOR CO_2 REDUCTION TO ALCOHOLS

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Within the CALCD EFRC we have an integrated experimental and theoretical effort to develop novel catalysts for the electrochemical reduction of CO_2 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 CO_2 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 CO_2 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 CO_2 reduction on these surfaces.

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

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Biomass conversion to liquid fuels may be accomplished through gasification to syngas ($CO+H_2$) 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 H_2 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 H_2S adsorption and hydrocarbon conversion. Initial efforts have examined the H_2S adsorption and incorporation process. Oxygen vacancy sites in the doped oxide are active for H_2S adsorption and dissociation. Relative rates of the initial H_2S activation step predict trends in experimental H_2S 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

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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 $[\mathrm{MCp2}]^{0/+}$, [MCp*2]0/+ and $[\mathrm{M(bpy)_3}]^{2+/3+}$, 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

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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 ressources 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 $\mathrm{Si_n/Ge_m/.../Si_p/Ge_q}$ superstructures grown on (001) $\mathrm{Si_{1-x}Ge_x}$. This search reveals a robust configurational motif -- $\mathrm{SiGe_2Si_2Ge_2SiGe_n}$ on (001) $\mathrm{Si_{1-x}Ge_x}$ substrate ($x<0.4$) -- which presents both a direct and dipole-allowed gap by coupling the CBM at Î” with the direct transition state at Î“.

P1-H08 - Computational Discovery and High Throughput synthesis of new A_2BX_4 and ABX semiconductors for Solar Energy

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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_3B0_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 Berger[1], Kendra Weaver[2], Ravishankar Sundararaman[2], Tomas Arias[2], Craig Fennie[2], and Jeff Neaton[1]
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This poster highlights two projects in the theory objective of the Energy Materials Center at Cornell (EMC^2). 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. Chathoth[1], Eugene Mamontov[1], Alexander I. Kolesnikov[1], Gernot Rother[1], Michael Rouha[2], Peter T. Cummings[2], Pasquale Fulvio[1], X. Wang[1], Sheng Dai[1], Jake McDonough[3], Volker Presser[3], and Yury Gogotsi[3]
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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 Ã… 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][Tf_2N] 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 Zhou[1], Paul Fenter[1], Volker Presser[2], Jake McDonough[2], Yury Gogotsi[2], Matthew Wander[2], Kevin Shuford[2], P. Ganesh[3], Paul R.C. Kent[3], De-en Jiang[3], Gernot Rother[3], Ariel Chialvo[3], Pasquale Fulvio[3], Sheng Dai[3], Michael Rouha[4], Guang Feng[4], and Peter T. Cummings[4]
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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 imbibed 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 Vlaisavljevich[1], Pere Miro[1], Christopher Cramer[1], Peter C. Burns[2], and [1]Laura Gagliardi
[1]University of Minnesota and [2]University of Notre Dame

The uranyl ion, $[UO_2]^{2+}$, 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 work[4-6] 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, $(UVIO_2)O_2L_3$, and dimer, $(UVIO_2)_2O_2L_{4\text{-}6}$, with various equatorial ligands, L (L=water, hydroxyl, or oxalate). Monomer formation is preferred over the dimer in the absence of countercations 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. Adduction 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. Burns[1], Ginger E. Sigmon[1], Daniel K. Unruh[1], Jie Ling[1], Jie Qiu[1], Christine Wallace[1], and Jennifer E.S. Szymanowski[1]
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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. Johnson[1], Stephen J. Harley[1], C. Andre Ohlin[1], Adele F. Panasci[1], and William H. Casey[1]
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There is little information about the mechanisms of reactions involving aqueous actinide elements and high-pressure ^{17}O- and ^{13}C-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 $[UO_2(OH)_4]^{2-}{}_{(aq)}$ 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 (Î”Vâ€¡) of -9.8Â±0.8 cm^3/mol for the reaction, which indicates a strongly associative pathway. We are now extending the work to examine the pressure dependence of ^{13}C and ^{17}O exchange in the $[UO_2(CO_3)_3]^{4-}{}_{(aq)}$ 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 U_{28} cluster (and others) prepared in collaboration with Dr. May Nyman of Sandia National Laboratory. We find that the U_{28} compound synthesized with ^{17}O-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 $^{99}TcO_4^-$ 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

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The U_{28} nanosphere, $[UO_2(O_2)_{1.5}]_{28}$ 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 U_{28} capsule. Successful anionic templates include $Nb(O_2)_4^{3-}$, $Ta(O_2)_4^{3-}$, $UO_2(O_2)_3^{4-}$ and $VO_{4-x}(O_2)_x^{3-}$. 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 U_{28} 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]
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Cubic ceria (CeO_2) 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, CeO_2 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 CeO_2 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 CeO_2 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[4]
[1]*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) Mahanti[1]
[1]*Michigan State University*

Heusler alloys have been studied extensively since they were first discovered by Heusler in 1903. Among those Fe_2VAl and Fe_2TiSn 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 Fe_2VAl 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. Webb[1], Travis M. Figg[2], Mark J. Pouy[1], Bruce M. Prince[2], T. Brent Gunnoe[1], Thomas R. Cundari[2], and John T. Groves[3]
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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 Jha[1], Vladimir Kuzovkov[2], Bartosz Grzybowski[1], and Monica Olvera de la Cruz[1]
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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

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[1]*University of Michigan and* [2]*Northwestern 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 Crowley[2], Michael Himmel[2], Shi-You Ding[2], Bryon Donohoe[2], Jeremy Madden[3], Garth Simpson[3], 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 Tischler[1], Ben Larson[1], Matt Brandes[2], Jonghan Kwon[2], Michael Mills[2], Wenjun Liu[3], and Gene Ice[1]
[1]Oak Ridge National Laboratory; [2]Ohio State University and [3]Advanced Photon Source

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 Trebotich[1], Chaopeng Shen[1], and Carl Steefel[1]
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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 CO_2 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 CO_2 sequestration, with an objective of upscaling these to the continuum scale.

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

[HeteroFoaM] Kevin Blinn[1], Xiaxi Li[1], Samson Lai[1], Mostafa El-Sayed[1], Andreas Heyden[2], and Meilin Liu[1]
[1]*Georgia Institute of Technology and* [2]*University 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. Kim[1], Christopher Lee[1], Daniel J. Cosgrove[1], Yong Bum Park[1], Jeffrey M. Catchmark[1], Jin Gu[1], Anna Barnette[1], and Laura Bradley[1]
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Lignocellulose, an agriculture feedstock containing semi-crystalline cellulose, hemicellulose and lignin, is economically appealing for energy demands because it is highly renewable and globally availible. 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. Amporphous 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 microfibirls, development of primary and secondary cell wall tissues, and chemical treatments for biofuels.

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

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[1]*Argonne National Laboratory and* [2]*Northwestern 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 Prieto[1], Jovana Zecevic[1], Dr. Heiner Friedrich[1], Prof. Krijn P. de Jong[1], and Dr. Petra E. de Jongh[1]
[1] *Utrecht 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 SiO_2 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). \r\n\r\nHighly dispersed SiO2-supported Cu/ZnO catalysts are obtained through NO-mediated nitrate activation. Nano-confined catalysts display catalytic acitivities (per Cu mass) comparable to a benchmark Cu/ZnO(Al_2O_3) 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 SiO_2-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

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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 Wen[1], Dylan H. Arias[1], Katherine W. Stone[1], and Keith A. Nelson[1]
[1]*Massachusetts 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 Bettinger[1], Yezhou Shi[1], Andriy Zakutayev[2], Paul Ndione[2], Philip Parilla[2], John Perkins[2], David Ginley[2], and Michael Toney[1]
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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 Armstrong[1], Mariola Macech[1], Gordon MacDonald[1], Samuel Graham[2], Yongjin Kim[2], Jeanne Pemberton[1], Oliver Monti, Anne Simon[1], Brooke Beam[1], Scott Saavedra[1], Bradley Macleod[1], and David Ginger[3]
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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 Khafizov[1], David Hurley[1], In-Wook Park[2], John Moore[2], Jianliang Lin[2], Ryan Deskins[3], and Anter El-Azab[4]
[1]*Idaho National Laboratory;* [2]*Colorado School of Mines;* [3]*Florida State University and* [4]*Florida 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

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[1]*Florida State University;* [2]*University of Wisconsin-Madison and* [3]*Florida 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 UO_2. 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 Stockum[1], James Mack[1], and Fritz Prinz[1]
[1]*Stanford 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 $Li[LiM]O_2$ Electrodes for Lithium-Ion Batteries

[CST] Karalee Jarvis[1], Zengquiang Deng[1], Eun Sung Lee[1], Penghao Xiao[1], Graeme Henkelman[1], Arumugam Manthiram[1], and Paulo Ferreira[1]
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With an aim to increase the energy density of lithium-ion batteries, lithium-rich layered oxides with the general formula $Li[M_{1-x}Li_x]O_2$ (M = Mn, Co, and Ni) have become appealing recently as they exhibit much higher capacities (250 mAh/g) relative to that of $LiCoO_2$ (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 $Li[M_{1-x}Li_x]O_2$ 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 $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ 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 $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ is a solid solution with C2/m monoclinic symmetry and multiple planar defects, suggesting that the $Li[M_{1-x}Li_x]O_2$ type materials can be single-phase and still exhibit high reversible capacity.

P1-I16 - Instrumentation for Nanoscale Thermometry and Picowatt Calorimetry

[CSTEC] Pramod Reddy[1], Seid Sadat[1], Yi-Jie Chau[1], and Aaron Tan[1]
[1]*University 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 (?Tres) of ~4 µK and a noise floor of ~6.4 µK. The small thermal conductance coupled with the excellent temperature resolution enable measurement of modulated heat currents (q = G x ?Tres) with a resolution better than 4 pW.

P1-I17 - Beam-Assisted Nanostructuring in Thin Films for Thermoelectrics

[CSTEC] Michael Warren[1], Yuwei Li[1], Vladimir Stoica[1], Lynn Endicott[1], Guoyu Wang[1], Adam Wood[1], Justin Canniff[1], Roy Clarke[1], Ctirad Uher[1], and Rachel Goldman[1]
[1] *University 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 Sb_2Te_3 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 Ko[1], Yingchao Yu[1], Manuel Plaza[1], Xin Huang[1], Alexander Kazimirov[1], Huolin Xin[1], Robert Hovden[1], Megan Holtz[1], Julia Mundy[1], David Muller[1], Joel Brock[1], and Hector Abruna[1]
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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. Unocic[1], Leslie A. Adamczyk[1], Nancy J. Dudney[1], P. Ganesh[1], Paul R.C. Kent[1],
De-en Jiang[1], and Karren L. More[1]
[1] *Oak 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 $LiClO_4$ 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, Junling[2], Ray, Natalie[1], Lee, Sungsik[2], Winans, Randall[2], Elam, Jeffrey[2], Stair, Peter[1], and Notestein, Justin[1]
[1]*Northwestern University;* [2]*Argonne 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 Lu[1], Hao Feng[1], Peter C. Stair[2], and [1]Jeffrey 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. Ahn[1], David Lorang[1], Ralph G. Nuzzo[1], and Jennifer A. Lewis[1]
[1]*University 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 In_2O_3 (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 Î¼m 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 Sadtler[1], Joseph Beardslee[1], and Nathan Lewis[1]
[1]*California 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 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. Shvareva[1], C. Armstrong[1], T.J. Park[1], B. Hanken[1], and A. Navrotsky[1]
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 La^{3+}-, Y^{3+}- and Ce^{4+}- doped ThO_2 are calorimetrically determined and supported by DFT calculations (M. Asta's group). Energetics of water adsorption on ThO_2 are measured and reveal exothermic chemisorption of eight water molecules per nm^2 of surface (in agreement with computational studies, M. Asta's group). Surface enthalpies of ThO_2 are 0.92 ± 0.10 J/m_2 for hydrous and 1.24 ± 0.16 J/m_2 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 MnO_2-LI-HOPG SYSTEMS: ELECTROCHEMICAL SPM AND UHV-STM INVESTIGATIONS

[NEES] Satyaveda C. Bharath[1], Wentao Song[1], Janice E. Reutt-Robey[1], and Kevin R. Zavadil[2]
[1]*University of Maryland and* [2]*Sandia 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 cathodes 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 MnO_2-Li-HOPG model system. This system consists of low-dimensional beta-MnO_2 and cubic spinel $Li_{1+x}Mn_{2-x}O_4$ 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-MnO_2 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- MnO_2 - C(0001) electrical conductivity, and efforts to overcome this limitation will be described. Additionally, alkali seeded growth of MnO_2 nanocrystals will be presented as a means to guide the formation of alternative MnO_2 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. Blum[1], Jiaqing He[1], John Androulakis[1], David N. Seidman[1], Vinayak P. Dravid[1], and Mercouri G. Kanatzidis[1]
[1] *Northwestern 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 $\text{PbTe-K}_{1.25\text{mol\%}}\text{-Na}_{1.4\text{mol\%}}$, 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 Schiros[1]
[1] *Columbia 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 Johnson[1], Kara Manke[1], Jeffrey Eliason[1], Alexei Maznev[1], Keith Nelson[1], Austin Minnich[1], Maria Luckyanova[1], Kimberlee Collins[1], Gang Chen[1], Adam Jandl[1], Mayank Bulsara[1], Eugene Fitzgerald[1], and Mildred Dresselhaus[1]
[1] *MIT*

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 Brennaman[1], John Papanikolas[1], Thomas Meyer[1], Andrew Moran[1], Christopher Fecko[1], and Malcolm Forbes[1]
[1]*UNC 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 O^{2-}(dpms)Pt^{II}Me(X)- Systems in Water (X = OH^-, I^-)

[CCHF] Anna V. Sberegaeva[1] and Andrei N. Vedernikov[1]
[1]*University 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 O_2 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 O_2 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 O_2 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)$Pt^{II}Me(OH_2)$ 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. Andreatta[1], Hung-Ting Chen[2], T. Brent Gunnoe[1], Victor S.-Y. Lin[3], and Brian G. Trewyn[3]
[1]*University of Virginia;* [2]*Iowa State University and* [3]*Iowa 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)][$BArF_4$] (tbpy = 4,4'-di-tert-butyl-2,2'-bipyridine; L = THF, NCMe or NC_5F_5, $BArF_4$ = 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 Paul[1], Aaron K. Vannucci[1], Jonathan F. Hull[1], Zuofeng Chen[1], Daniel H. Ess[2], Michael R. Norris[1], Javier J. Concepcion[1], and Thomas J. Meyer[1]
[1]UNC Chapel Hill and [2]Brigham Young University

Benzyl alcohol oxidation in aqueous medium was studied by $Ru^{IV}=O^{2+}$ and $Ru^{V}=O^{3+}$ forms of the water oxidation catalyst $[Ru(Mebimpy)(bpy)(OH_2)]^{2+}$. Three different pathways were identified for oxidation by $Ru^{IV}=O^{2+}$: 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 $Ru^{V}=O^{3+}$ compared to $Ru^{IV}=O^{2+}$. Oxidation of hydrocarbons- ethylbenzene, toluene, cumene- were studied by $Ru^{V}=O^{3+}$ 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. Bischof[1], Mu-Jeng Cheng[2], Robert J. Nielsen[2], T. Brent Gunnoe[3], William A. Goddard III[2], and Roy A. Periana[1]
[1]The Scripps Research Institute; [2]California Institute of Technology and [3]University 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. Umile[1], Wei Liu[1], Erika M. Milczek[1], Rodney D. Swartz, II[1], Dawn Wallace[1], and John T. Groves[1]
[1]Princeton 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-rhodum 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 O_2 ACTIVATION AT A SINGLE PALLADIUM CENTER

[CCHF] Dao-Yong Wang[1] and Andrei N. Vedernikov[1]
[1]University of Maryland

P1-I36 - *IN-SITU* NANOELECTROCHEMISTRY

[NECCES] Dongli Zeng[1], Feng Wang[1], Yimei Zhu[1], Jason Graetz[1], Y. Shirley Meng[2], Thomas McGilvray[2], Ming-Che Yang[2], and Danijel Gostovic[2]
[1]*Brookhaven National Laboratory and* [2]*University 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, Robert[1], Jones, Matthew[1], and Mirkin, Chad[1]
[1]*Northwestern 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 Ding[1], Daniel Haskel[2], Jungho Kim[2], Michel Van Veenendaal[2], Paul Chow[1], Yuming Xiao[1], and Ho-kwang Mao[1]
[1]*Carnegie Institution of Washington;* [2]*Argonne 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. Anjos[2], Avram M. Buchbinder[1], Yu Cai[3], Matthew Neurock[3], Steven H. Overbury[2], and Franz M. Geiger[1]
[1]Northwestern University; [2]Oak Ridge National Laboratory and [3]University 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 Ï€-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 Savoie[1], Jon Servaites[1], Mark Ratner[1], and Tobin Marks[1]
[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-Ortiz[1], Joel Yuen-Zhou[1], Sangwoo Shim[1], Geoffrey A. Lott[2], Andrew H. Marcus[2], Jacob J. Krich[1], Jacob Sanders[1], Patrick Rebentrost[1], Stephanie Valleau[1], and Alan Aspuru-Guzik[1]
[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 Arias[1], Patrick Wen[1], Kathy Stone[1], Brian Walker[1], Sebastiaan Vlaming[1], Moungi Bawendi[1], Robert Silbey[1], Vladimir Bulovic[1], Jeremy Baumberg[2], and Keith Nelson[1]
[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

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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

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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 C_{60}. 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-C_{60} 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

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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 Garcia[1], Thomas Vanderpoll[2], Gregory C. Welch[2], Sergio Paniagua-Barrantes[3], Seth Marder[3], Guillermo C. Bazan[2], David S. Ginley[1], Joseph J. Berry[1], and Dana Olson[1]
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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

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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 Burkhart[1], Petr P. Khlyabich[1], and Barry C. Thompson[1]
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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

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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. Roberts[1], R. Eric McAnally[1], Cody W. Schlenker[1], Vincent Barlier[1], Joseph N. Mastron[1], Yuyuan Zhang[1], Mark E. Thompson[1], and Stephen E. Bradforth[1]
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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 Schockley-Quiesser 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 Simon[1], Zeynep Ozkan Araci[1], Hsiao-Chu Lin[1], Neal Armstrong[1], Scott Saavedra[1], Nate Polaske[1], Dominic McGrath[1], Ajaya Sigdel[2], Joseph Berry[2], O'Neil Smith[3], Yanrong Shi[3], and Seth Marder[3]
[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

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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 Hernandez[1], Mayank Mayukh[1], Clarissa Sema[1], Jessica Roberts[1], Nate Polaske[1], Dominic McGrath[1], Diogenes Placencia[1], Neal Armstrong[1], Hsiao-Chu Lin[1], Scott Saavedra[1], and Erin Ratcliff [1]
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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 Meyer[1], Erin Ratcliff[2], Ajaya Sigdel[3], Xerxes Steirer[2], Andres Garcia[3], Joseph Berry[3], David Ginle[3], Dana Olson[3], Paul Ndione[3], Edwin Widjonarko[3], Neal Armstrong[2], and Antoine Kahn[1]
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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 MoO_3 and NiO_x are hole-extraction interlayers which function with very different mechanisms. MoO_3 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 Jenkins[1], Joseph Berry[2], Natalia Doubina[3], Sergio Paniagua[4], Neal Armstrong[1], Antoine Kahn[5], Jens Meyer[5], Seth Marder[4], Christine Luscombe[3], Ajaya Sigdel[2], Paul Ndione[2], and Erin Ratcliff[1]
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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. Willard[1], Loren Kaake[1], Jonathan Moussa[1], Xiaoyang Zhu[1], James R. Chelikowsky[1], and Peter J. Rossky[1]
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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 Brazard[1], Robert J. Ono[1], Takuji Adachi[1], Songsu Kang[1], Joshua C. Bolinger[1], Christopher W. Bielawski[1], Paul F. Barbara[1], and David A. Vanden Bout[1]
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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

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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 C_{60} 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 SQUARAINE MATERIALS

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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 Sykes[1], Kwang Hyup An[1], Brian Roberts[1], Pei-Cheng Ku[1], and Max Shtein[1]
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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 reduced exciton quenching 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 Kretchsmann 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. Aguirre[1], Bertrand Tremolet de Villers[1], Krastina Petrova[1], Robert Thompson[1], Benjamin J. Schwartz[1], Yves Rubin[1], and Sarah H. Tolbert[1]
[1]*UCLA*

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 Kumar[1], Akshay Kokil[1], J. Matthew Chudomel[2], Paul Homnick[2], and Paul M. Lahti[2]
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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

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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 Labastide[1], Mina Baghgar[1], Austin Cyphersmith[1], Harihara Venkatraman[1], D. Venkataraman[1], and Michael D. Barnes[1]
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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. Pandey[1], Jun Wang[1], T. J. Mountziaris[1], and Dimitrios Maroudas[1]
[1]*University 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 $ZnSe_{1-x}Te_x$ and $In_xGa_{1-x}As$ 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 Gorodetsky[1]
[1]*Columbia 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 Yardley[1], Louis Brus[1], and Tony Heinz[1]
[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 *Schuller* [1]
[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 Cox[1]
[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 Esfarjani[1], Zhiting Tian[1], Takuma Shiga[2], Tengfei Luo[1], Junichiro Shiomi[2], Jivtesh Garg[1], Olivier Delaire[3], and Gang Chen[1]
[1]*MIT;* [2]*U Tokyo and* [3]*ORNL*

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 (Bi_2Te_3) 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 Martinson[1], Noel Giebink[1], Gary Wiederrecht[1], Daniel Rosenmann[1], Michael Pellin[1-2], and Michael Wasielewski[1-2]
[1]*Argonne National Lab and* [2]*Northwestern University*

Dye-sensitized solar cells (DSSCs) differ from other phovoltaics 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 DeMarco[1], Patrick Shively[1], Michael DeVries[1], Hanning Chen[1], George Schatz[1], Michael Pellin[2], and Josepth Hupp[1]
[1]*Northwestern University and* [2]*Argonne 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. Simonds[1], Jeremy D. Fields[1], and P. Craig Taylor[1]
[1]*Colorado 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. Stewart[1], Aaron G. Midgett[2], Lazaro A. Padilha[3], Danielle K. Smith[1], Jeffrey M. Pietryga[2], Joseph M. Luther[1], Matthew C. Beard[2], Arthur J. Nozik[2], and Victor I. Klimov[2]
[1]*Los Alamos National Laboratory;* [2]*National Renewable Energy Laboratory and* [3]*University of Colorado*

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 experiential 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 (Eg), 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?) to Eg, while for both PbS and PbSSe QDs following an initial increase, the QY drops above a certain values of h?/Eg. 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 Law[1], Yao Liu[1], Markelle Gibbs[1], Jason Tolentino[1], and Rachelle Ihly[1]
[1]*University of California, Irvine*

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 Holman[1], Chin-Yi Liu[1], and Uwe Kortshagen[1]
[1]*University 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 cm^2/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. Madaria[1], Maoqing Yao[1], ChunYung Chi[1], Ruijuan Li[1], Chenxi Lin[1], Ningfeng Hunag[1], P. Daniel Dapkus[1], Michelle Povinelli[1], and Chongwu Zhou[1]
[1]*University 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 patterning techniques to obtain highly ordered pattern for SA-MOCVD and demonstrate wafer-scale fabrication of GaAs nanowires nanowire 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 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 Zakutayev[1], Tula Paudel[1], John Perkins[1], Nicola Perry[2], Thomas Mason[2], Joanna Bettinger[3], Yezhou Shi[3], Michael Toney[3], Stephan Lany[1], David Ginley[1], and Alex Zunger[1]
[1]*NREL;* [2]*Northwestern University and* [3]*SLAC 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 Co_2ZnO_4, 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 Co_2ZnO_4. Second is the enhancement of antisite disorder and for Co_2ZnO_4 we show that the intentional non-equilibrium growth of Zn-rich Co_2ZnO_4 enhances both the conductivity and optical transparency. Finally, third is the conversion, through alloying, of normal spinels, such as Co_2ZnO_4, into related inverse spinels, such as Co_2NiO_4 for which the maximum conductivity is ~ 200 S/cm, roughly 104 times higher than that for intrinsic Co_2ZnO_4. 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 Jung[1], Neil P. Dasgupta[1], Orlando Trejo[1], Matthew T. McDowell[1], Aaron Hryciw[1], Robert Sinclair[1], and Fritz B. Prinz[1]
[1]*Stanford 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 Huang[1], Divine P. Kumah[1], Jia-Hung Wu[1], Naji S. Husseini[1], Andrey V. Semichaevsky[2], Harley T. Johnson[2], Roy Clarke[2], and Rachel S. Goldman[2]
[1]*University of Michigan and* [2]*University 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 Gladden[1], Majid Gharghi[1], Ze'ev Abrams[1], and Avi Niv[1]
[1]*UC 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 Kosten[1], Emily Warren[1], and Harry Atwater[1]
[1]*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 noptics model to experimental data, we find that it shows reasonable agreement with large (4 um radius) wires, but underpredicts the absorption in smaller (1 um 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 Ning[1], Augstin Mihi[1], Erik Nelson[1], John Rogers[1], and Paul Braun[1]
[1]*UIUC*

The continuous demand for increasing the efficiency of photovoltaic devices has lead 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 Hill[1], Alexander G Krause[1], Amir Safavi-Naeini[1], and Oskar Painter[1]
[1]*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 Deng[1], Samuel Humphry-Baker[1], Weishu Liu[1], and Christopher Schuh[1]
[1]*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 Kraemer[1], Kenneth McEnaney[1], Bed Poudel[2], Hsien-Ping Feng[1], J. Christopher Caylor[2], Bo Yu[3], Xiao Yan[3], Yi Ma[3], Xiaowei Wang[3], Dezhi Wang[3], Andrew Muto[1], Matteo Chiesa[4], Zhifeng Ren[3], and Gang Chen[1]
[1]*MIT;* [2]*GMZ Energy;* [3]*Boston College and* [4]*Masdar 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 °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 Bermel[1], Michael Ghebrebrhan[1], Yi Xiang Yeng[1], Youngsuk Nam[1], Evelyn Wang[1], John Joannopoulos[1], Ivan Celanovic[1], and Marin Soljacic[1]
[1]*MIT*

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 Yeng[1], Michael Ghebrebrhan[1], Peter Bermel[1], Walker Chan[1], John Joannopoulos[1], Marin Soljacic[1], and Ivan Celanovic[1]
[1]*MIT*

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 $(Bi,Sb)_2(Te,Se,S)_3$

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We have found that a small amount of Cu added to $Bi_2Te_{2.7}Se_{0.3}$ can drastically improve the process repeatability of the thermoelectric properties of $Cu_{0.01}Bi_2Te_{2.7}Se_{0.3}$. 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 Bi_2Te_2S 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 $Bi_{0.4}Sb_{1.6}Te_3$ 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)

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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 Mn = 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

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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

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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" ($(P\text{-}P)_2M(N_2)_2$, 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

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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

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[1]*Purdue University and* [2]*University 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 C^3Bio, 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 Carey[1]
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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 ^{13}C 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-^{13}C Alanine, U-^{13}C Glutamine, or 80%1,2-^{13}C Glucose and 20%U-^{13}C Glucose. Also illustrated are select labeling differences between light levels analyzed by GCMS.

P2-C06 - BIOMIMETIC CATALYSTS FOR HYDROGEN EVOLUTION

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[1]*University of Illinois and* [2]*Northwestern 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 TiO_2 SURFACES

[ANSER] Julio L. Palma[1], Laura J. Allen[1], Rebecca L. Milot[1], Karin Brumback[1], Gary W. Brudvig[1], Charles A. Schmuttenmaer[1], Robert H. Crabtree[1], and Victor S. Batista[1]
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We characterize the electronic rectification properties of molecular linkers that covalently bind Mn catalysts to TiO_2 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 TiO_2 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 Cedeno[1] and Joseph J. Bozell[1]
[1]*University 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 Wei[1], Haibing Yang[2], Joe Cox[2], Bryon S. Donohoe[1], Peter N. Ciesielski[1], Michael E. Himmel[1], Angus Murphy[2], Wendy Peer[2], Maureen McCann[2], Melvin P. Tucker[1], and Mahdi M. Abu-Omar[2]
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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. Olek[1], Lake Paul[1], Catherine Rayon[1], Subhangi Ghosh[1], and Nicholas C. Carpita[1]
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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. Parsell[1], Laura J. Haupert[1], Lucas M. Amundson[1], Benjamin C. Owen[1], Christopher L. Marcum[1], Tiffany M. Jarrell[1], Christopher J. Pulliam[1], Padmaja Narra[1], Mohammad Sabir Aqueel[1], Nelson R. Vinueza[1], Joseph J. Bozell[1], Hilkka I. Kenttamaa[1], and Mahdi M. Abu-Omar[1]
[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 Gawecki[1], Andrew D. Smeltz[1], Matthew R. Hurt[1], David J. Borton II[1], Nelson R. Vinueza[1], Nicholas J. Nugent[1], Rakesh Agrawal[1], W. Nicholas Delgass[1], Hilkka I. Kenttamaa[1], William E. Anderson[1], and Fabio H. Ribeiro[1]
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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-Silva[1], Rebecca Cahoon[1], and Edgar Cahoon[1]
[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 Pieris[1]
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Photosynthesis occurs via light and dark reactions in the chloroplast thylakoid membranes and stroma respectively. Under saturating light and CO_2 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 CO_2 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 CO_2 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 chcloroplast 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 Deshpande[1] and Yair Shachar-Hill[1]
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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 (^{13}C 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 reinhardti* (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 reinhardti*. 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

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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-aristrochene 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 Dutta[1] and Anne K. Jones[1]
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[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 metallocenter 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 N_2S_2 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 metallocenters. 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

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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 m^2/g (equivalent to ~700 m^2 per 1 cm^3 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 cyclovoltammetric and UV-VIS studies.

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

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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 Rendek[1], Chad Simmons[1], Justin Flory[1], Sudipta Biswas[1], Xixi Wei[1], Chenxiang Lin[1], Sandip Shinde[1], Ingo Grotjohann[1], Raimund Fromme[1], Giovanna Ghirlanda[1], Hao Yan[1], Yan Liu[1], and Petra Fromme[1]
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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 Mn_4CaCl 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 Mn_4CaCl cluster have been identified through X-ray analysis of PSII. Truncated regions of the peptide sequences that contain Mn_4CaCl 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

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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 Sb_2O_3 (929 K). Because Sb_2O_3 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 Salciccioli[1], Weiting Yu[1], Mark Barteau[1], Jingguang Chen[1], and Dion Vlachos[1]
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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

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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/?-Al_2O_3, Ni/?-Al_2O_3, and NiPt /?-Al_2O_3 in a packed bed reactor. Under the experimental conditions used, the Ni catalyst deactivates quickly. The bimetallic catalyst NiPt /?-Al_2O_3 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

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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

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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, CO_2, H_2O 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

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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

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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

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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 HANSENII CELLULOSE SYNTHESIS

[CLSF] Prashanti R. Iyer[1], Jeffrey M. Catchmark[1], Nicole R. Brown[1], and Ming Tien[1]
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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

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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)-?-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

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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 developped 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 extend 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. Kittle[1], Xiaosong Du[1], Xiao Zhang[1], Chen Qian[1], Maeve Budi[1], Alan R. Esker[1], Feng Jiang[1], Maren Roman[1], Jing Gu[2], and Jeffrey M. Catchmark[2]
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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

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Cellulose, a crystallized polymer comprised of Î²-1,4 linkedglucose residues, is the earth's major biopolymer of enormous global economic importance. Cellulose synthase (CesA) integral membraneproteins are responsible for its synthesis in plants, algae, somebacteria, and animals such as sponges. In a broader context, CesA's are in the family of glycosyltransferases which are a diverse set ofenzymes 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 anunderstanding 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* structureprediction following by refinement by molecular dynamics simulations of the CesA protein of *Gossypium hirsutum* and CesAs 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

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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 interdigited 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 ï m, 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

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In the family of bio-inspired hydrogen production/oxidation catalysts, $[Ni(PR_2NR'_2)_2]^{2+}$, 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. ^{31}P lineshape analysis and 2D EXSY NMR experiments were used to characterize proton exchange between pendant amines in the hydrogen oxidation catalyst, $[Ni(PCy_2NBn_2H)_2]^{2+}$. 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

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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 ($PR_2NR'_2$). Chloride abstraction in aerobic solvent gives stable, cationic species with O_2 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 O_2 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 $Cp^*Ru(PR_2NR'_2)O_2^+$ are currently being examined.

P2-C37 - PLASMONS AND RUST FOR SOLAR ENERGY CONVERSION

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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

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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-$Ti_{15}O_{32}$(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 TiO_2 is considerable enhanced compared to that on TiO_2. Given that TiO_2 is extremely cheap, some of the systems considered here may serve as candidates for cheap alternatives to expensive RuO_2 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 MoS_2 BY ELECTROCATALYSIS AND SOLAR PHOTOELECTROCHEMISTRY

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We develop nanoparticles of MoS_2 for photoelectrochemical water splitting. Bulk MoS_2 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 MoS_2 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 MoS_2 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 MoS_2 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. Anjos[1], Glen Alliger[1], Alexander I. Kolesnikov[1], Yu Cai[2], Matthew Neurock[2], Zili Wu[1], John McDonough[3], Yury Gogotsi[3], Gilbert M. Brown[1], and Steven H. Overbury[1]
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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 chronoamperommetry and kinetic isotope effects. Finally, the application of PCET for improvement of photocatalysis for water splitting has been investigated by photoelectrochemistry of modified TiO_2.

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

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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 fuels 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 ^{13}C LABELING

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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 (PO_4^{3-}/niobic acid or Amberlyst 70 catalysts) by monitoring the ^{1}H and ^{13}C NMR spectra. Using ^{13}C-labeled fructose we have identified two key intermediates in the formation of HMF, and we have investigated the mechanism of HMF formation utilizing ^{13}C-labeled precursors. Results with ^{13}C 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 ^{13}C 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 Dietrich[1], Rodrigo Lobo[2], Neng Guo[2], Tianpin Wu[2], Bradley Fingland[2], Fabio Ribeiro[1], Nicholas Delgass[1], Jeffrey Miller[2], and James Dumesic[3]
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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, H_2, and H_2O 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

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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 Nb_2O_5 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 Î³-valerolactone (GVL) to pentanoic acid.

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

[PARC] Aaron M. Collins[1], Michelle Liberton[2], Sangeeta Negi[3], Howland D.T. Jones[1], Omar F. Garcia[1], Michael B. Sinclair[1], Himadri B. Pakrasi[2], Richard T. Sayre[3], and Jerilyn A. Timlin[1]
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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-call "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 absorbs 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 cyanbacterium, *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[1]
[1] *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[1]
[1] *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 PHOTSYNTHETIC LIGHT-HARVESTING COMPLEXES FOR BIO-HYBRID SOLAR UTILIZATION

[PARC] William Bricker[1] and Cynthia Lo[1]
[1] *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 Qy 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[1]
[1] *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 ~ 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 perfluoronated silanes in hexanes of ITO slides, that were pre-loaded with $[Ru(P_2bpy)_2(bpy)]^{2+}$ (as a chomophore 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. Weinberg[1], Zuofeng Chen[1], Peng Kang[1], Javier Concepcion[1], Chuncheng Chen[1], Aaron Vannucci[1], David Stewart[1], Marsha Massey[1], Maurice Brookhart[1], Cynthia Schauer[1], Shubin Liu[1], and Thomas J. Meyer[1]
[1]*The 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 Hu[1]
[1]*Duke 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 $[Ru^{II}(OH_2)(tpy)(bpm)]^{2+}$ (i.e, $[Ru^{II}\text{-}OH_2]^{2+}$) 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. Morse[1] and Hong-Li Zhang[1]
[1]*University 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 ^oC 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. Hayner[1] and Sudeshna Chattopadhyay[1]
[1]*Northwestern 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 story 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 Chan[1], Scott Kirklin[2], Hakim Iddir[1], Kah Chun Lau[1], Jishnu Bhattacharya[2], David Snydacker[2], Jeff Greeley[1], Chris Wolverton[2], and Larry Curtiss[1]
[1]*Argonne National Laboratory and* [2]*Northwestern 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 Fister[1], Maria Chan[1], Paul Fenter[1], Jeff Greeley[1], Jason Goldman[2], Brandon Long[2], Michael Cason[2], Ralph Nuzzo[2], and Andy Gewirth[2]
[1]*Argonne National Laboratory and* [2]*University 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 ($Li_4.4Si$), 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. Hersam[2], and Michael M. Thackeray[1]
[1]*Argonne National Laboratory and* [2]*Northwestern 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 TiO_2-carbon particles, prepared from a titanium alkoxide precursor, consist of 30-40 nm sized TiO_2 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^oC/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]
[1]*LBNL and* [2]*GE 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]
[1]*LBNL;* [2]*Yale University and* [3]*GE Global Research*

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. Luca[1], Steven J. Konezny[1], Jeremy M. Praetorius[1], Kurt M. Luthy[1], Ting Wang[1], Grigorii L. Soloveichik[2], Mark D. Doherty[2], Davide L. Simone[2], Victor S. Batista[3] and Robert H. Crabtree[3]
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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 Huang[1], Lakshmi Krishnan[1], Davide Simone[1], Mark D. Doherty[1], Grigorii L. Soloveichik[1], Guillermo D. Zappi[1], Matthew Rainka[1], Oltea Siclovan[1], Thomas Miebach[1], John Kerr[2], and Judith Stein[1]
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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 Vajo[1], Jun Liu[1], Wen Li[1], John Wang[1], and Ping liu[1]
[1]*HRL*

FeF_3 has been studied extensively as a high capacity cathode material for lithium batteries. During lithiation, FeF_3 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 Dathar[1], Daniel Sheppard[1], Nicholas Delone[1], Jing Wu[1], Keith J. Stevenson[1], and Graeme Henkelman[1]
[1]*University 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 $FePO_4$ and $LiFePO_4$ 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 $FePO_4$. The mechanism switches to single vacancy hopping with a higher barrier for cross-channel diffusion in $LiFePO_4$, 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 Wang[1], Huolin Xin[1], David Muller[1], Francis DiSalvo[1], and Hector Abruna[1]
[1]*Cornell 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 Rus[1], Hongsen Wang[1], Anna Legard[1], Michele Tague[1], Bruce van Dover[1], and Hector Abruna[1]
[1]*Cornell 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, IV[1], Timothy Clark[1], Nocholas Robertson[1], and Geoffrey Coates[1]
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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 ARCHITECHTURES

[EMC2] Michael Lowe[1], Zichao Yang[1], Jayaprakash Navaneedhakrishnan[1], Jennifer Nugent[1], Jie Gao[1], Hector Abruna[1], Lynden Archer[1], and Stephen Burkhardt[1]
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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 Smith[1], Michele Tague[1], John Gregoire[1], Darren Dale[1], Anna Legard[1], Bruce van Dover[1], Frank DiSalvo[1], Richard Hennig[1], and Hector Abruna[1]
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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 fluoremetry. 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. McDonough[1], P. Ganesh[2], P. Fulvio[2], V. Mochalin[1], V. Presser[1], S. Dai[2], P.R.C. Kent[2], and Y. Gogotsi[1]
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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 Song[1], Shuang Cheng[1], Feng Liu[2], and Meilin Liu[1]
[1] *Georgia Institute of Technology and* [2] *University 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 Augustyn[1], Zheng Chen[1], Jong Woung Kim[1], Thomas Quickel[1], Sarah Tolbert[1], Yunfeng Lu[1], and Bruce Dunn[1]
[1] *University 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. Moreoever, 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-TiS$_2$ System to a Li-Fe-F System

[NECCES] Hui-Chia Yu[1], Tapiwa Mushove[1], Jishnu Bhattacharya[1], Chen Ling[1], Anton Van der Ven[1], Katsuyo Thornton[1], Glenn G. Amatucci[2], and Nathalie Pereira[2]
[1]*University of Michigan and* [2]*Rutgers 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 Cu-Ti_2S_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. Chernova[1], Fredrick Omenya[1], Ruigang Zhang[1], M. Stanley Whittingham[1], Feng Wang[2], Jason Graetz[2], Glenn Amatucci[3], Nathalie Pereira[3], Thomas McGilvray[4], and Y. Shirley Meng[4]
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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 lead 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 Upreti[1], Ruigang Zhang[1], Natasha Chernova[1], Feng Wang[2], Lin-Shu Du[3], Jaroslaw Syzdek[4], [5]Faisal Alamgir, Christian Burger[3], Jun Wang[2], Cole Petersburg[5], Elaine Lin[5], Jason Graetz[2], Robert Kostecki[4], Clare P. Grey[3], and M.S. Whittingham[1]
[1]*Binghamton University;* [2]*Brookhaven National Laboratory;* [3]*Stony Brook University;* [4]*Lawrence Berkeley Laboratory;* [5]*Georgia Institute of Technology*

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 Li_xSn + Co products could occur. We investigate how the nano-SnCo alloy reacts with lithium in the electrochemical cell by ^{7}Li 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 Wang[1], Kyung-Wan Nam[1], Xiao-Qing Yang[1], Nathalie Pereira[2], and Glenn G. Amatucci[2]
[1]*Brookhaven National Laboratory and* [2]*Rutgers University*

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 $Li_{1-x}FePO_4$ 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 $LiFePO_4/FePO_4$ 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 Janssen[1], Shouhang Bo[1], Lin-Shu Du[1], Derek Middlemiss[1], Peter Khalifah[1], and Clare P. Grey[1]
[1]*Stony 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 - NANOELECTRODE NETWORKS: CHEMISTRY AND MECHANICS AT NANOSTRUCTURED INTERFACES

[NEES] Hongwei Liao[1], Alexandra H. Brozena[1], Khim Karki[1], Yin Zhang[1], John Cumings[1], and YuHuang Wang[1]
[1]*The University of Maryland, College Park*

Carbon nanotube (CNT) @amorphous Si (Î±-Si) core-shell structures are a promising anode material for lithium ion batteries because this heterogeneous structure combines the optimal properties of two materials: Î±-Si maximizes Li^+ storage capacity while the CNT core enhances structural stability and electrical conductivity. We have developed a synthetic approach for fabricating CNT@Î±-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 Î±-Si coating on CNTs. With plasma enhanced chemical vapor deposition, Î±-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 Î±-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 Î±-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 Î±-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 Cho[1], Xianglong Li[1], Xiao Hua Liu[2], Jian Yu Huang[2], and S. Thomas Picraux[1]
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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 $Li_{15}Si_4$ under fast charging condition. Furthermore, we are going to shows 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 SUPERCAPCITORS

[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 MnO_2/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 Depostion (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 ofthese 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 Barin[1], Ali Coskun[1], Jason M. Spruell[1], and J. Fraser Stoddart[1]
[1]*Northwestern 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 Yang[1], Chao Jin[1], and Fanglin (Frank) Chen[1]
[1]*University 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 SOCs 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 Liu[1] and Donald T. Morelli[1]
[1]*Michigan 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

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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 Curtin[1], Hong Lu[1], Jacqueline Hall[1], Chris Palmstrøm[1], Arthur Gossard[1], and John Bowers[1]
[1]*University 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. Santner[1], Michael P. Burke[1], Frederick L. Dryer[1], and Yiguang Ju[1], Swetaprovo Chaudhuri[1], Peng Zhang[1], Fujia Wu[1], and Chung K. Law[1], David F. Davidson[2] and Ronald K. Hanson[2], Bryan W. Weber[3], Mruthunjaya Uddi[3], Apurba Das[3], and Chih-Jen Sung[3], Fokion N. Egolfopoulos[4], and Stephen J. Klippenstein[5]
[1]*Princeton University;* [2]*Stanford University;* [3]*University of Connecticut;* [4]*University of Southern California and* [5]*Argonne 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 Zuo[1], Hefei Hu[1], Ivan Bozovic[2], Cedomir Petrovic[2], Genda Gu[2], Lei Fang[3], Wai-Kwon Kwok[3], Mercouri Kanatizidis[3], and Jim Eckstein[1]
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Superconductivity is observed in certain materials when cooled below a characteristic temperature, Tc , the electrical resistance becomes exactly zero. In superconducting metals, the Tc is well below the liquid nitrogen temperature (90K). The discovery of high Tc 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

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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 TC-SUPERCONDUCTING ORDER PARAMETER WITH PHOTOEMISSION AND POLARIZED X-RAYS.

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The Center for Emergent Superconductivity carries out studies of the physical properties of the high Tc 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

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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 Keszler[1], John Wager[1], Vorranutch Jieratum[1], Ram Ravichandran[1], Brian Pelatt, Emmeline Altschul[1], Robert Kykyneshi[1], and Liping Yu[1-2]
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Inorganic materials exhibiting band gaps > 1 eV and high absorption coefficients (Î± > 105 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 = 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

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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

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The existing Ni-YSZ (yttria-stablized 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 ºC. 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

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A series of complex perovskites $Ba_3Ca_{1.18}Nb_{1.82-x}Y_xO_9$-? (x=0, 0.1, 0.2, 0.3, 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 $5.3\times10_{-3}$ 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 Franco[1], Martin McCullagh[1], Mark A. Ratner[1], and George C. Schatz[1]
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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 Hermans[1] and Bartosz Grzybowski[1]
[1]*NERC*

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 PROPERITES OF VANADIUM BASED ORGANIC COMPOUNDS

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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 (100µV/K). Even if some can have high p, they are not known to be efficient thermoelectric materials. V-TCNE$_x$ or V-$(C_2(CN)_4)_x$ 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-TCNE$_x$ deposited by molecular layer deposition on glass. At room temperature S > 1mV/K and increases with decreasing temperature. The dependence of S and ? 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

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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 ($FeSb_2$) 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 $FeSb_2$ 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 $Yb_{0.6}Co_2Fe_2Sb_{12/x}FeSb_2$. 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 CoSi Alloys

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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

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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 Pb^{2+} 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 Î£ 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 $PbTe/Bi_2Te_3$ for thermoelectric applications

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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= (S2 p) T / k; S = Seebeck coefficient, p = 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 Bi_2Te_3 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

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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 faction 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

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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

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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 (4-6Î¼m long, 100-300nm diameter) at 266nm and at room-temperature. For the smallest diameter nanowires we measure lasing thresholds of 250kw/cm^2. 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 CO_2-BEARING FLUIDS AT NANOSCALE INTERFACES

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Injection of CO_2 into geologic formations has been identified as a key strategy for mitigating the impact of anthropogenic emissions of CO_2. 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 (SiO_2) and clays. We still lack a fundamental understanding of the structural and dynamic behavior of CO_2 (and CO_2-bearing aqueous fluids) in cap rock environments dominated by nanoporosity for state conditions encountered in injection systems. Even for a simple fluid such as CO_2 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 CO_2-matrix interactions relevant to sequestration, (iii) a MD assessment of adsorption behavior of gaseous and supercritical CO_2 interacting with a SiO_2 substrate, (iv) MD modeling of the microscopic behavior of CO_2-H_2O at SiO_2 surfaces and (v) a new MD description of CO_2 in slit pores (muscovite).

P2-F02 - CO_2 FROM BENCHTOP TO OUTCROP: MULTIPHASE REACTIVE TRANSPORT AND A NATURAL ANALOGUE FOR LEAKAGE

[CFSES] Hongkyu Yoon[1], Matt Balhoff[2], Steve Bryant[2], Peter Eichhubl[2], Tom Dewers[1], Yashar Mehmani[2], and Tie Sun[2]

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Development and mitigation of leakage pathways from subsurface CO_2 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 ($scCO_2$) in subsurface saline formations from the perspective of multiphase flow, reactive transport, and rock deformation. Pore-scale experiments on micromodel calcite precipitation, $scCO_2$-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 $scCO_2$ 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 $scCO_2$ breakthrough and wettability. The model allows for prediction of the formation of preferential pathways for CO_2 transport in porous media. All of these results bear on the transport and disposition of CO_2 and associated mineral precipitation patterns observed in outcrop samples from the Crystal Geyser, near Green River, Utah, a natural analog for subsurface CO_2 leakage.

P2-F03 - MULTIPHYSICS MODELS OF CAPROCK FRACTURING DURING CO_2 INJECTION

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Worldwide energy consumption, mainly through the use of fossil fuels, has contributed to a significant increase in atmospheric levels of carbon dioxide (CO_2), a so-called greenhouse gas. Long term sequestration of anthropogenic CO_2 by injection into deep saline formations has been espoused as a viable option for reducing atmospheric levels of CO_2 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 CO_2. Geologic trapping of CO_2 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 CO_2 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 CO_2 INJECTION -- IMPLICATIONS FOR FIELD SCALE MONITORING OF SEQUESTRATION PROCESSES

[CFSES] Mrinal Sen[1], Sean McKenna[2], Ranjana Ghosh[1], Hongkyu Yoon[2], Son Phan[1], Sanjay Srinivasan[1], and Rui Zhang[1]

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The effects of CO_2 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 CO_2 plume post-injection. Towards this goal, we have carried out three primary tasks: (1) laboratory measurements of elastic stiffness of cores from the Cranfield CO_2 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 CO_2 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 CO_2. 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 CO_2 SEEPAGE BASED ON FIELD OBSERVATIONS AT CRYSTAL GEYSER NATURAL ANALOG

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The Little Grand Wash normal fault in Green River, Utah, hosts 10-15 naturally occurring active and inactive CO_2 seeps. We studied the association of fault structure with CO_2-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 CO_2 systems. CO_2 seepage is focused along fault segment intersections within the 200-meter-wide fault zone. CO_2 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 CO_2 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 CO_2 flow conduits. The observed reduction in porosity and permeability would restrict the upward flow of CO_2-charged water through fault conduits over time. Field structural observations and available radiometric dates on travertine suggest, however, that CO_2 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 CO_2 CAPTURE TOWARD APPLICATION: AN EFRC/NETL COLLABORATION

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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

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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 CO_2 AND METAL-ORGANIC FRAMEWORKS

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Significant experimental efforts are focusing on the design of the optimal metal-organic frameworks (MOFs) to capture CO_2 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 CO_2-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 CO_2 molecule and different MOF sites. This study provides insight into the CO_2-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

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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 (CO_2/N_2 separations), pre-combustion capture (CO_2/H_2 separation), and oxyfuel combustion (O_2/N_2 separation). The pore surfaces of these materials can be modified post-synthetically to achieve selectivities for CO_2 over N_2 well over 10. The working capacity and selectivities for metal-organic frameworks for CO_2 in the presence of H_2 at high pressures relevant to CO_2/H_2 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 O_2 that cannot be achieved with N_2, 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

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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 CO_2 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 CO_2 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 CO_2 adsorption from first principles calculations. Since van der Waals (vdW) forces create much of the CO_2 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. Houndonougbo, 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. Let. 92, 246401 (2004)

P2-F11 - UNDERSTANDING GAS ADSORPTION IN ZEOLITIC IMIDAZOLATE FRAMEWORKS: EXPERIMENTAL SYNTHESIS AND CHARACTERIZATION

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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 CO_2, CO, and CH_4. 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 Zn^{2+} were studied. These frameworks showed that certain functionalities played an important role in CO_2 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 m^2/g for the specific surface area of the neoformed calcite, added to the initial calcite surface area of 0.012 m^2/g, results in good agreement with the continuum model.

P2-F13 - AGING IN DISSOLUTION AND PRECIPITATION RATES FOR MINERALS RELEVANT TO CO_2 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 CO_2 is converted to minerals or dissolved in aqueous solution, both in the context of long-term mineralization of CO_2 and short-term modification of the subsurface porosity and conductivity.

P2-F14 - CARBON DIOXIDE - WATER INTERFACIAL TENSION UNDER GEOLOGIC CO_2 STORAGE CONDITIONS: A MOLECULAR DYNAMICS SIMULATION STUDY

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Carbon dioxide storage in subsurface geologic formations, principally saline aquifers, is currently under development as a major approach for abating anthropogenic CO_2 emissions. To ensure the long-term viability of geologic carbon storage, buoyancy-driven escape of reservoir CO_2 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 CO_2 into the cap rock pore space. This force, which depends on closely related properties such as brine-CO_2 interfacial tension (IFT), remains poorly characterized in conditions relevant to CO_2 sequestration. In the present study, we tested the ability of molecular dynamics (MD) simulations to predict the properties of CO_2-water (and eventually CO_2-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 CO_2-water IFT data. Our results also showed that IFT is most sensitive to the short-range portion of the CO_2-H_2O interaction, thus indicating a future means for improving model parameters. Finally, our results confirmed that pressure—especially below the critical CO_2 pressure of 7 MPa—exerts the dominant control on IFT and, therefore, on the CO_2 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 CO_2, which are affected by changes in fluid chemistry and porosity-permeability during geologic CO_2 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 Ca^{2+} concentrations similar to those encountered in subsurface reservoir conditions were used. The solutions' ionic strengths ranged from 10 mM to 1M NaCl. $CaCO_3$ nucleation experiments on quartz (100) substrates showed a decrease of the nucleation rate with increasing salinity, as expected from the reduced activity of Ca^{2+} and CO_3^{2-} at high ionic strength. The GISAXS data from $CaCO_3$ 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 $CaCO_3$ 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.