

Bottling the Hydrogen Genie

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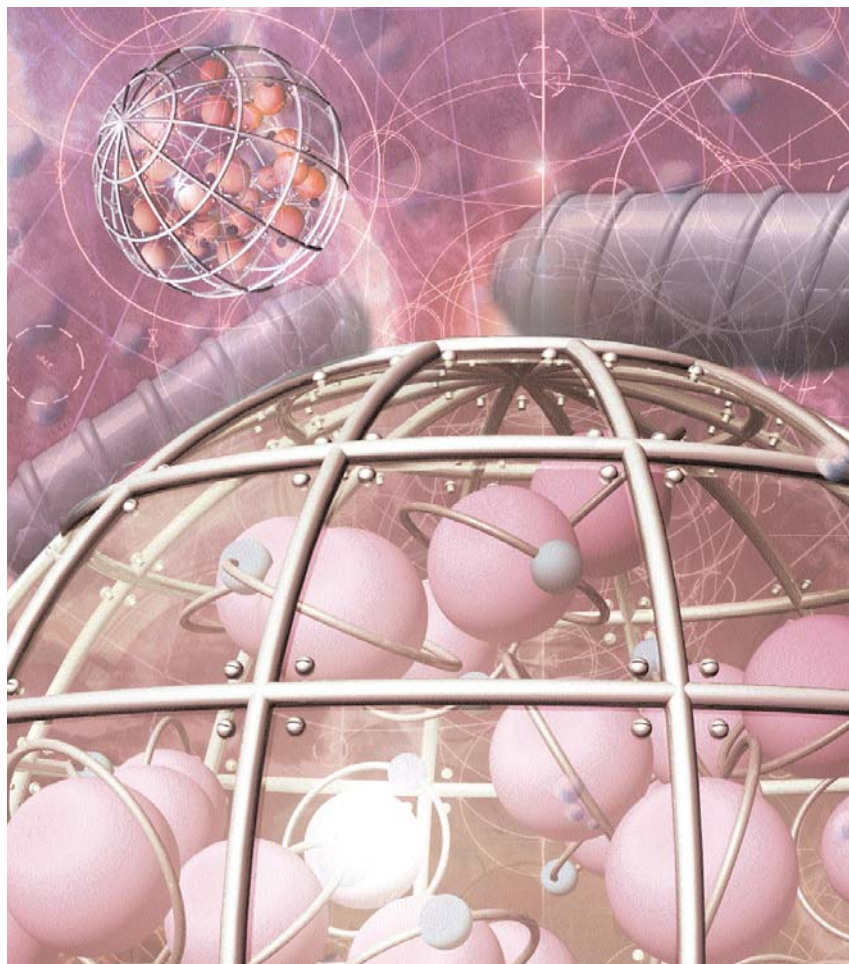
FEATURE

Hydrogen-powered vehicles will require better storage systems

As the dawn of a new century approached, a transportation revolution was brewing. Visionary inventors and small companies, inspired by new technologies and driven by public outcry for relief from urban pollution, set out to remake an entire industry. Their goal was nothing less ambitious than the creation of a completely new transportation infrastructure.

One by one, the competing technologies fell by the wayside. Commercial experiments with electric batteries and even steam came and went. The winner? A nuisance byproduct of kerosene refining—gasoline. Cheap, plentiful, and easy to transport and dispense, its fast, hot flame made the internal-combustion engine practical. The burgeoning automobile industry provided people with unprecedented independence and vanquished one of the most serious pollution problems of its day—horse manure, 1,200 tons of it daily in New York City alone. Gasoline has dominated transportation for more than a century since. Its environmental, political, and social consequences, good and ill, have shaped our culture.

As this new century unfolds, we stand on the threshold of another transportation revolution: the transformation from petroleum to clean hydrogen power. Success depends on three critical elements. First, we must develop a clean, efficient, cost-effective hydrogen-fueled power source. Although an internal-combustion engine can burn



hydrogen directly, the spotlight now focuses on electricity generated by proton-exchange-membrane (PEM) fuel cells. PEMs combine pure hydrogen fuel with oxygen from air with twice the energy efficiency of internal-combustion engines, and release only water vapor and heat as exhaust products. Second, the hydrogen revolution requires building an **infrastructure** to deliver hydrogen to the vehicle. And third, we need to find a means of **storing** useful quantities of hydrogen on-board vehicles.

Hydrogen vehicles can affect environmental cleanliness and energy independence only by entering the transportation mainstream; specialty and niche vehicles can make only incremental contributions at best. However, the uncompromised performance and reliability demanded by today's consumers mean that hydrogen fuel must offer the power, vehicle range, convenience, and affordability that people take for granted with gasoline. Only by more than satisfying the customer will hydrogen supplant gasoline.

VEHICULAR HYDROGEN-STORAGE SYSTEM REQUIREMENTS

METRIC	GOAL
Mass energy density	See Figure 1
Volumetric energy density	See Figure 1
Refueling time	<5 min
Durability (total distance maintaining 80% capacity)	150,000 miles
Hydrogen release rate (g/s/kW _{fuel cell})	0.025 (1.5 g/s at 60 kW)
H ₂ release temperature	<80 °C
Parasitic energy loss during H ₂ release	<5%

This places tough requirements on the vehicular hydrogen-storage system (Figure 1 and table). One kilogram of hydrogen provides about the same chemical energy (142 MJ) as 1 gal of gasoline (131 MJ). Factoring in the greater efficiency of PEMs, we need to store about 1 kg of hydrogen for every 2 gal of gasoline on a similar internal-combustion-engine vehicle. For U.S. transportation,



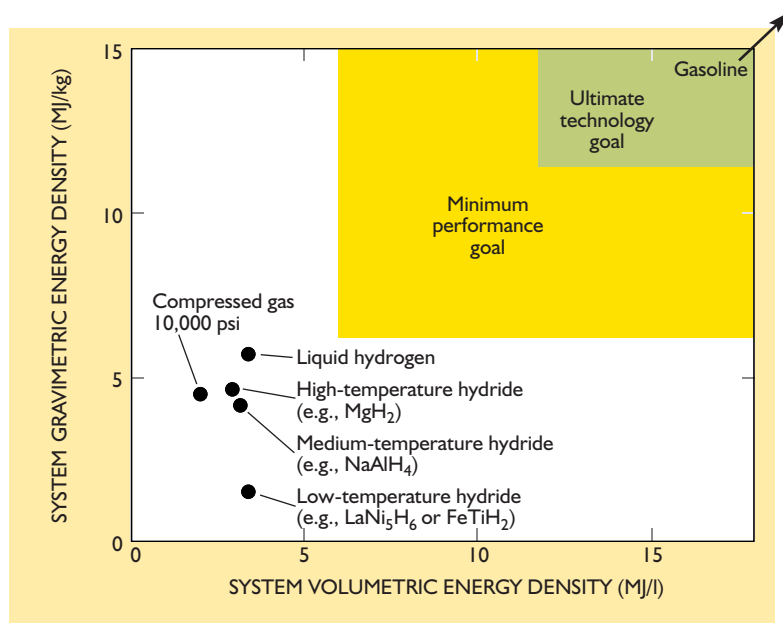
General Motors estimates that the entire on-board hydrogen fuel system—which includes the weight and volume of the hydrogen and its required fuel-delivery support such as the tank, pipes, pumps, and heat exchangers—must provide a volumetric energy density of at least 6 MJ/l and a gravimetric energy density of at least 6 MJ/kg energy equivalent of hydrogen to achieve significant market penetration. We will need about double those values to completely replace gasoline internal-combustion engines across the entire light-duty vehicle fleet.

These are system requirements; the hydrogen density, calculated from the weight and volume of the hydrogen alone (hydrogen basis) must be considerably higher to compensate for the weight and volume of the support hardware. Similarly, incorporating a hydride into an on-board storage system will substantially reduce its effective hydrogen density. There is no rule of thumb for the degree of reduction; it depends on the choice of storage medium and the required system design.

System safety is a given. Public perception and corporate citizenship will permit only an uncompromising attitude toward the safe implementation of a hydrogen economy. Fortunately, experts agree that hydrogen is inherently no more dangerous than gasoline, popular belief notwithstanding.

Storage challenges

Compressed gaseous storage is closest to technical feasibility and is fundamentally appealing because of its familiarity and conceptual simplicity. The major difficulty with compressed hydrogen is its volume. One kilogram of hydrogen stored in common laboratory gas cylinders at 2,200 psi occupies 91.2 l (1.6 MJ/l, hydrogen basis—the effective energy density in a storage sys-



tem will be substantially lower). For comparison, a mere 8.2 l of gasoline carries the same energy. Hydrogen tanks of 5,000 and 10,000 psi are being developed, but even at 10,000 psi, the volume of hydrogen is 27 l/kg (5.3 MJ/l, hydrogen basis).

At high pressures, deviations from the ideal gas law are large (Figure 2). The hydrogen gas density at 10,000 psi is only two-thirds that of an ideal gas. Doubling the pressure to 20,000 psi, if that were technically feasible, would increase the gas density by only about 50%. High-pressure tanks are complex structures containing multiple layers for hydrogen confinement, rupture strength, and impact resistance. Furthermore, the tank must be cylindrical or near-cylindrical in shape, which seriously limits the options for tank placement on a vehicle. High-pressure storage is most appealing for large vehicles, such as buses, which have more available space—on the roof, for example.

Demonstration fuel-cell vehicles have been built using liquid-hydrogen storage. Here, the volumetric situation is somewhat improved compared to compressed gas because liquid hydrogen occupies about 14 l/kg (10 MJ/l, hydrogen basis). But hydrogen vaporizes at $-253\text{ }^{\circ}\text{C}$, which necessitates an exotic superinsulated cryogenic tank. Inevitably, heat leaking into the tank will produce serious boil-off, and the tank will begin to empty itself in days in undriven vehicles. Liquid hydrogen seems best suited to fleet applications, where vehicles return nightly to a central station for refueling. Advanced tank designs may extend the boil-off period to perhaps a few weeks. Proposals that combine high-pressure and cryogenic capabilities in a single tank design could also mitigate boil-off.

There is a large energy penalty for hydrogen compression (equal to 10% of the energy content of the gas compressed) or liquefaction (30%). Although this affects the storage economics, it does not impact the on-board storage system because the penalty is paid before the hydrogen is delivered to the vehicle.

Figure 1. Existing hydrogen-storage systems using liquid, gas, or solid hydrides lack the gravimetric and volumetric energy density values to meet even the minimum performance goals required for vehicular transport.

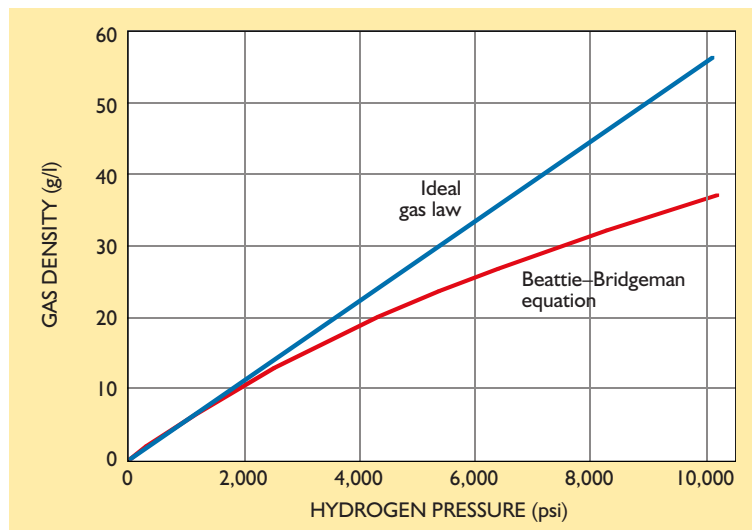


Figure 2. The Beattie-Bridgeman equation of state shows that higher gas density becomes increasingly difficult to attain with higher pressure.

Solid-hydride storage

Hydrogen can be chemically bound and stored as a solid compound. Solid-hydride storage materials release hydrogen gas under suitable conditions of temperature and hydrogen pressure (generally 2–5 bar) and, in some cases, in the presence of a further reactant. Solid hydrides can be loosely sorted into two groups:

- those for which the reverse hydriding reaction can be accomplished on-board the vehicle, generally by supplying hydrogen to the vehicle at a pressure higher than its working pressure, and
- those for which on-board rehydriding is impractical or impossible. In this case, refueling requires replacement of the storage medium itself, either by flush-and-fill or by exchanging the entire tank. The dehydrided material must then be recharged off-board; simply disposing of the spent material is unlikely to

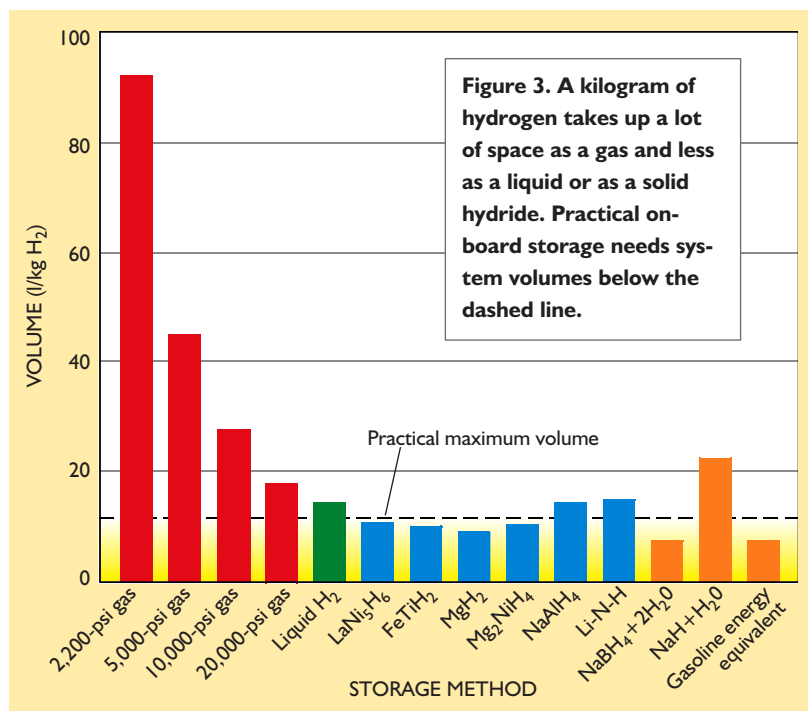


Figure 3. A kilogram of hydrogen takes up a lot of space as a gas and less as a liquid or as a solid hydride. Practical on-board storage needs system volumes below the dashed line.

be economically or environmentally acceptable for mainstream transportation applications.

Perhaps the best-known solid-storage media for hydrogen are the reversible metal hydrides, such as lanthanum nickel hydride (LaNi₅H₆). Among the more hydrogen-rich metal hydrides, volume is not the primary issue (Figure 3). In fact, many hydrides, including LaNi₅H₆, store more hydrogen per unit volume than does liquid hydrogen. Furthermore, at modest hydrogen pressures (a few bars), LaNi₅H₆ releases hydrogen at or near room temperature. Its hydriding kinetics are also acceptable, and laboratory quantities can be dehydrided and rehydrided in 5 to 10 min. The main challenge of metal hydrides is their weight. Because the hydrogen content of LaNi₅H₆ is only 1.4% by weight (wt%), storing 5 kg of hydrogen would require 360 kg of LaNi₅H₆.

Some reversible metal hydrides store larger specific masses of hydrogen. Magnesium hydride (MgH₂) contains 7.6 wt% hydrogen (10.8 MJ/kg, based on material weight only, excluding the support hardware), a value that approaches feasible energy density. Regrettably, MgH₂ suffers from a thermodynamic obstacle common to high-capacity metal hydrides: the hydrogen is too strongly bound (Figure 4). Its large enthalpy of hydride formation—the heat of formation (ΔH) = 37 MJ/kg H₂—has several important consequences. First, at the operating hydrogen pressure of the fuel cell (typically 2–5 bar), the hydrogen release temperature is commensurately high, nearly 300 °C. Second, because dehydriding is endothermic, the ΔH must be supplied as heat to release the hydrogen. This represents nearly a 30% parasitic energy loss incurred on-board the vehicle. Finally, all of that heat is released again during fueling. Rapid fueling, say in 5 min, requires roughly 1 MW of cooling power to extract the heat energy from MgH₂. What we need is a new, as-yet-undiscovered, light-metal hydride with a hydrogen capacity greater than that of MgH₂ but with ΔH similar to that of LaNi₅H₆.

The solid hydride NaAlH₄ (sodium alanate) lies intermediate between the low- and high-temperature metal hydrides. It decomposes on heating in two steps, first to sodium aluminum hydride (Na₃AlH₆) plus aluminum, and subsequently to sodium hydride (NaH) plus additional aluminum. (Further decomposition of the NaH requires impractically high temperatures for PEM fuel-cell applications.) The combined theoretical hydrogen capacity is 5.6 wt% (7.8 MJ/kg, material weight only). Incorporating titanium, or titanium and zirconium dopants, has yielded experimental dehydriding rates of 1 wt%/h at 110 and 160 °C for the first and second decomposition steps, respectively, but at the cost of lower hydrogen capacity (~4.5 wt%). Even relatively slow rehydriding requires high hydrogen pressure (~80 bar).

A new storage material based on transformations between a series of lithium–nitrogen–hydrogen compounds has been identified recently. Although interesting, this system still suffers from a relatively high ΔH

and a modest hydrogen capacity of only 6.5 wt%.

Nonreversible hydrides can store and release hydrogen. Sodium borohydride (NaBH_4) and NaH are examples of hydrolysis hydrides; adding water releases hydrogen and forms sodium metaborate (NaBO_2) or sodium hydroxide (NaOH). Although these materials generate considerable quantities of hydrogen, on-board system problems such as thermal control are significant, and off-board regeneration infrastructure and energy-efficiency considerations remain challenging.

Carbon nanomaterials

Since 1997, numerous reports in the technical literature and news releases have claimed that carbon nanofibers, nanotubes, and similar carbon nanostructures can sorb anywhere from 3 to 67 wt% hydrogen at room temperature. Most claims require hydrogen pressures of around 100 bar, but in a few cases, researchers claim high hydrogen capacity at ambient pressure. Although it is widely accepted that carbon nanotubes in 120-bar hydrogen gas can sorb up to 8 wt% hydrogen at cryogenic temperatures by simple physisorption, the binding energy is far too low to account for high hydrogen storage at room temperature. The amount of hydrogen physisorbed on activated carbon, for example, drops by an order of magnitude between 77 K and room temperature, to 0.7 wt% or less. Hydrogen capacities approaching 8 wt% (1 hydrogen atom/carbon atom) at room temperature would require a currently unknown carbon-hydrogen bonding mechanism intermediate in strength between physisorption and chemisorption.

Worldwide efforts to verify large hydrogen storage in nanostructured carbon have met with no real success. A few claims have been proven wrong (but nevertheless continue to be cited in the technical literature). Many “demonstrations” of hydrogen sorption rely on measurement of the drop in hydrogen pressure with time in a “leak-free” sample vessel. This technique appears simple but is deceptively vulnerable to error. Cooling of the hydrogen gas after pressurization can easily masquerade as sorption, and hydrogen is notorious for leaking. It cannot be overemphasized: there is no substitute for careful, deliberate research conducted using accurate techniques and with a full appreciation of the possible pitfalls.

It remains difficult to dismiss all such claims as spurious, and new, unverified claims continue to appear regularly. Hope persists that carbon nanomaterials might prove viable for hydrogen storage. Nevertheless, the early euphoria has largely given way to a more skeptical view of its prospects. For now, we have no independently verified evidence of technologically significant hydrogen sorption at room temperature.

Conclusion

The dawn of a hydrogen economy for mainstream vehicles may well depend on breakthrough research to find new storage materials or innovative storage concepts. To

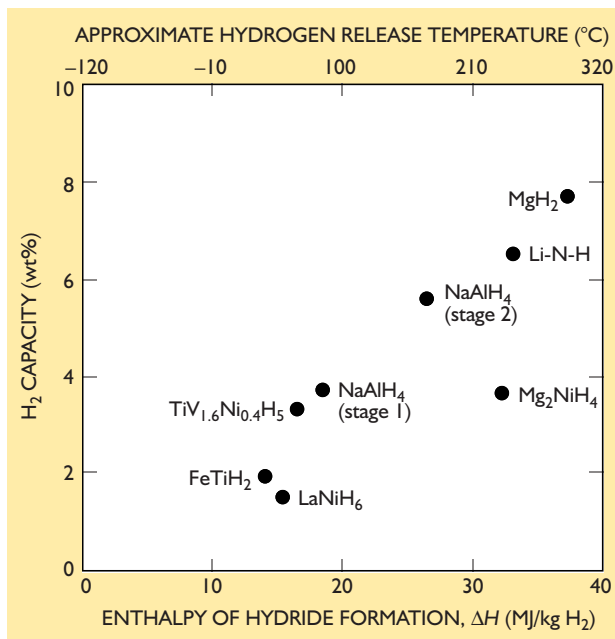


Figure 4. Unfortunately, the known reversible metal hydrides that store large specific masses of hydrogen also have high enthalpies of formation and require high temperatures to release the strongly bound hydrogen.

this end, the U.S. Department of Energy has issued what it calls a Grand Challenge for the research and development of hydrogen storage materials and technologies and has committed \$150 million to it over the next five years. Only by answering this challenge can hydrogen take its place as the transportation fuel of the future.

Further reading

Additional information about hydrogen storage technologies is available at <http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/storage.html>.

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B I O G R A P H Y

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