# GASSING UP *with* HYD

# ROGEN

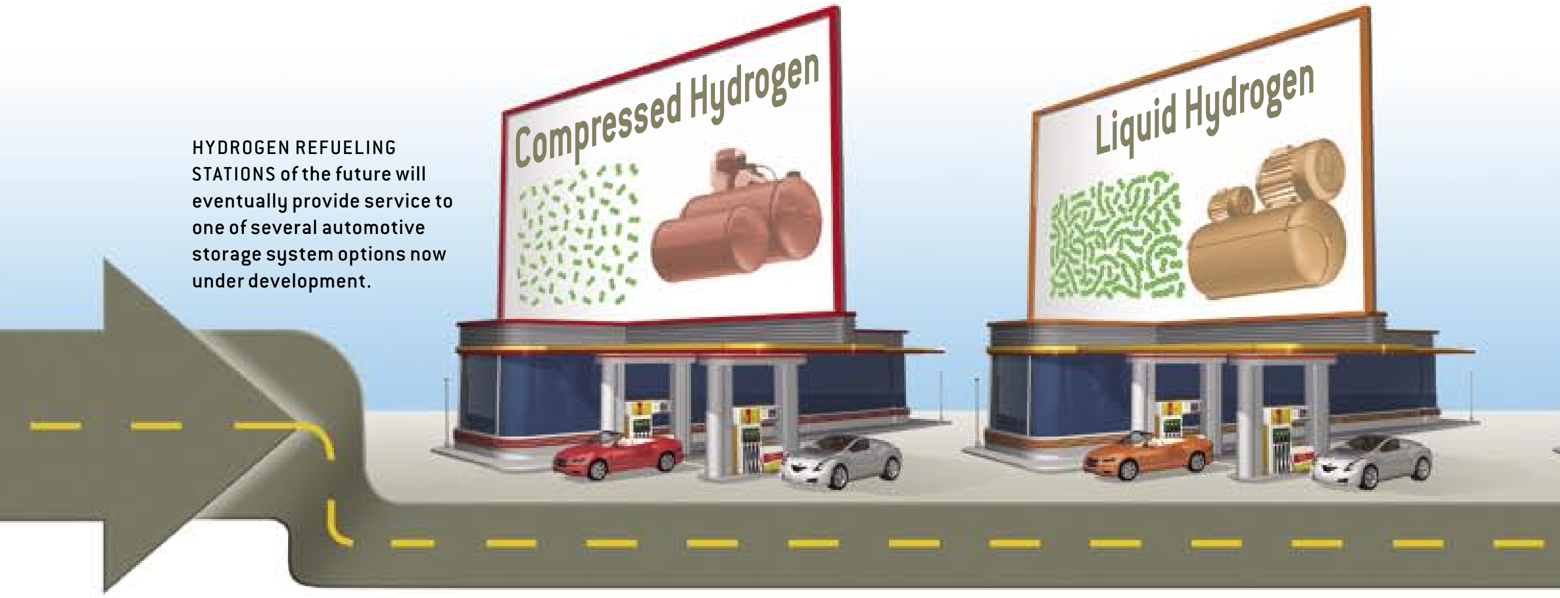
**Researchers are working on ways for fuel-cell vehicles to hold the hydrogen gas they need for long-distance travel**

By Sunita Satyapal, John Petrovic and George Thomas

On a late summer day in Paris in 1783, Jacques Charles did something astonishing. He soared 3,000 feet above the ground in a balloon of rubber-coated silk bags filled with lighter-than-air hydrogen gas. Terrified peasants destroyed the balloon soon after it returned to earth, but Charles had launched a quest that researchers two centuries later are still pursuing: to harness the power of hydrogen, the lightest element in the universe, for transportation.

Burned or used in fuel cells, hydrogen is an appealing option for powering future automotive vehicles for several reasons. Domestic industries can make it from a range of chemical feedstocks and energy sources (for instance, from renewable, nuclear and fossil-fuel sources), and the nontoxic gas could serve as a virtually pollution-free energy carrier for machines of many kinds. When it burns, it releases no carbon dioxide, a potent greenhouse gas. And if hydrogen is fed into a fuel-cell stack—a batterylike device that generates electricity from hydrogen and oxygen—it can propel an electric car or truck with only water and heat as by-products [see "On the Road to Fuel-Cell Cars," by Steven Ashley; Scientific American, March 2005]. Fuel-cell-powered vehicles could offer more than twice the efficiency of today's autos. Hydrogen could therefore help ease pressing environmental and societal problems, including air pollution and its health hazards, global climate change and dependence on foreign oil imports.

HYDROGEN GAS resists being crammed into the volume of a standard automotive gasoline tank.




HYDROGEN REFUELING STATIONS of the future will eventually provide service to one of several automotive storage system options now under development.

Yet barriers to gassing up cars with hydrogen are significant. Kilogram for kilogram, hydrogen contains three times the energy of gasoline, but today it is impossible to store hydrogen gas as compactly and simply as the conventional liquid fuel. One of the most challenging technical issues is how to efficiently and safely store enough hydrogen onboard to provide the driving range and performance that motorists demand. Researchers must find the "Goldilocks" storage solutions that are "just right." Storage devices should hold sufficient hydrogen to support today's minimum acceptable travel range—300 miles—on a tank of fuel in a volume of space that does not compromise passenger or luggage room. They should release it at the required flow rates for acceleration on the highway and operate at practical temperatures. They should be refilled or recharged in a few minutes and come with a competitive price tag. Current hydrogen storage technologies fall far short of these goals.

Researchers worldwide in the auto industry, government and academia are expending considerable effort to overcome these limitations. The International Energy Agency's Hydrogen Implementing Agreement, signed in 1977, is now the largest international group focusing on hydrogen storage, with more than 35 researchers from 13 countries. The International Partnership for the Hydrogen Economy, formed in 2003, now includes 17 governments committed to advancing hydrogen and fuel-cell technologies. And in 2005 the U.S. Department of Energy set up a National Hydrogen Storage Project with three Centers of Excellence and many industry, university and federal laboratory efforts in both basic and applied research. Last year alone this project provided more than $30 million to fund about 80 research projects.

## Infrastructural Hurdles

ONE OBSTACLE to the wide adoption of hydrogen fuel-cell cars and trucks is the sheer size of the problem. U.S. vehicles alone consume 383 million gallons of gasoline a day (about 140 billion gallons annually), which accounts for about two thirds of the total national oil consumption. More than half of that petroleum comes from overseas. Clearly, the nation would need to invest considerable capital to convert today's domestic auto industry to fuel-cell vehicle production and the nation's extensive gasoline refining and distribution network to one that handles vast quantities of hydrogen. The fuel-cell vehicles themselves would have to become cheap and durable enough to compete with current technology while offering equivalent performance. They also must address safety concerns and a lingering negative public perception—people still remember the 1937 *Hindenburg* airship tragedy and associate it with hydrogen, despite some credible evidence that the airship's flammable skin was the crucial factor in the ignition of the blaze.

Why is it so difficult to store enough hydrogen onboard a vehicle? At room temperature and atmospheric pressure (one atmosphere is about 14.5 pounds per square inch, or psi), hydrogen exists as a gas with an energy density about 1/3,000 that of liquid gasoline. A 20-gallon tank containing hydrogen gas at atmospheric pressure would propel a standard car only about 500 feet. So engineers must increase the density of stored hydrogen in any useful onboard hydrogen containment system.

A 300-mile minimum driving range is one of the principal operational aims of an industry-government effort—the FreedomCAR and Fuel Partnership—to develop advanced technology for future automobiles. Engineers employ a useful rule of thumb in making such calculations: a gallon of gasoline is equal, on an energy basis, to one kilogram (2.2 pounds) of

## Overview/*Hydrogen Storage*

- One of the biggest obstacles to future fuel-cell vehicles is how engineers will manage to stuff enough hydrogen onboard to provide the 300-mile minimum driving range that motorists demand.
- Typically hydrogen is stored in pressurized tanks as a highly compressed gas at ambient temperature, but the tanks do not hold enough gas. Liquid-hydrogen systems, which operate at cryogenic temperatures, also suffer from significant drawbacks.
- Several alternative high-density storage technologies are under development, but none is yet up to the challenge.

KENN BROWN (*preceding pages and these two pages*)

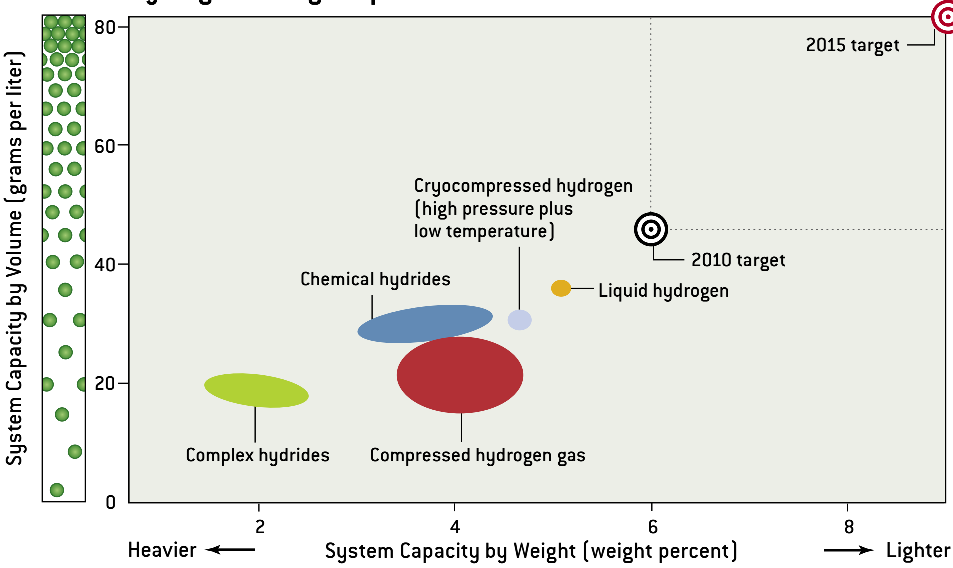

hydrogen. Whereas today's average automobile needs about 20 gallons of gasoline to travel at least 300 miles, the typical fuel-cell vehicle would need only about eight kilograms of hydrogen because of its greater operational efficiency. Depending on the vehicle type and size, some models would require less hydrogen to go that far, some more. Tests of about 60 hydrogen-fueled prototypes from several automakers have so far demonstrated driving ranges of 100 to 190 miles.

Aiming for a practical goal that could be achievable by 2010 (when some companies expect the first production fuel-cell cars to hit the road), researchers compare the performance of various storage technologies against the "6 weight percent" benchmark. That is, a fuel storage system in which 6 percent of its total weight is hydrogen. For a system weighing a total of 100 kilograms (a reasonable size for a vehicle), six kilograms would be stored hydrogen. Although 6 percent may not seem like much, achieving that level will be extremely tough; less than 2 percent is the best possible today—using storage materials that operate at relatively low pressures. Further, keeping the system's total volume to about that of a standard automotive gas-

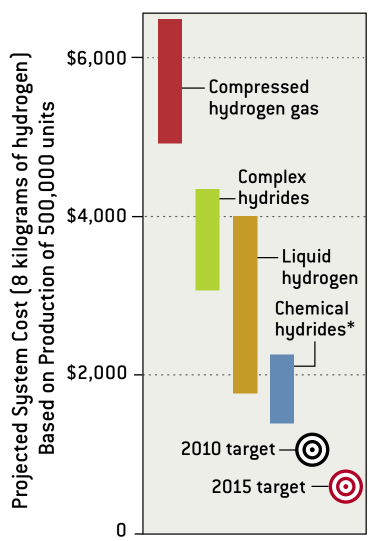
## The Storage Challenge

A hydrogen storage system must carry enough fuel for at least a 300-mile trip and also be compact and light enough to haul around in a car. A system that stored 6 percent by weight as hydrogen and 45 grams of hydrogen per liter by 2010 would likely meet the needs of first-generation fuel-cell vehicles (*black target on first graph*), but none of the current options can yet do this. Even better performance will be needed by 2015 for the wider range of vehicle types that will be available. Note that the values below include the equipment needed to run each system. Liquid hydrogen alone, for example, has a density of 71 grams per liter, but when the tank and ancillary components are included, the volume capacity falls to just under 40 grams per liter. Because hydrogen adsorbents [*see box on page 87*] are still at an early stage of development, capacity and cost data are not yet available.

### Hydrogen Storage Capacities




### Estimated Costs



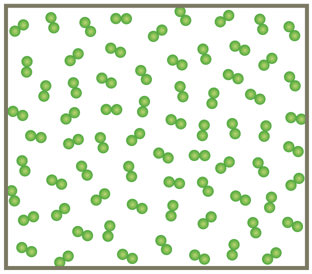

*Excludes recycling costs

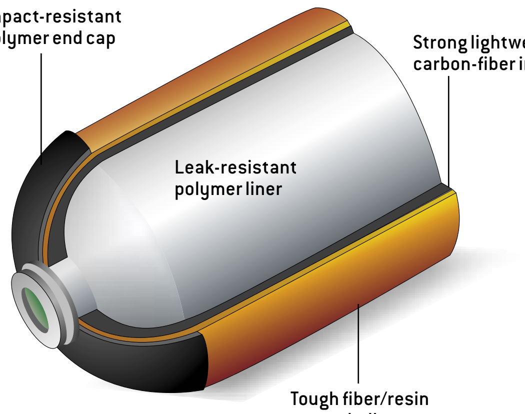
JEN CHRISTIANSEN

## COMPRESSED HYDROGEN

Lightweight but strong, high-pressure cylinders that resemble diving tanks store the compressed gas at 5,000 and 10,000 pounds per square inch.

STORAGE DENSITY




| Pros | Cons | Status |
|---|---|---|
| Low weight | High volume; requires high-pressure compression and refueling | Available |

oline tank will be even more difficult, given that much of its allotted space will be taken up by the tanks, valves, tubing, regulators, sensors, insulation and anything else that is required to hold the six kilograms of hydrogen. Finally, a useful system must release hydrogen at rates fast enough for the fuel-cell and electric motor combination to provide the power and acceleration that drivers expect.

## Containing Hydrogen

AT PRESENT, most of the several hundred prototype fuel-cell vehicles store hydrogen gas in high-pressure cylinders, similar to scuba tanks. Advanced filament-wound, carbon-fiber composite technology has yielded strong, lightweight tanks that can safely contain hydrogen at pressures of 5,000 psi (350 times atmospheric pressure) to 10,000 psi (700 times atmospheric pressure) [*see box above*]. Simply raising the pressure does not proportionally increase the hydrogen density, however. Even at 10,000 psi, the best achievable energy density with current high-pressure tanks (39 grams per liter) is about 15 percent of the energy content of gasoline in the same given volume. Today's high-pressure tanks can contain only about 3.5 to 4.5 percent of hydrogen by weight. Ford recently introduced a prototype "crossover SUV" called Edge that is powered by a combination plug-in hybrid/fuel-cell system that stores 4.5 kilograms of hydrogen fuel in a 5,000-psi tank to achieve a total maximum range of 200 miles.

High-pressure tanks would be acceptable in certain transportation applications, such as transit buses and other large vehicles that have the physical size necessary to accommodate storage for sufficient hydrogen, but it would be difficult to manage in cars. Also, the current cost of such tanks is 10 or more times higher than what is competitive for autos.

Liquefying stored hydrogen can improve its energy density, packing the most hydrogen into a given volume of any existing option. Like any gas, hydrogen that is cooled sufficiently condenses into a liquid, which at atmospheric pressure occurs around –253 degrees Celsius. Liquid hydrogen exhibits a density of 71 grams per liter, or about 30 percent of the energy density of gasoline. The hydrogen weight densities achievable by these systems depend on the containment and insulation equipment they use [*see box on opposite page*].

Liquefied hydrogen has important drawbacks, though. First, its very low boiling point necessitates cryogenic equipment and special precautions for safe handling. In addition, because it operates at low temperature, the containers have to be insulated extremely well. Finally, liquefying hydrogen takes more energy than compressing the gas to high pressures. This requirement drives up the cost of the fuel and reduces the overall energy efficiency of the cryocooling process.

Nevertheless, one carmaker is pushing this technology onto the road. BMW plans to introduce a vehicle this year called Hydrogen 7, which will incorporate an internal-combustion engine capable of running on either gasoline (for 300 miles) or on liquid hydrogen for 125 miles. Hydrogen 7 will be sold on a limited basis to selected customers in the U.S. and other countries with local access to hydrogen refueling stations.

## Chemical Compaction

SEARCHING FOR promising ways to raise energy density, scientists may be able to take advantage of the chemistry of hydrogen itself. In their pure gas and liquid phases, hydrogen molecules contain two bound atoms each. But when hydrogen atoms are chemically bound to certain other elements, they

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MELISSA THOMAS; QUANTUM TECHNOLOGIES (*cylinder*) can be packed even closer together than in liquid hydrogen. The principal aim of hydrogen storage research now is finding the materials that can pull off this trick.

Some researchers are focusing on a class of substances called reversible metal hydrides, which were discovered by accident in 1969 at the Philips Eindhoven Labs in the Netherlands. Investigators found that a samarium-cobalt alloy exposed to pressurized hydrogen gas would absorb hydrogen, somewhat like a sponge soaks up water. When the pressure was then removed, the hydrogen within the alloy reemerged; in other words, the process was reversible.

Intensive research followed this discovery. In the U.S., scientists James Reilly of Brookhaven National Laboratory and Gary Sandrock of Inco Research and Development Center in Suffern, N.Y., pioneered the development of hydride alloys with finely tuned hydrogen absorption properties. This early work formed the basis for today's widely used nickel–metal hydride batteries. The density of hydrogen in these alloys can be very high: 150 percent more than liquid hydrogen, because the hydrogen atoms are constrained between the metal atoms in their crystal lattices [*see top box on next page*].

Many properties of metal hydrides are well suited to automobiles. Densities surpassing that of liquid hydrogen can be achieved at relatively low pressures, in the range of 10 to 100 times atmospheric pressure. Metal hydrides are also inherently stable, so they require no extra energy to maintain storage, although heat is required to release the stored gas. But their Achilles' heel is mass. They weigh too much for practical onboard storage. Metal hydride researchers have so far attained a maximum hydrogen capacity of 2 percent of the total material weight (2 weight percent). This level translates into a 1,000-pound hydrogen storage system (for a 300-mile driving range), which is clearly too heavy for today's 3,000-pound car.

Metal hydride studies currently concentrate on materials with inherently high hydrogen content, which researchers then modify to meet the hydrogen storage system requirements of operating temperatures in the neighborhood of 100 degrees C, pressures from 10 to 100 atmospheres and delivery rates sufficient to support rapid vehicle acceleration. In many cases, materials that contain useful proportions of hydrogen are a bit too stable in that they require substantially higher temperatures to release the hydrogen. Magnesium, for example, forms magnesium hydride with 7.6 weight percent hydrogen but must be heated to above 300 degrees C for release to occur. If a practical system is to rely on waste heat from a fuel-cell stack (about 80 degrees C) to serve as the "switch" to liberate hydrogen from a metal hydride, then the trigger temperature must be lower.

## Destabilized Hydrides

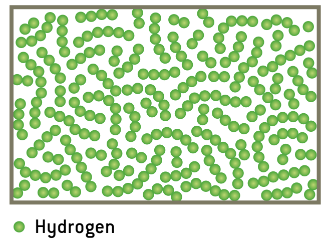
CHEMISTS John J. Vajo and Gregory L. Olson of HRL Laboratories in Malibu, Calif., as well as researchers elsewhere are exploring a clever approach to overcoming the temperature problem. Their "destabilized hydrides" combine several substances to alter the reaction pathway so that the resulting compounds release the gas at lower temperatures.

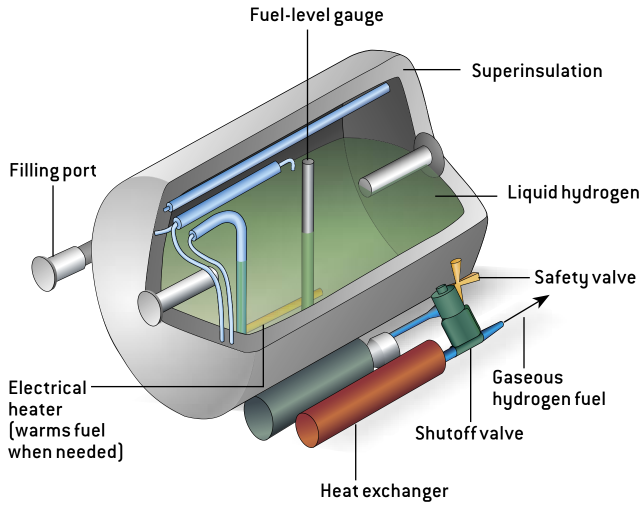
Destabilized hydrides are part of a class of hydrogen-containing materials called complex hydrides. Chemists long thought that many of these compounds were not optimal for refueling a vehicle, because they were irreversible—once the hydrogen was freed by decomposition of the compounds, the materials would require reprocessing to return them to a hydrogenated state. Chemists Borislav Bogdanovic and Manfred Schwickardi of the Max Planck Institute of Coal Research in Mülheim, Germany, however, stunned the hydride research community in 1996 when they demonstrated that the complex hydride sodium alanate becomes reversible when a small amount of titanium is added. This work triggered a flurry of activity during the past decade. HRL's lithium borohydride destabilized with magnesium hydride, for example, holds around 9 percent of hydrogen by weight reversibly and features a 200 degree C operating temperature. This improvement is notable, but its operating temperature is still too high and its hydrogen release rate too slow for automotive applications. Nevertheless, the work is promising.

Although current metal hydrides have limitations, many automakers see them as the most viable low-pressure approach in the near- to mid-term. Toyota and Honda engineers, for

## LIQUID HYDROGEN

Cooled to −253 degrees Celsius, hydrogen condenses and liquefies. Considerable amounts of insulation and ancillary equipment are required to maintain this low temperature.



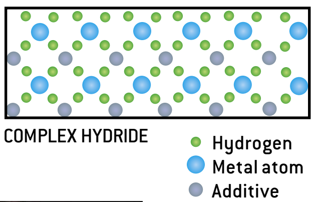

| Pros | Cons | Status |
| --- | --- | --- |
| Low weight and volume | Continual loss because of boil-off; energy penalty to liquefy hydrogen | Available |

MELISSA THOMAS; LINDE [*container*]

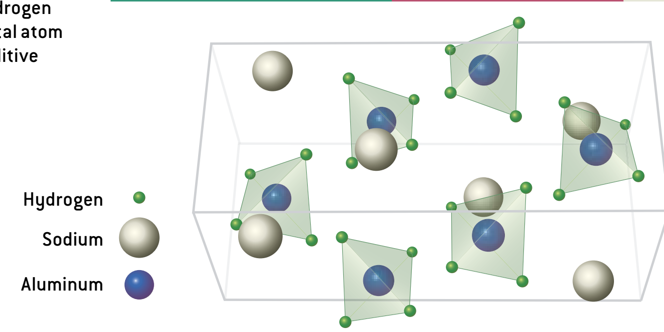
# COMPLEX HYDRIDES

Combining hydrogen chemically with metals and other substances produces metal hydrides (*below*) and complex hydrides (*right*). Heat liberates the fuel from these compounds when needed.

STORAGE DENSITY




| Pros | Cons | Status |
| --- | --- | --- |
| Low volume; potential for recharging onboard; potential for moderate to low-pressure operation | High weight; high temperatures required; insufficient fuel flow | In development |




SODIUM ALUMINUM HYDRIDE (example of complex hydride)

example, are planning a so-called hybrid approach in a system that combines a solid metal hydride with moderate pressure (significantly lower than 10,000 psi), which they predict could achieve a driving range of more than 300 miles. General Motors has teams of storage experts, including Scott Jorgensen, who are supporting research on a wide range of metal hydride systems worldwide (including in Russia, Canada and Singapore). GM is also collaborating with Sandia National Laboratories on a four-year, $10-million effort to produce a prototype complex metal hydride system.

## Hydrogen Carriers

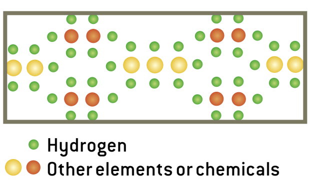
OTHER HYDROGEN STORAGE options have the potential to work well in cars, but they suffer a penalty in the refueling step. In general, these chemical hydride substances need industrial processing to reconstitute the spent material. The step requires offboard regeneration; that is, once hydrogen stored onboard a vehicle is released, a leftover by-product must be reclaimed at a service station and regenerated in a chemical plant [*see box below*].

More than 20 years ago Japanese researchers studied this approach using, for example, the decalin-naphthalene system. When decalin ($C_{10}H_{18}$) is heated, it converts chemically to naphthalene (a pungent-smelling compound with the formula $C_{10}H_8$) by changing the nature of its chemical bonds, which liberates five hydrogen molecules. Hydrogen gas thus bubbles out of the liquid decalin as it transforms into naphthalene. Exposing naphthalene to moderate hydrogen gas pressures reverses the process; it absorbs hydrogen and changes back to decalin (6.2 weight percent for the material alone). Research chemists Alan Cooper and Guido Pez of Air Products and Chemicals in Allentown, Pa., are investigating a similar technique using organic (hydrocarbon-based) liquids. Other scientists, including S. Thomas Autrey and his co-workers at the

# CHEMICAL HYDRIDES

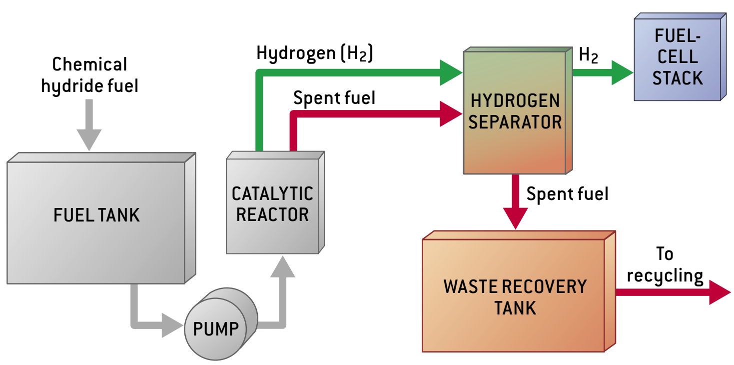
These hydrogen-containing compounds, which can be liquids or solids, release the fuel when they are heated and exposed to a catalyst (*photograph at right*). The flowchart (*far right*) shows how a representative chemical hydride must be recycled offboard to recharge it with hydrogen after use.

STORAGE DENSITY




*N*-ETHYL CARBAZOLE

| Pros | Cons | Status |
| --- | --- | --- |
| Low weight and volume; potentially a liquid | Materials need to be removed from the vehicle for regeneration; cost of offboard recycling and related infrastructure | In development |

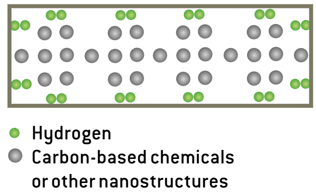


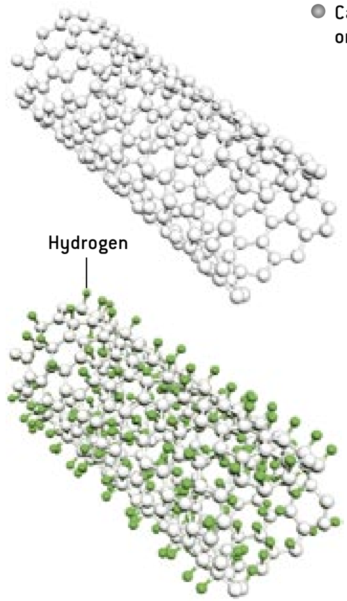

MELISSA THOMAS; ENERGY CONVERSION DEVICES (*researcher with hydride*); INSTITUTE FOR ENERGY TECHNOLOGY (*complex hydride*); AIR PRODUCTS AND CHEMICALS (*test tube*)

## HYDROGEN ADSORBENTS

Hydrogen atoms readily stick (adsorb) to certain "designer" materials.

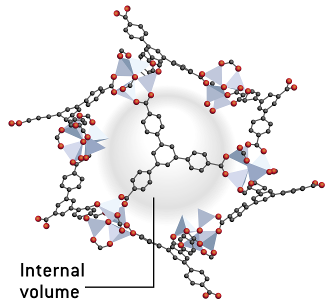
STORAGE DENSITY




CARBON NANOTUBES

Carbon nanotubes (*top left*) can hold onto hydrogen until needed (*bottom left*). Chemists designed the metal-organic framework molecule (*below*) so that hydrogen molecules could readily attach themselves to the structure.




METAL-ORGANIC FRAMEWORK

| Pros | Cons | Status |
|---|---|---|
| Low weight; reversible onboard; potential for room-temperature operation | High volume; low temperatures for operation may be required | Early R&D stage |

Pacific Northwest National Laboratory and chemistry professor Larry G. Sneddon of the University of Pennsylvania, are working on new liquid carriers, such as aminoboranes, that can store large amounts of hydrogen and release it at moderate temperatures.

## Designer Materials

YET ANOTHER APPROACH to the hydrogen storage problem centers on lightweight materials with very high surface areas to which hydrogen molecules stick (or adsorb) [*see box at right*]. As one might expect, the amount of hydrogen retained on any surface correlates with the material's surface area. Recent developments in nanoscale engineering have yielded a host of new high-surface-area materials, some with more than 5,000 square meters of surface area per gram of material. (This amount equates to about three acres of surface area within just a teaspoon of powder.) Carbon-based materials are particularly interesting because they are lightweight, can be low cost and can form a variety of nanosize structures: carbon nanotubes, nanohorns (hornlike tubes), fullerenes (ball-shaped molecules) and aerogels (ultraporous solids). One relatively cheap material, activated carbon, can store up to about 5 weight percent hydrogen.

These carbon structures all share a common limitation, however. Hydrogen molecules bond very weakly with the carbon atoms, which means that the high-surface-area materials must be kept at or near the temperature of liquid nitrogen, –196 degrees C. In contrast to hydride research, in which scientists are struggling to lower the hydrogen binding energy, carbon researchers are exploring ways to raise the binding energy by modifying the surfaces of materials or by adding metal dopants that may alter their properties. These investigators employ theoretical modeling of carbon structures to discover promising systems for further study.

Beyond the carbon-based approaches, another fascinating nanoscale engineering concept is a category of substances called metal-organic materials. A few years ago Omar Yaghi, then a chemistry professor at the University of Michigan at Ann Arbor and now at the University of California, Los Angeles, invented these so-called metal-organic frameworks, or MOFs. Yaghi and his co-workers showed that this new class of highly porous, crystalline materials could be produced by linking inorganic compounds together with organic "struts" [*see box at right*]. The resulting MOFs are synthetic compounds with elegant-looking structures and physical characteristics that can be controlled to provide various desired functions. These heterogeneous structures can have very large surface areas (as high as 5,500 square meters per gram), and researchers can tailor chemical sites on them for optimal binding to hydrogen. To date, investigators have demonstrated MOFs that exhibit hydrogen capacities of 7 weight percent at –196 degrees C. They continue to work on boosting this performance.

Although current progress on hydrogen storage methods is encouraging, finding the "just right" approach may take time, requiring sustained, innovative research and development efforts. Over the centuries, the basic promise—and challenge—of using hydrogen for transportation has remained fundamentally unchanged: Holding onto hydrogen in a practical, lightweight container allowed Jacques Charles to travel across the sky in his balloon during the last decades of the 18th century. Finding a similarly suitable container to store hydrogen in automobiles will permit people to travel across the globe in the coming decades of the 21st century without fouling the sky above. SA

MELISSA THOMAS; ANTON NIKITIN *Stanford Synchrotron Radiation Laboratory* (*nanotubes*); OMAR M. YAGHI *U.C.L.A.* (*metal-organic framework*)

### MORE TO EXPLORE

**The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs.** National Research Council and National Academy of Engineering. National Academies Press, 2004. Available at **www.nap.edu/catalog.php?record_id=10922**

**Hydrogen Program: 2006 Annual Merit Review Proceedings.** U.S. Department of Energy. Available at **www.hydrogen.energy.gov/annual_review06_proceedings.html**

United States Council for Automotive Research: **www.uscar.org**

International Energy Agency's Hydrogen Implementing Agreement: **www.ieahia.org**

International Partnership for the Hydrogen Economy: **www.iphe.net**