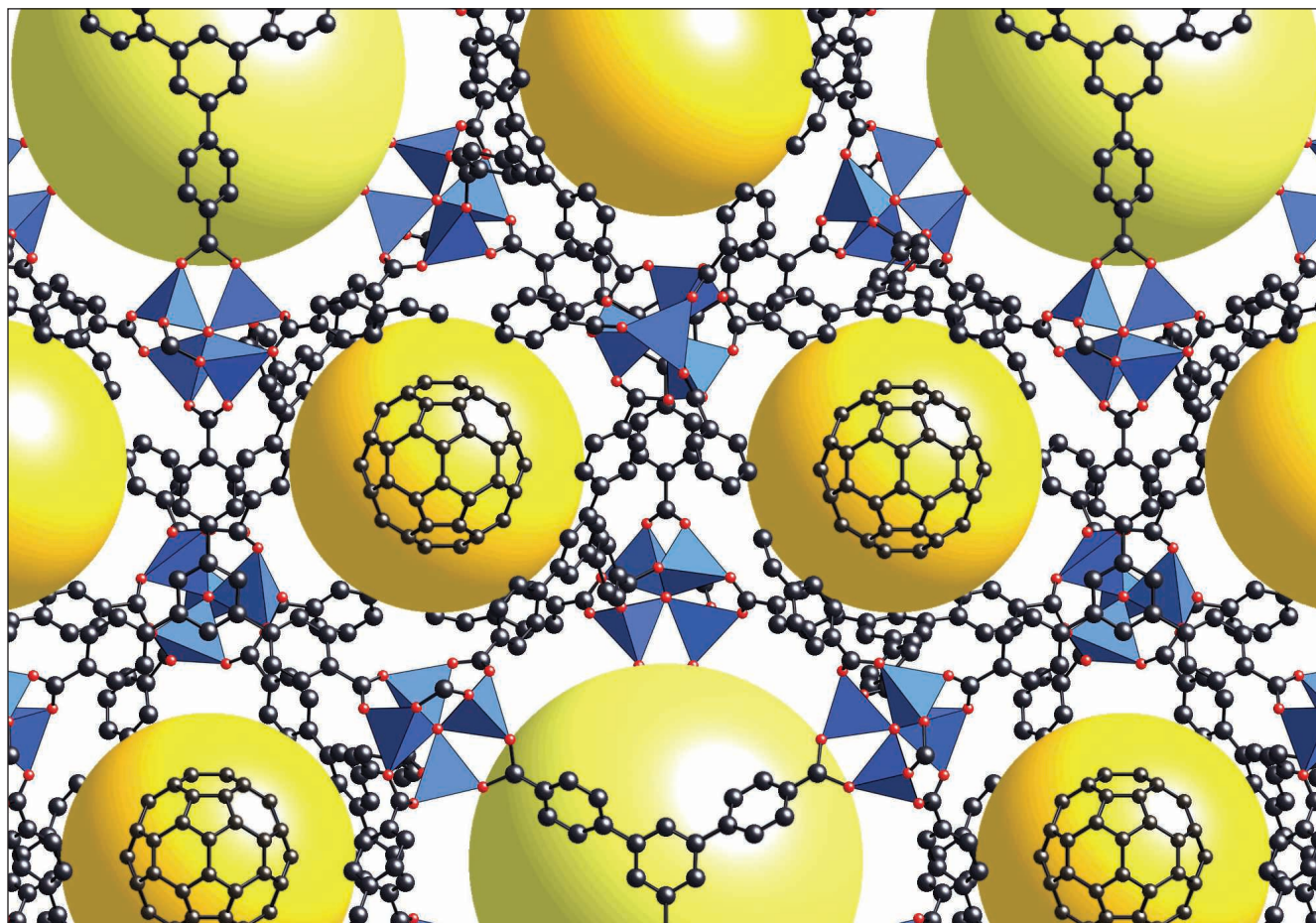


COURTESY OF MICHAEL O'KEEFE



MOLECULAR CONTAINERS Developing suitable storage media for hydrogen is critical to capitalizing on the gas's potential benefits as an energy carrier. Among other candidates, this metal-organic framework compound—MOF-177, composed of zinc clusters (blue) and 1,3,5-benzenetricarboxylate units—is being studied for gas uptake because of its large pore volume (yellow spheres).

FILLING UP WITH HYDROGEN

New materials and methods are improving hydrogen storage and production technology, but significant challenges remain

MITCH JACOBY, C&EN CHICAGO

SUPPLYING 1.21 GIGAWATTS TO THE DELOREAN'S FLUX capacitor precisely at the moment that the time-traveling sports car reached 88 miles per hour was no small feat, but that's what was needed to propel the protagonists through time in the science-fiction film trilogy "Back to the Future." The movies' madcap scientist achieved time travel by tapping the power of lightning and harnessing Mr. Fusion, a handheld nuclear device that generated energy from garbage.

In the real world, though, finding new energy sources is considerably more challenging. Researchers are working to replace fossil-fuel sources with hydrogen in a variety of applications, including transportation. Switching from petroleum to hydrogen may offer major benefits in terms of pollution, energy security, and other issues. But the change to a hydrogen economy won't happen overnight. Numerous scientific and technological hurdles need to be overcome before the switch to hydrogen can be implemented on a large scale. Working toward that goal, scientists are developing a variety of new materials and methods for producing and storing hydrogen.

As an energy carrier, hydrogen is attractive for several reasons. The gas can be burned or combined with oxygen in a fuel cell to release energy and produce water with no pollutants. Likewise, those reactions do not generate greenhouse gases. In addition, hydrogen can be produced from plentiful sources such as water, thereby reducing a growing dependence on fossil fuels.

Capitalizing on those benefits—for example, in a fuel-cell-powered automobile—remains challenging. One reason is that no infrastructure exists through which ordinary motorists can acquire hydrogen conveniently and safely. And there is no uniform procedure for storing the fuel in a car's gas tank.

George J. Thomas, a retired Sandia National Laboratories scientist and a participant in the Department of Energy National Hydrogen Storage Project, says one of the key enabling technologies on which a future hydrogen economy rests is hydrogen storage. The topic is central to all aspects of hydrogen usage: production, distribution, and utilization, he says.

TO BE ACCEPTED by the public as a transportation fuel, hydrogen needs to be accessible and easily stored onboard an automobile in suitable quantities. Today's cars, Thomas notes, can be refueled in a few minutes and generally travel some 300 miles on a tank of gasoline. DOE has set similar targets for the performance of hydrogen-powered cars. For light-duty vehicles, the targets call for being able to fill up with roughly 5 to 10 kg of hydrogen. The trick is being able to store the fuel compactly.

Thomas points out that hydrogen has roughly three times the energy content of gasoline on a per-weight basis. On a volumetric basis, however, hydrogen's energy content is only 8 megajoules (MJ) per liter for the cryogenic liquid compared with gasoline's 32 MJ/L. DOE's 2010 targets call for developing a hydrogen-storage system with an energy density of 7.2 MJ/kg and 5.4 MJ/L. Energy density refers to the amount of usable energy that can be derived from the fuel system. The figures include the weight and size of the container and other fuel-delivery components—not just the fuel, Thomas stresses.

The 2010 values work out to be 6 wt % of hydrogen and 45 kg of hydrogen per cubic meter. Further down the road, the targets will be even more stringent. For 2015,

DOE is calling for fuel systems with 9 wt % of hydrogen and 81 kg of hydrogen per cubic meter, which is greater than the density of liquid hydrogen (approximately 70 kg/m³ at 20 K and 1 atm).

Many approaches to packing a large quantity of hydrogen in low-weight, low-volume systems are being studied. Research on liquid and high-pressure gas-storage systems is ongoing, and international safety certifications have been issued recently for compressed gas cylinders designed to hold hydrogen at 10,000 psi. But those methods cannot satisfy long-term storage goals. Most scientists working on the problem are focusing on storing the gas in solids and solid matrices—forms in which it's possible to exceed the density of liquid hydrogen.

Storing hydrogen in hydrides, carbon-based materials, hydrogen-containing compounds, and other solids offers a number of potential advantages over other storage methods. Theodore Motyka, a manager in the Hydrogen Technology Section at Savannah River National Laboratory (SRNL), points out that hydrogen can be stored in solids at low pressure, which is reassuring from a safety standpoint. The fuel tank itself may offer another benefit, he adds. Compared with standard containers such as high-pressure gas cylinders, storage for solids permits design flexibility in terms of the shape of a container and its location on (or under) an automobile. In addition, waste heat from fuel cells may be able to drive hydrogen evolution from some solids.

Motivated by properties of solids that seem promising, numerous research groups have examined a large number of metal hydrides over the years. The list of materials includes hydrides of nickel and other transition metals, rare-earth alloys, and related materials. According to Motyka, scientists have found that, in general, only about 2 wt % of hydrogen can be stored and released by this class of compounds under temperature and pressure conditions that are suitable for onboard storage (up to about 100 °C and a few atmospheres).

Much larger quantities of hydrogen can be stored in other simple hydrides, such as magnesium hydride (MgH₂, about 7

wt % H₂), but the temperatures required to evolve hydrogen are too high for that material and other high-capacity materials to be of practical use in transportation applications.

A key advance in the field was reported in a landmark study in 1997 by researchers Manfred Schwickardi and Borislav Bogdanovi² at Max Planck Institute for Coal

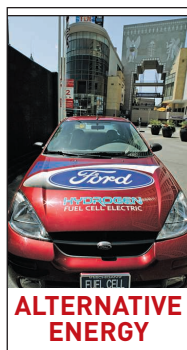


Thomas



Motyka

PHOTOS BY MITCH JACOBY



Research, in Mülheim an der Ruhr, Germany. The team found that some 3.7 wt % of hydrogen could be absorbed and desorbed reversibly under fairly mild conditions using titanium-doped sodium aluminum hydride, a complex hydride also known as sodium alanate (NaAlH₄) (*J. Alloys Compd.* 1997, 253, 1).

The investigation also showed that sodium alanate releases hydrogen in a two-step process. The reported 3.7 wt % H₂ corresponds to a reversible reaction in which NaAlH₄ is converted to Na₃AlH₆, aluminum, and hydrogen at low temperature. Additional hydrogen (about 1.8 wt %) is released in a second step as NaH is formed, but that reaction occurs at higher temperature, according to the study.

The Bogdanovi² paper, which is cited regularly in presentations on hydrogen storage, touched off a wave of investigations in search of metal dopants and other substances that can be added to sodium alanate to take advantage of the full 5.5 wt % of hydrogen held by the material.

"We need new preparation methods and new compounds for hydrogen storage," Motyka says. "The goal is to develop lighter materials with an even higher reversible hydrogen-storage capacity than sodium aluminum hydride," he adds.

At SRNL, scientists recently developed a molten-state synthesis method in which reagents used for preparing hydrides are mixed at near-melting-point temperatures. The simple method leads to high yields of homogeneous products and can boost hydrogen-evolution kinetics, Motyka notes.

As proof-of-concept, the method was used to prepare $\text{Na}_2\text{LiAlH}_6$, which, according to Motyka, can also be prepared by conventional wet chemistry methods or ball milling (vigorous mixing of solids). The team, led by SRNL staff scientist Ragaiy Zidan, has also made compounds based on magnesium and MgNi, Motyka says. "Some of them look promising," he says, "but we are still looking."

Recently, Zidan teamed up with chemical engineering professor James A. Ritter and coworkers at the University of South Carolina, Columbia, to examine synergistic effects of graphite and titanium dopants on hydrogen uptake and release from sodium alanate. Used alone, graphite induced almost no change in the hydride, the team reports. In contrast, the graphite-titanium combination lowered the dehydrogenation temperature by some 15 °C compared with TiNaAlH_4 (*J. Alloys Compd.* 2005, 395, 252).

In related work, researchers in England are developing new techniques for activating high-capacity metal hydrides such as MgH_2 . One way to boost the material's sluggish gas absorption and desorption behavior is through high-velocity ball milling—an energy-intensive process. Now, a more energy-efficient method has been reported: Chemistry professors Peter P. Edwards at the University of Oxford and Paul A. Anderson at the University of Birmingham and their coworkers find that adding a minute amount of LiBH_4 to MgH_2 (0.1 mole ratio), followed by heat treatment, leads to a product that is as active for gas storage as the ball-milled material (*Chem. Commun.* 2005, 2823).

Studies of similar materials are being conducted at Sandia National Laboratories, Livermore, Calif. Sandia leads a DOE Center of Excellence in metal hydride research that includes SRNL; Brookhaven National Laboratory; the University of Hawaii, Honolulu; and other institutions. This center is one of three DOE Centers of Excellence in hydrogen storage.

Motivated by work conducted a few years ago at National University of Singapore, Sandia researchers have turned their attention to lithium-based materials. James C. Wang, a research manager at Sandia and director of the Sandia-based Center of Excellence, explains that lithium amide

but the temperature needs to be around 300 °C for the reactions to occur." He adds that the reactions take place at very low pressures, which is another strike against this hydrogen-storage candidate for vehicular applications.

So Sandia staff scientist Weifang Luo reasoned that replacing some of the lithium in the lithium amide-lithium hydride step with magnesium should improve the gas sorption properties because MgH_2 is less stable (more reactive) than LiH. That's exactly what the researchers found. Adding MgH_2 to the lithium amide-lithium hydride system lowered the reaction temperature by more than 80 °C and also bumped up the pressure—bringing both parameters closer to a range that's suitable for use in transportation (*J. Alloys Compd.* 2004, 381, 284).

Scientists have been unable to tap the full 5.5 wt % of hydrogen bound up in sodium alanate, and as a result the focus is shifting away from that hydride. But NaAlH_4 has been studied in detail, so it remains a model system for investigation. Scientists at Sandia are developing processing methods that reduce the level of impurities in the material and improve its gas-uptake kinetics. Other Sandia researchers, such as Eric H. Majzoub, have been working to uncover reaction mechanisms that govern sodium alanate's hydrogen-storage behavior.

A key question Majzoub and colleagues are trying to answer is, What role do titanium dopants play in stimulating hydrogen desorption reactions? To begin answering that question, the team recently conducted Raman spectroscopy experiments on single crystals of NaAlH_4 . They observed that the AlH_4^- anions remain intact as the temperature is raised to the melting point of sodium alanate.

On the basis of the spectroscopy measurements and quantum calculations, Majzoub proposes that breaking the AlH_4^- anions is the rate-limiting step in the hydrogen desorption reaction and that tita-



HANDS ON Sandia engineer Daniel E. Dedrick prepares equipment for hydrogen-storage experiments on sodium aluminum hydride.

(LiNH_2) can store and release on the order of 11.5 wt % of hydrogen in a reversible two-step process.

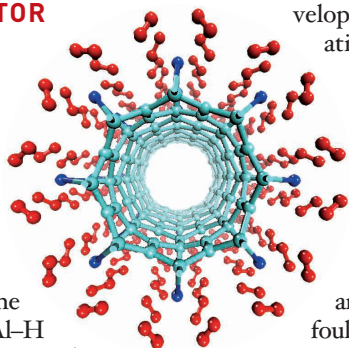
Reacting lithium amide with lithium hydride (LiH) forms lithium imide (Li_2NH) and liberates approximately 6.5 wt % of hydrogen, Wang says. Subsequent reaction of lithium imide with lithium hydride yields lithium nitride (Li_3N) and another 5 wt % of hydrogen. Wang points out that "11.5 wt % hydrogen makes it a pretty attractive material for storage applications,

“Energy density figures include the weight and size of the container and other fuel-delivery components—not just the fuel.”

EXTERIOR DECORATOR

Computational studies predict that carbon nanotubes doped with titanium (dark blue) can bind four hydrogen molecules (red) per metal atom.

COURTESY OF TANER YILDIRIM



nium dopants promote the reaction by lowering the Al-H bond strength (*Phys. Rev. B* 2005, 71, 024118).

Another hydride—one that was investigated 20 years ago for its potential as a rocket fuel—is being considered nowadays for a job in the hydrogen-storage business. Aluminum hydride (AlH_3) has some promising-looking properties, Wang remarks. The material contains 10.1 wt % of hydrogen and roughly 150 kg of H_2/m^3 . When blended with about 20% LiH, AlH_3 evolves hydrogen at approximately 100 °C, according to Wang. “But it’s a one-way street,” he says. “For now, the reaction is essentially irreversible.” He adds that a team led by Brookhaven scientists that includes researchers at Sandia and SRNL is searching for efficient ways to rehydride the material.

THE HYDROGEN-STORAGE spotlight is also being shared with boron compounds. In a well-publicized example a few years ago, DaimlerChrysler unveiled the Natrium, a fuel-cell-powered concept car based on the automaker’s Town & Country minivan. The Natrium runs on hydrogen derived from an aqueous sodium borohydride solution via a hydrogen generator developed by Millennium Cell, Eatontown, N.J. Fuel is generated when sodium borohydride is converted to sodium metaborate and hydrogen in the presence of a supported ruthenium or other transition-metal catalyst. The spent metaborate solution needs to be reprocessed off-board.

Somewhat off the beaten path, ammonia borane (NH_3BH_3 , also known as borazane) is being studied as a hydrogen-storage compound. Gert Wolf, a professor in the Physical Chemistry Institute at the Technical University of Freiberg, in Germany, notes that roughly 15 wt % of hydrogen can be released by the compound either through direct thermal decomposition of the solid or by way of catalytic decomposition of aqueous ammonia borane solutions. Wolf’s research group has studied the thermodynamics of the decomposition reactions and is de-

veloping methods for regenerating the spent material.

As ammonia borane decomposes, the material evolves hydrogen and is converted to polyamino-borane-type compounds and related substances.

The reaction also forms borazine, a boron-nitrogen analog of benzene that can foul fuel cells.

S. Thomas Autrey, Maciej S. Gutowski, Anna Gutowska, and coworkers at Pacific Northwest National Laboratory (PNNL) sought to remove borazine from the hydrogen stream by carrying out the reaction in a highly porous silica support. They got more than they bargained for. In addition to removing borazine, the team found that dispersing ammonia borane in the nanometer-sized pores of silica increased the hydrogen desorption kinetics by a factor of 100 relative to the bulk form



Dow Biocides. FIRST.

Think biocides at the start of your formulation process and solve microbial challenges before they occur. With the industry’s most comprehensive biocides product portfolio, our people will help you select the most effective solutions for your unique applications. Ask us how Dow Biocides’ laboratory, regulatory, toxicology and scientific expertise can help ensure your success.

www.biocidesfirst.com
Tel. 1 800 447 4369
1 989 832 1560

Ioana
Water Treatment
Personal Care
ioana@dow.com

Sanjay
Building & Construction
Metalworking Fluids
sanjay@dow.com

Tina
Paints & Coatings
Adhesives
tina@dow.com

George
Regulatory
EH&S
george@dow.com

Bei
High Level Disinfection
Leather Tanning
bei@dow.com

Ask Us.



Request more at AdInfoNow.org



ROOM FOR DISCUSSION Michigan chemists (from left) Nathan W. Ockwig, Andrew R. Millward, Yaghi, David J. Tranchemontagne, and Adrien P. Côté discuss crystal properties.

of ammonia borane (*Angew. Chem. Int. Ed.* 2005, 44, 3578). According to Autrey, the source of the rate increase is not fully understood. “We have more questions now than before we started the experiments,” he confesses.

Organosilanes don’t come up regularly in discussions on hydrogen storage unless you talk to researchers such as Mahdi M. Abu-Omar, an associate professor of chemistry at Purdue University. Abu-Omar recently demonstrated a method for producing hydrogen via hydrolytic oxidation of organosilanes using water and an oxorhenium oxazoline complex to catalyze the reaction (*J. Am. Chem. Soc.* 2005, 127, 11938).

SOAK IT UP Composed of $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel-shaped units that are joined by biphenyltetracarboxylic acid linker groups, this porous metal-organic framework compound (MOF-505) can store 2.5 wt % hydrogen at 77 K. Yellow sphere indicates cavity volume. Cu is blue, C is black, and O is red.

Carbon-based materials—and in particular, carbon nanotubes—have been considered promising candidates for high-density storage of hydrogen for more than a decade. A few years ago, some researchers reported storing 5–10 wt % of hydrogen in single-walled carbon nanotubes (SWNTs) at room temperature and under moderate pressure. But a number of those studies were disputed, and in some cases the high gas uptake was attributed to the presence of metal contaminants. In other cases, water absorption was

blamed (C&EN, Jan. 14, 2002, page 25).

Since that time, several research teams have focused on uncovering the role of metals in hydrogen storage in carbon nanotubes and related structures. For example, physicist Taner Yildirim of the National Institute of Standards & Technology and Salim Ciraci, a physicist at Bilkent University in Ankara, Turkey, used computational methods to model hydrogen uptake on the surface of titanium-decorated SWNTs. The team reports that each titanium atom can bind up to four hydrogen molecules—a finding they describe as “quite remarkable and unanticipated.”

The results predict that as hydrogen comes in contact with the binding sites, the first H_2 molecule to latch onto the surface dissociates upon adsorbing. The other three molecules become elongated but do not dissociate. At high titanium coverage, up to 8 wt % of hydrogen can be adsorbed, they say (*Phys. Rev. Lett.* 2005, 94, 175501).

Similarly, Michael J. Heben, Shengbai Zhang, and their coworkers at the National Renewable Energy Laboratory find that some organometallic buckyballs can store

up to 9 wt % of hydrogen under mild conditions. Their computational results predict that $\text{C}_{48}\text{B}_{12}[\text{ScH}]_{12}$ can bind up to 11 hydrogen molecules per transition-metal atom, 10 of which adsorb reversibly near room temperature (*Phys. Rev. Lett.* 2005, 94, 155504).

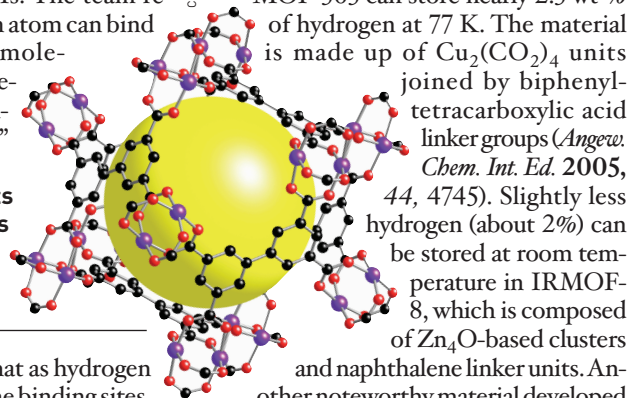
Another class of carbon-rich materials under investigation for hydrogen storage is metal-organic framework compounds (MOFs)—highly porous crystalline materials composed of metal clusters and organic linkers. At the University of Michigan, Ann Arbor, chemistry professor Omar M. Yaghi and coworkers have been designing, synthesizing, and characterizing MOFs for several years, with an eye to customizing their structures and gas-storage properties.

The components that make up the porous materials can be varied widely, leading to a large class of robust crystalline compounds with potential for high-capacity hydrogen storage, Yaghi says. Some of the design strategies for boosting gas uptake include customizing pore size, impregnating large pores with guest molecules for additional adsorption, and preparing interpenetrating (catenating) frameworks. To date, the Michigan group has prepared nearly 500 MOFs, some of which are described in a recent review article (*Angew. Chem. Int. Ed.* 2005, 44, 4670). And that’s just a small fraction of the MOFs that have been made in labs around the globe, he asserts.

Recently, Yaghi’s group reported that MOF-505 can store nearly 2.5 wt % of hydrogen at 77 K. The material is made up of $\text{Cu}_2(\text{CO}_2)_4$ units joined by biphenyltetracarboxylic acid linker groups (*Angew. Chem. Int. Ed.* 2005, 44, 4745). Slightly less hydrogen (about 2%) can be stored at room temperature in IRMOF-8, which is composed of Zn_4O -based clusters

and naphthalene linker units. Another noteworthy material developed by Yaghi’s group is MOF-177. Its surface area was determined to be an unprecedented $4,500 \text{ m}^2/\text{g}$, which exceeds the surface areas of other MOFs, carbon materials, and zeolites (C&EN, Feb. 9, 2004, page 10).

After years of focusing on a large class of highly symmetric structures, Yaghi observes that “there may be real opportunities for gas storage and other important applications in structures made from less



symmetric building blocks." But he advises against working on their synthesis without clearly defined target structures.

Fundamental studies of catalytic materials may have an impact on issues related to hydrogen production and storage. For example, at Rutgers University, Piscataway, N.J., chemistry and physics professor Theodore E. Madey is studying ammonia decomposition on iridium (which forms N₂ and H₂) in response to proposals that ammonia may serve as a clean source of hydrogen. Madey and coworkers showed that simple procedures can be used to prepare iridium crystals with custom-sized nanometer-scale facets and that these surface features control the ammonia decomposition process (*J. Am. Chem. Soc.* 2005, 127, 5014).

Meanwhile, at the University of Wisconsin, Madison, Manos Mavrikakis, an associate professor in the department of chemical and biological engineering, recently conducted a theoretical investiga-



MAKING PLANS At PNNL, Autrey (left) and Wendy J. Shaw discuss lab results and plan experiments on hydrogen-storage materials.

tion that points the way to new types of transition-metal alloy catalysts that bind hydrogen weakly yet dissociate H₂ readily. That combination of properties may make the new materials useful catalysts for hydrogen-storage applications

it the future to see how hydrogen-storage issues are resolved. Unfortunately, a real time-traveling DeLorean is not an option. So scientists will need to search for answers, not by going back to the future, but by going back to the lab. ■

(C&EN, Nov. 29, 2004, page 25).

Similarly, David S. Sholl, an associate professor of chemical engineering at Carnegie Mellon University, also applied computational techniques to discover new materials with useful properties. Sholl's study revealed new types of sulfur-tolerant transition-metal alloy membranes for hydrogen purification (*Science* 2005, 307, 569).

The list of materials under investigation for hydrogen-storage applications is extensive. Many materials exhibit properties that render them ideal in terms of volumetric or gravimetric (weight-based) storage capacity, but they may suffer shortcomings with regard to cost, durability, safety, and practical usage.

It would be enlightening to vis-

New Polythiophenes from Rieke Metals, Inc.

Today's Materials for Tomorrow's Electronics

Useful for printed electronics of all types: OLED's, sensors, displays, and a wide range of smart materials

Exceptional quality and reproducibility

Expanded manufacturing capabilities ranging from grams to kilograms

Significantly reduced prices

www.riekemetals.com

phone: 402-434-2775

fax: 402-434-2777

Contact us for specific details: riekemetals@hotmail.com



Rieke Metals, Inc.

Offering:

98.5 % Regioregular
3-Alkyl Polythiophenes

Regiorandom 3-Alkyl
Polythiophenes

Water Soluble
Polythiophenes

Electronic Grade 3-Alkyl
Polythiophenes

Wide Range of
Functionalized
Polythiophenes

Request more at AdInfoNow.org