Hydrogen Storage and Its Limitations

by Giselle Sandí

Hydrogen storage is a crucial step for providing a ready supply of hydrogen fuel to an end use, such as a car, as it is considered by many to be the most technically challenging aspect of achieving a hydrogen-based economy. Current hydrogen storage materials or systems are still far short of meeting target goals set for either 2010 or 2015.

Two kinds of storage functions with very different requirements are needed for effective storage and delivery of hydrogen. Hydrogen storage systems used for such stationary applications as residential heating and air-conditioning, neighborhood electrical generation, and many industrial applications can occupy a large area, employ multistep chemical charging/recharging cycles that operate at high temperature and pressure, and compensate for slow kinetics with extra capacity. In contrast, hydrogen storage for transportation must operate within minimum volume and weight specifications, supply enough hydrogen to enable a 480 km (300 mile) driving range, charge/recharge near room temperature, and provide hydrogen at rates fast enough for fuel cell locomotion of cars, trucks, and buses.

Two-thirds of U.S. oil consumption is used to meet transportation energy needs. Therefore, this sector presents not only the most difficult challenges, but it also provides the most intense drive for the hydrogen economy. Developing effective hydrogen storage for transportation is a central challenge for basic research and a key factor in enabling the success of the hydrogen economy.

The operating requirements for effective hydrogen storage for transportation include appropriate thermodynamics, fast kinetics, high storage capacity, effective heat transfer, high gravimetric and volumetric densities, long cycle lifetime for hydrogen absorption/desorption, high mechani-
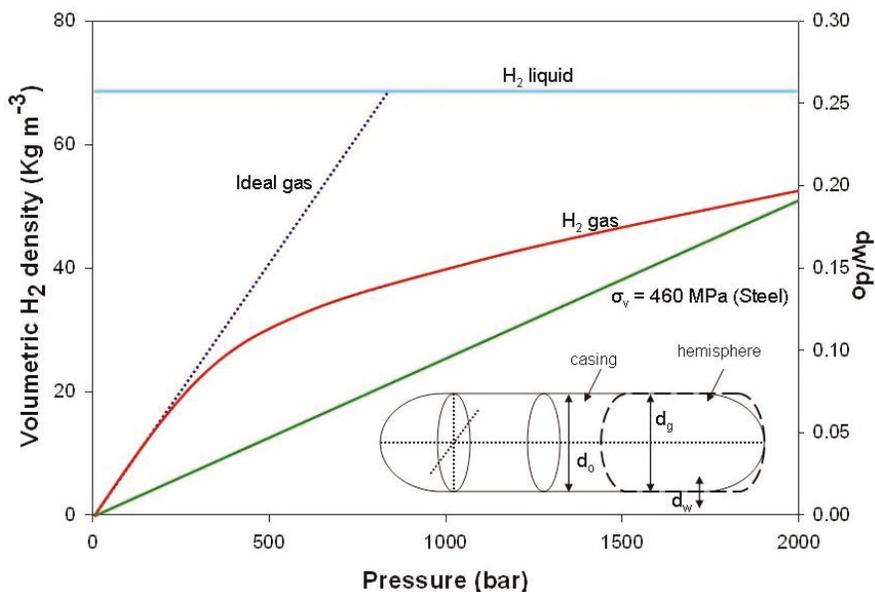

FIG. 1. Volumetric density of compressed hydrogen gas as a function of gas pressure, including the ideal gas and liquid hydrogen. The ratio of the wall thickness to the outer diameter of the pressure cylinder is shown on the right side for steel with a tensile strength of 460 MPA. A schematic drawing of the pressure cylinder is shown as an inset.

cal strength and durability, safety under normal use, and acceptable risk under abnormal conditions. Depending on the vehicle, a storage capacity of approximately 5-10 kg of usable hydrogen is needed to provide a 480 km range for a fuel cell/electric vehicle. A refueling time of less than 5 min is targeted for 2015. Current technology for hydrogen storage involves tanks in which hydrogen is stored as a compressed gas or as a cryogenic liquid. With compressed gas and liquid storage, the hydrogen is easily accessible for use. However, these storage methods fall far short of the FreedomCAR targets[1] because of the volume of the tanks that would be required using present technology. Solid-state storage, in which the hydrogen is absorbed in a solid material, holds considerable promise for meeting the FreedomCAR targets, but no completely satisfactory material has been identified as yet.

The current methods of hydrogen storage are described below, along with fundamental research issues that are needed to achieve the required hydrogen storage goals.

Gaseous and Liquid Hydrogen Storage

Storage of hydrogen as a gas in tanks is a mature technology. Recently 10,000 psi tanks have been demonstrated and certified.[2] These high-pressure tanks use new lightweight tank materials, such as carbon-fiber reinforced composites. The major drawback of gaseous storage for transportation applications is the small amount of hydrogen that may be stored in a reasonable volume. Even at 10,000 psi pressure, the energy content is significantly less than that for the same volume of gasoline, 4.4 MJ/L (10,000 psi) for hydrogen compared with 31.6 MJ/L for gasoline. The energy used in com-

pressing the gas is another consideration, as is the large pressure drop during use. Because many of the system parts exposed to hydrogen will be metallic, researchers need a better understanding of the atomic-level processes responsible for hydrogen embrittlement in candidate materials to develop strategies to prevent failure resulting from long exposure to hydrogen.

For liquid hydrogen, researchers predict 8.4 MJ/L compared with 4.4 MJ/L for compressed gas (at 10,000 psi).[3] The density of liquid hydrogen is 70.8 kg/m^{3} at standard temperature and pressure. These values are still less than half those required to meet the FreedomCAR goals. A major drawback of liquid storage is the large quantity of energy required for liquefaction. The loss of hydrogen through evaporation is also an issue, especially with small tanks. High-pressure cryogenic tanks are also being explored to alleviate the requirement for very low temperature storage.[4] New approaches are needed to reduce the cost of liquefaction and make it more energy efficient. Figure 1 shows the volumetric density of hydrogen inside the cylinder and the ratio of the wall thickness to the outer diameter of the pressure cylinder for stainless steel with a tensile strength of 460 MPa. The volumetric density increases with pressure and reaches a maximum above 1000 bar, depending on the tensile strength of the material. However, the gravimetric density decreases with increasing pressure, and the maximum gravimetric density is found for zero overpressure. Therefore, the increase in volumetric storage density is sacrificed with the reduction of the gravimetric density in pressurized gas systems.

Solid-State Storage

Solid-state storage refers to the storage of hydrogen in metal hydrides, in chemical storage materials, and in nanostructured materials. This method of hydrogen storage offers the best opportunities for meeting the requirements for onboard storage. In these materials, hydrogen can be stored both reversibly and irreversibly. Reversible storage means that hydrogen is released by raising the temperature, for example, of a metal hydride at a suitable pressure; hydrogen is subsequently replaced (stored) through the control of temperature and hydrogen pressure. Although temperature and pressure are the two typically controlled thermodynamic parameters, other types of ener-

gy (e.g., mechanical and acoustical) can be employed to control both the release and uptake of hydrogen.[5] Ideally, storage and release of hydrogen should take place at temperatures between 0 and 100°C and pressures of 1-10 bar and on time scales suitable for transportation applications. Some materials contain strongly chemically bound hydrogen that is not readily retrievable. Only hydrogen that can be made easily accessible meets the hydrogen storage requirements for transportation applications. Hydrogen is irreversibly stored in some materials, including chemical hydrides, and is released by chemical reaction with another substance, such as water. The heat released upon hydrolysis is energy that can be captured and used. The resulting hydrolysis product cannot be used again to store hydrogen without chemical reprocessing. Hydrogen storage using recyclable hydrocarbon carriers, such as methylcyclohexane, has also been demonstrated. However, these liquid carriers store low ratios of usable hydrogen for their weight. In addition, these carriers require a long release time, because the catalyst used for dehydrogenation must first be brought up to operating temperature.

Metal hydrides may represent ideal storage systems. Although a database published at Sandia National Laboratory[6] lists more than 2,000 elements, compounds, and alloys that form hydrides, no material has yet been demonstrated to meet all the FreedomCAR targets. Conventional metal hydrides, which are well characterized and have well-established values for interstitial hydrogen storage, include intermetallics of the types AB, AB2, AB5, A2B, and body-centered cubic metals. These materials typically store between 1.4 and 3.6 wt % hydrogen. Examples of these intermetallic compounds are TiFe, $ZrMn_2$, $LaNi_5$, and Mg_2Ni. Generally, the hydrogen storage capabilities are a factor of three lower than the FreedomCAR requirements.[1]

Metal Hydrides and Complex Hydride Materials

Over the past four decades, materials for solid-state hydrogen storage have been nearly exclusively metals and metallic alloys, in which the metal matrix is expanded and filled with absorbed hydrogen atoms that are usually located in tetrahedral or octahedral interstitial sites. Atomic hydrogen stored in these interstitial sites recombines at particle surfaces to form mole-

cular hydrogen upon release. A major emphasis of materials-related research has been to encapsulate hydrogen. Capacities exceeding two hydrogen atoms per metal atom have been demonstrated with this approach. However, most metal matrices investigated to date consist of relatively heavy elements, and gravimetric storage capacities usually do not exceed 2 wt % hydrogen when transition metals are major components. Light elements, such as Mg, have shown promising levels of stored hydrogen (3-7 wt % hydrogen), but they release hydrogen at high temperature (e.g., 552 K at one atmosphere).[7] Although improvements in the kinetics of magnesium-based alloys have been achieved by nanostructuring and adding catalysts,[8] the thermodynamics remain virtually unchanged. In comparison, $NaAlH_4$, a low-temperature hydride, and Na_3AlH_6, a medium-temperature hydride, offer promise for lowering the hydrogen release temperature while attaining high storage capacity (above 5 wt %) using both phases to provide hydrogen. Hydride formation in nearly all metal systems generally involves about a 15-25% volume change that must be accommodated in storage vessel designs. Another issue that must be addressed is the thermal management of the heats of absorption and desorption to (1) enhance the kinetics during filling and discharge of the hydrogen storage systems and (2) avoid degradation effects during long-life operation.

The stability of metal hydrides is usually presented in the form of Van't Hoff (see Fig. 2). The most stable binary hydrides have enthalpies of formation of ΔH_f = -226 kJ mol^{-1} H_2. The least stable hydrides are $FeH_{0.5}$, $NiH_{0.5}$, and $MoH_{0.5}$ with enthalpies of formation of ΔH_f = +20 kJ mol^{-1} H_2, ΔH_f = +20 kJ mol^{-1} H_2, and ΔH_f = +92 kJ mol^{-1} H_2, respectively.[9]

Another concept in solid-state storage of hydrogen is to encapsulate by hydrogen, thus opening the possibility of approaching the hydrogen content of methane. Methane seems to be the ultimate hydrogen storage compound, in which four hydrogen atoms surround a single carbon atom. However, because CH_4 is gaseous, it offers little practical benefit over storage of hydrogen itself. Further, the hydrogen-carbon bonds of methane are too strong for easy hydrogen recovery. Novel solids — such as alanates (aluminohydrides), borohydrides, and imides — in which the metal atom is surrounded by four to six hydrogen atoms

forming a complex negatively charged anion, mimic the structure of methane and may provide a much-needed breakthrough in the solid-state storage of hydrogen. Their theoretical total hydrogen capacities are high (from 7 to 18 wt %).[10] Solid storage materials with a high volumetric density of hydrogen (up to 100 g H_2/L) would exceed the density of a cryogenic liquid at 20 K (~70 g H_2/L). Use of these materials is critically dependent on whether the stored hydrogen can be conveniently released at a temperature that is within acceptable bounds and how the materials can be recharged with hydrogen. Mixing hydrides to make complex, multicomponent hydrides, potentially allows the synthesis of storage materials with specifically tailored properties. For example, the ionic bonding of hydrogen-rich [MeHn]p- anions with various light-element cations provides a means for precise chemical substitutions in the cation sublattice, thus bridging the gap between hydrogen-poor intermetallic hydrides and hydrogen-rich LiH, BeH_2, and MgH_2 compounds. Thus, these complex hydrides have perhaps the greatest potential to provide both a high weight percent hydrogen and desirable release/absorption kinetics.

The majority of complex hydrides have been prepared via lengthy solvent-based synthesis; only a few (*e.g.*, $LiAlH_4$ and $NaBH_4$) have been prepared without solvents. Novel materials and processing approaches must be developed for these and other lightweight hydrides, and these materials must be evaluated in terms of their potential for enhanced hydrogen storage performance. One important, but little understood, finding is the critical role of dopants in achieving reasonable kinetics and reversibility of complex hydrides. For example, the addition of Ti-based compounds (such as $TiCl_3$ or $Ti[OBu]_4$ to $NaAlH_4$) lowers the first decomposition temperature of the hydride, so that 3.7 wt % is released at 353 K, but at the expense of lowering the hydrogen content from 5.5 wt % in the hydride without a catalyst.[11] Also $TiCl_4$-catalyzed $LiAlH_4$ releases 5 wt % hydrogen at ambient temperature during mechanochemical processing and 2.5 wt % hydrogen at temperatures below 423 K during heating. However, the reversibility of hydrogen in this material is yet to be demonstrated.[12]

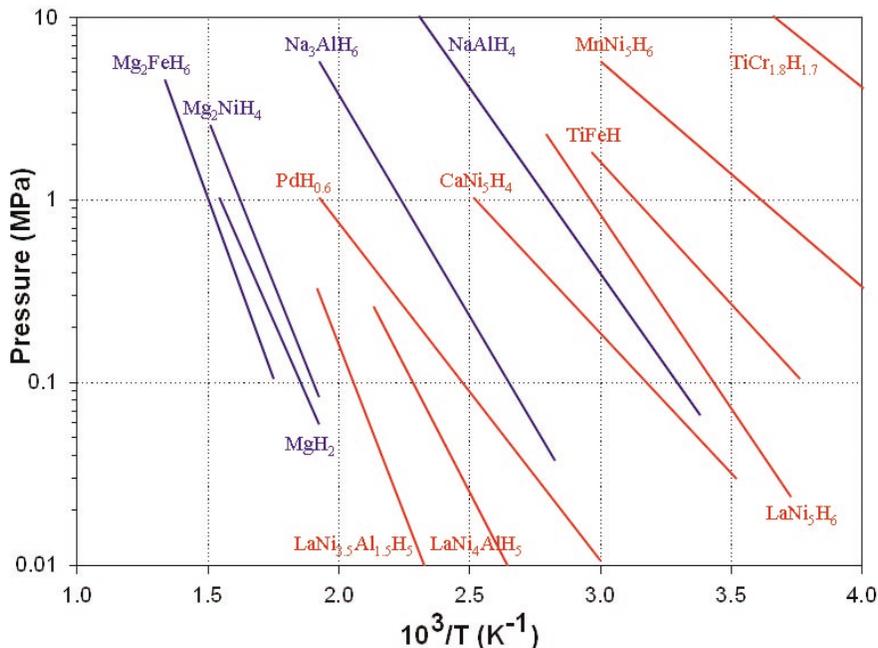Recently, Chen *et al.*[13] reported hydrogen storage in lithium nitride of

Fɪɢ. 2. *Van't Hoff plots of some selected hydrides. The stabilization of the hydride of LaNi$_5$ by the partial substitution of Ni with Al in LaNi$_5$ is shown.*

11.4 wt % (6 wt % cyclable) under pressure. This report sparked interest in the potential for nitrides and imides as hydrogen storage media. While the temperature required to release the hydrogen was high in this initial study, alkali metal nitrides and related compounds deserve additional study.

Nanostructured Materials

Researchers have demonstrated that at the nanoscale, materials may have distinctly different properties than those observed in their bulk-material analogs. New synthesis techniques have opened the door to designing materials with specific architectures to yield desired properties. Currently, there is considerable excitement about a new class of materials with unique properties that stem from their reduced length scale (1 < d < 100 nm). Examples of these types of materials include both carbon-based materials — such as nanotubes, nanohorns, fullerenes — and non-carbon-based nanomaterials made of other atoms (including nanoscale versions of the hydride materials discussed above). The small size of nanostructured materials strongly influences the thermodynamics and kinetics of hydrogen adsorption and dissociation by increasing the diffusion rate, as well as by decreasing the required diffusion length. The diffusion rate also may be influenced in general by

changes in the phonon modes, which directly influence the transport rate. In addition, materials at the nanoscale offer the possibility of controlling material parameters more independently than in their bulk counterparts. The advantages that can be realized because of nanoscale size may thus potentially minimize some current limitations of bulk complex hydrides, for example, and make some materials attractive for hydrogen storage.

A major advantage of nanostructured materials for hydrogen storage is that specific architectures can be designed into these materials to enhance the weight percentage of stored hydrogen and to control the kinetics involved in the adsorption/release of hydrogen. Incorporation of tailored nanostructures may allow dissociative hydrogen storage materials, such as the metal and complex hydrides currently used in bulk for hydrogen storage, to demonstrate substantial improvements in storage/release. Carbon nanostructures (including nanotubes and nanohorns) and the analogous non-carbon-based nanostructures show particular promise for effective nondissociative hydrogen storage. In both types of hydrogen storage, fundamental studies of the atomic and molecular processes involved in hydrogen adsorption and release are needed to enable the design of improved storage materi-
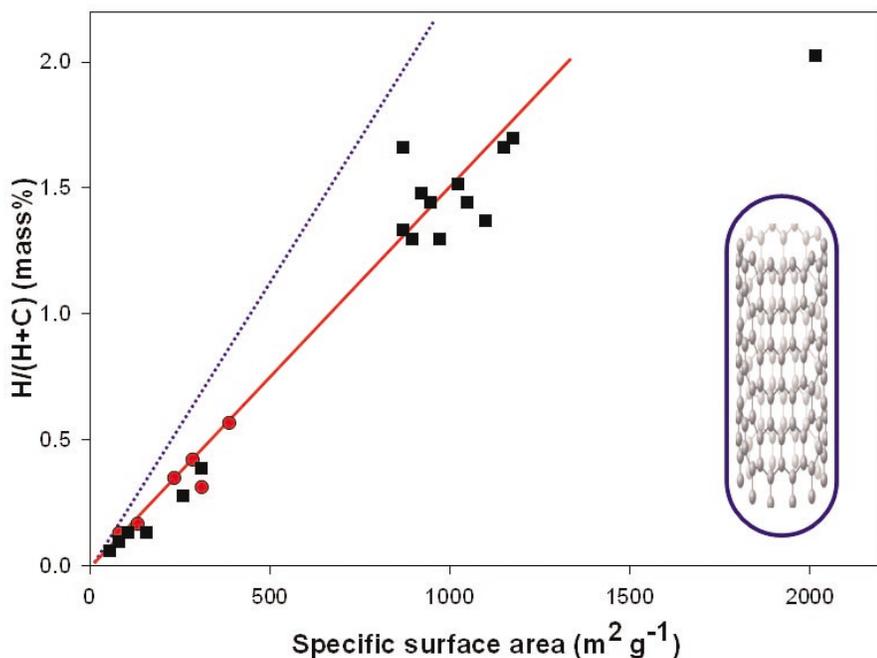
FIG. 3. *Reversible amount of hydrogen adsorbed* vs. *the surface area (red circles) of carbon nanotube samples including two measurements on high surface area graphite samples. Literature values of hydrogen gas adsorption at 77 K (black squares) are included (13). The dotted line represents the calculated amount of hydrogen in a monolayer at the surface of the substrate.*

Theory and Computation

A fundamental understanding of the hydrogen interaction in materials requires a synergistic approach involving both theory and experiment. Theory and computation may be used not only to understand experimental results, but also to guide them. The large advances in methodology (theory and algorithms) and increases in computational power in recent years have opened up new possibilities for theoretical studies of hydrogen storage. Broadly speaking, four classes of theoretical approaches are available for studying these systems: (1) the quantum mechanical approach, which yields information about electronic structure and chemical bonds; (2) the empirical and semiempirical approaches, which yield atomistic information about hydrogen trapping at vacancies and impurities; (3) the mesoscale approach, which yields information about average trapping at distributions of defects; and (4) the continuum methods, which yield information about transport through a real material.

Coupled with molecular dynamics, these approaches can predict the thermodynamic properties and time evolution resulting from thermally activated processes such as diffusion and chemical reactions. Direct simulations of time evolution can cover time scales of picoseconds (10^{-12} s) when using quantum mechanical methods to evaluate atomic forces, but up to nanoseconds (10^{-9} s) when empirical and semiempirical potential energy functions are used. Mesoscale approaches, such as kinetic Monte Carlo, can cover much longer time scales (up to seconds), and continuum methods can cover time scales from seconds to hours. The behavior of hydrogen spans all these length and time scales and thus poses serious challenges for theory and computation. There is no general approach for integrating simulations on different length and time scales. Modeling is mainly carried out separately at each length and time scale with limited integration. Researchers must find ways to integrate these methods to address the problems involving hydrogen production, storage, and use. The real challenge is to couple these approaches so that predictions of real materials behavior may be made with a solid physical and chemical basis.

als. Figure 3 shows the maximum amount of hydrogen in mass % for the physisorption of hydrogen on carbon nanotubes.[14] The theoretical maximum amount of adsorbed hydrogen is 3.0 mass % for single-wall nanotubes (SWNTs) with a specific surface area of 1315 m^2 g^{-1} at 77 K. A large variety of different nanostructured carbon samples have been investigated by high-pressure microbalance[15,16] at 77 K, electrochemical galvanostatic measurements at room temperature,[17,18] and volumetric (mass flow) gas-phase measurements at 77 K. From adsorption-desorption experiments, it is evident that reversible physisorption takes place with all samples. The amount of adsorbed hydrogen correlates with the specific surface area of the sample.

Nanoscale hydrogen storage materials can be divided into two general categories. The first is "atomic" hydrogen storage materials ("dissociative" materials), which require the reversible dissociation of molecular hydrogen into hydrogen atoms and the bonding of these atoms with the lattice of the storage medium. Dissociative materials would include such storage materials as the complex hydrides discussed previously. The second category is "molecular" hydrogen storage materials ("nondissociative" materials), which store hydrogen in the molecular state via weak molecular-surface interactions

(*e.g.*, van der Waals forces or physisorption). These materials include nanotubes, nanohorns, and non-carbon-based structures that have been tailored to have various sizes, surface areas, surface modifications, and other properties to control the physical characteristics of the materials. For nondissociative materials, in which hydrogen is bound in molecular form, a means for increasing the hydrogen-surface interactions must be developed to facilitate storage at the target operational temperatures. For example, the strength of the molecular binding may be enhanced by adding suitable dopants.

Great care is required to characterize the structure, surface, and hydrogen storage/release properties of high-surface-area nanomaterials. Clearly, researchers must identify the structure and surface properties of high-performance nanomaterials to facilitate modeling and provide an understanding of the structure-property relationships. Characterization of nanoscale materials presents a considerable challenge primarily because, at the nanoscale, existing analytical tools lack the required detection sensitivity. Thus, new characterization tools that have increased detection sensitivity, while retaining high detection selectivity, must be developed.

Theory and computation can play two important roles in the development of hydrogen storage materials. First, each approach allows researchers to understand the physics and chemistry of the hydrogen interactions at the appropriate size scale. Researchers can use information generated at any level to help choose new hydrogen storage materials. The second, and perhaps more powerful, application of theory and computation lies in the boot-strapping of information between theoretical levels. For example, the energetics data obtained from quantum mechanical calculations is used directly in the development of the semi-empirical potentials. The trapping energetics and kinetics obtained by using these potentials are used in a mesoscale calculation to determine effective properties as a function of microstructure. These results are then used directly in continuum calculations to predict the recycling properties of an engineering material. In principle, the entire process of material selection, processing, and — ultimately — material performance in service, can be accurately simulated.

To ensure that the modeling is accurate, it is critical that predictions at each size scale be compared with appropriate experimental information. Perhaps the largest contribution that theory and computation can make in the development of new hydrogen storage materials is to reduce the number of choices (and thus reduce the required development time) that researchers must investigate. Only through a multiscale approach, such as the one described above, may we expect predictions accurate enough to be useful in materials development. Examples of research areas for theory and computation are outlined in the sections that follow.

Computational tools are needed to understand the interaction of hydrogen with surfaces and determine how hydrogen diffuses and interacts with step edges. The sites that hydrogen atoms occupy in the bulk, the energy barriers for its diffusion, its effect on the electronic structure of the host, its interaction with lattice defects (such as vacancies, voids, impurities, grain boundaries, and dislocations), and the effect of temperature and pressure on hydrogen interaction — all of these elements are important for a comprehensive understanding of hydrogen storage in materials. Theory can help elucidate how the ionic and covalent bonding between hydrogen and metal atoms in light complex metal hydrides may be changed by alloying. Similarly, an understanding of the role of catalysts/dopants in altering the nature of hydrogen bonding in these hydrides may be provided by

theory and modeling. Computational modeling also may provide insights into the relationship of size and shape to the nature of hydrogen bonding and binding energies in nanostructured materials, and may thus help with the design of nanostructured versions of hydrides that may provide more efficient hydrogen storage capabilities.

Conclusion

Hydrogen storage is a key technology required for attaining a hydrogen-based economy. It represents the most challenging technical hurdle to reaching this goal. The storage capabilities of current technologies, such as gas and liquid hydrogen storage in containers or use of simple hydrides, are far from the requirements for viable onboard automotive storage. Simple, incremental improvements in these technologies will not allow researchers to meet the rigorous storage requirements. Understanding these chemical and physical processes will allow new, higher efficiency, recyclable hydrogen storage materials to be designed. Nanoscience has the potential to provide revolutionary new capabilities that will have a profound impact on hydrogen storage. Improvements in today's metal and complex hydrides may be achieved by careful design of two- and three-dimensional nanoarchitectures that include dopants and tailored voids to improve the weight percentages of stored hydrogen and provide control of the kinetics and thermodynamics of hydrogen storage/release. Carbon and non-carbon nanostructures have shown particular promise for the storage of molecular hydrogen. New insights into the mechanisms of hydrogen uptake and release in these materials are needed to design new functionalization strategies and architectures for improved hydrogen storage.

Fundamental studies of nanomaterials used in hydrogen storage will require the availability of new highly sensitive and selective analytical tools to match the scale requirements of these nanomaterials. The discovery of new hydrogen storage materials will require close coupling between experimental and computational research activities to elucidate the physical and chemical processes involved in hydrogen storage and release, while modeling and prediction of these processes are needed so that improved materials may be designed efficiently. ∎

Acknowledgments

References

1. J. Milliken, Office of Hydrogen, Fuels Cells and Infrastructure Technologies, U.S. Department of Energy, Private communication (April 16, 2003).
2. B. Bogdanovic and G. Sandrock, *MRS Bull.*, **27**, 712 (2002).
3. L. Schlapbach and A. Zuttel, *Nature*, **414**, 353 (2001).
4. A. Zuttel and S. Orimo, *MRS Bull.*, **27**, 705 (2002).
5. M. G., Nijkamp, J. E. Raaymakers, A. J. Van Dillen, and K. P. De Jong, *Appl. Phys.,* **A72**, 619 (2001).
6. http://hydpark.ca.sandia.gov
7. G. Sandrock, *J. Alloys Compd.*, **887**, 293 (1999).
8. W. Oelerich, T. Klassen, and R. Bormann, *J. Alloys Compd.,* **315**, 237 (2001).
9. R. Griessen and T. Riesterer, in *Hydrogen in Intermetallic Compounds I*, L. Schlapbach, Editor, p. 219, Springer, New York (1988).
10. G. Barkhordarian, T. Klassen, and R. Bormann, *Scr. Mater.,* **49**(3), 213 (2003).
11. B. Bogdanovic and M. Schwickardi, *J. Alloys Compd.,* **253**, 1 (1997).
12. V. P. Balema, K. W. Dennis, and V. K. Pecharsky, *Chem. Commun.,* **17**, 1655 (2000).
13. P. Chen, Z. Xiong, J. Z. Luo , J. Y. Lin, and K. L. Tan, *Nature*, **420**, 302 (2002).
14. A. Züttel, *Int. J. Hydrogen Energy,* **27**, 203 (2002).
15. W. B. Leung, *Phys. Lett.,* **56**, 425 (1976).
16. R. A. Beebe, *J. Am. Chem. Soc.,* **69**, 95 (1947).
17. C. Nützenadel, in *Science and Technology of Molecular Nanostructures*, H. Kuzmany, Editor, p. 462, American Institute of Physics, New York (1999).
18. Ch. Nützenadel, in *Sciences and Application of Nanotubes*, D. Tománek, and R. J. Enbody, Editors, p. 205, Kluwer Academic Publishing/Plenum Press, Dordrecht (2000).

About the Author

G. Sandí is a member of the Chemical Transformations Mechanisms Group at the Chemistry Division, Argonne National Laboratory, working on the development and characterization of novel materials for energy applications, including rechargeable lithium batteries (anodes and polymer electrolytes), catalytic membranes for hydrogen separation and purification, and hydrogen storage. She is also an Adjunct Associate Research Professor at the Center for Electrochemical Science and Engineering, Department of Chemical and Environmental Engineering, Illinois Institute of Technology. She can be reached at gsandi@anl.gov.