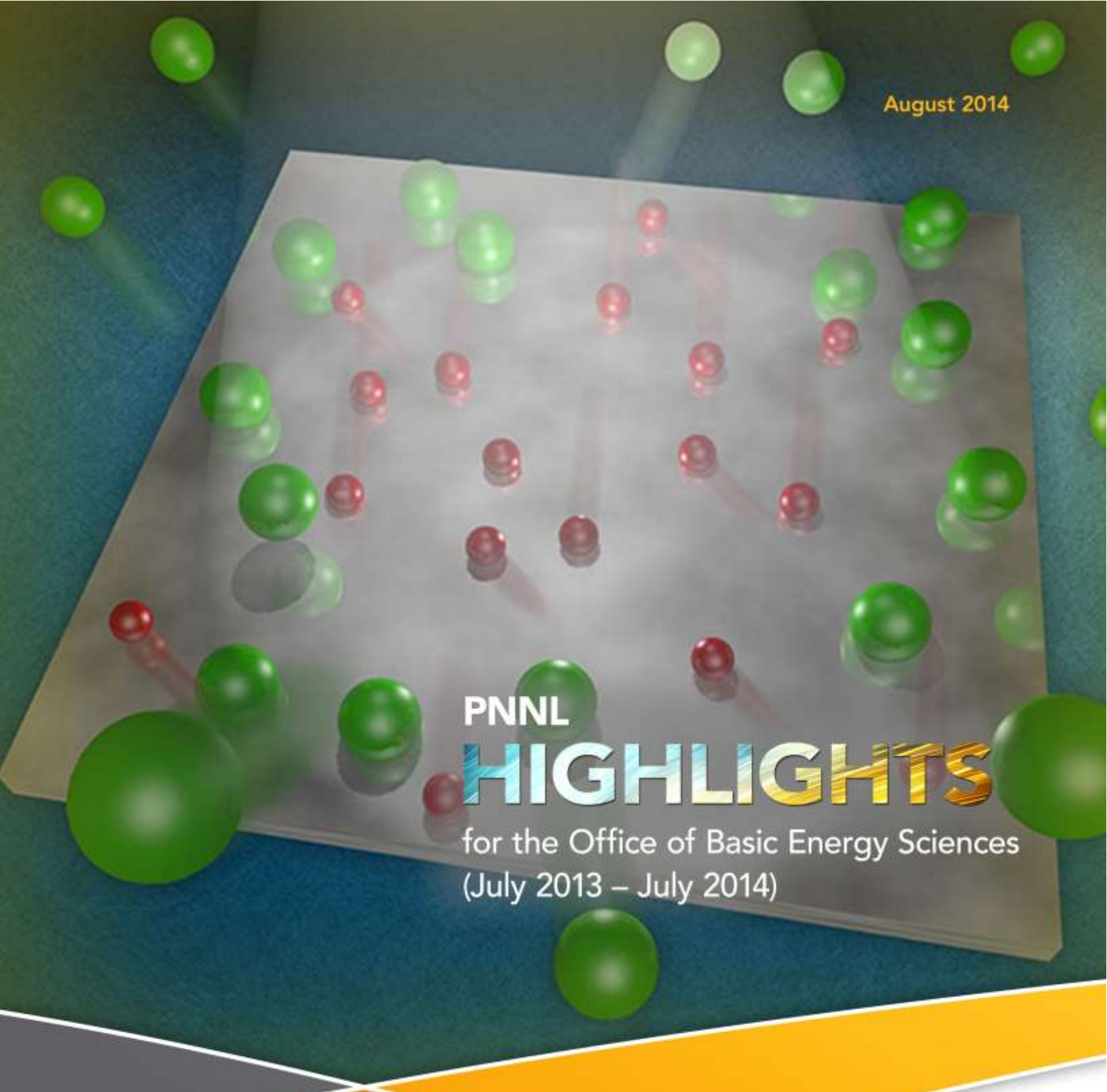

August 2014

PNNL HIGHLIGHTS

for the Office of Basic Energy Sciences (July 2013 – July 2014)

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About the Cover: Long thought to be unresponsive to ultraviolet light, oxygen adatoms actually respond to light. PNNL researchers made this discovery by coating the surface of the catalyst titanium dioxide with krypton reporters. When light strikes the catalyst, the oxygen adatoms become electronically excited and knock the krypton off the surface.

PNNL Highlights for the Office of Basic Energy Sciences (July 2013 – July 2014)

August 2014
Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Pacific Northwest National Laboratory Highlights for the Office of Basic Energy Sciences showcases our fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels to provide the foundations for new energy technologies and to support the U.S. Department of Energy's missions. The highlights are from July 2013 to July 2014.

In addition to reading about outstanding fundamental research that appeared in key scientific publications, you'll also see invited review articles, where our staff were asked to provide the definitive examination of a topic. The BES leadership highlights showcase our experts' contributions to the chemical sciences, geosciences, biosciences, and materials sciences. You'll see new fellows in the Materials Research Society, Royal Society of Chemistry, and other organizations along with awards from professional societies in the United States and abroad.

As you leaf through these pages, you will see that Pacific Northwest National Laboratory's contributions to BES programs are making significant impacts in the basic energy sciences. PNNL is poised to deliver even more important science to the nation in the future.

We are pleased to share this limited edition compilation with you.

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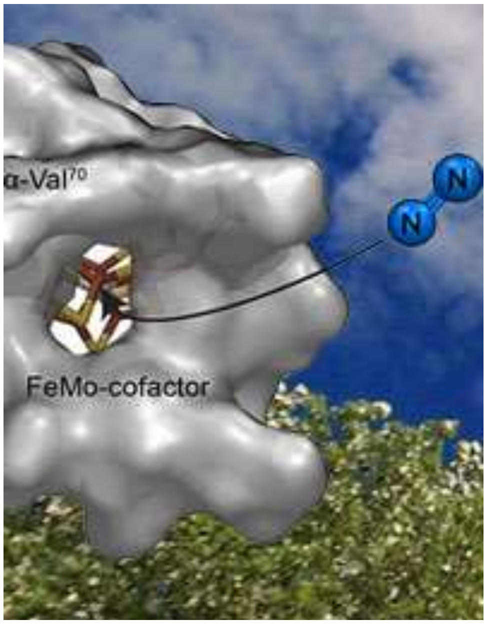
Research Highlights

Catalysis

Navigating the Nitrogen Passage

Scientists discover channel used by catalyst to produce ammonia, vital for food and fuel crops

May 2014



The enzyme nitrogenase uses molybdenum and iron to turn nitrogen from the air into ammonia. How does the nitrogen gas reach the heart of the catalyst? A team from Pacific Northwest National Laboratory and Utah State University discovered the actual channel the nitrogen uses. The open conformation of the nitrogen channel in a molybdenum-dependent nitrogenase is shown here.

Results: Mother Nature's helper in turning nitrogen from the air into ammonia is an enzyme called nitrogenase that uses molybdenum and iron; scientists want to learn natural catalysts' secrets and apply them to synthetic catalysts. To do so, they first need to know how the nitrogen gas reaches the heart of the catalyst. While scientists have posited long, convoluted routes, a team from Pacific Northwest National Laboratory and Utah State University discovered the actual channel the nitrogen uses. It is short and direct. They discovered the channel by identifying groups of proteins on the catalyst's surface that guard access to the metal atoms, twisting aside to allow nitrogen in.

"Our channel is the only one anyone has seen in action," said Dr. Simone Raugei, a theoretical chemist at PNNL who worked on the study.

Why It Matters: Producing ammonia for use in fertilizer is an energy-intense reaction, known as the Haber-Bosch reaction, that requires high temperatures, around 500°C. The reaction consumes hydrogen gas derived from fossil fuels. Nitrogenase takes fundamentally different process to produce ammonia, and this natural reaction happens quickly at room temperature. If a synthetic catalyst could be designed that operates efficiently at room temperature and consumes available protons and electrons instead of hydrogen gas, it would greatly benefit both the agricultural and energy sectors. The discoveries made in this study provide vital information for designing such catalysts.

"We knew where the reaction happened," said Dr. Dayle Smith, a computational chemist at PNNL who conducted the study. "But, we didn't know how the nitrogen got there. Now we do."

Methods: The researchers modeled molybdenum-dependent nitrogenase, a fast, efficient, and prevalent enzyme. The natural catalyst drives a reaction that turns 1 nitrogen molecule into 2 ammonia molecules. The reaction happens at the active site, buried deep inside the molecule. To access the metals at the active site, nitrogen gas must traverse channels from the surface to the active site.

Previously, scientists suggested three possible channels that directed the nitrogen to the active site. Each of these channels was long and convoluted. To determine the actual channel, the team ran submicrosecond atomistic molecular dynamics simulations using a supercomputer at EMSL. The simulations provide the location and trajectories of each atom as the enzyme catalyzes the reaction.

"Being able to see how the atoms move — you can get a lot out of that," said Smith.

In analyzing the data, the team found the channel was short and not far away at all, but rather close to where the chemistry happens. The channel is covered by protein groups on the surface that act as flaps that open to allow the nitrogen to enter.

"Nobody could see it before because you had to have the protein moving to see it," said Smith.

The team further analyzed the viability of the channel by studying the energy required for the nitrogen to move through the catalyst. Their calculations showed that nitrogen uptake occurs along a low-energy path.

What's Next? The team's next steps include determining how other small molecules enter and exit the catalyst.

If a synthetic catalyst could be designed that operates efficiently at room temperature and consumes available protons and electrons instead of hydrogen gas, it would greatly benefit both the agricultural and energy sectors. The discoveries made in this study provide vital information for designing such catalysts.

Acknowledgments:

Sponsors: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division (DS, SR) and a separate DOE Office of Science grant (LCS, KD)

User Facility: EMSL for computational resources

Research Team: Dayle Smith and Simone Raugei, Pacific Northwest National Laboratory; Karamatullah Danyal, Utah State University; and Lance C. Seefeldt, Utah State University and Pacific Northwest National Laboratory (joint appointment)

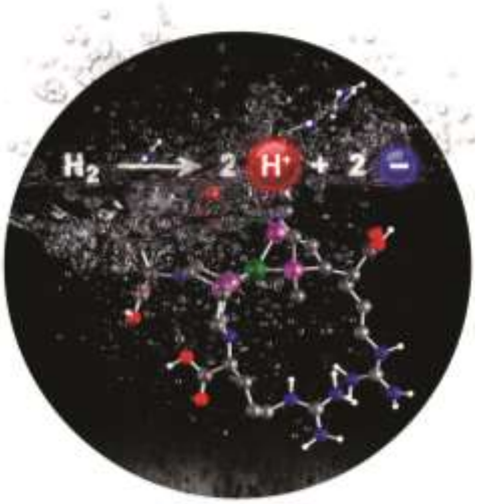
Reference: Smith D, K Danyal, S Raugei, and LC Seefeldt. 2014. "Substrate Channel in Nitrogenase Revealed by a Molecular Dynamics Approach." *Biochemistry* 53(14):2278-2285. DOI: 10.1021/bi401313j

Getting into the Fast Lane Means Minor Adjustments Far from the Catalyst's Core

Adding an amino acid increases speed by 400 percent and requires little energy

May 2014

Results: When it comes to making catalysts that quickly snap chemical bonds and free the stored energy, researchers often focus on the active site. However, small changes far from the active site can also have a large impact. Taking a cue from enzymes, researchers at Pacific Northwest National Laboratory (PNNL) placed the amino acid arginine at the periphery of a hydrogen-splitting catalyst that cleaves hydrogen into protons and electrons. The arginine's carboxylic acid groups accelerated proton transfer and made the catalyst more energy efficient. At the same time, the arginine guanidinium groups interacted with each other to increase the rate of hydrogen binding and activation. With the appended arginine and at 133 atm hydrogen, this nature-inspired catalyst can split 144,000 molecules of hydrogen in a single second.



Including an arginine in the ligand of a hydrogen oxidation catalyst results in water solubility, enhances proton movement through the carboxylic acid groups, and alters that active site structure through intramolecular guanidinium:guanidinium interactions.

"Here we are incorporating minimal elements of natural enzymes into synthetic catalysts to understand their role and begin defining how much is necessary to make molecular catalysts as good as, or better than, the enzyme," said Dr. Arnab Dutta, a postdoctoral fellow at PNNL who worked on the study.

Why It Matters: Few people want electricity only when the sun shines. Solar and wind energy could play a larger role if the energy they capture were to be stored in the chemical bonds of fuels such as hydrogen in fuel cells, then recovered later as electricity. Hydrogenase enzymes do exactly this, and quickly: some can cleave 10,000 molecules of hydrogen a second with little excess energy and without precious metals such as platinum. The enzyme is made up of an active site and a protein scaffold. The active site is where the action is; however, the core or active site is not the whole story.

The PNNL team hypothesized that to mimic enzymes' speed and energy efficiency, they must keep selective parts of the protein scaffold or outer coordination sphere, in this case a single amino acid. With this study, scientists are getting closer to enzymatic speed and energy efficiency — all with changes far from the active site, and in a system that is much more stable than the enzyme under fuel cell conditions.

Methods: The team began with the nickel-based DuBois catalyst, which has a proton relay. They added a second proton relay to build a proton channel that moves protons from the active site to the surrounding solution. Within these channels, the proton is passed from one relay to the next like a baton in a relay race. The team added arginine to the complex, with the idea of putting another player in the race.

The revised catalyst is abbreviated $[Ni^{II}(P^{Cy}{}_2N^{Arg}{}_2)_2]^{8+}$; Arg stands for arginine.

Arginine was chosen because it plays important roles in moving protons and stabilizing structures in proteins and enzymes. In the synthetic catalyst, this amino acid's carboxylic acid groups make protons move quickly, decreasing the excess energy required for catalysis. The $[Ni^{II}(P^{Cy}{}_2N^{Arg}{}_2)_2]^{8+}$ system is one of the most energy-efficient synthetic catalysts now known.

"Energy efficiency is extremely relevant to energy technologies, and our research is allowing us to put together a general understanding of what affects or alters energy efficiency," said Dr. John A. S. Roberts, a PNNL chemist who worked on the study.

While the arginines' guanidinium groups were introduced with the idea of further enhancing proton movement, they serve a different role, interacting to cause a change in the shape of the active site, resulting in a catalyst that splits 210 hydrogen molecules a second at 1 atm hydrogen, 4 times faster than previously reported complexes. When the hydrogen pressure was increased to 133 atm, the catalyst breaks 144,000 molecules a second, orders of magnitude faster.

In some ways, the team's catalyst is better suited for real-world energy technologies than its natural inspiration, because extreme solution acidity can deactivate certain enzymes. The catalyst works in both basic and neutral conditions, and operates best under the highly acidic conditions found in fuel cells.

The study demonstrates a bottom-up approach based on understanding enzymes' functions and adding the components that perform these functions to a simple synthetic catalyst.

"Our methodology is broadly applicable," said Dr. Wendy Shaw, a PNNL biophysical chemist who led the study. "As we increase our understanding of how the outer coordination sphere functions, we can take our bottom-up approach to other catalysts to improve their reactivity, operation, specificity, and all of the things that enzymes do so well."

What's Next: To understand the structural role of the guanidinium pairing in the proton channel, the team is studying how the environment alters the catalyst's behavior and the impact of other structural elements. In addition, they are collaborating with two organizations to attach the catalyst to carbon nanotubes, for use in fuel cells, and to attach it to quantum dots for photocatalysis applications.

Acknowledgments:

Sponsors: Office of Science Early Career Research Program through the U.S. Department of Energy's Office of Basic Energy Sciences (AD, WJS), and the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science's Office of Basic Energy Sciences (JASR)

User Facility: EMSL

Research Team: Arnab Dutta, John A. S. Roberts, and Wendy Shaw, PNNL

Reference: Dutta A, JAS Roberts, and WJ Shaw. 2014. "Arginine Containing Ligands Enhance H_2 Oxidation Catalyst Performance." *Angewandte Chemie International Edition. Communications*.
DOI: 10.1002/anie.201402304

State of the Science: Making Plastics from Biomass, Not Fossil Fuels

Researchers review advances in catalysts that turn bioethanol into valuable chemicals

May 2014

Results: Ethanol from garbage and other sources could replace fossil fuels in manufacturing plastics, rubber, and other chemicals if scientists can gain the needed knowledge of catalysis, according to scientists at Pacific Northwest National Laboratory (PNNL) and Washington State University (WSU). In their invited article, Dr. Yong Wang and Dr. Junming Sun review the current state of understanding on converting ethanol into a host of other chemicals. They also identify future research directions, including one-step ethanol conversions.

Plastic bottles, traditionally made from fossil fuels, could be created from biomass, according to an invited review by scientists at Washington State University and Pacific Northwest National Laboratory.

Wang and Sun were asked to write the article, which appears in *ACS Catalysis*, because of their applied research, including their one-step process for upgrading ethanol to isobutene. Wang has a joint appointment with PNNL and WSU. At PNNL, he is an Associate Director at the Institute for Integrated Catalysis; at WSU, he is the Voiland Distinguished Professor. Sun completed a postdoctoral fellowship at PNNL and is now a research professor at WSU.

Why It Matters: Renewable fuel requirements are increasing the availability and decreasing the cost of ethanol, with the production in the United States expected to reach more than 30 billion gallons in 2017. With only 15 to 16 billion gallons needed for fuel blending, the additional alcohol could be used to produce plastic water bottles, carpet backing, and thousands of other products. This study provides a detailed summary of the research to date, giving scientists a needed overview.

“We need to debottleneck the process, from lignocellulose to the end products,” said Wang.

Methods: In the article, the team reviewed the progress made on deconstructing ethanol to provide hydrogen for use in proton exchange membrane fuel cells. Ethanol is of interest because of its easy-to-use form, nontoxicity, and high hydrogen content. Highly stable and selective catalysts, based on cobalt and other earth-abundant metals, appear promising for hydrogen production. Yet, efficiency and deactivation issues remain.

The team also discussed the production of light olefins, which can be used in building alkenes, alkanes, and aromatics, longer chained or ring-structured hydrocarbons. For example, producing the light olefin, *i.e.*, ethylene, using gamma aluminum oxide is a commercial success; however, the reaction requires high temperatures when water is present. Mixed metal oxides with balanced acid-base pairs can enable direct production of 1-butanol and 1,3-butadiene from ethanol. However, questions remain, including the formatting of key intermediates, which inhibit the effective conversion of ethanol.

“Olefins are exciting because they are a nice platform molecule that can be further converted to other chemicals,” said Wang. “Essentially, the potential is great, but if you look at the current status, a significant amount of research is needed before commercialization.”

What’s Next? The researchers are continuing to better understand the catalysts and the reaction mechanisms involved, including the influence of impurities introduced with the bioethanol. They are also looking at the coupling thermochemical conversions to biological processes that produce the ethanol.

Acknowledgments:

Sponsor: U.S. Department of Energy Office of Science’s Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

Research Team: Junming Sun, Washington State University; Yong Wang, Washington State University and Pacific Northwest National Laboratory

Reference: Sun J and Y Wang. 2014. “Recent Advances in Catalytic Conversion of Ethanol to Chemicals.” *ACS Catalysis* 4:1078-1090. DOI: 10.1021/cs4011343

The Science of Creating Catalysts for Energy Storage

Dan DuBois at Pacific Northwest National Laboratory reviews key advances in catalytic design

March 2014

Dan DuBois authored an invited review of key advances in catalytic design that appears in *Inorganic Chemistry*.

Results: In *Inorganic Chemistry,* Dr. Dan DuBois at Pacific Northwest National Laboratory shares three fundamental discoveries made to build catalysts that drive the storage of electrical energy inside chemical bonds. He was invited to write this review article after winning the American Chemical Society Inorganic Chemistry Award in 2012. DuBois was recognized for his scientific leadership in a career highlighted by outstanding science, popular seminars and talks, and a reputation as an insightful, gregarious mentor.

Why It Matters: Replacing fossil fuels with wind and solar energy requires a method of storing the energy generated and releasing it when needed. “Both of these renewable energy sources can contribute significantly to our energy needs, but their energy output can vary over periods as short as a few minutes to as long as a year. This leads to mismatches between energy production and demand that could be overcome by energy storage,” said DuBois.

One option is to store the energy in chemical bonds (*i.e.*, fuels), and then break those bonds when the energy is needed. The necessary reactions demand an efficient catalyst based on nickel or other abundant transition metal. Designing catalysts means understanding the underlying scientific principles. With his colleagues at the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy’s Office of Basic Energy Sciences, DuBois has answered fundamental questions about what makes a catalyst work.

“His work is the foundation we use to design a catalyst to do what we want to do. Without this basic knowledge, catalyst development relied largely on trial and error,” said Dr. Monte Helm, Deputy Director of the Center for Molecular Electrocatalysis.

Methods: In his review, DuBois focuses on three themes: thermodynamic modeling, catalyst structure, and proton movement. Designing a catalyst involves creating a reaction path that avoids troubling intermediates with excessively high or low energy barriers. To examine intermediates, DuBois and his colleagues built comprehensive thermodynamic models to provide detailed simulations. The models include new approaches to measure thermodynamic hydride acceptor and donor abilities. They also include data about redox potentials and the solvent.

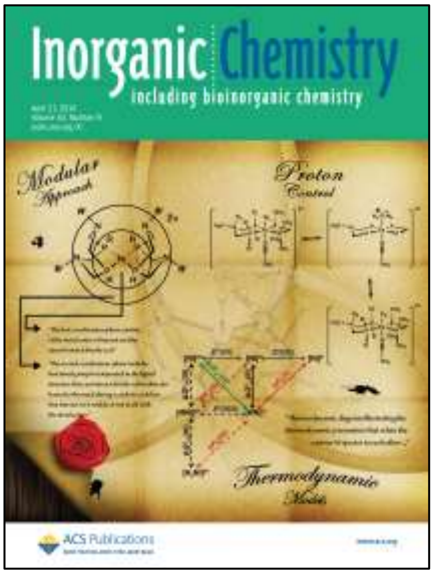
“We’ve used relationships extracted from the thermodynamic models to create powerful tools for predicting and understanding the relative free energies of intermediates,” said DuBois.

The second advance DuBois discusses is conceptually partitioning catalysts into first, second, and outer coordination spheres. The first coordination sphere is closest to the active site at the heart of the catalyst.

Understanding the proton-transfer reactions that involve the second and outer spheres, once dismissed as “shrubbery,” and the associated energy barriers is vital to designing needed catalysts.

Finally, the review covers the motion of protons, specifically via pendant amines, small dangling molecules with strategically placed nitrogen atoms in the second coordination sphere. The amines create paths for intra- and intermolecular proton transfers. “Dan’s influence on our research at PNNL is profound, as is obvious when you read this article,” said Dr. Morris Bullock, Director of the Center for Molecular Electrocatalysis.

What’s Next? Further discoveries critical for designing the needed catalysts are being made at Pacific Northwest National Laboratory, and DuBois continues to be a part of the Center. He currently serves as an advisor, working on research and counseling other scientists.



Artwork representing the article was featured on the cover of *Inorganic Chemistry*. ©American Chemical Society, 2014.

Acknowledgments:

Sponsor: Funding for the research described in this manuscript was provided as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center supported by the U.S. Department of Energy’s Office of Science and through individual grants from the Office of Science’s Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

Research Team: DuBois acknowledges enjoyable and productive collaborations over many years with his colleagues Mary Rakowski DuBois, R. Morris Bullock, and Calvin J. Curtis. He also thanks other collaborators, students, and postdocs who have contributed to the research described in this manuscript: Alex Miedaner, William Bell, John Linehan, Jim Franz, Michel Dupuis, Wendy Shaw, Aaron Appel, Jenny Yang, John Roberts, Mike Mock, Simone Raugei, Roger Rousseau, Molly O’Hagan, Monte Helm, Eric Wiedner, Dan Blake, Mark Nimlos, Carl Koval, Rich Noble, Arlie Norman, John Bercaw, Jay Labinger, Dorothy Gibson, Jim Muckerman, Etsuko Fujita, Cliff Kubiak, Rebecca Ciancanelli, Renee Henry, Aaron Wilson, George Jacobsen, Rachel Newell, Kendra Fraze, Stuart Smith, Uriah Kilgore, Doug Pool, Michael Stuart, Shentan Chen, Ming-Hsun Ho, Tianbio Liu, Brandon Galan, Brian Boro, Andy Herring, Paul Bernatis, Doug Berning, Paul Scovazzo, Sherry Wander, Bryan Steffey, Andrew Price, Jim Raebiger, Wallace Ellis, Stefan Weise, Charles Weiss, Jonathan Darmon, Ming Fang, Zachariah Heiden, Elliott Hulley, Wesley Hoffert, and Michael Stewart.

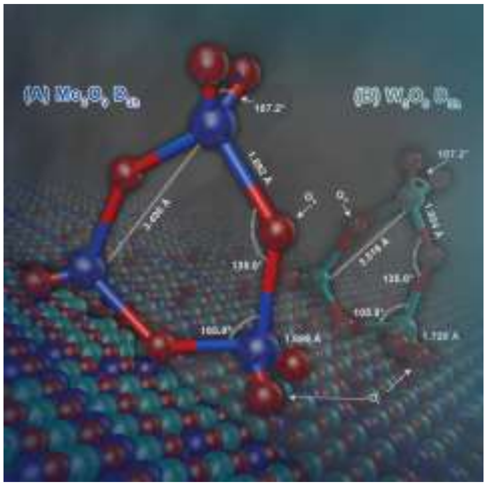
Reference: DuBois DL. 2014. “Development of Molecular Electrocatalysts for Energy Storage.” *Inorganic Chemistry* 53(8):3935-3960. DOI: 10.1021/ic4026969

Building Complexity Through Collaboration

Scientists draw unified picture of alcohol's interactions with early transition metal oxide catalysts

March 2014

Results: Based on 8 years of study, scientists at Pacific Northwest National Laboratory (PNNL) and the University of Alabama described in exquisite detail how alcohols behave on two early transition metal catalysts, molybdenum trioxide and tungsten trioxide, in a 17-page article in *Chemical Society Reviews*. All the catalysts were prepared using an innovative method introduced at PNNL that allows for the preparation of monodispersed catalytic clusters of identical size and structure. Such model systems can be utilized by scientists needing a structurally well-known material. The review provides a detailed discussion of the reaction mechanisms of these prepared catalysts for dehydration, dehydrogenation, and condensation reactions of small aliphatic, or open chain, alcohols.



In their review article, researchers at Pacific Northwest National Laboratory and the University of Alabama discuss how alcohols behave on two catalysts: cyclic $(WO_3)_3$ and $(MoO_3)_3$.

"I'm happy that we could summarize the research and publish it in a high-profile review journal," said Dr. Zdenek Dohnálek, a PNNL scientist who worked on the experimental research. "The only way we could afford to do this review and the underlying research was with long-term Basic Energy Sciences funding."

Why It Matters: Catalysts drive countless reactions, such as converting alkenes and other petroleum-derived chemicals into plastics that are used in everyday items from carpets to capacitors. Replacing the petroleum in these reactions with alcohols derived from biomass demands a new catalyst. To build that catalyst, scientists need to understand how catalysts drive reactions that convert propanol, ethanol, and other alcohols into those same alkenes and other hydrocarbons. The team's research into molybdenum and tungsten trioxides and the resulting review article reveals important catalyst characteristics.

"We came up with a pretty simple picture of how these things work," said Dr. Roger Rousseau, a PNNL scientist who worked on the computational simulations. "We found the small changes in the molecular structure that determine whether the molybdenum or tungsten oxide catalyst is good for a reaction."

Methods: Initially, the team's goal was to prepare catalytic metal oxide clusters supported on other oxides and determine how the clusters react. "You'd look in the literature in the past, and you would see all types of poorly defined clusters in the experiment, making it hard to determine anything," said Dohnálek.

The team devised a new method to obtain identical clusters. They evaporated the oxide into the gas phase, getting primarily cyclic trimers. The clusters could then be dispersed on different supporting materials.

Now, this method is used by other scientists at other research institutes to study catalysts properties. Their work and that of PNNL's appears in the review article.

Using the monodispersed preparation method, the authors and their colleagues spent years studying the catalysts. "Frequently researchers focus only on the characteristics of the system or the chemistry, not both. Whatever we prepare as the model system, we understand the structure and understand how the reactions work, or don't," said Dohnálek.

Rousseau added, "Some of the reactions were very disappointing, although overall even the disappointing ones showed us what was important in the reactions."

What's Next? Now, the team is focusing on how tungsten and molybdenum oxides catalyze deoxygenation of diols and other more complex molecules.

Acknowledgments:

Sponsors: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division (RR, BDK, ZD) and the Robert Ramsay Endowment of the University of Alabama (DAD)

Research Team: David A. Dixon, University of Alabama; Roger Rousseau, Bruce D. Kay, and Zdenek Dohnálek, PNNL

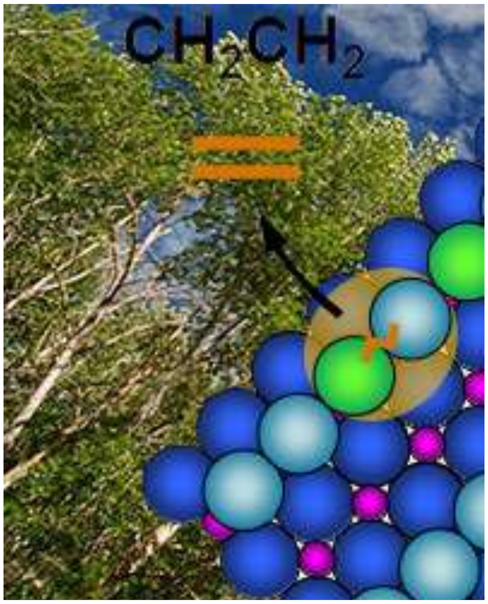
Reference: Rousseau R, DA Dixon, BD Kay, and Z Dohnálek. 2014. "Dehydration, Dehydrogenation, and Condensation of Alcohols on Supported Oxide Catalysts Based on Cyclic $(WO_3)_3$ and $(MoO_3)_3$ Clusters." *Chemical Society Review*. Advance Article. DOI: 10.1039/C3CS60445D

The Complexity of Catalytically “Cracking” Cellulose

Molecule’s carbon chain length affects oxygen’s departure in key reaction for building bio-fuels

December 2013

Results: In a maze of blindingly complex reactions that snap oxygen atoms off cellulose or other bio-sources to create energy-dense fuel, the starting molecule’s size has a curious effect. If the oxygen-rich molecule is too short to comfortably stretch to a catalyst’s active site, oxygen atoms are split from its hydrocarbon chain instead of staying together as happens when the molecule can reach across, according to scientists at Pacific Northwest National Laboratory (PNNL) and Baylor University. The team uncovered this steric effect by comparing 2 cellulose stand-ins that each have 2 oxygens or hydroxyl groups. Iterating between experimental and computational studies, they learned that the longer molecule keeps its last oxygen until the last step. The shorter one drops its oxygen atoms earlier as it struggles to fit on the catalyst’s surface.



Replacing fossil fuels in industrial applications could reduce economic, environmental, and security concerns. However, transforming bio-feedstocks into fuels means quickly and efficiently removing oxygen atoms.

“It’s safe to say that we didn’t expect the chemistry to be this complex,” said Dr. Roger Rousseau, a computational chemist at PNNL who worked on the study. “We’ve done a lot of research into alcohols, but extrapolating from 1 hydroxyl group to 2 was an order of magnitude more complex.”

Why It Matters: Economic, environmental, and security concerns are tied to the global need for energy. World energy consumption is predicted to grow by 56 percent between 2010 and 2040, with almost 80 percent of that energy coming from fossil fuels. Replacing those fuels in industrial applications could reduce these concerns. However, transforming bio-feedstock into fuels means quickly and efficiently removing oxygen atoms. To do this, scientists need to understand how and why the atoms behave as they do. This study uncovers the hidden reactions using molecular stand-ins, known as diols, on a prototypical catalyst.

“It looks as if it should be simple; you pull the oxygen off the biomass and get hydrocarbons. The reality is that it is a pretty complex reaction with a lot of intermediate steps,” said Dr. Zdenek Dohnálek, an experimental chemist at PNNL who led the research. “Our research — generating the elementary steps in oxygen removal — is contributing to an uncharted area.”

Methods: To resolve the complexity of the reactions, the team compared the reaction of 2 diols on the prototypical oxide catalyst titanium dioxide. The diols were a longer 1,3-propylene glycol ($HO(CH_2)_3OH$) with a three-carbon backbone and the shorter ethylene glycol ($HO(CH_2)_2OH$) with just 2 carbon atoms.

"It took more than 3 years to compare and contrast the reactions," said Rousseau. "We'd come up with new ideas to explain what we were seeing. We'd measure. We'd do the calculations. And then, we'd do it all again until we knew what was happening," said Rousseau.

The measurements came from scanning tunneling microscopy (STM); the calculations, from complex density functional theory. Using STM and temperature-programmed desorption, the team determined which bonds were broken and which intermediates formed. "STM was critical to providing information," said Dohnálek. "In a sense, it was the only way we could disentangle what was happening — imaging one molecule at a time."

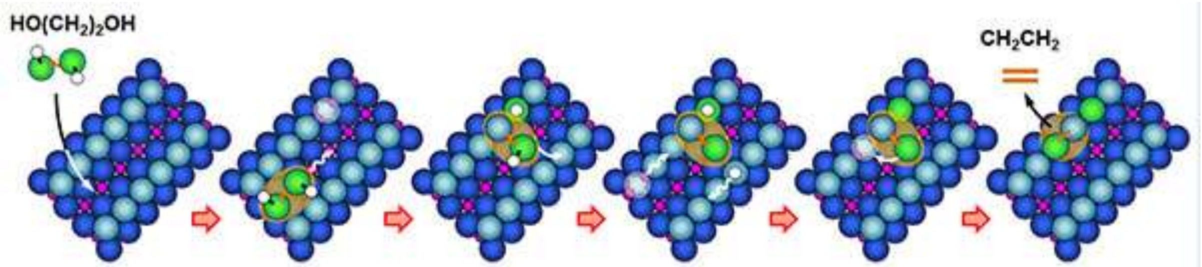
The experimental team deposited each diol in a thin layer on titanium dioxide at low temperatures. The diol landed on the titanium rows of the catalyst with the molecule's oxygen atoms resting on the row of titanium atoms. The attached hydrogen in the hydroxyl group hopped on and off.

"This was as expected," said Dohnálek. "Then, it got surprisingly complex."

The team determined that the longer 1,3-propylene glycol reached out. The hydroxyl dropped into a nearby oxygen vacancy, a "hole" in the surface. The associated hydrogen broke off. "This was a standard acid-base reaction that we have seen for alcohols," said Dohnálek.

The shorter ethylene glycol couldn't quite reach the oxygen vacancy. The hydroxyl group broke off from the hydrocarbon chain completely as the molecule struggled to reach the oxygen vacancy.

"This mechanism is different than what we typically see for alcohols," said Rousseau.



Ethylene glycol lands on titanium dioxide catalyst, with the oxygen atoms (green) resting on the row of titanium atoms. The attached hydrogen atoms (white) hop onto the nearby oxygen atoms (light blue). One of the molecule's oxygen atoms falls into a nearby oxygen vacancy. At higher temperatures, the second oxygen atom also falls into another oxygen vacancy, which migrated across the surface. Heating leads to the cleavage of both oxygen atoms, leaving behind a hydrocarbon that comes off the surface. This sequence of steps, which are of interest to catalytic scientists, was described by the research team at PNNL and Baylor University. ©American Chemical Society, 2013

When the temperature was raised above ~400 K, they saw a new stable intermediate centered on the bridging oxygen row. This intermediate was a new dioxo species. Further heating led to the homolytic cleavage of the other oxygen, and the hydrocarbon then left the surface when the temperature was raised above ~500 K.

"Again this process was very different from the one we saw for alcohols as it proceeded by a hemolytic rather than heterolytic bond breaking and was a nonadiabatic," said Rousseau.

"The reactions are wonderfully complex and fun to study," said Dohnálek.

What's Next? The team will be diving into further complexity when they apply what they've found here to tungsten trioxide catalysts and other catalytic materials.

Acknowledgments:

Sponsors: Xiao Lin was funded by the Linus Pauling Distinguished Postdoctoral Fellowship Program funded by PNNL's Laboratory Directed Research and Development Program. Zhenrong Zhang was funded by the American Chemical Society Petroleum Research Fund. The other authors were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

User Facility: EMSL

Research Team: Danda P. Acharya, Yeohoon Yoon, Zhenjun Li, Xiao Lin, Rentao Mu, Long Chen, Bruce D. Kay, Roger Rousseau, and Zdenek Dohnálek, PNNL; and Zhenrong Zhang, Baylor University

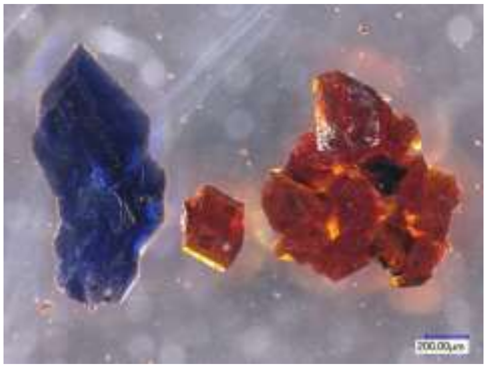
Reference: Acharya DP, Y Yoon, Z Li, Z Zhang, X Lin, R Mun, L Chen, BD Kay, R Rousseau, and Z Dohnálek. 2013. "Site-Specific Imaging of Elemental Steps in Dehydration of Diols on $TiO_2(110)$." *ACS Nano* 7(2013):10414-10423. DOI: 10.1021/nn404934q

A Crystal of a Different Color

One chemical forms two colors of crystals, gives insight into agostic bonds vital in industrial catalysis

August 2013

Results: Chemists at Pacific Northwest National Laboratory have unexpectedly made two differently colored crystals — one orange, the other blue — from one chemical in the same flask while studying a special kind of molecular connection called an agostic bond. The discovery is providing insights into important industrial chemical reactions such as those that occur while making plastics and fuels.



At Pacific Northwest National Laboratory, researchers described the first example of a metal-based catalyst that contains two different agostic bonds. The different forms, which create orange or blue crystals, illuminate the versatility of agostic bonding. This work will help scientists get a better handle on some catalytic reactions found in common industrial processes such as making plastic or fuels.

"We were studying agostic bonds in a project to make liquid fuels like methanol from carbon dioxide to replace fuels we get from oil," said Dr. Morris Bullock, a chemist at PNNL. "We knew the molecule we were making would have an agostic bond, but we had no idea there'd be two flavors of these metal complexes."

While chemists have studied these bonds in chemicals in liquid form, no one had crystallized one chemical with multiple forms of its agostic bonds. And no one expected different forms to give rise to different colors.

Why It Matters: The metal in a catalyst is usually the reactive heart of the molecule. Bullock and postdoctoral chemist Edwin van der Eide knew an agostic bond in their catalyst would help protect the reactive metal from working at the wrong time: The carbon-hydrogen bond blocks the reactive metal until conditions are right, which in turn would help the scientists better control the catalytic reactions to use renewable materials instead of fossil fuels, which present security, environmental and economic issues.

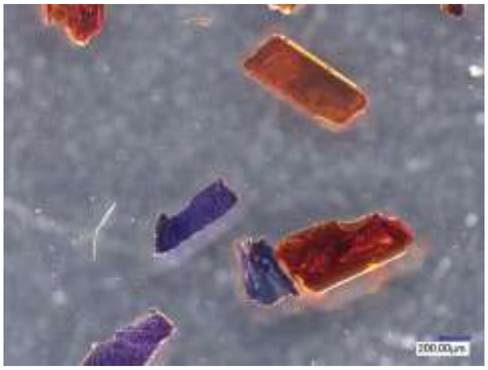
Methods: Van der Eide began with a violet solution of the molybdenum-containing catalyst; he added another liquid to crystallize the molybdenum complex. Crystals formed at the bottom of the flask and others formed near the top.

Oddly, the crystals were two different colors.

Orange crystals formed at the bottom of the flask and blue above. If van der Eide dissolved either the orange or blue crystals in a fresh flask of the original solvent, the violet color returned, with the same properties as the original violet solution. These results suggested that either molecule in the two colored solids could give rise to both structures in liquid, where they easily change back and forth.

The researchers examined the differently colored crystals to determine their structures. The molecule forms a shape like a piano stool: a ringed section forms a stool seat on top of the molybdenum atom, with multiple legs connecting to the molybdenum at the bottom.

One of the legs, however, is longer than the others and contains a chain of 3 carbon atoms, each with at least one protruding hydrogen. The team found that the long leg was involved in the agostic bonds, with the middle carbon atom involved in the orange crystals and an end carbon involved in the blue crystals.



One flask of chemicals gives rise to either blue or orange crystals.

Ping Yang used EMSL's supercomputer Chinook to perform theoretical calculations on the orange and blue structures. Chemically, the two structures were almost equally likely to form, with the blue one having a slight edge. The analysis also revealed why the crystals were different colors, which is due to subtleties within the structures.

What's Next? This work is part of PNNL's ongoing research into the fundamental questions of catalytic structures and bonding.

Acknowledgments:

Sponsors: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

User Facility: EMSL

Research Team: Edwin F. Van der Eide, Ping Yang, and R. Morris Bullock, PNNL

Reference: van der Eide EF, P Yang, and RM Bullock. 2013. "Isolation of Two Agostic Isomers of an Organometallic Cation: Different Structures and Colors." *Angewandte Chemie International Edition* 52(39):10190-10194. DOI: 10.1002/anie.201305032

Analyzing the Status of Oxide Surface Photochemical Reactivity

Invited review shows power of scanning tunneling microscopy to understand and control the surface photochemistry of oxide materials

July 2013

In their invited review, Dr. Michael Henderson and Dr. Igor Lyubinetsky, Pacific Northwest National Laboratory, show that scanning probe microscopy techniques give scientists detailed molecular information to shed new light on fundamental interactions that are key to our energy future. This research graced the cover of *Chemical Reviews*. ©American Chemical Society, 2013.

As shown by Pacific Northwest National Laboratory's Dr. Michael Henderson and Dr. Igor Lyubinetsky in their invited review article, using scanning probe microscopy techniques, in particular scanning tunneling microscopy (STM), allows scientists to understand fundamental interactions that are key to our energy future. Adsorbates, their adjacent neighbors, defects, and impurities of the surface topography all influence the surface's photochemistry. Knowing the locations and residence times of each molecule is important to understanding and controlling surface chemistry, vital for solar energy and other forms of renewable energy.

"The scanning tunneling microscopy technique correlates atomic-level details of the active surface environment with photocatalytic processes, which enables researchers to design catalysts to achieve desired chemical transformations," said Henderson.

STM enables researchers to follow and understand the photochemical reactions on various surface sites. With STM's sensitivity to the electronic structure of a surface, scientists can identify the locations of adsorbates and determine which make the best and worst neighbors so that photocatalysts can be designed to control chemical reactions.

In the article, Henderson and Lyubinetsky highlight the growing use of scanning probe microscopy techniques. They focus on the ability to provide molecular-level insights into surface photochemistry on the model photocatalyst surface of rutile $TiO_2(110)$ to illustrate the unique knowledge that scanning probe techniques have already provided the field of photocatalysis. They also strive to motivate a new generation of effort into the use of such approaches to obtain insights into the molecular-level details of photochemical events occurring at interfaces.

Acknowledgments:

Sponsors: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division with IL partially supported by PNNL's Chemical Imaging Initiative

Research Team: Michael A. Henderson and Igor Lyubinetsky, PNNL

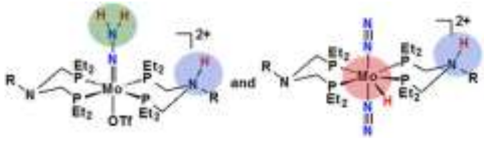
Reference: Henderson MA and I Lyubinetsky. 2013. “Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO_2(110).” *Chemical Reviews* 113:4428-4455.
DOI: 10.1021/cr300315m

Energy Frontier Research Center

Building the Ideal Rest Stop for Protons

Determining preferences provides insight into molybdenum complex's ability to produce ammonia precursor

July 2014



When protons rest on the metal-bound dinitrogen groups (green), this is the desired location for producing ammonia. If the protons rest on the metal center (red), the reaction halts. Subtle differences in the amine groups (blue) greatly change where the protons end up. Understanding the motion of protons is critical to understanding and then designing catalysts for energy and chemical production.

Results: Where protons, or positive charges, decide to rest makes the difference between proceeding towards ammonia production or not, according to scientists at Pacific Northwest National Laboratory (PNNL) and Villanova University. By designing and examining the reactivity of five complexes with molybdenum metal centers, the team found that subtle differences in the complexes greatly change where the protons end up. The differences were in the structure of the ligands, molecular frameworks that surround the metal. When the ligands were more willing than a metal-bound dinitrogen group to take in a proton, the protons ended up binding with the molybdenum center, essentially ending up stuck in the wrong place. But, when the ligands' ability to accept protons was more closely matched with that of the dinitrogen group, the protons ended up going to the desired location for producing NH_3.

"We showed how the metal compound works and how it facilitates proton movement," said Dr. Liezel Labios, a synthetic organometallic chemist who led the experiments as a postdoctoral associate in the Center for Molecular Electrocatalysis, an Energy Frontier Research Center led by PNNL.

Why It Matters: Renewable energy. Available food. Effective medicines. The reactions behind these products and countless more are not as efficient or effective as we want. Too much waste. Too much energy. Or simply not possible with today's chemistry. To improve the reactions, scientists must first understand and then design catalysts, the molecules that drive reactions without being consumed by them. Specifically, scientists need to know how catalysts move protons, so they are delving into one reaction — ammonia production from dinitrogen molecules — that is a six proton, six electron process. Understanding the in's and out's of how the complexes react with protons could lead to more efficient catalysts.

"This study is leading us toward optimizing complexes to facilitate difficult reactions by giving us details about how altering the molybdenum compounds ligand structure will influence their reactivity," said Dr. Michael Mock, who leads the nitrogen studies at the Center for Molecular Electrocatalysis.

Methods: The researchers are studying the conversion of dinitrogen molecules to ammonia and are focused on understanding how, where, and why the 6 protons involved in the reaction move. In designing the metal-based scaffolding to study the first step in ammonia production, the team was inspired by both natural processes and industrial processes that produce ammonia. Natural processes, which are catalyzed by nitrogenase enzymes, proceed at ambient temperature and pressure. In industry, the Haber-Bosch process uses a heterogeneous catalyst and produces millions of tons of ammonia every year under conditions using high temperatures and pressures.

"Our work is inspired by these processes, and we are striving to understand proton movement from a molecular perspective in this challenging multi-proton, multi-electron reaction," said Labios.

To improve the reactions involved in storing renewable energy, scientists must first understand and then design catalysts, the molecules that drive reactions without being consumed by them. Specifically, scientists need to know how catalysts move protons.

The team took on the first step in producing ammonia: forming a molybdenum-hydrazido intermediate (Mo-NNH_2). They tested five different compounds with different ligands bound to molybdenum at a low oxidation state, Mo(0). Each molecule had different ligands containing different amine groups as proton relays, which are basic sites designed to facilitate proton movement in the presence of acid to the metal-bound dinitrogen group. Using nuclear magnetic resonance spectroscopy, *in situ* infrared spectroscopy, and their expertise with proton motion, they determined the protonated products that were formed.

In complexes where the ligands and the dinitrogen groups did not have similar pK_a values, measures of their capacity to donate protons, the reactions produced molybdenum-hydride compounds, in which the protons were attached to the molybdenum center. This molecule is not readily converted into the desired molybdenum-hydrazido intermediate, Mo-NNH_2. Further, certain ligands resulted in complexes that were not highly soluble, limiting their ability to work in the reaction's solutions.

When the pK_a values between the ligands and the dinitrogen groups were more closely matched, the reactions generated a greater ratio of the molybdenum-hydrazido triflate complex, the desired precursor.

What's Next? The researchers in the Center for Molecular Electrocatalysis are more closely studying the structural influence of the proton relays. Their results could lead to gaining further insight into how to match the pK_a values and optimize the role of the proton relays in these complexes. They are also screening an array of molecules in the presence of protons and electrons to find one that can serve as a catalyst to produce ammonia.

Acknowledgments:

Sponsors: This work was supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (LAL, CJW, JDE, RMB, MTM, WGD, WSK). Sheri Lense was supported by the DOE Office of Science, Early Career Research Program through the Office of Basic Energy Sciences.

Research Team: Liezel A. Labios, Charles J. Weiss, Jonathan D. Egbert, Sheri Lense, R. Morris Bullock, and Michael T. Mock, Pacific Northwest National Laboratory; William G. Dougherty and W. Scott Kassel, Villanova University

Reference: Labios LA, CJ Weiss, JD Egbert, S Lense, RM Bullock, WG Dougherty, WS Kassel, and MT Mock. 2014. "Synthesis and Protonation Studies of Molybdenum(0) Bis(dinitrogen) Complexes Supported by Diphosphine Ligands Containing Pendant Amines." *Journal of Inorganic and General Chemistry (ZAAC).* DOI: 10.1002/zaac.201400119

Researchers Propose a Common Yardstick to the Efficiency of Molecular Electrocatalysts

Finding a consistent and accurate overpotential description to compare catalytic performance

June 2014

Results: In an invited *ACS Catalysis* Viewpoint paper, scientists at Pacific Northwest National Laboratory (PNNL) proposed a way to measure and report the energy efficiency of molecular electrocatalysts, small molecules that quickly convert electrical energy into chemical bonds or break those bonds to release energy. The definition and process they propose is designed to clear up inconsistencies in describing and reporting overpotential, a measure of the catalyst's efficiency. By adhering to a set of uniform procedures and metrics, researchers can consistently compare one catalyst to another.

Pacific Northwest National Laboratory scientists suggest a consistent and accurate approach to compare the performance of molecular catalytic reactions using overpotential.

Why It Matters: In chemical reactions, a catalyst is like a matchmaker, fanning the marriage proposal flames without actually walking down the aisle. Increased interest in fuels made from renewable energy has ignited the discovery and testing of many new efficient, robust and effective catalysts. Propelled by the desire to replace expensive and rare metal catalysts with less expensive and abundant sources, researchers are also looking for catalysts that are fast and efficient. Researchers use the measure of overpotential as a way to quantify the catalyst's energy efficiency. In the competitive bid to find this catalytic brass ring, researchers have used different metrics to determine and report the overpotentials of their catalysts. The Viewpoint presented by Dr. Aaron M. Appel and Dr. Monte L. Helm at PNNL offers a clear and consistent path for the determination of overpotential, allowing an easy and consistent comparison.

Methods: The idea of finding a consistent and accurate way to compare the performance of molecular catalytic reactions intrigued the PNNL team. The scientists are researchers at the Center for Molecular Electrocatalysis (a U.S. Department of Energy (DOE)-funded Energy Frontier Research Center) led by PNNL. After working to compare many different catalysts through the literature, they noted that there was no easy way to view catalysts' performance without a consistent and uniform measure of efficiency. Overpotential is one such measure, yet they found various methods and approaches for describing and measuring overpotential that did not enable an "apples-to-apples" comparison. Even conversion of previous measurements into a common system proved out of reach.

Noting the inconsistencies in the way overpotential has been reported, the researchers set about finding metrics that allowed the scientific community to easily compare different catalysts. They discussed and analyzed options and arrived at the recommendations they present in this article. Their innovative idea for a common language or description of overpotential can be used in future research in this fast-growing field. Their Viewpoint paper describes the method to determine and measure potential and overpotential, in an accurate and consistent way that works within and across all catalyst families.

What's Next? The researchers have adopted this process in their research and continue to build consensus on this method in their research community.

Acknowledgments

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: Aaron M. Appel and Monte L. Helm, PNNL

Reference: Appel A and M Helm. 2014. "Determining the Overpotential for a Molecular Electrocatalyst." *ACS Catalysis* 4(2):630-633. DOI: 10.1021/cs401013v

Predicting Potholes on the Road to Renewable Energy

Storing wind-generated electricity as fuels means catalysts must avoid low energy states

May 2014

Results: When it comes to driving reactions to store electrons from wind turbines in the chemical bonds of use-any-time fuels, the path the catalyst takes matters. Researchers want to avoid low-energy and high-energy catalytic intermediates that could either represent a thermodynamic sink (even stopping the reaction) or require adding excessive amounts of energy to reach the final products. Scientists at the Center for Molecular Electrocatalysis (CME) devised a new computation-based method to predict the intermediates. The Center is an Energy Frontier Research Center led by Pacific Northwest National Laboratory (PNNL) and funded by the U.S. Department of Energy's Office of Basic Energy Sciences.

To create fast catalysts that avoid dangerous and delaying potholes, scientists built a scientific model that they can use to map the road a catalyst will take. The model predicts and allows scientists to avoid unnecessary stops or detours.

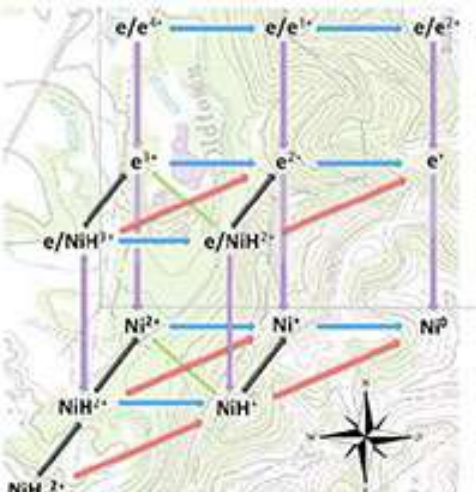
Image provided by *Frontiers in Energy Research,* the EFRC Newsletter.

"Our goal is to avoid bottlenecks," said Dr. Simone Raugei, a PNNL theorist who led the study. "To make the reactions fast and efficient, we need to take out those undesirable intermediates."

Why It Matters: Cooling and heating our homes and offices with renewable energy would reduce environmental issues of fossil fuel use. However, wind and solar energy fluctuate greatly depending on the time of day and the location of the turbines or solar stations. One option is to store the generated electrons in chemical bonds. Making these bonds and then breaking them to get the electrons back to do work requires catalysts. This study provides scientists with an important tool in designing catalysts that work as quickly and efficiently as possible.

Methods: Using computational resources at EMSL and the National Energy Research Scientific Computing Center, the team devised a new computation-based method to calculate *free energy maps,* which show the energy required or given off in each step of the reaction. They tested the new method against nickel-based catalysts with a pendant amine in the second coordination sphere of the metal center; these catalysts were designed and characterized by scientists at the Center. The catalysts can either split hydrogen gas into protons and electrons or produce hydrogen from protons and electrons. The team input three easily accessible data points: redox potentials for the Ni(II)/Ni(I) and Ni(I)/Ni(0) couples of the nonprotonated complex, as well as the pK_a or proton donating ability of the parent primary aminium ion.

The result was an accurate prediction of the thermodynamics of intermediates as well as information on the reduction potentials, hydride donor abilities, and pK_a values of both the protonated nickel center and the pendant amine. In addition to predictability under the normal conditions, the model allows for predictions at high temperatures and extreme pressures. While this method was built specifically for the hydrogen-specific catalytic system, the strategy is amenable to almost any catalytic system.



Energy correlation diagrams serve as road maps in catalytic processes by identifying high- and low-energy intermediates that should be avoided.

Image provided by *Frontiers in Energy Research*, the EFRC Newsletter.

What's Next? This work continues to be implemented in new catalyst design in the CME. The catalyst team has begun work on a complementary model to fill in some of the other potential bottlenecks to complete the energy landscape.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: Shentan Chen, Ming-Hsun Ho, R. Morris Bullock, Daniel L. DuBois, Michel Dupuis, Roger Rousseau, and Simone Raugei, PNNL

User Facilities: Computational resources were provided at EMSL at Pacific Northwest National Laboratory and the National Energy Research Scientific Computing Center at Lawrence Berkeley National Laboratory

Reference: Chen S, MH Ho, RM Bullock, DL DuBois, M Dupuis, R Rousseau, and S Raugei. 2014. "Computing Free Energy Landscapes: Application to Ni-based Electrocatalysts with Pendant Amines for H_2 Production and Oxidation." *ACS Catalysis* 4:229-242. DOI: 10.1021/cs401104w

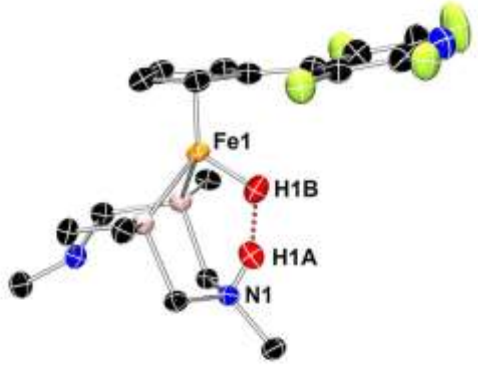
Halving Hydrogen

First view of nature-inspired catalyst after ripping hydrogen apart provides insights for better, cheaper fuel cells

April 2014

Results: Like a hungry diner ripping open a dinner roll, a fuel cell catalyst that converts hydrogen into electricity must tear open a hydrogen molecule. Now researchers have captured a view of such a catalyst holding onto the two halves of its hydrogen feast. The view confirms previous hypotheses and provides insight into how to make the catalyst work better for alternative energy uses.

This study is the first time scientists have shown precisely where the hydrogen halves end up in the structure of a molecular catalyst that breaks down hydrogen, the team reported online April 22 in *Angewandte Chemie International Edition*. The design of this catalyst was inspired by the innards of a natural protein called a hydrogenase enzyme.



Neutron crystallography shows this iron catalyst gripping two hydrogen atoms (red spheres). This arrangement allows an unusual dihydrogen bond to form between the hydrogen atoms (red dots).

“The catalyst shows us what likely happens in the natural hydrogenase system,” said Dr. Morris Bullock of Pacific Northwest National Laboratory (PNNL). “The catalyst is where the action is, but the natural enzyme has a huge protein surrounding the catalytic site. It would be hard to see what we have seen with our catalyst because of the complexity of the protein.”

Why It Matters: Hydrogen-powered fuel cells offer an alternative to burning fossil fuels, which generates greenhouse gases. Molecular hydrogen — 2 hydrogen atoms linked by an energy-rich chemical bond — feeds a fuel cell. Generating electricity through chemical reactions, the fuel cell spits out water and power.

If renewable power is used to store energy in molecular hydrogen, these fuel cells can be carbon-neutral. But fuel cells aren’t cheap enough for everyday use.

To make fuel cells less expensive, researchers turned to natural hydrogenase enzymes for inspiration. These enzymes break hydrogen for energy in the same way a fuel cell would. But while conventional fuel cell catalysts require expensive platinum, natural enzymes use cheap iron or nickel at their core.

Methods: Researchers have been designing catalysts inspired by hydrogenase cores and testing them. In this work, an important step in breaking a hydrogen molecule so the bond’s energy can be captured as electricity is to break the bond unevenly. Instead of producing 2 equal hydrogen atoms, this catalyst must produce a positively charged proton and a negatively charged hydride.

The physical shape of a catalyst — along with electrochemical information — can reveal how it does that. So far, scientists have determined the overall structure of catalysts with cheap metals using X-ray crystallography, but hydrogen atoms can’t be located accurately using X-rays. Based on chemistry and X-ray methods, researchers have a best guess for the position of hydrogen atoms, but imagination is no substitute for reality.

Bullock, Dr. Tianbiao "Leo" Liu, and their colleagues at the Center for Molecular Electrocatalysis at PNNL, one of the U.S. Department of Energy's Energy Frontier Research Centers, collaborated with scientists at the Spallation Neutron Source at Oak Ridge National Laboratory in Tennessee to find the lurking proton and hydride. Using a beam of neutrons like a flashlight allows researchers to pinpoint the nucleus of atoms that form the backbone architecture of their iron-based catalyst.

To use their iron-based catalyst in neutron crystallography, the team had to modify it chemically so it would react with the hydrogen molecule in just the right way. Neutron crystallography also requires larger crystals as starting material compared to X-ray crystallography.

"We were designing a molecule that represented an intermediate in the chemical reaction, and it required special experimental techniques," Liu said. "It took more than 6 months to find the right conditions to grow large single crystals suitable for neutron diffraction. And another 6 months to pinpoint the position of the split H_2 molecule."

If renewable power is used to store energy in molecular hydrogen, fuel cells can be carbon-neutral.

Crystallizing their catalyst of interest into a nugget almost 40 times the size needed for X-rays, the team succeeded in determining the structure of the iron-based catalyst.

The structure, they found, confirmed theories based on chemical analyses. For example, the barbell-shaped hydrogen molecule snuggles into the catalyst core. On being split, the negatively charged hydride attaches to the iron at the center of the catalyst; meanwhile, the positively charged proton attaches to a nitrogen atom across the catalytic core. The researchers expected this set-up, but no one had accurately characterized it in an actual structure before.

In this form, the hydride and proton form a type of bond uncommonly seen by scientists — a dihydrogen bond. The energy-rich chemical bond between 2 hydrogen atoms in a molecule is called a covalent bond and is very strong. Another bond called a "hydrogen bond" is a weak one formed between a slightly positive hydrogen and another, slightly negative atom.

Hydrogen bonds stabilize the structure of molecules by tacking down chains as they fold over within a molecule or between two independent molecules. Hydrogen bonds are also key to water surface tension, ice's ability to float and even a snowflake's shape.

The dihydrogen bond seen in the structure is much stronger than a single hydrogen bond. Measuring the distance between atoms reveals how tight the bond is. The team found that the dihydrogen bond was much shorter than typical hydrogen bonds but longer than typical covalent bonds. In fact, the dihydrogen bond is the shortest of its type so far identified, the researchers report.

This unusually strong dihydrogen bond likely plays into how well the catalyst balances tearing the hydrogen molecule apart and putting it back together. This balance allows the catalyst to work efficiently.

What's Next? "We're not too far from acceptable with its efficiency," said Bullock. "Now, we just want to make it a little more efficient and faster."

Acknowledgments:

Sponsors: This research was supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Research conducted at the Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

User Facility: Spallation Neutron Source

Research Team: Tianbiao Liu, Daniel L. DuBois, and R. Morris Bullock, PNNL; Xiaoping Wang and Christina Hoffmann, Oak Ridge National Laboratory

Reference: Liu T, X Wang, C Hoffmann, DL DuBois, and RM Bullock. 2014. "Heterolytic Cleavage of Hydrogen by an Iron Hydrogenase Model Investigated by Neutron Diffraction." *Angewandte Chemie International Edition*, April 22, 2014. DOI: 10.1002/anie.201402090

Uncovering the Details of Proton Relays Vital to Creating New Catalysts for Energy Storage

Invited article reviews the science behind proton motion in hydrogen-generating catalysts

March 2014

Results: Storing intermittent solar and wind energy in chemical bonds for later use requires a detailed understanding of how protons flow. In their invited review for *Chemical Communications*, Dr. R. Morris Bullock, Dr. Aaron Appel, and Dr. Monte Helm at Pacific Northwest National Laboratory (PNNL) describe how proton relays and other factors influence the catalysts that produce the desired chemical bonds. They were asked to write this review for a special themed collection in the journal on electrocatalytic hydrogen evolution because of their groundbreaking research in proton movements in reactions that break and form hydrogen. Dr. Jonathan Darmon and Dr. Charles Weiss at PNNL designed artwork that graces the journal's cover.

An invited review of proton relays in nickel catalysts graced the cover of Chemical Communications' cover. Cover reprinted with permission of the authors and the Royal Society of Chemistry.

Controlling protons' motion and the release of the hydrogen molecule produces fast, efficient catalysts based on abundant metals, rather than precious metals. The scarcity of platinum, rhodium, and other metals makes them unsustainable for use on a large scale. "Our ultimate goal is to use cheap metals for noble tasks," said Bullock, Director of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy's Office of Basic Energy Sciences.

Why It Matters: Would you want a car that only ran when the sun shined? A dishwasher that only ran when the wind blew? Solar and wind energy are sustainable, carbon-neutral energy sources, but their role on the nation's energy stage may be limited unless the resulting electricity can be stored. One option is to store the energy as chemical energy in the hydrogen-hydrogen bond.

"We are gaining the understanding necessary to rationally design catalysts that match the functionality of enzymes, natural catalysts that use nickel and other abundant metals," said Appel.

Methods: In the article, the authors focus on pendant amines, dangling molecular chains with nitrogen atoms that act as proton relays. Placing pendant amines correctly puts the reaction's hydride or hydrogen anion and proton in the right spot to interact. A poorly placed or missing amine can stall the reaction. "We don't necessarily need more proton relays to improve catalytic performance," said Helm, the Center's Deputy Director. "The research demonstrates that delivering protons to the right spots for the catalyst to use productively is the most important factor in determining catalytic performance."

Another key factor is how quickly the catalyst releases the hydrogen, once formed. The release rate is strongly influenced by the thermodynamics of breaking both the hydride and the proton from the catalyst; both of the hydricity (hydride donor ability) and acidity (proton donor ability) can be varied in the catalyst.

In addition to the internal design of the catalyst, the environment also matters. Protons move more quickly, speeding the catalyst, when the basicity of the pendant amine is thermodynamically matched to the acid, also known as pK_a matching.

What's Next? While this review focuses on nickel electrocatalysts for creating hydrogen, the science and the underlying principles can be applied to other catalysts. For example, further research is being carried out on cobalt, iron, and manganese complexes. These findings apply to more complicated reactions involving oxygen and nitrogen that are also critical in energy science.

"We want to store energy as densely as possible. Chemical bonds can store a huge amount of energy in a small amount of physical space," said Bullock.

Solar and wind energy are sustainable, carbon-neutral energy sources, but their role on the nation's energy stage may be limited unless the resulting electricity can be stored. One option is to store the energy as chemical energy in the hydrogen-hydrogen bond.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: R. Morris Bullock, Aaron M. Appel, and Monte L. Helm, PNNL

Reference: Bullock RM, AM Appel, and ML Helm. 2014. "Production of Hydrogen by Electrocatalysis: Making the H-H Bond by Combining Protons and Hydrides." *Chemical Communications* 50:3125-3143. DOI: 10.1039/c3cc46135a

Revving Up Catalysts by Building in Proton-Only Offramp

Simple addition to catalyst's outer edge speeds bond breaking and electron release

February 2014

If water is used as a base to remove the protons, compared to a strong amine base, the proton's behavior and the catalyst's response changes, according to scientists at the Center for Molecular Electrocatalysis. Cover reprinted with permission of the authors and the Royal Society of Chemistry.

Results: Do protons speed through a catalyst, take the scenic route, or stop altogether? Using their understanding of a proton's choices, scientists at the Center for Molecular Electrocatalysis revised their nickel-based catalyst to quickly handle one of a fuel cell's tough challenges: breaking chemical bonds and freeing the stored electrons to work. The catalyst's speed comes from an additional, second proton relay, a molecular fragment, on the outer edge. With the second proton relay, the catalyst quickly transforms through three different isomers, or forms, and the proton goes on its way. Without the relay, the catalyst sticks in one form and moving the proton from the active site takes much longer. Also, the team discovered that the proton's behavior and the catalyst's response changes if water is used as a base to remove the protons, compared to a strong amine base. The catalyst's response to the different bases graces the cover of *Dalton Transactions.* The artwork was designed by Dr. Jonathan Darmon at Pacific Northwest National Laboratory.

"We need to control proton movement over greater distances to generate catalysts that operate efficiently and quickly," said Dr. Monte Helm, who worked on the study and serves as the Center for Molecular Electrocatalysis' Deputy Director. "This study is just one example of our progress."

The Center for Molecular Electrocatalysis is an Energy Frontier Research Center led by Pacific Northwest National Laboratory and funded by the U.S. Department of Energy's Office of Basic Energy Sciences.

Why It Matters: Fuel cells could store massive quantities of intermittent solar- or wind-generated energy and release it when needed. The cells can store energy or electrons in a bond between 2 hydrogen atoms. When needed, the fuel cell breaks the hydrogen-hydrogen bond, freeing the electrons to do work. However, fuel cells do not play a major role in our nation's energy economy because they require platinum catalysts, which are too expensive to be used on a large scale.

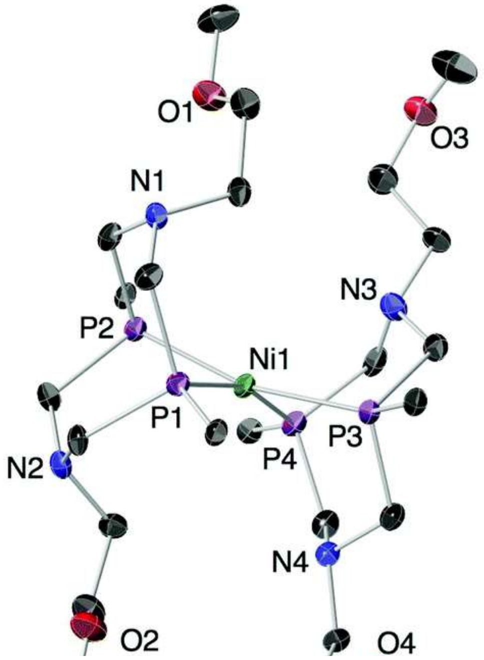
"Changing our nation's energy landscape requires us to devise efficient catalysts from cheap, abundant metals," said Dr. R. Morris Bullock, who worked on the study and directs the Center for Molecular Electrocatalysis.

Methods: The research team began by adding a methoxy group (-CH_2CH_2OMe) to the pendant amine to serve as a second proton relay in the outer coordination sphere of a nickel bis(diphosphine) catalyst. The methoxy group was added to move protons away from the active site quickly so that the next reaction could begin. They synthesized the compounds they needed and characterized them with nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallography, and a variety of other spectroscopic techniques. Once characterized, the compound's catalytic H_2 oxidation properties were studied by electrochemistry.

They found that in moving protons, this nickel catalyst does not behave the way others in its class do. To move the protons, the catalyst twists and turns. The added methoxy group weakened key bonds between nickel and hydrogen atoms, allowing the catalyst to isomerize quickly.

"What we'd seen previously was that the transfer can take days; what we found is that the catalyst can do this isomerization very quickly — faster than any other catalysts we've tested so far," said Dr. Molly O'Hagan, a chemist at PNNL who worked on the study.

When the catalyst was placed under 1 atm of H_2 pressure, it broke 5 hydrogen bonds every second (overpotential of 720 mV) when water was used as a base to remove the protons. When a strong base was used to remove the protons, the rate went up to 18 molecules per second, with a lower overpotential. The team discovered the faster reaction did not follow the same twists and turns as the slower reaction in water.



Scientists at the Center for Molecular Electrocatalysis demonstrated their ability to control the speed and energy of a catalyst (X-ray crystal structure of $Ni(P^{Cy}{}_2N^{(CH2)2OMe})_2](BF_4)_2 \cdot 2CH_3CN)$.

"This research demonstrates our ability to control both the speed and required energy of the catalyst by modifying the outer layers of the catalyst, an area once thought to be unimportant for synthetic catalysts," said Helm.

What's Next? "Scientists at the Center have learned how to move protons to and from the metal center over short distances using proton relays in the secondary coordination sphere. We've realized now that we need to control proton movement at greater distances," said Helm. The team is working to move the protons greater distances and to answer other fundamental questions involved in efficiently moving protons to create catalysts with platinum's speed and efficiency, but not its cost.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: Parthapratim Das, Ming-Hsun Ho, Molly J. O'Hagan, Wendy J. Shaw, R. Morris Bullock, Simone Raugei, and Monte L. Helm, PNNL

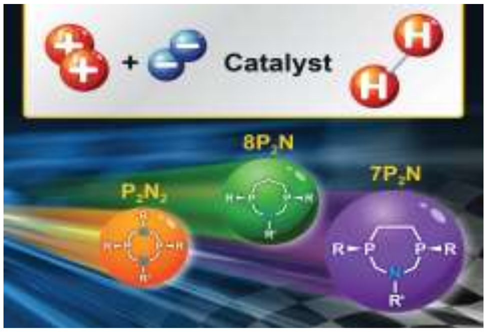
Reference: Das P, MH Ho, MJ O'Hagan, WJ Shaw, RM Bullock, S Raugei, and ML Helm. 2014. "Controlling Proton Movement: Electrocatalytic Oxidation of Hydrogen by a Nickel(II) Complex Containing Proton Relays in the Second and Outer Coordination Spheres." *Dalton Transactions* 43:2744-2754. DOI: 10.1039/C3DT53074D

When Less Is More: Fewer Proton Relays Improve Catalytic Rates

First direct comparison of 3 nickel-based complexes shows that those with 2 proton relays outperform 4

January 2014

Results: By directly comparing three closely related catalysts, scientists at the Center for Molecular Electrocatalysis established that hydrogen production speed and efficiency are influenced by the molecules' structure and proton relay arrangement, not the total number relays. They found that a catalyst built with the ligand called $8P_2N$, with a total of 2 proton relays in its nickel complex, is faster than a catalyst with double the number. Further, catalysts built with the related $7P_2N$, with its smaller ring of atoms, is faster than its $8P_2N$ counterpart, with a larger ring.



With just two proton relays or pendant amines and a smaller ring structure, nickel-based catalyst $7P_2N$ is faster than similar catalysts according to a detailed comparison by scientists at the Center for Molecular Electrocatalysis.

"We don't necessarily need more proton relays to improve catalytic performance," said Dr. Monte Helm, Deputy Director, Center for Molecular Electrocatalysis. "This work demonstrates that delivering protons to the right spots for the catalyst to use productively is the most important factor in determining catalytic performance."

The Center is an Energy Frontier Research Center, funded by the U.S. Department of Energy's Office of Basic Energy Sciences and led by Pacific Northwest National Laboratory (PNNL).

Why It Matters: Storing energy from wind farms and other renewable sources in chemical bonds relies on platinum-based catalysts, which excel at turnover frequency and overpotential. Turnover frequency is the rate at which the desired molecules are created. Overpotential, the difference between the theoretical energy and the actual energy used, measures the reaction's efficiency. Because platinum is scarce, a catalyst based on earth-abundant metals is needed to store large volumes of renewable energy and release it when needed. This study sheds light on protons' behavior in such catalysts, key to synthesizing catalysts that can match or beat platinum's high turnover frequency and low overpotential.

"Right now, the catalyst used to store energy in chemical bonds with fuel cells is platinum, which we can't implement on a large scale because of cost and availability," said Helm. "To increase the use of renewable sources of energy, we need a way to store the energy during times of high production to balance those times of low production."

Methods: The team began with 3 nickel-based electrocatalysts, which are working models of hydrogenase enzymes that split and form hydrogen for water-dwelling microbes. The models allowed for two comparisons:

- **Comparing proton relays.** The team compared catalysts with P_2N_2 and with $8P_2N$ ligands; the catalysts are identical except for the number of proton relays. Nickel complexes with P_2N_2 have 4 relays, and those with $8P_2N$ have 2.

- **Comparing structure.** The team compared catalysts with $8P_2N$ and $7P_2N$ ligands; these catalysts differ only in the size of the rings that contain the proton relays. $8P_2N$ has an eight-membered cyclic ligand, while $7P_2N$ has a smaller seven-membered ring.

In doing the two comparisons, the team found that the nickel catalyst with P_2N_2 was the slowest, generating 1,040 molecules of hydrogen per second with an overpotential of 570 mV. The nickel catalyst with $8P_2N$ achieved a maximum turnover frequency for H_2 production of 3,300 molecules/second with an overpotential of 760 mV. The nickel catalyst with $7P_2N$ achieved a maximum of 17,000 molecules/second with an overpotential of 860 mV.

“The turnover frequency of the nickel complex with $8P_2N$ is limited by the formation of catalytically less productive protonated forms of the complex,” said Dr. Simone Raugei, who performed the computational studies for the team. “These forms divert the catalyst away from its work, slowing it down.”


“To increase the use of renewable sources of energy, we need a way to store the energy during times of high production to balance those times of low production,” said Dr. Monte Helm, Deputy Director, Center for Molecular Electrocatalysis.

With a smaller ring that allowed it to better position the protons for the reaction, $7P_2N$ clocked in at 17,000 molecules per second with an overpotential of 860 mV. “This is good news, but we want to know more,” said Helm. “Our focus now is to understanding how to make catalyst modifications that will lower the overpotentials while maintaining the fast rates.”

What’s Next? The team at the Center for Molecular Electrocatalysis is continuing to answer fundamental questions about the behavior of protons in reactions important to energy storage and production. Look for follow-on work on the electronic nature in the catalytic complexes that control the energy of reaction intermediates as the team works to uncover more ways to ratchet down the overpotential.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: Stefan Wiese, Uriah J. Kilgore, Ming-Hsun Ho, Simone Raugei, Daniel L. DuBois, R. Morris Bullock, and Monte L. Helm, PNNL

Reference: Wiese S, UJ Kilgore, MH Ho, S Raugei, DL DuBois, RM Bullock, and ML Helm. 2013. “Hydrogen Production Using Nickel Electrocatalysts with Pendant Amines: Ligand Effects on Rates and Overpotentials.” *ACS Catalysis* 3(11):2527-2535. DOI: 10.1021/cs400638f

A Better Bit of Binding

New catalyst-free method decorates electrode with designer molecules for fuel cells, sensors

December 2013

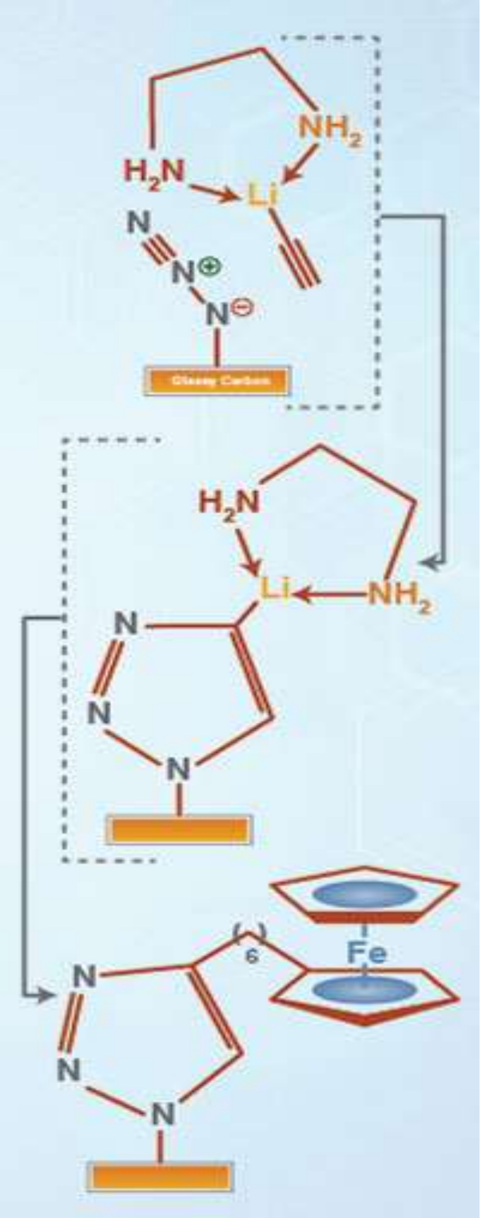
Results: In studying how to modify carbon electrodes for catalyzed reactions, scientists at the Center for Molecular Electrocatalysis designed a process for creating a plethora of specialized electrodes at room temperature. The Center is an Energy Frontier Research Center, funded by the U.S. Department of Energy's (DOE) Office of Basic Energy Sciences. Pacific Northwest National Laboratory (PNNL) leads the center. Today's reactions require metal catalysts or high temperatures and concentrated acids. In just three steps, the new method produces electrodes with the same coverage as traditional methods, but with less energy, in less time, and with no catalyst.

"Mild conditions allow better selectivity," said Dr. John A. S. Roberts, the chemist who led the study. "With aggressive conditions, the thing you want might happen, but other things you don't want might, as well."

Why It Matters: Designing and perfecting synthesis of revolutionary new forms of matter with tailored properties can change our nation's energy landscape. Fuel cells, longer lasting batteries, and other energy challenges require materials with unique features. This new synthetic route provides the desired materials quickly and efficiently.

"The method provides interesting energy-related materials, but it is not specific to energy-related problems," said Roberts. "It could be useful in other areas where carbon material modifications are of interest, including sensors."

Methods: Starting with a glass-like carbon electrode, the team attached an azide group using iodine azide (IN_3). The addition-elimination reaction replaces a hydrogen atom on the electrode (specifically, an atom on the edge of an sp^2 carbon) with an azide. The team then added lithium acetylide-ethylenediamine, which reacts with the azide to form a 5-membered 1,2,3-triazolyl ring. This surface-attached group



Scientists developed an efficient, flexible method of adding tailored molecules to a conductive carbon electrode. The team's new method attaches a nitrogen-based molecule, reacts it with a triple-bonded lithium-based hydrocarbon, and swaps part of that molecule for the desired one. The method results in a variety of materials with possible uses in energy and security technologies.

retains the lithium atom, providing an anchor point that reacts cleanly with a variety of electrophilic coupling reagents including alkyl halides, organic carbonyl compounds such as esters and aldehydes, and silyl chlorides.

"If you look at the number of compounds in these categories, it is very, very large," said Roberts. "We now have dozens of functional groups to choose from, and we don't need a catalyst."

The team measured the resulting materials. Using voltammetry, they showed that the attachments were made. Taking X-ray photoelectron spectroscopy measurements at DOE's EMSL, a scientific user facility at PNNL, the team determined the elemental composition of the surface. With these measurements, the team confirmed that the new method achieved the same coverage as the more conventional and less synthetically flexible copper-catalyzed reaction between azides and alkynes.

"We discovered a fairly general way of covalently binding things to conductive carbon materials," said Roberts.

What's Next? The team is following up on the research using the time-of-flight secondary ion mass spectrometer, also in EMSL, to study the process and resulting materials. They are also applying the new route to fabricate catalytically active materials with molecular-scale control over surface structures.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by DOE, Office of Science, Office of Basic Energy Sciences

User Facility: EMSL

Research Team: Atanu K. Das, Mark H. Engelhard, R. Morris Bullock, and John A. S. Roberts, PNNL; Fei Liu, University of Wyoming

Reference: Das AK, MH Engelhard, F Liu, RM Bullock, and JAS Roberts. 2013. "The Electrode as Organolithium Reagent: Catalyst-Free Covalent Attachment of Electrochemically Active Species to an Azide-Terminated Glassy Carbon Electrode Surface." *Inorganic Chemistry* 52(23):13674-13684.
DOI: 10.1021/ic402247n

New Catalyst Dives into Water to Produce Hydrogen

Earth-abundant metal at heart of material that creates 170,000 molecules a second

August 2013

Results: Few catalysts are energy efficient, highly active, stable, and operate in water, but a nickel-based catalyst designed at the Center for Molecular Electrocatalysis at Pacific Northwest National Laboratory quickly produces hydrogen molecules in solutions with 75 percent water. This catalyst contains tailored relays that allow the catalyst to quickly shuttle protons from the solution to the heart of the catalyst, where they are added to electrons. The catalyst is known to be energy efficient, stable, and highly active. With the modified design, it now operates in water, producing up to 170,000 hydrogen molecules per second. The study on this catalyst was highlighted as a hot article in *Chemical Communications*. Dr. John Darmon and Dr. Charles Weiss at the national laboratory captured this research in an image that was selected for the journal's cover.

"We've moved from pure organic solvents to solutions with increasing amounts of water," said Dr. Monte Helm, Deputy Director of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center. "We found that our catalyst performed better with water than in an organic solvent alone."

Why It Matters: Solar power is not a large part of our nation's energy grid, in part because of its intermittent nature and the challenges involved in storing the energy. One option is to combine the electrons generated with protons and create molecular hydrogen. The hydrogen stores the energy for later use. Catalysts are needed to drive this reaction, and this study answers a fundamental question about these catalysts by showing how to design proton relays that achieve fast, energy-efficient materials able to work in water.

ChemComm

RSC Publishing

Few catalysts are energy efficient, highly active, stable, and able to operate in water; however, a redesigned nickel-based catalyst quickly and efficiently turns protons and electrons into hydrogen. One day, power generated by solar farms and wind turbines could be used to drive this transformation. This catalyst works in solutions with 75 percent water.

We report a synthetic nickel complex containing proton relays that catalyzes the production of hydrogen in aqueous acetonitrile with turnover frequencies of 750-170,000/s at experimentally determined overpotentials of 310-470 mV.

Cover reprinted with permission of the authors and the Royal Society of Chemistry.

"We are getting closer to what we need for a real-world catalyst," said Dr. Morris Bullock, Director of the Center for Molecular Electrocatalysis.

Methods: The team began with a stable, efficient nickel-based catalyst. The catalyst is $[Ni(P^{Ph}{}_2N^{C_6H_4OH}{}_2)_2](BF_4)_2$, where $P^{Ph}{}_2N^{C_6H_4OH}{}_2$ equals 1,5-bis(ρ-hydroxyphenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octane. The catalyst drives a reaction that produces hydrogen by adding protons and electrons.

The ρ-hydroxyphenyl groups in the catalyst's structure make it hydrophilic, able to easily mix with water. They synthesized the catalyst in the quantities needed for experiments and determined the maximum amount of water that the catalyst could tolerate. They found that the catalyst would work in a solution with up to 75 percent water.

The scientists conducted a host of electrochemical hydrogen production studies. The energy efficiency or overpotential was determined to be 310 to 470 mV with turnover rates of up to 170,000/second, one of the fastest and most efficient of its kind.

Further, the team determined the catalyst's behavior in the presence of different amounts of acid. The acid supplies the protons that are relayed via pendant amines to the catalyst's active site. The team found that there is an optimum pH where the catalyst performs best.

"This work underscores the important roles that the pendent amine, acid and solvent medium all play in determining the catalyst's performance," said Dr. John Roberts, a scientist at the EFRC.

One option to make solar power a larger part our nation's energy grid is to combine the electrons generated with protons and create hydrogen, storing the energy for later use. Catalysts are needed to drive this reaction, and this study answers a fundamental question about these catalysts.

What's Next? The team continues to uncover the basic design principles for catalysts capable of hydrogen oxidation and hydrogen production.

Acknowledgments:

Sponsor: Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

Research Team: Wesley A. Hoffert, John A. S. Roberts, R. Morris Bullock and Monte L. Helm, PNNL

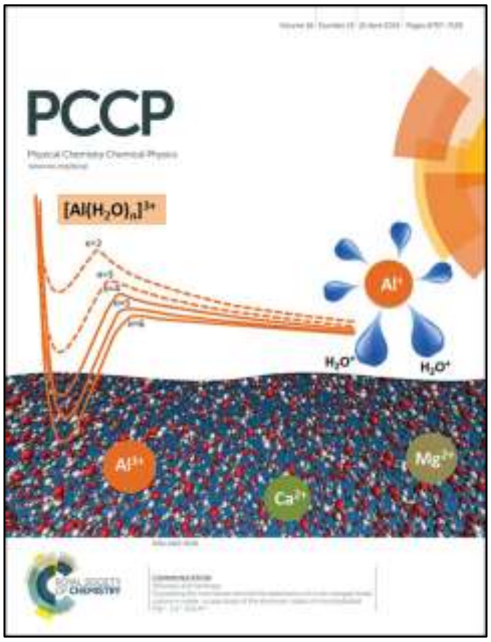
Reference: Hoffert WA, JAS Roberts, RM Bullock, and ML Helm. 2013. "Production of H_2 at Fast Rates using a Nickel Electrocatalyst in Water-Acetonitrile Solutions." *Chemical Communications* 49:7767-7769. DOI: 10.1039/C3CC43203C

Condensed Phase and Interfacial Molecular Science

Satisfying Metals' Thirst Vital for High-Capacity Batteries

Scientists show how to stabilize certain multiply charged metal cations and keep them from shredding water molecules

May 2014



This research graced the cover of *Physical Chemistry Chemical Physics.* Cover reprinted with permission of the authors and the Royal Society of Chemistry.

Results: When a multiply charged aluminum or magnesium cation encounters a single water molecule, the result can be explosive. The metal ion rips an electron from the water molecule, causing a molecular-level explosion, triggered by the Coulombic repulsion of the 2 positive charges on each fragment. But multiply charged metal ions exist in water in countless ways, such as the calcium ions in your chocolate milkshake. At Pacific Northwest National Laboratory, scientists determined the paths that lead to either the hydrolysis of water or the creation of stable metal ion clusters peaceably surrounded by water. It comes down to the pH of the solution, the number of water molecules nearby and the energy needed to remove electrons from the metal, known as the ionization potential.

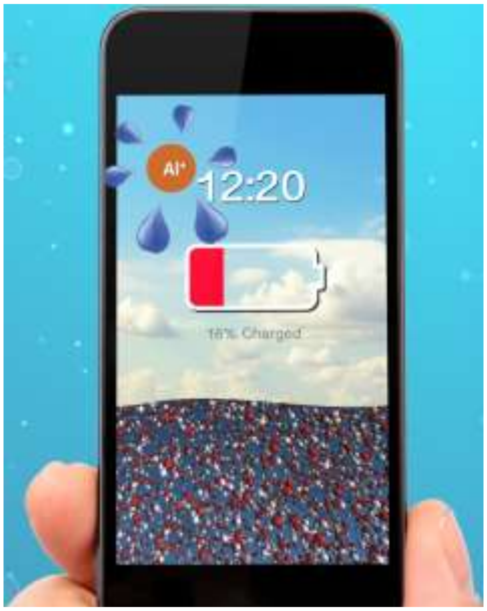
This research was featured on the cover of a recent issue of *Physical Chemistry Chemical Physics* and in a special issue of *Theoretical Chemistry Accounts* dedicated to Prof. Thomas H. Dunning, Jr. on the occasion of his 70th birthday.

"This paper describes an elegant use of computational modeling to understand a phenomena that is of fundamental importance in chemistry, yet has many practical applications as well," said Dunning, co-director of the Northwest Institute for Advanced Computing, operated by PNNL and the University of Washington.

Why It Matters: Imagine a cell phone battery that lasted for a whole week on a single charge. A car battery that worked for months between charges. A massive battery that stores the intermittent electricity from wind turbines and releases it when needed. In all three cases, today's batteries simply do not hold enough charge. Replacing lithium, which is in the +1 oxidation state, with other metals with multiple charges could greatly increase battery capacity. A roadblock to this future is understanding how to keep multiply charged ions stable.

"We want to use other metals that have +2 or +3 oxidation states," said Dr. Sotiris Xantheas, who led the research at PNNL. "This would double or triple the amount of charge that could be stored in a battery, but before this study, we had no insights on how the ions are either stabilized or destabilized when their local environment changes."

Methods: Numerous experiments show that multiple charged metal ions can generate hydrolysis products through the hydrolysis channel or metal-water clusters through the association channel, depending on the pH. Experiments, however, could not delve into "why" the different products appeared. Using accurate



Imagine a cell phone battery that worked for days between charges. At Pacific Northwest National Laboratory, scientists are answering fundamental science questions that could make batteries work more efficiently. Replacing lithium, which is in the +1 oxidation state, with metals that can carry multiple charges could potentially increase battery capacity.

computational models, Xantheas and Dr. Evangelos Miliordos calculated the different electronic states corresponding to those different channels for 3 metal ions with several water molecules in the gas phase. The ions were Al^{+3}, Ca^{+2}, and Mg^{+2}.

To accurately calculate the location and behavior of the electrons on these metal cation-water clusters, the scientists computed all the states that led to the different channels. The hydrolysis channels, seen at low pH, were also computed for the alkaline earth dication (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) microsolvated clusters.

The team found that each of the various metal ions require different numbers of water molecules to be stable as a microsolvated cluster. For example, the magnesium ion requires at least 2 water molecules for stability. For aluminum, 4 water molecules are needed. This stability is due to complex interactions between the ions and the water. The water cluster has an effective ionization potential; that is, the energy needed to pull an electron from a water cluster. The ionization potential increases as more water molecules are added. Eventually, at the right number of water molecules, the ionization potential of the water cluster gets larger than the corresponding ionization potential of the metal, preventing the removal of electrons from the water and creating stability for the metal-water cluster.

While these calculations required extensive computing time, the challenge is the analysis. Both scientists spent considerable time analyzing and refining the calculations. “A lot of analysis is required to decide what the next step is. At every step you need to decide what the next step is in the process. What did you learn and where do you want to go?” said Miliordos, a postdoctoral fellow from the University of Athens who is working with Xantheas.

What’s Next? The researchers are now working to extend their computational protocol to the solution phase and at interfaces. Extending the methodology will allow the team to better understand the dynamic interactions occurring, eventually leading to better battery technologies.

Acknowledgments:

Sponsor: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

User Facility: National Energy Research Scientific Computing Center

Research Team: Evangelos Miliordos and Sotiris Xantheas, Pacific Northwest National Laboratory

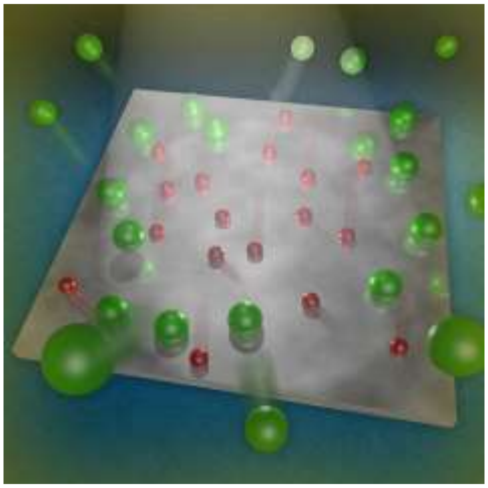
References: Miliordos E and SS Xantheas. 2014. “Elucidating the Mechanism Behind the Stabilization of Multi-Charged Metal Cations in Water: A Case Study of the Electronic States of Microhydrated Mg^{2+}, Ca^{2+} and Al^{3+}.” *Physical Chemistry Chemical Physics* 16:6886-6892. DOI: 10.1039/C3CP53636J

Miliordos E and SS Xantheas. 2014. “Unimolecular and Hydrolysis Channels for the Detachment of Water from Microsolvated Alkaline Earth Dication (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) Clusters.” *Theoretical Chemistry Accounts* 133:1450. DOI: 10.1007/s00214-014-1450-4

Krypton Reporter Uncovers Oxygen's Antics

On the surface of a popular catalyst, certain atoms and molecules flee when light appears

March 2014



When light strikes oxygen adatoms (red) on the surface of a titanium dioxide catalyst, the adatoms are excited by reactions with electrons and/or holes created in the catalyst. The adatoms undergo a change in their charge state and transfer energy to nearby krypton atoms (green), causing the reporting atoms to depart. A similar result was seen for chemisorbed molecular oxygen.

Results: Long thought to be unresponsive to ultraviolet light, negatively charged oxygen ions stuck to the catalyst's surface, known as oxygen adatoms, actually respond to light, according to scientists at Pacific Northwest National Laboratory (PNNL). The researchers made this discovery by coating the surface of common catalyst titanium dioxide with krypton reporters. When light strikes the catalyst, the oxygen adatoms become electronically excited and knock the krypton off the surface. The alteration occurs because the adatoms react with electrons and/or holes created by the ultraviolet light.

"The adatoms could be an additional source of photochemical interactions on titanium dioxide or other transition metal surfaces," said Dr. Nikolay Petrik, a physical chemist at PNNL and one of two authors on the yearlong study. "Potentially, the adatoms could participate in other photochemical reactions."

Why It Matters: Despite being part of numerous devices and industrial processes, photocatalytic reactions on metal oxides, such as titanium dioxide, are not well understood. This study answers basic questions about the behavior of oxygen adatoms and other forms of chemisorbed oxygen, where the oxygen is adsorbed onto the surface and held by chemical bonds. Fundamental knowledge could lead to innovations in catalysis and energy production technologies, such as solar and fuel cells. "Oxygen on titanium dioxide is important because most applications involve oxygen in some way or another," said Dr. Greg Kimmel, a PNNL chemical physicist and the other scientist on the study.

Methods: A challenge in studying the photochemistry of titanium dioxide, such as the light-induced breakdown of water or organic solvents, is that the oxygen adatoms and other forms of chemisorbed oxygen stay put. Most of the chemisorbed oxygens do not desorb thermally, and it is difficult to analyze the oxygen using other techniques. "There are few tools available to tell scientists what is happening with oxygen on the surface," said Petrik. "What we were looking for was a way to probe oxygen left on the surface."

To examine the oxygen's behavior, Petrik came up with the idea of adding reporter molecules to the surface and seeing what they would tell. Reporter molecules have been used for decades, but they had not been applied to this situation. Working together, Petrik and Kimmel began with a slightly reduced crystal of titanium dioxide. They absorbed different forms of chemisorbed oxygen, including oxygen adatoms and molecular oxygen, onto the crystals. Next, they added weakly bonding krypton and shined light on the surface. They found the krypton is knocked off the surface and can be easily measured.

This study answers basic questions about the behavior of oxygen adatoms and other forms of chemisorbed oxygen. Fundamental knowledge could lead to innovations in catalysis and energy production technologies, such as solar and fuel cells.

Petrik offers this analogy for understanding the technique. Imagine a large room with an invisible person in it. How do you determine their location, their choices? You could fill the room with balloons. While you can't see the person move, you can determine their actions by the movement of the "reporter" balloons. Photo-active molecules, such as oxygen adatoms or molecular oxygen (O_2), are like that invisible person. The departure of the krypton tells the scientists about how the oxygen prowls across the surface.

In this case, the oxygen adatoms are excited by reactions with electrons and/or holes created in the substrate by ultraviolet photon irradiation. The oxygen adatoms undergo a change in their charge state. This change causes the adatoms to move and collide with, and transfer energy to, nearby krypton atoms, overcoming the atoms' binding energy and desorbing them from the surface. The krypton reporters did not depart under other circumstances, including when ultraviolet light hit the surface without adsorbed oxygen. Further, the krypton's departure was not primarily due to its collision with the 11 to 50 percent of molecular oxygen that photo-desorbs.

What's Next? In regard to oxygen's behavior, Petrik and Kimmel are studying reactions of oxygen with considerably more complicated molecules, such as acetone, via infrared spectroscopy.

Acknowledgments:

Sponsor: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

User Facility: EMSL

Research Team: Nikolay G. Petrik and Greg A. Kimmel, PNNL

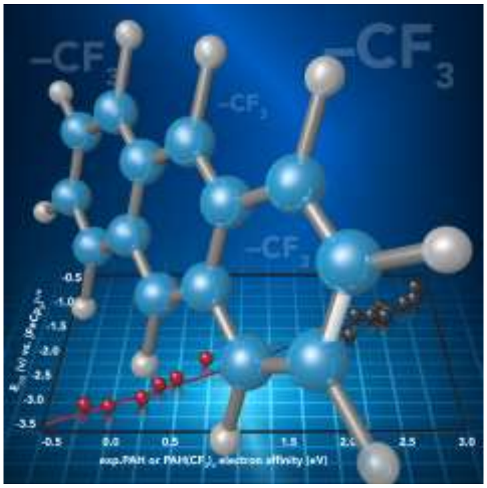
Reference: Petrik NG and GA Kimmel. 2014. "Probing the Photochemistry of Chemisorbed Oxygen on TiO_2(110) with Kr and Other Co-Adsorbates." *Physical Chemistry Chemical Physics* 16:2338-2346. DOI: 10.1039/c3cp54195a

Hot Radicals Change Material, Giving It an Affinity for Electrons

One-pot synthesis transforms ubiquitous hydrocarbons into electron attractors

February 2014

Results: Without using a solvent, catalyst, or promoter, scientists at Pacific Northwest National Laboratory (PNNL) and Colorado State University transformed a common molecule that abhors electrons into one with a strong affinity for them. The team's synthesis route begins with polycyclic aromatic hydrocarbons, or PAHs. These molecules contain common carbon and hydrogen, and scientists want to quickly tailor or functionalize them to replace materials that use rare metals. The new synthesis route adds perfluoroalkyl groups (-CF_3) via thermally hot radicals to a PAH; the resulting molecule has a strong affinity for electrons.



Replacing materials that use rare metals with ones that use polycyclic aromatic hydrocarbons could provide sustainable, lower cost solar devices. Creating tailored materials requires expertise, insights, and a foundational understanding of the material's behavior at molecular level. This study demonstrates a direct, one-pot synthesis route for building "textbook" molecules, which will be pored over to understand the material's electronic properties and solid-state shapes.

"PAHs don't like electrons at all," said Dr. Xue-Bin Wang, a PNNL chemical physicist who led the gas phase characterization of the study. "We've made them like them."

Why It Matters: Replacing metal-based materials with tailored ones made from abundant carbon, hydrogen, or other elements could provide sustainable, lower cost solar devices, catalysts, and other materials. Creating tailored materials requires expertise, insights, and a foundational understanding of the material's behavior at molecular level. This study demonstrates a direct, one-pot synthesis route, but not for creating high yields of the material, rather for building "textbook" molecules, which will be pored over to understand the material's electronic properties and solid-state shapes. The subsequent gas phase study elucidates a close correspondence among electron affinity, number of added CF_3 groups, and PAH molecular structure.

Methods: While scientists have tried to fine-tune PAHs to build new materials for some time, functionalizing PAHs has been notoriously complex and resulted in low yields of delicate products. Scientists want a process that does not require complex steps. The team's route uses only one "pot" and is free from solvents, catalysts, or other promoters. The reaction mixes a thermally stable PAH with gaseous CF_3I and high heat.

"Using a solvent-free, catalyst-free approach is very new," said Wang.

After combining PAH and CF_3I, the following steps probably occur — the exact reaction steps will need to be delineated in a follow-on study:

1. “Hot” CF_3 radicals form as a result of the gaseous CF_3I dissociating in the heat. A radical is an atom, ion, or piece of a molecule that has an unpaired electron. The unpaired electron makes the radical highly reactive.
2. The radical removes a hydrogen atom on the outer edge of the PAH, creating a CHF_3 radical and a PAH radical.
3. The PAH radical reacts with another CF_3 radical, resulting in the functionalized PAH.

These three steps can continue for some time, resulting in a PAH with one or more new functional groups and a high affinity for electrons.

To test the synthesis route, the team created 7 functionalized PAHs, $PAH(CF_3)_n$. To measure the electron affinity of each functionalized PAH and to characterize other intrinsic molecular properties, the team first converted neutral molecules into the corresponding anions, $PAH(CF_3)_n^{\bullet-}$, by adding one extra electron in solutions. They used electrospray ionization to generate gaseous $PAH(CF_3)_n^{\bullet-}$ anions from such solutions. The respective electron affinity and electronic structure of each $PAH(CF_3)_n$ were directly obtained by a photodetaching electron from each corresponding $PAH(CF_3)_n^{\bullet-}$ anion in the gas phase using low-temperature photoelectron spectroscopy.

Such a gas phase study rendered an accurate and quantitative measurement of incremental increase in the electron affinity per CF_3 group for isomer-selective functionalized PAHs, and the study also revealed substantially different stepwise increases of electron affinity per CF_3 for different classes of PAHs, thus providing the most fundamental molecular information to shed light on designing principles for rational synthesis of targeted materials with desired electron affinities. The resulting 7 materials were stable under a range of conditions and had other traits that could make them ideal candidates for fundamental studies of the connection between structure and function.

“The actual affinity can be finely tuned,” said Wang. “Specifically, we can control how many CF_3 groups are added and in what position.”

What’s Next: The team is continuing to examine how changes to the structure of the molecules affect their function. They are examining other PAHs, including corannulene, with chlorine-based molecules.

Acknowledgments:

Sponsors: National Science Foundation and Colorado State University Research Foundation (IVK, KPC, SHS, OB), and U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division (SHMD, SBW)

User Facility: EMSL

Research Team: Igor V. Kuvychko, Karlee P. Castro, Steven H. Strauss, Olga Boltalina, Colorado State University; Shihu M. Deng and Xue-Bin Wang, Pacific Northwest National Laboratory

Reference: Kuvychko IV, KP Castro, SHM Deng, XB Wang, SH Strauss, and OV Boltalina. 2013. “Taming Hot CF_3 Radicals: Incrementally Tuned Families of Polyarene Electron Acceptors for Air-Stable Molecular Optoelectronics.” *Angewandte Chemie International Edition* 52:4871-4874.
DOI: 10.1002/anie.201300085

Strong Forces at Work in Simple Table Salt

Intense electric fields alter electrons arrangement to produce light during NaCl crystallization

August 2013

Results: Inside the chemical processes to synthesize simple table salt crystals, or NaCl, intense electric fields, typically associated with particle accelerators, occur, according to Pacific Northwest National Laboratory scientists. The 5 GV/m fields can alter the NaCl solution's electronic structure. These findings are the next step in determining the exact mechanism underlying salt's crystallization and the long-lived cobalt blue light emitted (luminescence) during salt formation.

"The fields in the reactions are intense and can have dramatic effects on the electronic states inside the system," said Dr. Shawn Kathmann, the chemical physicist who led the study.

Why It Matters: The ultimate goal is to control the synthesis of matter to make materials capable of innovative leaps in capturing, storing, and transducing energy. Exquisite control over material synthesis could lead to solar cells that capture more light to improve their efficiency or catalytic nanoparticles with significantly less precious metals, reducing financial and environmental costs. This level of control requires a fundamental understanding of synthesis at the molecular and electronic levels.

Inside the chemical processes to synthesize simple table salt crystalsl, intense electric fields, typically associated with particle accelerators, occur, according to Pacific Northwest National Laboratory scientists. ©American Chemical Society, 2013.

"Our goal is to control the synthesis of matter to make whatever we want, whenever we want, out of whatever we want," said Kathmann.

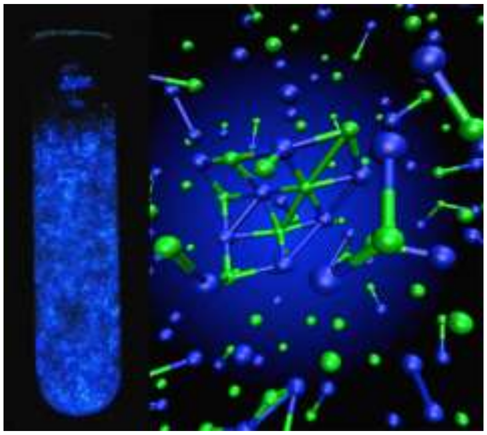
Methods: When NaCl crystallizes out of water at room temperature with no additional energy added, it emits a cobalt blue glow, indicating that electronic transitions are occurring and in direct contradiction to the general belief that salt crystallization does not involve a change in electronic structure or that the NaCl retains its ionic character.

"The basic point is that if luminescence occurs, something very different is actually happening than what we think is happening," said Dr. Bernhard Sellner, a PNNL postdoctoral fellow and a theoretical chemist on the study. "A photon of light cannot be emitted unless something exciting is happening to the electrons."

Using large-scale molecular dynamics simulations on NaCl solutions at the National Energy Research Scientific Computing Center, the team determined the fluctuations in the charges, electric potentials and fields.

"This is the first time these fields have been quantified and analyzed," said Dr. Marat Valiev, a PNNL chemical physicist and theorist on the project who works in EMSL.

In addition, the team analyzed the charge redistribution of the salt in aqueous solution as a function of concentration. They wanted to know if the charges on the water molecules and ions were what they expected. They discovered that the ion charges are not equal and opposite to each other. Some of the electronic charge on the chloride ion (Cl^-) ends up on the water molecules in the first solvation shells around the chloride and sodium ions, with the waters around sodium being the most negative — the waters effectively act as an electronic sink.



Crystalluminescence was a critical "hint" to the team that the conventional wisdom underlying salt formation was incomplete. This led them to ask if intense electric fields actually occur in concentrated aqueous electrolytes and thus could be responsible for driving the electronic processes leading to the emission of blue light. The answer? Yes.

What's Next? The next step is to understand how long these intense fields last in aqueous electrolytes, determine what types of molecular configurations are needed to create these long-lasting fields, and quantify the distribution of energy gaps between the various excited electronic states. The near-term goal is to understand the electronic mechanisms of the process and the influence of trace impurities, such as silver or copper.

Acknowledgments:

Sponsor: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

User Facility: National Energy Research Scientific Computing Center

Research Team: Bernhard Sellner, Marat Valiev, and Shawn M. Kathmann, PNNL

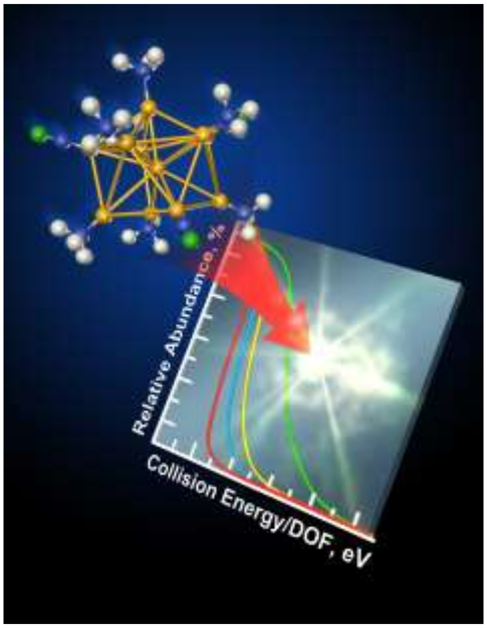
Reference: Sellner B, M Valiev, and SM Kathmann. 2013. "Charge and Electric Field Fluctuations in Aqueous NaCl Electrolytes." *Journal of Physical Chemistry B* 117(13):10869-10882.
DOI: 10.1021/jp405578w

Chemical Analysis

The Stability of Gold Clusters: Every Ligand Counts

The number of molecules attached to gold clusters has a previously unrecognized influence

July 2014



What determines the stability of gold clusters, which may be the building blocks for new energy technologies? By colliding the ultra-small particles with a surface and analyzing the resulting fragments, scientists found that the binding energy between the gold center and the surrounding molecular framework is key.

Results: By colliding ultra-small gold particles with a surface and analyzing the resulting fragments, a trio of scientists at Pacific Northwest National Laboratory discovered how and why the particles break. This information is important for controlling the synthesis of these tiny building blocks that are of interest to catalysis, energy conversion and storage, and chemical sensing. The team showed that the particles break along three competing pathways. The path chosen by a specific cluster depends on the amount of energy that binds it together as well as whether a given pathway leads to rapid or slow fragmentation. Particles with 8 gold atoms wrapped with 6 ligands or phosphorus-based strands proved exceptionally stable in part because the ligands tightly bind to the gold core.

“There is substantial interest in many disciplines that wish to control the synthesis of metal clusters,” said Dr. Julia Laskin, a physical chemist and Laboratory Fellow who led the study. “These particles’ optical and electronic properties make them promising candidates for applications in catalysis, photovoltaics, and drug delivery.”

Why It Matters: Today’s materials will not likely solve our nation’s mounting energy challenges. They simply don’t have the necessary properties to produce more efficient catalysts or solar cells that create, store, and use energy on a massive scale. Employing ultra-small particles, scientists are synthesizing highly tailored materials with the desired stability and chemical reactivity. However, in many cases, researchers lack basic thermodynamic and kinetic information about how the particles behave. The study done at PNNL — which is the first of its kind — provides fundamental knowledge that allows researchers to control the synthesis of gold particles or other nanosized clusters in a more rational manner.

“By understanding the fundamentals of cluster synthesis through thermochemistry, we may control and exploit these processes to create superior materials for a variety of energy-related applications,” said Dr. Grant Johnson, a PNNL physical chemist who worked on the study.

Methods: The team began by synthesizing a variety of ionic gold clusters in solution. The clusters had 7, 8, or 9 gold atoms and 6 or 7 triphenylphosphine ligands. Their chemical formulas were $Au_7L_6^{2+}$, $Au_8L_6^{2+}$, $Au_8L_7^{2+}$, and $Au_9L_7^{2+}$ (Au = gold, L = ligand). They filtered out the clusters of interest one by one in the gas phase using mass spectrometry. “We isolate clusters of the exact size that we want,” said Johnson. “In solution, this is very challenging to accomplish — so measurements are typically made on poorly defined distributions of particles.”

Next, they collided the clusters they selected with a special surface inside the mass spectrometer in a process known as surface-induced dissociation. The instrument showed the fragments produced when the clusters fragmented at different collision energies and times. Using a unique modeling approach developed by Laskin, they determined the energy involved in breaking the clusters apart and whether each route to fragmentation is rapid or slow for a specific cluster.

They found the clusters dissociate through one of three competing pathways. The particles may break

- With the loss of an uncharged phosphine ligand.
- Through asymmetrical fission, with a gold atom and two ligands breaking off.
- Through more symmetrical fission, with two fragments having nearly the same number of gold atoms and ligands.

The team showed that a cluster containing 8 gold atoms and 6 ligands is exceptionally stable compared to other clusters. It turns out that this cluster is also the predominant species formed during the early stages of reduction synthesis in solution. This observation demonstrates that experiments with gas-phase ions are indispensable for understanding the thermochemistry of complex processes occurring in solution.

The Value of Gold: The chemistry of creating small clusters and nanoparticles of gold goes back more than 1000 years to the production of stained glass windows. The color and other properties, including surface area to volume ratio, and electrical conductivity are all influenced by the size of the particles. Different sizes of particles have potential uses in catalysis and chemical sensing.

“This is an old chemistry that is widely used now because it is scalable and generates materials with interesting and highly-tunable properties,” said Dr. Julia Laskin, who led the research.

The study also provides theorists with benchmark values for their calculations and simulations of ligated gold clusters. Experimental benchmarks give theorists important complementary information that aids them in selecting the most computationally efficient and accurate methods.

What’s Next: The team expects that the surface-induced dissociation experiments will play an increasing role in understanding the initial steps of cluster nucleation and growth in solution. They are currently examining different ligated clusters to understand how the spatial arrangement of the atoms in the ligands alters the abundance of clusters formed in solution and their stability in the gas phase.

Acknowledgments:

Sponsors: U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Thomas Priest also received partial support from the DOE Science Undergraduate Laboratory Internship. Grant Johnson also received partial support from the Linus Pauling Fellowship and the Laboratory Directed Research and Development Program at PNNL

User Facility: EMSL

Research Team: Grant E. Johnson, Thomas Priest, and Julia Laskin, PNNL

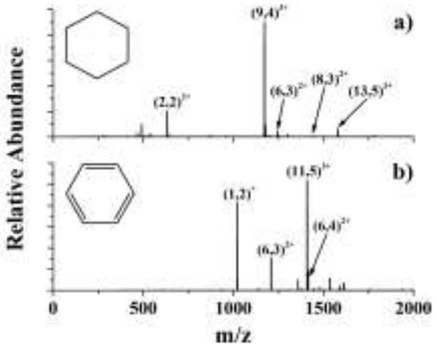
Reference: Johnson GE, T Priest, and J Laskin. 2014. “Size-Dependent Stability toward Dissociation and Ligand Binding Energies of Phosphine Ligated Gold Cluster Ions.” *Chemical Science* 5:3275-3286.
DOI: 10.1039/C4SC00849A

Strong Influence of a Minor Substitution in Gold Clusters

Ligand change controls size, stability, and charge state of nanoparticles synthesized in solution

October 2013

Results: What could you change about our nation's energy, transportation, and other sectors if you could synthesize a material with exactly the properties that you needed on demand and with high purity? The answer to creating these materials may lie in sub-nanometer building blocks called clusters that have a precisely defined size and composition. Producing commercially relevant quantities involves the reduction in solution of positively charged metal ions to neutral atoms in the presence of organic molecules called ligands, which arrest the growth at a particular number of metal atoms. Researchers at Pacific Northwest National Laboratory showed that changes at a diphenylphosphine ligand's phosphorus centers alter the size of clusters synthesized in solution and the fragmentation pathways of otherwise identical clusters.



Using a combination of synthesis in solution and high-resolution mass spectrometry, scientists at Pacific Northwest National Laboratory demonstrated that the substitution of diphosphine ligands (top: phenyl; bottom: cyclohexane) dramatically influences the size and fragmentation pathways of otherwise identical gold clusters.

"Until now, scientists assumed that substitutions in certain ligands did not influence the size or stability of clusters formed," said Dr. Julia Laskin, a PNNL physical chemist involved with the project.

Why It Matters: Future materials that will decrease energy consumption and waste associated with manufacturing, detect harmful contaminants in foods and medicines, and enable the ultimate miniaturization of complex electronic devices will be composed of clusters containing different numbers and types of atoms. Clusters exhibit large variations in critical properties, such as electron affinity and ionization energy, with changing size that may be exploited to tune their stability and chemical reactivity for specific applications.

"By understanding the fundamentals of cluster synthesis, we may control and exploit them to create these superior materials," said Dr. Grant Johnson, a physical chemist at PNNL who led the study.

Methods: Diphenylphosphine ligands, which consist of 2 phenyl (C_6H_5) substituted phosphorus centers separated by a carbon chain of variable length, produce gold clusters with extremely narrow distributions in size; that is, the synthesis route produces a large quantity of clusters with the same number of gold atoms as well as a small number of clusters with similar numbers of atoms. The length of the carbon chain between the 2 phosphorus centers determines the size and monodispersity of the gold clusters. In contrast, the substituents (*e.g.*, phenyl (C_6H_5)) at the 2 phosphorus centers are generally regarded as not exerting an influence on the selectivity of diphosphine ligands towards gold clusters of a particular size. Furthermore, theoretical calculations on diphosphine capped gold clusters often involve the substitution of simpler hydrogen atoms in the place of computationally demanding substituents such as phenyl groups with the assumption that the substitution does not alter the stability of the cluster.

The team wanted to see if this assumption would hold up. They focused on gold clusters capped with diphosphine ligands. The team prepared 2 gold cluster solutions that differed only in the substitution of either cyclohexane groups or phenyl groups at the phosphorus centers of diphosphine ligands.

Thomas Priest, a DOE Science Undergraduate Laboratory intern at PNNL, synthesized the gold clusters, creating a purple solution that Johnson electrosprayed into a high-resolution mass spectrometer at EMSL. The electrospray process turns the gold clusters in the liquid into positively charged ions in a gaseous stream. The team analyzed the composition of the solution including the number of gold atoms and ligands in each cluster using the mass spectrometer. In addition, they isolated representative ions with the instrument and fragmented these clusters through high kinetic energy collisions with an inert background gas to provide insight into the structure and stability of the clusters.

To reduce industry's energy demands, scientists must build innovative materials; this research provides foundational insights into directing atomic clusters to create these materials.

They found that clusters synthesized using the phenyl ligand contained predominantly 11 gold atoms. In contrast, clusters prepared using the cyclohexane ligand contained 9 gold atoms. In addition, gold clusters with the phenyl-containing ligand fragmented through a wide range of dissociation channels involving the loss of gold atoms as well as activation of the phosphorus-carbon bonds of the ligands. The gold clusters with the cyclohexane ligands exhibited far less activation of the ligands. By swapping cyclohexane (C_6H_{11}) for phenyl (C_6H_5) groups in otherwise identical diphosphine ligands, the team showed that gold clusters of completely different size may be synthesized in solution under the same reaction conditions.

“This work demonstrates that the substitution of the phosphorus centers is another powerful parameter that may be used to direct the size-selected synthesis of a broad range of gold clusters,” said Johnson.

What's Next? Johnson and members of Laskin's team are now studying how the composition of the solutions evolves from the initial stages of reaction through the formation of the final products. These kinetic studies are aimed at determining the appropriate conditions of reaction time, temperature, and concentration to produce a continuous flow of a wide array of different size clusters for studies in the gas phase using mass spectrometry and on surfaces through soft landing of mass selected ions.

Acknowledgments:

Sponsors: Grant Johnson acknowledges the support of the Linus Pauling Postdoctoral Fellowship Program and the Laboratory Directed Research and Development Program at the Pacific Northwest National Laboratory. Julia Laskin and Thomas Priest acknowledge support from the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and

Biosciences Division. Thomas Priest was supported in part by DOE's Science Undergraduate Laboratory Internship at PNNL.

Research Team: Grant Johnson, Thomas Priest, and Julia Laskin, PNNL

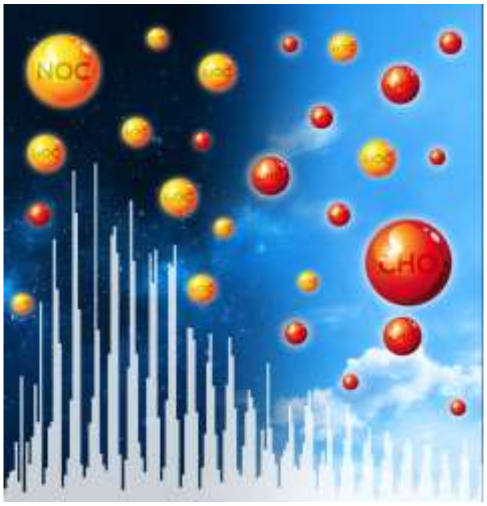
User Facility: EMSL

Reference: Johnson GE, T Priest, and J Laskin. 2013. "Synthesis and Characterization of Gold Clusters Ligated with 1,3-Bis(dicyclohexylphosphino)propane." *ChemPlusChem* 78:1033-1039.
DOI: 10.1002/cplu.201300134

The Changing Face of Aerosols

New study reveals chemical transformations of ambient organic aerosols

July 2013



Changes in the chemical composition of organic aerosols throughout the day indicate the potential role of ammonium-carbonyl reaction chemistry in forming the nitrogen-containing organic constituents of aerosols.

Results: Throughout the day, the composition of organic aerosols that influence our climate changes: molecules containing carbon, hydrogen, and oxygen, or CHO, compounds dominate the composition of fresh aerosol during the day time, while nitrogen-containing organics increase at night, according to a new study by scientists at Pacific Northwest National Laboratory and two California universities. The formation of nitrogen-containing organic compounds is caused by reactions of CHO molecules with ammonium ions, a pervasive atmospheric constituent. To probe the compositional changes during a diurnal cycle and the distribution of unique species over different lengths of time, the team employed the Nanospray Desorption Electrospray Ionization (nano-DESI) coupled to high-resolution mass spectrometry (HR-MS) to characterize more than 850 molecular species.

Why It Matters: Deciphering the molecular composition of organic aerosols in the atmosphere is essential for understanding how these complex aerosols impact climate forcing. The chemical composition of organic aerosols influences how sunlight is absorbed. For example, nitrogen-containing organic compounds in the aerosols may greatly alter the particle's light-absorption properties, affecting how the aerosols influence regional haze and the Earth's climate. Organic aerosol sources, their atmospheric transformation, and radiative effects are key contributors of uncertainty in today's atmospheric climate models. At present, the understanding of organic aerosols composition is limited, hence their impact cannot be accurately predicted and mitigated.

Methods: Using nano-DESI/HR-MS, the team performed sensitive direct analysis of minute amounts of organic aerosol samples from the National Oceanic and Atmospheric Administration's CalNex 2010 field study. The analysis accurately assesses the transforming reactions and their plausible causes.

The analyses revealed increased nitrogen-containing compounds in samples taken at night while organic aerosols containing only CHO were more common in the afternoon. High ozone concentrations correlated with the predominant CHO compounds, indicating they were secondary products of daytime oxidation, including ozonolysis and/or photochemical reactions. Meanwhile, the observed nighttime enhancement of nitrogen-containing compounds showed evidence of being formed by reactions that transform carbonyls into imines, which require aqueous-phase chemistry of ammonium and organic compounds in liquid-phase particles. Thus, the team hypothesized ammonium chemistry may be an important pathway for nitrogen-containing compound formation.

What's Next? In addition to providing an alternate technique for investigating organic aerosols, and potentially more precise models, this work is another step in the scientific community's understanding of climate change ramifications stemming from the chemical transformations of organic aerosols.

Deciphering the molecular composition of organic aerosols in the atmosphere is essential for understanding how these complex aerosols impact climate forcing.

Acknowledgments:

Sponsors: Rachel O'Brien, Robin Weber, Lynn Russell, Allen Goldstein, Shang Liu, and Lynn Russell acknowledge support from the California Air Resources Board (CARB). Alexander Laskin acknowledges support from the Atmospheric System Research program, Office of Biological and Environmental Research, Office of Science, U.S. Department of Energy (DOE). Julia Laskin acknowledges support from the from the DOE, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

User Facility: EMSL

Research Team: Rachel O'Brien, Robin Weber, Lynn Russell, and Allen Goldstein, University of California, Berkeley; Alexander Laskin and Julia Laskin, Pacific Northwest National Laboratory; Shang Liu and Lynn Russell, University of California, San Diego

Reference: O'Brien RE, A Laskin, J Laskin, S Liu, R Weber, LM Russell, and AH Goldstein. 2013. "Molecular Characterization of Organic Aerosol Using Nanospray Desorption/Electrospray Ionization Mass Spectrometry: CalNex 2010 Field Study." *Atmospheric Environment* 68:265-272.
DOI: 10.1016/j.atmosenv.2012.11.056

Geosciences

Just in Time

Parallel-in-time algorithms enable simulation of long-lasting chemical processes

January 2014

Results: Molecular dynamics simulations often require too much time to be practical for simulating important chemical processes that take place on long timescales. Using EMSL-developed NWChem, researchers provided evidence that time integration algorithms working in parallel can significantly speed up computationally demanding molecular dynamics simulations, opening new avenues for studying complex, long-lasting chemical processes.

Why It Matters: New parallel-in-time algorithms that speed up high-level molecular dynamics simulations can enable scientists to predict the properties of complex materials. They are designed to use NWChem and other molecular simulation programs. This research is important for toxic waste disposal, nuclear waste storage, carbon sequestration, energy storage, drug discovery, disease treatment, efficient catalysis, the optimization of electronic device performance, and other applications relevant to addressing the nation’s major energy and environmental problems.

Methods: Molecular dynamics simulations provide valuable information about the physical movements and interactions of atoms and molecules over time. Unlike classical approaches, *ab initio* molecular dynamics (AIMD) simulations provide accurate calculations of the movements of electrons, enabling scientists to study chemical reactions that involve the breaking or formation of covalent bonds. Although AIMD simulations are useful for a wide range of important problems in areas such as liquid structure, acid–base chemistry, industrial and biological catalysis, atmospheric and aerosol chemistry, geochemistry, nanotechnology, and materials science, their use is limited because they are very computationally costly.

More time-efficient simulations have been made possible by massively parallel supercomputers and parallel algorithms, which distribute the computational workload across different processors or computers. Still, AIMD approaches currently take several months to simulate events that span picoseconds, even though many important chemical processes take much longer.

To address this problem, researchers from EMSL and the University of Chicago tested several parallel algorithms that distribute computations for different time intervals of a chemical event to different processors. These parallel-in-time algorithms sped up a conventional molecular dynamics simulation of 1,000 silicon atoms by a factor of 3, and a challenging AIMD simulation of an atmospherically important chemical reaction involving hydrochloric acid by a factor of 14. When the AIMD simulation of this chemical process was performed on the massively parallel Chinook computer at EMSL, a DOE national scientific user facility, the use of parallel-in-time algorithms compared with sequential algorithms reduced the duration of each computational time step from 32 seconds to 7 seconds.

The parallel-in-time algorithms are suitable for cloud computing — running the programs using a large number of computers connected through a real-time communication network such as the Internet. The speedup provided by these algorithms occurred even when they were implemented on machines connected by very slow networks such as WiFi or in different time zones connected by the Internet. Moreover, these algorithms can be implemented using scripting languages such as Python as well as standard quantum chemistry packages, such as NWChem, an open-source computational chemistry code developed at EMSL. Taken together, the findings demonstrate that parallel-in-time algorithms can allow researchers to use powerful AIMD simulations to study realistic and complex chemical processes that take place on long timescales.

What's Next: This research is part of ongoing efforts to speed up computationally demanding molecular dynamics simulations.

Sponsor: This research was supported by the ASCR Petascale Tools program (development of advanced parallel algorithms contained in the manuscript) and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES) Chemical Sciences, Geosciences, and Biosciences Division (initial applications of this technique contained in the paper including the grant for National Energy Research Scientific Computing Center time), and the National Science Foundation (Jonathan Weare's efforts at the University of Chicago)

User Facility: National Energy Research Scientific Computing Center and EMSL

Research Team: Eric Bylaska, Jonathan Weare, and John Weare

Reference: Bylaska EJ, JQ Weare, and JH Weare. 2013. "Extending Molecular Simulation Timescales: Parallel in Time Integrations for High-Level Quantum Chemistry and Complex Force Representations." *Journal of Chemical Physics* 139(7):074114. DOI: 10.1063/1.4818328

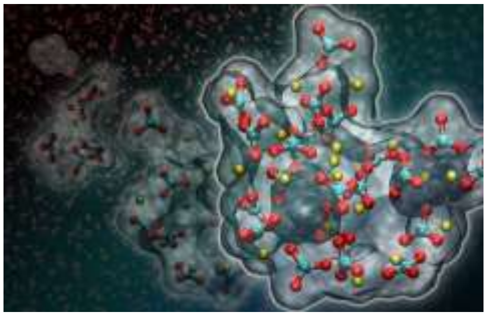
Computer Simulations Indicate Calcium Carbonate Has a Dense Liquid Phase

Research could help scientists predict how carbon is stored underground

August 2013

This research was done as part of Center for Nanoscale Control of Geologic CO_2, an Energy Frontier Research Center, led by Lawrence Berkeley National Laboratory.

Results: Led by Pacific Northwest National Laboratory's Dr. James De Yoreo when he was at Lawrence Berkeley National Laboratory, computer simulations could help scientists make sense of a recently observed and puzzling wrinkle in important natural processes. It turns out that calcium carbonate — a huge player in the planet's carbon cycle — may momentarily exist in liquid form as it crystallizes from solution. The team's work appears in the August 23 issue of *Science*.



Artistic rendition of liquid-liquid separation in a supersaturated calcium carbonate solution. New research suggests that a dense liquid phase (shown in red in the background and in full atomistic detail based on computer simulations in the foreground) forms at the onset of calcium carbonate crystallization. (Credit: Berkeley Lab).

Why It Matters: The existence of a dense liquid phase could influence the response of Earth's oceans to rising atmospheric carbon dioxide levels, and help scientists predict the extent to which geological formations can act as carbon storage reservoirs, among other examples. The research may also reconcile confounding experimental observations. For more than a century, scientists believed that crystals nucleate from solution by overcoming an energy barrier. But recent studies of calcium carbonate revealed the presence of nanosized clusters which, under certain conditions, appear to circumvent the barrier by following an alternative aggregation-based crystallization pathway.

"Because nucleation is ubiquitous in both natural and synthetic systems, those findings have forced diverse scientific communities to reevaluate their longstanding view of this process," said the study's co-corresponding author De Yoreo.

Acknowledgments:

Sponsor: Center for Nanoscale Control of Geologic CO_2, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences

User Facilities: Molecular Foundry and National Energy Research Scientific Computing Center

Reference: Wallace AF, LO Hedges, AF Fernandez-Martinez, P Raiteri, S Whitelam, GA Waychunas, JD Gale, JF Banfield, and JJ De Yoreo. 2013. "Microscopic Evidence for Liquid-Liquid Separation in Supersaturated $CaCO_3$ Solutions." *Science* 341(6148):885-889. DOI: 10.1126/science.1230915

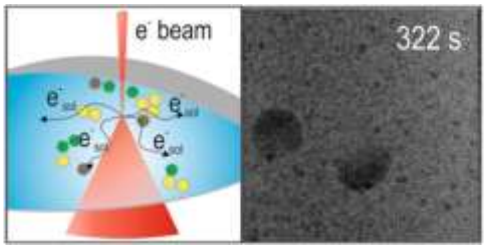
Joint Center for Energy Storage Research

Degradation Mechanisms Uncovered in Li-Ion Battery Electrolytes

In situ scanning transmission electron microscopy helps characterize stability, degradation

March 2014

Results: A team led by Pacific Northwest National Laboratory has uncovered information about high-demand batteries that could improve an essential component impacting their performance and longevity. The scientists characterized the stability and interconnected degradation mechanisms in electrolytes commonly used for lithium-ion, or Li-ion, batteries. They obtained detailed chemical imaging data using an environmental liquid stage in a scanning transmission electron microscope (STEM).



Left: Cartoon illustrating concept of electron-beam-induced degradation of lithium-ion battery electrolytes under conditions similar to those during battery operation. A fluid cell is analyzed with a scanning transmission electron microscope, or STEM. Electrons in the solvent and other electron-beam-induced radical species will interact through secondary chemical reactions with a lithium salt and solvent. Right: STEM image showing electron beam-induced breakdown — the two large, dark particles — of lithium salt in an electrolyte mixture.

Why It Matters: To develop new battery technologies, novel electrolytes with increased electrochemical stability are needed, preferably solid electrolytes such as inorganic or salt complexes. Finding these electrolytes requires non-invasive tools that can be used *in situ* at the active particle size level — the nanoscale — to observe the processes that occur during battery operation. In this study, the researchers used STEM.

“Currently, STEM is the only experimental technique that gives information at the nanoscale during the operation of lithium-ion batteries,” said Dr. Nigel Browning, Chief Science Officer for PNNL’s Chemical Imaging Initiative. “The *in situ* liquid stage in a STEM allows the reactions inside a battery to be characterized in real time. This study is a proof of principle of the STEM approach that avoids the standard post-mortem analysis of lithium electrolyte breakdown products.”

The detailed characterization offered by liquid-stage STEM can provide unique insights into electrolyte behavior, either for use in future *in situ* battery studies or to test new electrolytes, winnowing the library of candidate solutions for further characterization and reducing the experimental time spent on less effective electrolytes.

Methods: In their study, the scientists explored the stability of 5 different electrolytes commonly used for Li-ion and LiO_2 battery applications: three that contained lithium hexafluoroarsenate salt, one containing lithium hexafluorophosphate, and one containing lithium triflate.

The researchers placed miniature environmental chambers with different electrolytes in the path of the STEM’s electron beam. By allowing the electrolytes to be examined in a liquid state, even when inserted into the high vacuum of the microscope, these chambers simulated what is found inside an actual battery. Then, the electron beam caused a localized electrochemical reaction inside the liquid cell that sped up electrolyte degradation,-the breakdown of a range of inorganic/salt complexes. The microscope acquired real-time images with nanoscale resolution, showing the earliest stages of damage nucleation.

The scientists also used electron energy loss spectroscopy to verify the presence of the electrolyte and measure other experimental parameters.

"Each electrolyte behaved differently in the analysis," said Dr. Patricia Abellan, a PNNL postdoctoral fellow and materials scientist. "The stability of the electrolytes investigated here correlates with electrochemical trends reported in the literature, which suggests that this technique could potentially give new insights into the reduction and degradation processes that take place during the operation of lithium-ion batteries."

What's Next? Once the effect of the imaging electrons is fully calibrated, this approach could potentially provide insights into the degradation mechanisms that occur during the first stages of solid electrolyte interphase, or SEI, formation, which electrically insulates the electrolyte and prevents further deterioration.

"One day in the near future, *in situ* STEM could be used to study different processes through direct visualization and in real time," Abellan said. "We could use it to optimize current state-of-the-art and next-generation electrolytes."

Acknowledgments:

Sponsors: This work was supported by PNNL's Chemical Imaging Initiative (CII) (PA, MG, JE, CW, NB); Laboratory Directed Research and Development project (IA, LP); and the Joint Center for Energy Storage Research (JCESR) (BM, WX, YZ, NB, CW, JGZ), an Energy Innovation Hub funded by DOE Office of Science, Office of Basic Energy Sciences; the National Science Foundation (CP); Florida State University Ralph E. Powe Junior Faculty Enhancement Award (CP). Nigel Browning and Chongmin Wang were jointly funded by JCESR and CII.

User Facility: EMSL

Research Team: Patricia Abellan Baeza, Nigel D. Browning, B. Layla Mehdi, Lucas R. Parent, Meng Gu, Wu Xu, Yaohui Zhang, Ilke Arslan, Ji-Guang Zhang, Chong-Min Wang, and James E. Evans, PNNL; and Chiwoo Park, Florida State University

Reference: Abellan P, BL Mehdi, LR Parent, M Gu, C Park, W Xu, Y Zhang, I Arslan, J Zhang, CM Wang, JE Evans, and ND Browning. 2014. "Probing the Degradation Mechanisms in Electrolyte Solutions for Li-Ion Batteries by In Situ Transmission Electron Microscopy." *Nano Letters* 14(3):1293-1299. DOI: 10.1021/nl404271k

Batteries as They Are Meant To Be Seen

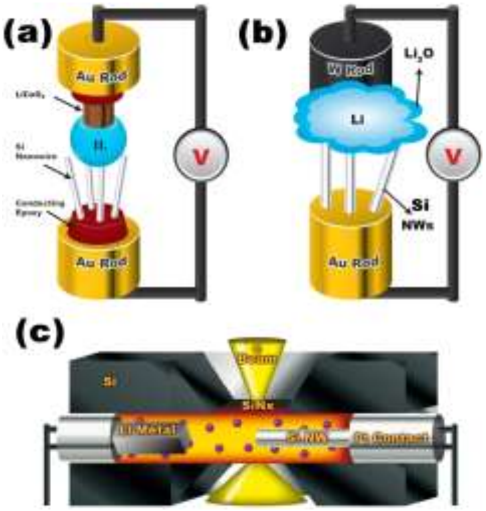
In the search for long-lasting, inexpensive rechargeable batteries, researchers develop more realistic methods to study the materials in action

January 2014

Results: Researchers at a host of national laboratories and universities have developed a way to microscopically view battery electrodes while they are bathed in wet electrolytes, mimicking realistic conditions inside actual batteries. While life sciences researchers regularly use transmission electron microscopy to study wet environments, this time scientists have applied it successfully to rechargeable battery research.

The results, reported in December 11's issue of *Nano Letters*, are good news for scientists studying battery materials under dry conditions. The work showed that many aspects can be studied under dry conditions, which are much easier to use. However, wet conditions are needed to study the hard-to-find solid electrolyte interphase layer, a coating that accumulates on the electrode's surface and dramatically influences battery performance.

"The liquid cell gave us global information about how the electrodes behave in a battery environment," said materials scientist Dr. Chong-Min Wang of Pacific Northwest National Laboratory. "And it will help us find the solid electrolyte layer. It has been hard to directly visualize in sufficient detail."



(a) The newly devised open-cell approach to viewing battery electrodes; (b) Open cell approach using lithium metal as lithium source and Li_2O as a solid electrolyte; (c) Setup of the liquid cell battery. Image courtesy of Gu et al., *Nano Letters* 2013

Why It Matters: Wang and colleagues have used high-powered microscopes to watch how the ebbing and flowing of positively charged ions deform electrodes in batteries. Metal ions squeezing into the electrode's pores makes the electrodes swell, and repeated use can wear them down. For example, recent work funded through the Joint Center for Energy Storage Research, a DOE Energy Innovation Hub established to speed battery development, showed that sodium ions leave bubbles behind, potentially interfering with battery function.

But up to this point, the transmission electron microscopes have only been able to accommodate dry battery cells, which researchers refer to as open cells. In a real battery, electrodes are bathed in liquid electrolytes that provide an environment ions can easily move through.

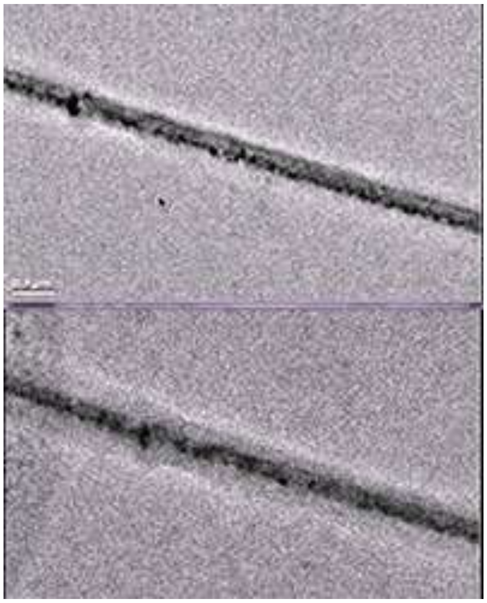
So, working with JCESR colleagues, Wang led development of a wet battery cell in a transmission electron microscope at EMSL, giving scientists a more realistic view of what's happening.

Methods: It began with the team building a battery so small that several could fit on a dime. The battery had one silicon electrode and one lithium metal electrode, both contained in a bath of electrolyte. When the team charged the battery, they saw the silicon electrode swell, as expected. However, under dry conditions, the electrode is attached at one end to the lithium source — and swelling starts at just one end as the ions push their way in, creating a leading edge. In this study's liquid cell, lithium could enter the silicon anywhere along the electrode's length. The team watched as the electrode swelled all along its length at the same time.

"The electrode got fatter and fatter uniformly. This is how it would happen inside a battery," said Wang.

The total amount the electrode swelled was about the same, though, whether the researchers set up a dry or wet battery cell. That suggests researchers can use either condition to study certain aspects of battery materials.

"We have been studying battery materials with the dry, open cell for the last 5 years," said Wang. "We are glad to discover that the open cell provides accurate information with respect to how electrodes behave chemically. It is much easier to do, so we will continue to use them."



Liquid battery electrolytes makes this view of an uncharged electrode (top) and a charged electrode (bottom) a bit fuzzy. Image courtesy of Gu et al., *Nano Letters* 2013

What's Next: As far as the elusive solid electrolyte interphase layer goes, Wang said they couldn't see it in this initial experiment. In future experiments, they will try to reduce the thickness of the wet layer by at least half to increase the resolution, which might provide enough detail to observe the solid electrolyte interphase layer.

"The layer is perceived to have peculiar properties and to influence the charging and discharging performance of the battery," said Wang. "However, researchers don't have a concise understanding or knowledge of how it forms, its structure, or its chemistry. Also, how it changes with repeated charging and discharging remains unclear. It's very mysterious stuff. We expect the liquid cell will help us to uncover this mystery layer."

Acknowledgments:

Sponsors: The work at PNNL and Stanford was supported as part of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES). The development of the electrochemical liquid cell was supported by Chemical Imaging Initiative at PNNL and Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of DOE, under the Batteries for Advanced Transportation Technologies program. The work in Oak Ridge was supported by the Fluid Interface Reactions Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by BES. Work at Northwestern University was supported by the National Science Foundation.

User Facility: EMSL

Research Team: Meng Gu, B. Layla Mehdi, Wu Xu, Patricia Abellan, Xilin Chen, Yaohui Zhang, Daniel E. Perea, James E. Evans, Ji-Guang Zhang, Jun Liu, Nigel D. Browning, Ilke Arslan, and Chong-Min

Wang, Pacific Northwest National Laboratory; Lucas R. Parent and Pinghong Xu, University of California-Davis; Raymond R. Unocic and Robert L. Sacci, Oak Ridge National Laboratory; Matthew T. McDowell, Stanford University; Justin Grant Connell and Lincoln J. Lauhon, Northwestern University; and Yi Cui, SLAC National Accelerator Laboratory

Reference: Gu M, LR Parent, BL Mehdi, RR Unocic, MT McDowell, RL Sacci, W Xu, JG Connell, P Xu, P Abellan, X Chen, Y Zhang, DE Perea, JE Evans, LJ Lauhon, JG Zhang, J Liu, ND Browning, Y Cui, I Arslan, and CM Wang. 2013. "Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes." *Nano Letters* 13(12):6106-6112. DOI: 10.1021/nl403402q

Synthesis and Processing Science

Battery Development May Extend Range of Electric Cars

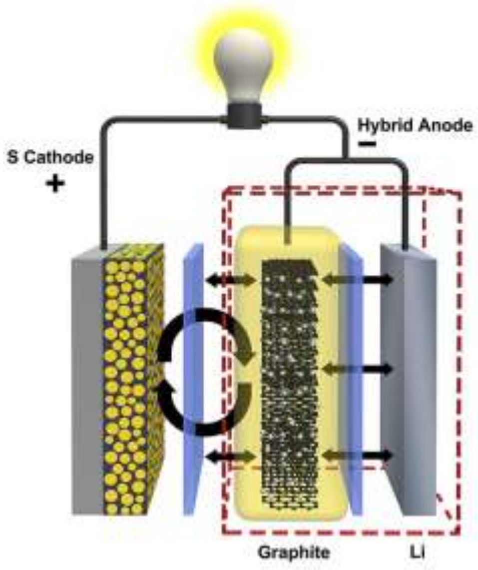
New anode quadruples life of lithium-sulfur battery, could also help store renewable energy more cheaply

January 2014

Results: It's known that electric vehicles could travel longer distances before needing to charge and more renewable solar energy could be saved for a rainy day if lithium-sulfur batteries can just overcome a few technical hurdles. Now, a novel design for a critical part of the battery has been shown to significantly extend the technology's lifespan, bringing it closer to commercial use.

A "hybrid" anode developed at the Pacific Northwest National Laboratory could quadruple the life of lithium-sulfur batteries. *Nature Communications* recently published a paper describing the anode's design and performance.

"Lithium-sulfur batteries could one day help us take electric cars on longer drives and store renewable wind energy more cheaply, but some technical challenges have to be overcome first," said Pacific Northwest National Laboratory (PNNL) Laboratory Fellow Jun Liu, who is the paper's corresponding author. "PNNL's new anode design is helping bringing us closer to that day."



Researchers at Pacific Northwest National Laboratory have developed a hybrid anode made of graphite and lithium that could quadruple the lifespan of lithium-sulfur batteries. Image courtesy of Huang *et al.*, *Nature Communications* 2014

Why It Matters: Today's electric vehicles are commonly powered by rechargeable lithium-ion batteries, which are also being used to store renewable energy. But the chemistry of lithium-ion batteries limits how much energy they can store. One promising solution is the lithium-sulfur battery, which can hold as much as 4 times more energy per mass than lithium-ion batteries. This would enable electric vehicles to drive longer on a single charge and help store more renewable energy when using similar sized batteries. The down side of lithium-sulfur batteries, however, is they have a much shorter lifespan.

Methods: The lithium-sulfur battery's main obstacles are unwanted side reactions that reduce the battery's lifetime. One undesirable attribute is the dissolution of the battery's sulfur-containing cathode into the battery's electrolyte liquid, forming molecules called polysulfides that then form a non-conductive deposit on the surface of the lithium anode, making the battery inoperable.

Most lithium-sulfur battery research to date has centered on stopping sulfur leakage from the cathode. But PNNL researchers determined stopping that leakage can be particularly challenging. Besides, recent research has shown a battery with a dissolved cathode can still work if the detrimental side reactions at the lithium metal anode can be prevented. So, the PNNL team focused on the battery's other side by adding a protective shield to the anode.

"Lithium-sulfur batteries could one day help us take electric cars on longer drives and store renewable wind energy more cheaply, but some technical challenges have to be overcome first," said PNNL Laboratory Fellow Jun Liu, who is the paper's corresponding author. "PNNL's new anode design is helping bringing us closer to that day."

The new shield is made of graphite, a thin matrix of connected carbon molecules that is already used in lithium-ion battery anodes. In a lithium-sulfur battery, PNNL's new anode design, a thin layer of carbon is electrically connected to the lithium metal, forming a unique electrochemical structure. The graphite shield moves the sulfur side reactions away from the lithium surface, preventing it from growing the debilitating insulating layer. Combining graphite from lithium-ion batteries with lithium from conventional lithium-sulfur batteries, the researchers dubbed their new anode a hybrid of the two.

The new anode quadrupled the lifespan of the lithium-sulfur battery system when compared to identical cells with conventional lithium anodes. When equipped with a conventional anode, the battery stopped working after about 100 charge-and-discharge cycles. But the system worked well beyond 400 cycles when tested under the same conditions using PNNL's hybrid anode.

"Sulfur is still dissolved in a lithium-sulfur battery that uses our hybrid anode, but that doesn't really matter," Liu said. "Tests showed a battery with a hybrid anode can successfully be charged repeatedly at a high rate for more 400 cycles, and with just an 11-percent decrease in the battery's energy storage capacity."

What's Next? This and most other lithium-sulfur battery research is conducted with small, thin-film versions of the battery that are easy to fabricate for lab tests. For commercial viability, larger, thicker electrodes would be needed to power electric cars and store renewable energy. Liu noted tests with a larger battery system would better evaluate the performance of PNNL's new hybrid anode for real-world applications.

Acknowledgments:

Sponsors: The development and demonstration of the hybrid design are supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division. The mechanistic study on the symmetric cell and overpotentials of the electrode materials were supported by DOE's Advanced Research Projects Agency—Energy. The cathode used in this work is supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the DOE under contract number DE-AC02-05CH11231 and subcontract number 18769 under the Batteries for Advanced Transportation Technologies programme.

User Facility: EMSL

Research Team: Cheng Huang, Jie Xiao, Yuyan Shao, Jianming Zheng, Wendy D. Bennett, Dongping Lu, Laxmikant V. Saraf, Mark Engelhard, Liwen Ji, Ji-Guang Zhang, Xiaolin Li, Gordon L. Graff, and Jun Liu, PNNL

Reference: Huang C, J Xiao, Y Shao, J Zheng, WD Bennett, D Lu, LV Saraf, M Engelhard, L Ji, J Zhang, X Li, GL Graff, and J Liu. 2014. “Manipulating Surface Reactions in Lithium-Sulphur Batteries using Hybrid Anode Structures.” *Nature Communications* 5:3015. DOI: 10.1038/ncomms4015

The Character of a Cathode

Nickel segregation, cation spatial distribution, and tightly integrated phases occur in pristine battery material

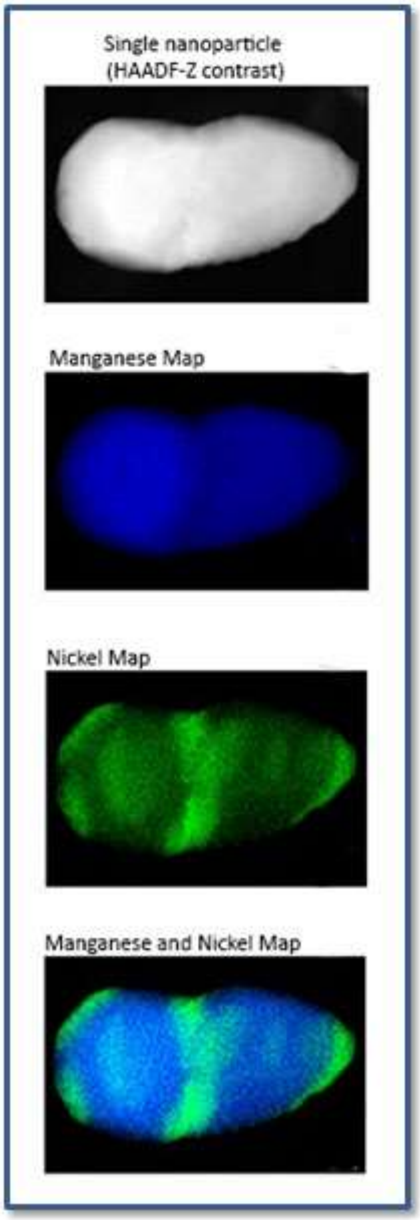
November 2013

Results: To prevent fading in a layered lithium cathode that holds promise for heavy duty transportation use, scientists at Pacific Northwest National Laboratory, FEI Company, and Argonne National Laboratory obtained a definitive view of a pristine cathode made of lithium, nickel, manganese, and oxygen. The cathode is known as $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ or LMNO. Controversy has encircled this material. Some state it's a solid solution; others, a composite. To address this debate, the team used a suite of instruments and determined the material is a composite with tightly integrated phases where the surface contains higher concentrations of nickel and low concentrations of oxygen and electron-rich manganese.

"If we want to improve the cycle life and capacity of the layered cathode, we must have this type of clarity around the atomic structure and possible cation ordering," said Dr. Nigel Browning, the Chief Science Officer of PNNL's Chemical Imaging Initiative and a microscopy expert who worked on the study.

Why It Matters: Replacing gasoline-powered cars with electric-powered ones could drop U.S. reliance on oil imports by up to 60 percent, and reduce harmful emissions as much as 45 percent, depending on the technological mix used. The key is long-lasting, energy-dense batteries. Innovative LMNO cathodes possess high voltage and high specific capacity. Yet, the material is far from ideal. Capacity and voltage fading issues are linked to the cathode's structure during charging and discharging. The team's characterization research provides the foundation necessary for needed discoveries.

"The ever-growing energy demand of information and transportation relies on lithium-ion batteries for power storage, because of their relatively high energy density and design flexibility. We need it better and we need it now, which contributes to the main driving force for creating new materials for energy storage," said Dr. Chong-Min Wang, chemical imaging expert at PNNL and lead investigator on this study.



Scientists obtained a definitive view of an LMNO cathode. The X-ray energy-dispersive spectroscopy maps are shown here, which indicate the distribution of manganese and nickel.

Method: Using a combination of aberration-corrected scanning transmission electron microscopy, X-ray energy-dispersive spectroscopy, electron energy loss spectroscopy, and complementary multi-slice image simulation, the team probed $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoparticles. On the particle's surface, they made several discoveries. A surface with a unique structural characteristic is prone to contain a higher concentration of nickel atoms than the core of the particle, while manganese atoms are more prevalent at the core than the surface. Oxygen vacancies on the particle's surface result in manganese atoms having a valence state or electron configuration of +2.2 on the surface, while the manganese at the particle's center is +4.0.

"This finding indicates a big variation in the local stoichiometry," said Dr. Jun Liu, a materials expert who worked on this study and who is also Director of PNNL's Energy Processes and Materials Division.

Finally, each particle contains both of the material's parent phases. The lattice parameter and crystal structure similarity of the layered $LiMO_2$ phase and the layered Li_2MO_3 phase allow for the structural integration.

"This detailed characterization allowed us to gain a more complete picture of the material," said Wang. "Clarification of the material's structure — nanoscale phase separation, cation ordering, and oxygen vacancy formation — will undoubtedly shine a new light on probing how the material behaves during battery performance and will inspire us to improve its functionality via controlled synthesis."

What's Next: The team is now working to understand how the material evolves during charge/discharge cycles.

Acknowledgments:

Sponsors: The research described in this paper is part of the Chemical Imaging Initiative at PNNL. It was conducted under the Laboratory Directed Research and Development Program at PNNL; JZ acknowledges the support of the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of DOE, under the Batteries for Advanced Transportation Technologies program; JL acknowledges the support of the DOE, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division. IB and KA acknowledge the support from DOE's Freedom CAR and Vehicle Technologies Office.

User Facilities: EMSL and National Center for Electron Microscopy

Research Team: Meng Gu, Suntharampillai Thevuthasan, Donald R. Baer, Ji-Guang Zhang, Nigel D. Browning, Jun Liu, and Chong-Min Wang, Pacific Northwest National Laboratory; Arda Genc, FEI Company; Ilias Belharouak, Dapeng Wang, and Khalil Amine, Argonne National Laboratory

Reference: Gu M, A Genc, I Belharouak, D Wang, K Amine, S Thevuthasan, DR Baer, JG Zhang, ND Browning, J Liu, and C Wang. 2013. "Nanoscale Phase Separation, Cation Ordering, and Surface Chemistry in Pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ for Li-Ion Batteries." *Chemistry of Materials* 25(11):2319-2326. DOI: 10.1021/cm4009392

Electron and Scanning Probe Microscopies

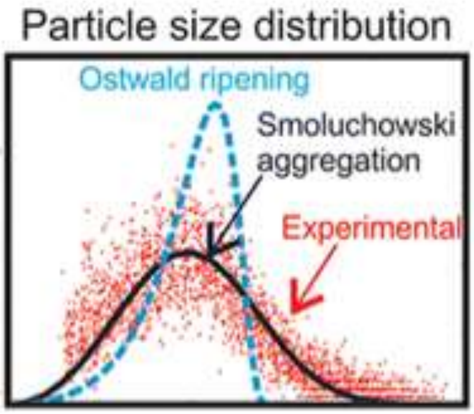
Watching Nanoparticles Grow

New approach shows particles and ensembles follow different growth patterns, explaining a frustrating discrepancy in experimental results

February 2014

Results: Individual silver nanoparticles in solutions typically grow through single atom attachment, but importantly, when they reach a certain size they can link with other particles, according to scientists at Pacific Northwest National Laboratory, the University of California, Davis, and Florida State University. This seemingly simple result has shifted a long-held scientific paradigm that did not consider kinetic models when explaining how nanoparticle ensembles formed.

Conventional methods have either 1) been limited to "post-mortem" analysis long after the growth subsided, 2) "cherry picked" the particles being examined, thereby missing the mesoscale implications, or 3) only analyzed the population average and missed the individual particle variances. Now, by considering the kinetics of the average growth rate and the distribution of particle sizes, the team explains why scientists see what they see when nanoparticle ensembles form via non-classical mechanisms.



As shown here, the Smoluchowski model quantitatively captures the mean growth rate and particle size distribution of a silver nanoparticle, while Ostwald ripening does not. By considering the kinetics of the average growth rate and the distribution of particle sizes, scientists can explain what they see when nanoparticle ensembles form via non-classical mechanisms.

"The team's findings shed light on previously unexplained observations of aggregative nanoparticle growth," said Dr. Louis Terminello, who leads the Chemical Imaging Initiative at PNNL, which funded much of the work. "Such understanding of mesoscale interactions provides more precision in material synthesis, bringing us closer to tailored materials for catalysis, energy storage, and other uses."

Why It Matters: Whether storing renewable energy for later use or designing longer lasting batteries for electric-powered vehicles, many of today's energy problems will not be solved with today's materials. New materials are needed. The key to avoiding time-consuming trial-and-error research is to tightly control nanoparticle growth to build the materials needed, from the bottom up. This study provides important information about nano-ensembles grown by non-classical mechanisms, including aggregation and coalescence.

Methods: Since the early 1960s, scientists have interpreted nanoparticle growth quantitatively using a model called Lifshitz-Slyozov-Wagner (LSW). This model addresses the dissolution of small crystals and deposition of the dissolved material onto larger ones — a process called Ostwald ripening. But until now, little attention has been paid to modeling the corresponding particle size distribution — a global property that often dictates important functional properties, such as catalytic activity.

"At the atomic scale, Ostwald ripening fits the observed growth. But at the mesoscale, we need to know more about particle size distribution," said Dr. Nigel Browning, Chief Science Officer for the Chemical Imaging Initiative and lead of this project.

The scientists used *in situ* liquid scanning transmission electron microscopy to grow and directly observe silver nanoparticle ensembles. The team found that the Smoluchowski aggregation kinetic model quantitatively matched the mean growth rate and the particle size distribution of the ensemble. The researchers also used an algorithm created by Dr. Chiwoo Park at Florida State to capture all the particles and analyze all the data, another difference from previous methods.

“Using the combined imaging and analytical approach, we can map out the complete particle size distribution, and see how one mechanism takes over from the other,” said Browning.

Although the mean growth rate observed during the *in situ* growth experiments was consistent with the LSW model and suggested that Ostwald ripening was the dominant growth mechanism, the Smoluchowski model showed that the ensemble-scale mean growth rate is ~20 percent larger than for non-aggregating nanoparticles. The corresponding particle size distribution is broader and more symmetric (see figure) than that predicted by Ostwald ripening in the LSW. And, it more closely matches the experimental data. The team’s results suggest that the particles must reach a certain size before they are capable of growing into bigger ensembles.

“Our results really highlight the need for the field to consider both classical and non-classical growth mechanisms when trying to understand and ultimately control the final characteristics of nanoparticles,” said Dr. James Evans, a coauthor and scientist within EMSL.

What’s Next? This study is a first step in allowing researchers to accurately predict and tune nanoparticle size distributions in lab-scale syntheses based on physical theories and empirical observations. The team will continue to answer fundamental questions about mesoscale phenomena.

Acknowledgments:

Sponsors: National Institutes of Health (JEE and NDB for developing DTEM); U.S. Department of Energy Office of Basic Energy Sciences, Materials Sciences and Engineering Division (NDB and TJW, project led by Nigel Browning when he worked at the University of California at Davis); Presidential Early Career Award for Scientists and Engineers (IA); University of California Lab Fee Program and the University of California Academic Senate (TJW); Florida State University COFRS and the Ralph E. Powe Junior Faculty Enhancement Award, and National Science Foundation (CP); Chemical Imaging Initiative, funded by PNNL’s Laboratory Directed Research and Development Program (NDB and JEE, project led by Nigel Browning at PNNL)

User Facility: EMSL

Research Team: Taylor J. Woehl and William D. Ristenpart, University of California, Davis; Nigel D. Browning, James E. Evans, and Ilke Arslan, Pacific Northwest National Laboratory; and Chiwoo Park, Florida State University

Reference: Woehl TJ, C Park, JE Evans, I Arslan, WD Ristenpart, and ND Browning. 2014. “Direct Observation of Aggregative Nanoparticle Growth: Kinetic Modeling of the Size Distribution and Growth Rate.” *Nano Letters* 14(1):373-378. DOI: 10.1021/nl4043328

Leadership Highlights

Window into Liquid Analysis Earns PNNL an R&D 100 Award

SALVI enables real-time imaging of liquid samples by more than one analytical instrument

July 2014

Many studies rely on precise knowledge of how solids and liquids interact on a molecular level, but liquids evaporate in the vacuum of certain instruments. Pacific Northwest National Laboratory developed the System for Analysis at the Liquid Vacuum Interface, or SALVI, that for the first time allows these instruments to image liquid samples in real time and space. Today, *R&D Magazine* honored SALVI's research team with an R&D 100 award. *R&D Magazine* selects the 100 most innovative scientific and technological breakthroughs of the year from nominations spanning private, academic, and government institutions.

This System for Analysis at the Liquid Vacuum Interface, or SALVI, enables for the first time imaging of liquid samples in real-time and space by more than one analytical instrument. It eliminates the need for sample preparations such as freezing or drying biological cells.

With SALVI, scientists can gain new insights about nanoparticles, bacteria, batteries, and more.

The portable system fits on a block the size of half a sheet of paper. It connects with many types of vacuum-based instruments, including time-of-flight secondary ion mass spectrometers and scanning electron microscopes.

SALVI can take a sample as small as 2 drops. The sample flows through a channel to a window the size of a pinhole, where an ion beam performs analysis. Surface tension keeps the liquid from escaping the window.

The flow and small window reduce evaporation in a vacuum and protect the sample from beam damage, making many forms of liquid analysis possible.

SALVI enables imaging in real time and space by more than one analytical instrument. And it eliminates the need for sample preparations such as freezing or drying biological cells.

Structure Probe Inc., based in West Chester, Pennsylvania, has licensed the patents covering the technology and plans to introduce a commercial version of SALVI by the end of the year.

The team recognized for developing SALVI includes PNNL's Xiao-Ying Yu, Martin Iedema, Bingwen Liu, Zihua Zhu, and Matthew Marshall; former PNNL staff member James Cowin; and Evans Analytical Group's Li Yang. The team developed SALVI in collaboration with scientists at EMSL.

These honors bring PNNL's total to 93 since the awards' inception in 1969.

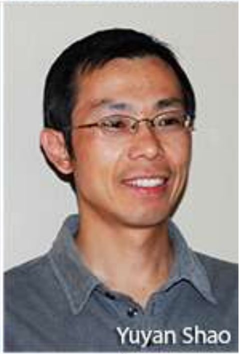
Other 2014 winners were Avegant's Glyph™, a headset display that contains a PNNL-developed virtual retinal display, which reflects light onto the back of the viewer's eyes. Because the display mimics natural vision, it reduces nausea and eye strain even with extended use. The team recognized for developing Glyph™ includes PNNL's Bruce Bernacki and Avegant's Allan Evans, Edward Tang, and Neil Welch.

In addition, the Solar Thermochemical Advanced Reactor System, or STARS, was recognized. It converts natural gas and sunlight into a more energy-rich fuel called syngas, which power plants can burn to make electricity. The team recognized for developing STARS includes PNNL's Robert Wegeng, Paul Humble, Robert Dagle, Daryl Brown, Dustin Caldwell, Richard Cameron, Richard (Feng) Zheng, Brad Fritz, and Ward TeGrotenhuis; former PNNL staff members, Shankar Krishnan, Steven Leith, Dan Palo, and Jair Lizarazo-Adarme; and DiverSolar LLC's Richard Diver.

R&D Magazine will honor award winners November 7 at an event in Las Vegas.

Five PNNL Researchers Named Most Cited

July 2014



Five researchers at Pacific Northwest National Laboratory have been named to a comprehensive list of the world's most referenced scientists.

The researchers are named in Thomson Reuters' Highly Cited Researchers 2014. The list includes more than 3,200 researchers whose scientific publications were in the top 1 percent of papers receiving the most references. Only 250 researchers in each field were selected based on total citations to their papers published during this period. The ranking was compiled using InCites, a Thomson Reuters analytical tool that combed their database of indexed published papers from 2002-2012.

The five PNNL researchers and their most cited subject areas are

- Jun Liu: chemistry, engineering, and materials science
- Alex Guenther: geosciences
- Phil Rasch: geosciences
- Yuyan Shao: engineering
- Yuehe Lin: chemistry (Washington State University professor, has joint appointment with PNNL)

Jay Grate Elected Electrochemical Society Fellow

July 2014


Dr. Jay Grate was named an Electrochemical Society Fellow.

Congratulations to Dr. Jay Grate at Pacific Northwest National Laboratory on being named a Fellow in the Electrochemical Society (ECS) for his contributions to chemical sensors and the scientific community. The nonprofit professional society, which has more than 8,000 members from over 70 countries, advances electrochemistry and solid-state science, and provides educational opportunities.

Since the mid-1980s, Grate has been a leader in developing chemical sensors. He pioneered a systematic understanding of vapor-polymer interactions critical to the selectivity of polymer-coated vapor sensors. Further, he developed methods to convert array responses into molecular descriptors. The result was the knowledge needed to select or rationally design polymers for sensors and arrays. His work also led to an understanding of the possibilities and limitations of polymer-coated sensors and the information they could provide. At PNNL, he pioneered radionuclide sensors for alpha and beta emitters in water; these sensors selectively collect radionuclides for radiometric detection in pre-concentrating mini-column sensors.

Grate has volunteered countless hours in service. At ECS, he participated in developing the society’s Sensor Division. He has served on the division’s executive committee since its inception, with activities from developing symposia to revising bylaws. Also, he recently served on the Linford Award committee. Beyond the society, he has been invited to participate in workshops on chemical sensing, chemical measurements, and threat detection. He has worked with the National Research Council, National Science Foundation, and the U.S. Department of Energy, among others.

A prolific author and inventor, Grate has written or co-written over 130 peer-reviewed articles and invited reviews along with 15 book chapters. He has 20 patents to his credit, in areas including separations, sensing polymers, vapor preconcentration, and biocatalysis. Several of these patents have been licensed through various mechanisms with PNNL’s commercialization organization.

Grate will accept his fellowship in Cancun, Mexico, at the fall society meeting.

DOE to Renew Energy Frontier Research Center at PNNL

Center for Molecular Electrocatalysis unites experts from many fields to conquer problems in energy production, storage, and use

June 2014

Directed by PNNL chemist Dr. Morris Bullock, the Center for Molecular Electrocatalysis will receive $3.5 million a year for 4 years.

The Pacific Northwest National Laboratory (PNNL) welcomed one of the 32 multi-million dollar Energy Frontier Research Centers announced by U.S. Department of Energy this week. The centers are charged with pursuing the scientific underpinnings of various aspects of energy production, storage, and use. As a renewal of an EFRC established in 2009, the Center for Molecular Electrocatalysis is poised to take on new scientific challenges exploring chemical reactions at the core of technologies such as solar energy and fuel cells.

Funded by the DOE's Office of Science, the centers across the nation will pursue scientific research that addresses big questions called Grand Challenges outlined by DOE that will transform how we make and use energy. The research to address these challenges will delve into problems such as matter that self-assembles into unique materials, converts electricity into chemical bonds for long or short-term storage, or mimics needed expertise found in the natural world.

"I have full confidence that the caliber of our exceptional staff and our scientific leadership will allow DOE to further enable and accelerate transformative discovery in an area that is so critical to our nation's energy future," said PNNL Director Mike Kluse.

Directed by PNNL chemist Dr. Morris Bullock, the Center for Molecular Electrocatalysis will receive $3.5 million a year for 4 years and involve researchers from several disciplines.

"We need the kind of diverse expertise Morris has assembled in this EFRC to surmount the challenge of moving towards zero carbon energy," said Dr. Doug Ray, Associate Laboratory Director of Fundamental & Computational Sciences. "They've made remarkable advances understanding the complex chemical reactions at the heart of converting between electricity and chemical bonds. Their work will surely contribute to inexpensive catalysts that will enable more effective energy storage in the future."

In addition to leading one center, PNNL will also partner on two others. PNNL's Johannes Lercher, director of PNNL's Institute for Integrated Catalysis, and others will contribute to the University of Delaware-led Catalysis Center for Energy Innovation and the University of Minnesota-led Inorganometallic Catalyst Design Center.

The Center for Molecular Electrocatalysis

Since 2009, researchers at the Center for Molecular Electrocatalysis have been studying molecules called catalysts that convert electrical energy into chemical bonds and back again. Of interest are catalysts that pack energy into bonds involving hydrogen, oxygen, or nitrogen. These reactions are at the core of technologies such as solar energy and fuel cells.

In the past 5 years, the researchers have dramatically improved their understanding of details of catalytic reactions, designing exceptionally fast catalysts that produce molecular hydrogen and others that split it, inexpensive metal-based catalysts that split molecular oxygen to make water, and have found new ways to split molecular nitrogen.

In the next 4 years, the team will work to make the hydrogen reactions faster and more efficient, to discover more selective catalysts to split molecular oxygen, and improve important aspects of molecular nitrogen catalysts.

“Our team has made some really great progress,” said Bullock. “We are excited about moving forward with new research.”

The Center for Molecular Electrocatalysis will include researchers from PNNL and the University of Illinois, the University of Wisconsin, and Yale University.

Heat Treatment of Copper-Based Zeolite Catalysts Is a Hot Topic

Material drives reactions that destroy nitrogen oxides in vehicle emissions

June 2014

Congratulations to Ja Hun Kwak, Diana Tran, Sarah Burton, Janos Szanyi, Jong Lee, and Chuck Peden at Pacific Northwest National Laboratory's Institute for Integrated Catalysis on being highly cited authors in the *Journal of Catalysis*. The Elsevier-published journal just released the most cited authors for 2012-2013. This team made the list for their article on how very high temperatures change the reactivity of certain copper-containing zeolite catalysts. The materials' ability to selectively turn nitrogen oxides into benign dinitrogen gas in cooler engine exhaust systems makes them of interest.

Congratulations to our team at Pacific Northwest National Laboratory's Institute for Integrated Catalysis on being highly cited authors in the *Journal of Catalysis* for their work on how very high temperatures change the reactivity of certain copper-containing zeolite catalysts.

The 6-page article discusses the results of hydrothermally treating 3 catalysts: Cu-ZSM-5, Cu-beta, and Cu-SSZ-13. The first two were significantly less active at low temperatures after the thermal treatment. The third catalyst was not affected. The scientists also determined aluminum placement, which is directly related to activity, in the 3 catalysts. More than 40 other articles have cited the research since its publication in 2012.

The research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy/Vehicle Technologies Program. The research described in this paper was performed at EMSL.

Reference: Kwak JH, D Tran, SD Burton, J Szanyi, JH Lee, and CHF Peden. 2012. “Effects of Hydrothermal Aging on NH_3-SCR Reaction over Cu/Zeolites.” *Journal of Catalysis* 287:203-209. DOI: 10.1016/j.jcat.2011.12.025

Jim Amonette Revises Model to Provide Detailed Data for Philanthropy Report

May 2014

Dr. James Amonette adapted an earlier model to assess the climate-mitigation potential of sustainable biochar use at the regional and national level.

Congratulations to Dr. James Amonette at Pacific Northwest National Laboratory for adapting an earlier model that assesses the climate-mitigation potential of sustainable biochar use at the global scale to one that also operates at the regional and national level. The biochar approach converts carbon captured by plants to relatively stable charcoal, which is then used as a long-lived soil amendment that can improve the fertility of croplands and pastures. In addition to the carbon that is stored, energy produced during the conversion offsets carbon dioxide emissions by other sources. Results from the new model were used by California Environmental Associates and ClimateFocus to recommend philanthropic investments in biochar technology in key test markets such as Brazil and China and to promote the development of biochar-industry standards.

The recommendations appear in *Strategies for Mitigating Climate Change in Agriculture: Recommendations for Philanthropy*.

Amonette has more than 35 years of research experience. He has written extensively on biochar, nanosized iron particles, chlorinated hydrocarbon degradation, and other topics. His applied research resulted in 6 patents. He also mentors early career scientists.

Aaron Appel's Invited Article on Catalysts for Renewable Fuels Appears in *Nature*

April 2014

Congratulations to Dr. Aaron Appel, Pacific Northwest National Laboratory, on having his invited News & Views article published in the April 9 issue of *Nature*, an important scientific journal. A News & Views article is an invited piece, written for a general audience, about a study that appears in the issue. Appel wrote about Stanford University's extremely fast and efficient copper catalyst that turns carbon monoxide into ethanol fuel. The catalyst is more active, not because of the size of the copper particles on the supporting material but, rather, because of the junctions between the particles.

The catalyst generates ethanol with fewer byproducts than previous catalysts. Also, it is more energy efficient. The team's catalyst is a major step in storing wind or solar energy in liquid fuel.

Dr. Aaron Appel had an invited article (News & Views) published in *Nature*, April 9, 2014.

Appel's invitation to write for *Nature* came about because of his expertise in the electrocatalytic conversions. An organometallic chemist at PNNL's Institute for Integrated Catalysis, he is the principal investigator on a project designing fast, efficient catalysts that turn carbon dioxide into fuel. The U.S. Department of Energy's Office of Basic Energy Sciences funds the research. He also works at the Center for Molecular Electrocatalysis, an Energy Frontier Research Center led by PNNL, where he provides expertise on thermochemical measurements relevant to catalysis.

The *Nature* article led to Appel being quoted in a story by Reuters' Will Dunham that appeared in multiple outlets, including the *Wichita Eagle*, the *New Hampshire Union Leader*, the *Toledo Blade*, and *Deutschlandfunk*.

Tiffany Kaspar Honored by American Physical Society for Outstanding Reviews

March 2014

Congratulations to Dr. Tiffany Kaspar at Pacific Northwest National Laboratory on being named an outstanding referee of the *Physical Review* and *Physical Review Letters* journals. She was selected for her quick and high-quality reviews. Kaspar, who began reviewing articles as a graduate student, referees several articles each year. She strives to provide a thorough review, pointing out weaknesses and noting ideas for improving the paper. When the research is outside her area of expertise, she often spends time learning how the results complement the broader context. She often finds herself counseling authors to not read more into their data than can be supported.

Dr. Tiffany Kaspar was named an outstanding referee by the American Physical Society.

At PNNL, Kaspar studies the growth and properties of epitaxial thin films of novel oxides for energy applications. Her work includes the electronic, photo-active, and magnetic properties of doped binary and complex oxides. Further, she studies lattice-mismatched epitaxial metal films on oxide substrates for radiation damage studies. Her fundamental research in pulsed laser deposition of complex oxides is providing new insights for solid oxide fuel cells.

Jim De Yoreo Elected Materials Research Society Fellow

March 2014

Dr. Jim De Yoreo, Chief Scientist of Pacific Northwest National Laboratory's Materials Synthesis and Simulation across Scales Initiative, was elected a Materials Research Society Fellow.

Congratulations to Dr. Jim De Yoreo, Pacific Northwest National Laboratory, on being selected as a Materials Research Society (MRS) Fellow for his pioneering research in the field of bio-inspired materials science and engineering along with his distinguished leadership and service to the materials community. A prestigious society, MRS has 16,000-plus members in more than 60 countries; the society's goal is to advance interdisciplinary materials research to improve the quality of life.

At Pacific Northwest National Laboratory, De Yoreo leads the initiative in materials synthesis and simulation across scales. During his career, he has pioneered the use of *in situ* molecular-scale imaging techniques to visualize self-assembly and crystallization in real time. He was the first to visualize multi-step self-assembly of proteins and oriented attachment in mineral systems and measure the forces involved. Further, this American Physical Society Fellow designed novel approaches to develop functional materials using template-driven synthesis.

A well-respected member of the scientific community, De Yoreo has served as the MRS President, a member of the MRS Board of Directors, and as Chair of a number of MRS subcommittees. He has chaired national and international materials science conferences, contributed to national efforts in public outreach, and edited journals. Also, he has written or co-written 175 articles. He has several patents and won both the International Organization for Crystal Growth's Laudise Prize and the American Association for Crystal Growth's AACG Award. He has mentored extensively and serves as an Affiliate Professor in Materials Science and Engineering at the University of Washington.

Ilke Arslan Joins *Microscopy & Microanalysis* Editorial Board

March 2014

Dr. Ilke Arslan is now an editor with *Microscopy & Microanalysis*.

Congratulations to Dr. Ilke Arslan, Pacific Northwest National Laboratory, on joining the editorial board for *Microscopy & Microanalysis*. The journal provides original research articles on imaging and compositional analysis to biologists, materials scientists, and others interested in microscopy. The international publication is the official journal of the Microscopy Society of America and eight other societies, including the European Microbeam Analysis Society and the Australian Microscopy and Microanalysis Society. It is also affiliated with South African and German societies. As a member of the 18-person board, Arslan will assist in the review of manuscripts, help select the best manuscripts from the journal for the annual award and for inclusion on the journal's website. She will also attend editorial board meetings and provide assistance, as requested, with editing a special issue or writing a review article.

Arslan is well known for bringing her physics expertise to chemical imaging and catalysis, working on PNNL's Chemical Imaging Initiative and Institute for Integrated Catalysis. A talented speaker, she recently lectured at the National Academy of Sciences' Kavli Frontiers of Science symposium and is a Microscopy Society of America tour speaker. She has received the Presidential Early Career Award for Scientists and Engineers (PECASE) and the research fellowships from the Royal Society USA and the National Science Foundation.

PNNL's Condensed Phase Research Proves Popular with Scientists

February 2014

Experimental and theoretical scientists at Pacific Northwest National Laboratory had three articles on the most-accessed list in the Liquid, Glasses, and Crystals category of *The Journal of Chemical Physics.*

Congratulations to our experimental and theoretical chemical physicists at Pacific Northwest National Laboratory (PNNL) who had three articles among the most-accessed ones in the Liquid, Glasses, and Crystals category of *The Journal of Chemical Physics*. The publication is the most highly cited journal in atomic, molecular, and chemical physics according to Thomson Reuters, making it *the* place to publish for leaders in the field. Scientists from PNNL routinely publish their research, sponsored by the U.S. Department of Energy's Office of Basic Energy Sciences (BES), in this journal.

Two of the popular articles explained how cracks form in amorphous solid water films. The researchers proved that in some cases, gases trapped under the water films are released via fissures that form during crystallization. When thicker layers of gas are trapped, the gas can escape before crystallization.

One of the articles, "The Release of Trapped Gases from Amorphous Solid Water Films. I. "Top-Down" Crystallization-Induced Crack Propagation Probed Using the Molecular Volcano," by R. Alan May, R. Scott Smith, and Bruce D. Kay, was viewed more than 400 times since March 2013. The abstract was viewed more than 1000 times. The companion article, "The Release of Trapped Gases from Amorphous Solid Water Films. II. "Bottom-Up" Induced Desorption Pathways," was downloaded 215 times; the abstract was viewed more than 400 times. Artwork from the articles graced the journal's cover.

The third popular article, "Molecular Origin of the Difference in the HOH Bend of the IR Spectra Between Liquid Water and Ice," by Sho Imoto, Sotiris Xantheas, and Shinji Saito, demonstrated, through molecular simulations, the molecular origin of the observed difference in the HOH bend between liquid water and ice. The simulations were performed with the Thole-Type Model (TTM3-F), an *ab initio*-based flexible, polarizable interaction potential for water that was developed at PNNL under BES support. The abstract has been viewed more than 700 times, and the full paper has been downloaded 424 times since February 2013. Imoto visited PNNL for 2 months during this graduate research as part of a national grant for overseas visits from the government of Japan. He spent the other month of his scholarship at the Massachusetts Institute of Technology. There, he worked with experimentalists who measure the structure and dynamics of liquid water using infrared spectrometry.

The research for all of the articles was supported by the BES Division of Chemical Sciences, Geosciences, and Biosciences: Condensed Phase Chemical Physics program. The fact that these articles are among the most often downloaded is evidence of the impact and leadership the program is having on the condensed phase chemical physics community at large.

Articles

May RA, RS Smith, and BD Kay. 2013. "The Release of Trapped Gases from Amorphous Solid Water Films. I. "Top-Down" Crystallization-Induced Crack Propagation Probed Using the Molecular Volcano." *The Journal of Chemical Physics* 138:104501. DOI: 10.1063/1.4793311

May RA, RS Smith, and BD Kay. 2013. "The Release of Trapped Gases from Amorphous Solid Water Films. II. "Bottom-Up" Induced Desorption Pathways." *The Journal of Chemical Physics* 138:104502. DOI: 10.1063/1.4793312

Imoto S, SS Xantheas, and S Saito. 2013. "Molecular Origin of the Difference in the HOH Bend of the IR Spectra Between Liquid Water and Ice." *The Journal of Chemical Physics* 138:054506. DOI: 10.1063/1.4789951

Sebastien Kerisit Appointed Associate Editor for *Geochemical Transactions*

February 2014

Congratulations to Dr. Sebastien Kerisit, geochemist at Pacific Northwest National Laboratory, who was appointed an associate editor for *Geochemical Transactions*. Kerisit was chosen for his expertise in geochemistry, modeling, and materials science as well his experience as a reviewer. As an associate editor, Kerisit will review manuscripts and find qualified peers to review each article. After analyzing the reviewers' comments, he will recommend or reject articles with just a few weeks of the article's submission.

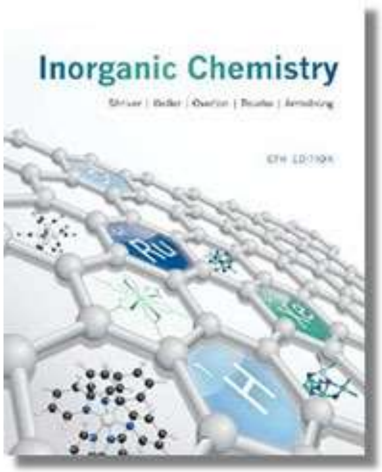
Geochemical Transactions is the official publication of the American Chemical Society's Geochemistry Division and serves up articles on the chemistry of terrestrial and extraterrestrial systems. This open-access journal delivers articles for free online, allowing scientists worldwide easy access. Further, the journal is available through widely recognized repositories.

Dr. Sebastien Kerisit named *Geochemical Transactions* Associate Editor.

At Pacific Northwest National Laboratory, where he has worked since 2004, Kerisit is investigating mineral nucleation and growth, especially as it relates to carbonates which are of interest for carbon sequestration. He also develops and refines models for nuclear waste vitrification, which traps highly radioactive waste in glass and away from the environment. Kerisit volunteers extensively with the American Chemical Society, with session organizer and program chair being just a few of the roles he's served.

Fast Nickel Catalyst Breaks into College Textbook

February 2014



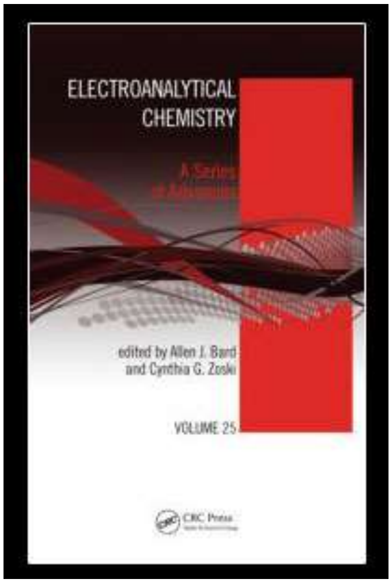
A nickel-based catalyst developed by scientists at the Center for Molecular Electrocatalysis was discussed in *Inorganic Chemistry*.

Congratulations to the scientists at the Center for Molecular Electrocatalysis, who had their nickel-based catalyst discussed in *Inorganic Chemistry*, a popular undergraduate college textbook. Students will read about the catalyst, with two seven-membered cyclic diphoshine ligands attached to a nickel atom, that uses proton relays to efficiently make H_2. Designing catalysts with earth-abundant metals instead of platinum and other rare metals is a critical challenge for upcoming scientists if we are to store intermittent renewable energy and release it when needed.

The Center for Molecular Electrocatalysis is an Energy Frontier Research Center funded by the U.S. Department of Energy’s Office of Basic Energy Sciences. Pacific Northwest National Laboratory leads the center.

Scientists' Advances in Measuring Water's Surface Potential Referenced in Electrochemical Book

January 2014



Electroanalytical Chemistry: A Series of Advances cites the work of Dr. Shawn Kathmann, Dr. Christopher Mundy, Dr. Gregory Schenter at Pacific Northwest National Laboratory and Dr. IFW Kuo at Lawrence Livermore National Laboratory.

Congratulations to Dr. Shawn Kathmann, Dr. Christopher Mundy, Dr. Gregory Schenter at Pacific Northwest National Laboratory and Dr. IFW Kuo at Lawrence Livermore National Laboratory on having their work mentioned in *Electroanalytical Chemistry: A Series of Advances.* In the 249-page book, noted scientists review advances in electroanalytical chemistry, which influences nanosynthesis, life sciences, and other fields. The team is mentioned for answering an ages-old question as to how to accurately measure the surface potential of water.

As stated in Chapter 1, "Kathmann *et al.* report that the large surface potential values obtained from QM [quantum mechanical] methods arise because these values include the potential for regions within the atoms of the solvent molecules...Gradually excluding the atomic volume of the atoms of the solvent molecules from the calculations results in values for the surface potential of water that...[are] in much better agreement with the estimates from electrochemical measurements and with the values obtained using classical force fields."

The team's research into the surface potential of water was funded by the U.S. Department of Energy's Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. This research used computational resources in EMSL, a national scientific user facility; the National Energy Research Scientific Computing Center; and Livermore Computing.

Bard AJ and CG Zoski. 2013. *Electroanalytical Chemistry: A Series of Advances: Volume 25*. CRC Press, Boca Raton, Florida.

Scott Chambers Assembles Oxide Interfaces Collection for Physics Journal

December 2013

Dr. Scott Chambers assembled a collection of articles on oxide interfaces for the *Journal of Physics: Condensed Matter.*

Congratulations to Dr. Scott Chambers, Pacific Northwest National Laboratory, on being invited to assemble a collection of articles on oxide interfaces for the *Journal of Physics: Condensed Matter*. As Chambers points out in his introduction, “metal oxides exhibit the widest range of properties in nearly every category of interest in materials science, including structural, electronic, optical, magnetic and photochemical properties. Accordingly, the interfaces oxides form are also highly diverse.” The papers he selected represent the scientific community’s progress in uncovering the fundamental truths of oxide interfaces with water, metals, silicon, graphene, and other oxides.

Chambers was invited to build this collection because he is an expert on the growth and properties of crystalline oxide films. His research focuses on the fundamental relationships between composition and structure, and the resulting electronic, magnetic, and photochemical properties. Understanding these structure-function relationships enables new technological applications of these materials in solid-state electronics and energy conversion.

Chambers is an American Association for the Advancement of Science Fellow, an American Vacuum Society Fellow, a Wiley Research Fellow, and Affiliate Professor in the Departments of Chemistry, and Materials Science and Engineering at the University of Washington.

Morris Bullock's Perspective on Cheap Metals and Precious Performance Appears in *Science*

December 2013

Dr. Morris Bullock authored a *Science* Perspective article.

Congratulations to Dr. Morris Bullock, Pacific Northwest National Laboratory, on having his Perspective article appear in the November 29 issue of *Science*, a highly respected journal published by the American Association for the Advancement of Science. A Perspective is an invited opinion piece that covers recent findings. In his article, Bullock discusses advances in using iron and other earth-abundant metals for catalysts in organic synthesis and other applications. These metals are needed to replace precious metals, such as ruthenium and platinum, which present cost and toxicity challenges. Bullock discusses three recent studies that describe iron or cobalt catalysts with impressive activities and selectivities, comparable to, or exceeding, conventional precious metal catalysts.

The article in *Science* resulted in Bullock being quoted in the December 2 issue of the *New York Times*, an American daily newspaper that has won 112 Pulitzer Prizes, and in the December 16 issue of *Chemical & Engineering News* as well as in *Chemistry World*, the Royal Society of Chemistry's magazine.

Bullock was asked to share his opinion with the approximately one million people who read *Science* because of his research on catalysis and his leadership of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. With an impressive track record of writing journal articles, editing a recent book on catalysis, and a host of invited talks, Bullock has been honored by his colleagues in the United States and abroad. He is a Fellow of the Royal Society of Chemistry and American Chemical Society. He also received the Royal Society of Chemistry's Homogeneous Catalysis Award in 2013.

Ilke Arslan Presents at National Academy of Sciences’ Kavli Symposium

November 2013

Congratulations to Dr. Ilke Arslan at Pacific Northwest National Laboratory on being chosen to attend the 25th U.S. Kavli Frontiers of Science Symposium. This invite-only National Academy event is designed to foster discussions among high-profile young scientists across a wide range of disciplines. Ninety scientists under the age of 45 were asked to attend. They were chosen from those who have prestigious awards and honors or are nominated by Academy members or other participants.

Dr. Ilke Arslan at Pacific Northwest National Laboratory focuses on a technique used to reconstruct the 3D morphology of nanoparticles based on a series of 2D images. The images Arslan and her colleagues make possible will answer key questions in catalysis, critical for improving our global energy landscape.

Arslan is well known for bringing her physics expertise to chemical imaging and catalysis. She completed her doctorate in physics at the University of California in Davis and her postdoctoral work at the University of Cambridge, United Kingdom. She won research fellowships from the Royal Society USA and the National Science Foundation. She received a U.S. Presidential Early Career Award for Scientists and Engineers to delve into materials research for 5 years. She is also a Microscopy Society of America tour speaker.

“There are many who have tried to become a Kavli speaker, and this recognition of Ilke’s science is noteworthy and highly warranted,” said Dr. Louis Terminello, her mentor and director of PNNL’s Chemical Imaging Initiative.

At the Kavli symposium, Arslan will share insights on her team’s work on the three-dimensional morphological changes observed in zeolite and Fisher-Tropsch catalysts. She will discuss how cobalt’s distribution changes in a Fisher-Tropsch catalyst as the material is reduced. During reduction, some of the cobalt moves a surprising distance on the order of tens of nanometers — from inside the alumina support to the outer surface — to combine with other cobalt atoms.

“If you just look at the catalyst in the oxidized state in a microscope, I don’t think you can make any assumptions about its activity based on its morphology because the morphology changes as it is reduced to its active state,” said Arslan, who is a member of PNNL’s Chemical Imaging Initiative and Institute for Integrated Catalysis.

This year’s Kavli symposium will be held at the Arnold and Mabel Beckman Center of the National Academies of Science and Engineering in Irvine, California, November 7-9.

International Scientific Conference Dedicates Session to Honor Jean Futrell

October 2013

Congratulations to Dr. Jean Futrell, Battelle Fellow Emeritus at Pacific Northwest National Laboratory, on having the high-resolution mass analysis session at the Innovations in Mass Spectrometry Instrumentation 2013 Conference in St. Petersburg dedicated in honor of his 80th birthday. This conference was co-sponsored by the United States and Russia to promote exchange of ideas and information sharing among academia, industry, and government agencies that rely on mass spectrometry for advanced chemical, pharmaceutical, and environmental applications.

Dr. Jean Futrell was honored at the Innovations in Mass Spectrometry Instrumentation 2013 Conference.

Futrell was chosen for this honor because of his outstanding work in the theory and practice of mass spectroscopy. Throughout his career, he has pursued innovation in mass spectrometry fundamentals and application, including the development or significant modification of some 20 new mass spectrometers with enhanced performance for research purposes. He is also widely recognized for the invention of tandem mass spectrometry, now deployed in nearly every commercial mass spectrometer.

In the scientific community, Futrell is known as a highly effective and diplomatic leader. He has served in leadership roles with the American Society of Mass Spectrometry, the Council for Chemical Research, and the American Chemical Society. His work has garnered four fellowships and numerous awards, including German Mass Spectrometry Society’s Wolfgang Paul Distinguished Lecturer and the FH Field and JL Franklin Award, a prestigious honor given by the American Chemical Society. The first director of EMSL, Futrell is a prolific writer with hundreds of articles and invited reviews to his name.

He retired from his position at PNNL on October 1, 2013, and rejoined the Laboratory as Battelle Fellow Emeritus the same day.

Patricia Abellan Earns International Award for Doctoral Thesis

October 2013

Congratulations to Dr. Patricia Abellan at Pacific Northwest National Laboratory on receiving the Best Ph.D. Thesis in Materials Science award from the Microscopy Society of Spain. She conducted her doctoral research at the Autonomous University of Barcelona. There, she studied how strain state and interface structure in oxide nanostructured materials grown by a solution route changed the material's superconductivity, magnetism, and other properties. She also discovered a novel mechanism for lattice parameter relaxation.

Dr. Patricia Abellan earned the Best Ph.D. Thesis in Material Science in the biennial 2011-2012 award from the Microscopy Society of Spain.

At Pacific Northwest National Laboratory, Abellan is obtaining and analyzing *in situ* electron microscopy images of nanomaterials in liquids. This work is part of the Chemical Imaging Initiative. She is also on the team installing the dynamic transmission electron microscope in DOE's EMSL, a national scientific user facility. The microscope will allow detailed study of chemical and biological structures with nanosecond to microsecond temporal resolution. Dr. Nigel Browning and Dr. James Evans are mentoring her on these projects.

On September 20 at the society's biennial meeting in Tarragona, Spain, Abellan talked about her thesis research. Her thesis is titled *Interfacial Structure and Microstructural Evolution of Solution-Derived Dissimilar Oxide Nanostructures: Implications on Their Functional Properties*. She also spoke on her PNNL research.

Scientists Discuss How Catalysts Transform Waste into Fuels

Basic and applied research explain how to turn carbon dioxide, agricultural waste into hydrocarbons

October 2013

Reducing our reliance on fossil fuels for industrial and home uses means increasing our use of renewable sources, such as agricultural waste and the coal-fired power plant pollutant carbon dioxide.

What if we could heat our homes and power our industries with fuels derived from pollution, instead of fossil fuels? Each year, nearly 40 billion tons of carbon dioxide is released from burning coal, gasoline, and other fossil fuels in the United States alone. Another potential feedstock is agricultural wastes and other biomass. At the 246th National Meeting & Exposition of the American Chemical Society (ACS), numerous teams from Pacific Northwest National Laboratory shared their progress in understanding the fundamental reactions needed to ease our reliance on fossil fuels.

Dr. Aaron Appel, who is leading the efforts to rationally design catalysts for carbon dioxide conversion PNNL’s Institute for Integrated Catalysis, shared his team’s work on 2 groups of catalysts that are involved in the first step of turning carbon dioxide into liquid transportation fuels. The first group of catalysts, based on cobalt, hydrogenates the carbon dioxide to produce formate. The second group, analogs of previously reported palladium triphosphine complexes, removes an oxygen molecule to create carbon monoxide, a precursor to another series of reactions that lead to fuel. In addition, Appel shared information gained on balancing the energetics of the reaction steps.

“We are gaining the understanding necessary to rationally design catalysts that match the functionality of enzymes,” said Appel.

Appel was took part in a press conference as part of the symposium in which he presented. The symposium was titled “CO_2 Conversion: Thermo, Photo and Electrocatalytic Pathways.”

Also, at the ACS meeting, Dr. Mariefel V. Olarte shared her team’s work on turning pyrolysis oil, a liquid produced from thermal decomposition of agricultural wastes and other renewable sources, into transportation fuels and valuable chemicals. One of the most important challenges faced by many bio-oil researchers is fouling of the upgrading catalysts, where catalyst activity is slowly lost and eventually plugs, often after only 50 hours. By tuning the bio-oil stabilization reactions, specific catalysts, and exotherm management in their multi-stage approach, the team demonstrated 1440 hours on the hydrodeoxygenation catalyst while producing a high-quality product.

“This is a noteworthy achievement, as most of the reported research in continuous bio-oil upgrading have not demonstrated long catalyst lifetime,” said Mr. Alan Zacher, who is the study’s project manager.

The team’s goal is a product that is sustainable. “This would entail having a stable, continuous process that has a catalyst lifetime similar to what the petroleum industry has. We are not there yet, but we are working towards that,” said Olarte, a chemical engineer who worked on the applied study.

The talks were given at the 246th National Meeting & Exposition of the American Chemical Society, the world's largest scientific society. Thousands of scientists and others attended the meeting, which featured almost 7,000 reports on new discoveries in science and other topics.

Appel AM, JC Linehan, BJ Boro, BR Galan, MS Jeletic, and SM Peterson. 2013. "Molecular Catalysts for the Reduction of CO_2 to CO or Formate." Presented by Aaron M. Appel (Invited Speaker) at 246th ACS National Meeting, Indianapolis, IN on September 8, 2013.

Olarte MV, DC Elliott, GG Neuenschwander, LJ Rotness Jr, SD Burton, B Schwenzer, AB Padmaperuma, and AH Zacher. 2013. "Towards Long-Term Fast Pyrolysis Oil Catalytic Upgrading." Presented by Mariefel V. Olarte at 246th ACS National Meeting, Indianapolis, IN on September 11, 2013.

Scientists Write Invited Review to Commemorate 60th Anniversary of Scientific Journal

September 2013

Congratulations to Don Baer, Mark Engelhard, Grant Johnson, Julia Laskin, Jinfeng Lai, Karl Mueller, Prabhakaran Munusamy, Suntharampillai Thevuthasan, Hongfei Wang, and Nancy Washton, Pacific Northwest National Laboratory, on developing an invited review featured in the AVS 60th anniversary *Journal of Vacuum Science & Technology A* commemorative issue, published online August 27.

Titled “Surface Characterization of Nanomaterials and Nanoparticles: Important Needs and Challenging Opportunities,” the review examines characterization challenges inherently associated with understanding nanomaterials and the roles surface and interface characterization methods can play in meeting some of the challenges.

Also contributing are Alison Elder and Brittany Baisch, both with the University of Rochester, NY; Ajay Karakoti and Satyanarayana Kuchibhatla, both with Battelle Science and Technology India, Pune, Maharashtra, India; and DaeWon Moon at Daegu Gyeongbuk Institute of Science and Technology, Daeju, Korea.

The journal’s September/October 2013 issue is a collection of invited review articles and perspectives by expert scientists and leaders in disciplines and fields represented by AVS for more than 60 years. A printed special cover edition of the commemorative issue will be available at the AVS 60th International Symposium & Exhibition, October 27 - November 1, Long Beach, Calif.

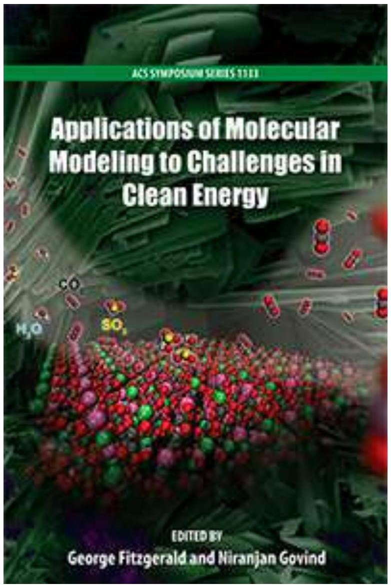
Acknowledgments: Portions of the research presented in the article were done using EMSL resources. As the article’s acknowledgments state, it evolved from research programs, research conducted as part of the EMSL User Program, and interactions with colleagues from around the world. Aspects of the work were supported by DOE’s Offices of Basic Energy Science and Biological and Environmental Research, and the National Institute of Environmental Health Sciences. The Linus Pauling Fellowship and PNNL’s Laboratory Directed Research and Development Program also provided support.

Reference: Baer DR, MH Engelhard, GE Johnson, J Laskin, J Lai, K Mueller, P Munusamy, S Thevuthasan, H Wang, N Washton, A Elder, BL Baisch, A Karakoti, SVNT Kuchibhatla, and D Moon. 2013. “Surface Characterization of Nanomaterials and Nanoparticles: Important Needs and Challenging Opportunities.” *Journal of Vacuum Science and Technology A — Vacuum, Surfaces and Films* 31(5):Article No. 050820. DOI:10.1116/1.4818423

Scientists Write Book on Answering the Challenges of Clean Energy with Molecular Modeling

September 2013

Congratulations to the scientists at Pacific Northwest National Laboratory for their outstanding contributions towards *Applications of Molecular Modeling to Challenges in Clean Energy*. This 245-page book, published by the American Chemical Society, is based on invited talks from a multi-day symposium at the society's 2012 spring meeting. The peer-reviewed book focuses on using computational modeling to answer fundamental questions in catalysis, bio-fuels, and other sustainable solutions.



Researchers at Pacific Northwest National Laboratory contributed chapters and the cover art to *Applications of Molecular Modeling to Challenges in Clean Energy*, published by the American Chemical Society. The cover artwork depicts the potential of carbonate minerals to remove sulfur dioxide, a troubling compound in the quest for clean energy. ©American Chemical Society, 2013.

Niranjan Govind at PNNL and George Fitzgerald at Accelrys, Inc. organized the ACS symposium and edited the book. Govind, who works in EMSL, develops methods and algorithms in electronic structure theory and applies these theories to real-world problems.

Vanda Glezakou and B. Peter McGrail, PNNL, discuss computational studies of the chemical processes involved in wet supercritical carbon dioxide, which is used in carbon sequestration. Their 18-page chapter focuses on bonds breaking and forming as the fluid interacts with mineral surfaces and other solids. See Chapter 3, "Density Functional Simulations as a Tool to Probe Molecular Interactions in Wet Supercritical CO_2."

Yeohoon Yoon, PNNL, explains carbon dioxide's behavior on the surface of rutile $TiO_2(110)$. He also covers the role of oxygen vacancy defects in changing carbon dioxide's performance, providing a fundamental understanding of a topic with implications in carbon sequestration and fuel production. His 15-page chapter shows how these insights were obtained using dispersion-corrected density functional theory and *ab initio* molecular dynamics. See Chapter 4, "Characterization of CO_2 Behavior on Rutile $TiO_2(110)$ Surface."

Ming-Hsun Ho, Shentan Chen, Roger Rousseau, Michel Dupuis, R. Morris Bullock, and Simone Raugei, PNNL, show how their nickel-based catalysts, inspired by fast and efficient enzymes, produce dihydrogen at speeds comparable to those of bio-processes. Their 22-page chapter is based on their research at the Center for Molecular Electrocatalysis, an Energy Frontier Research Center led by the national laboratory. See Chapter 6, "Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production."

In addition, Vanda Glezakou provided the artwork that graces the book's cover. The image, based on her work and that of PNNL's H. Todd Schaef, depicts the potential of carbonate minerals to remove sulfur dioxide, a troubling compound in the quest for clean energy. The image was created by Cortland Johnson**,** also from PNNL.

Morris Bullock Named Fellow of the Royal Society of Chemistry

September 2013

Congratulations to Dr. Morris Bullock, Director of the Center for Molecular Electrocatalysis, a DOE Energy Frontier Research Center led by PNNL, on being selected as a Fellow in the Royal Society of Chemistry, the largest organization in Europe for advancing the chemical sciences.

Bullock was recognized for his "significant contributions to the chemical sciences" and for winning the Society's 2013 Homogeneous Catalysis award earlier this year. The Society is supported by a worldwide network of members and an international publishing business. Their activities include education, conferences, science policy and the promotion of chemistry to the public.

In addition to his internationally recognized research efforts, Bullock is also focused on developing a comprehensive understanding of how chemical and electrical energy is stored and used for applications in the development of non-fossil fuel sources. He joined PNNL as a Laboratory Fellow in 2006 and has authored more than 110 scientific publications.

Dr. Morris Bullock became a Royal Society of Chemistry Fellow in 2013.

Johannes Lercher Receives Francois Gault Lectureship Award

September 2013

Johannes Lercher earns the 2013 Francois Gault Lectureship Award, Europe’s highest honor in catalysis.

Congratulations to Dr. Johannes Lercher, Director of Pacific Northwest National Laboratory’s Institute for Integrated Catalysis, on earning the 2013 Francois Gault Lectureship Award, Europe’s highest honor in catalysis. Lercher leads catalysis research at the national lab and is a Professor of Chemistry at the Technische Universität München, Germany. The award recognizes his groundbreaking contributions in understanding molecular interactions in solid catalysts through elegant combinations of physicochemical and kinetic analyses. His work includes research on catalyzed reactions involving fossil fuels and bio-based feedstocks.

As the award recipient, Lercher will give plenary lectures across Europe between the two biennial EUROPACAT meetings held in Lyon in September 2013 and in Kazan in September 2015.

The award is sponsored by EFCATS, a European federation of catalysis societies from 25 European countries. This honor is given every 2 years to a distinguished scientist in the field of heterogeneous catalysis.

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