

# Hydrogen Storage Technologies: Present and Future

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*Storage Technologies: Status and Challenges*

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by

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## 1 Introduction

We describe herein our recent work for the US Department of Energy, Office of Transportation Technologies, in which we evaluated methods of hydrogen storage from the perspective of fuel cell powered vehicles. Given our goal of providing DOE with demonstration hardware within the next year and a half, we focussed on those technologies now available or predictably available soon. As we did, we encountered several developing technologies, some of which may hold promise.

The criteria for hydrogen storage aboard fuel cell powered vehicles differ from those for hydrogen storage aboard IC engine powered vehicles. IC engines generate waste heat at higher temperatures, and in greater amount, than do the fuel cells under consideration for transportation applications; this is the flip side of the relatively high efficiency of fuel cells. Thus, IC engines are more suited than are fuel cells to the generally endothermic demands of dehydriding.

The criteria for hydrogen storage for bulk transport of hydrogen/energy differ, too, from those for vehicular hydrogen storage. The cost, weight and bulk of hydrogen-producing process equipment penalizes any vehicle, whereas only the cost of such equipment is of consequence to a stationary facility.

From the perspective, then, of fuel cell powered vehicles, what are the criteria by which one evaluates hydrogen storage systems?

- *System volumetric density* - the weight of stored hydrogen divided by the volume of the hydrogen storage and regeneration systems ( $\text{kg}_{\text{HYDROGEN}}/\text{m}^3_{\text{SYSTEM}}$ )
- *System gravimetric density* - the weight of stored hydrogen divided by the weight of the storage and regeneration systems ( $\text{kg}_{\text{HYDROGEN}}/\text{kg}_{\text{SYSTEM}}$ )
- *Stored energy efficiency* - one minus the percentage of the stored hydrogen's high heating value (HHV) that must be expended to release it from storage
- *Regeneration temperature* - the temperature to which the storage medium must be raised in order that it release its hydrogen
- *System simplicity* - the minimization of numerous components or complicated controls; and the lack of a tricky or lengthy refueling process, or a messy startup or shutdown procedure
- *Other criteria* - response rate, cost, refueling time, and safety

Different transport sectors will rank the importance of these criteria differently. Fuel cells are being considered for such diverse applications as passenger cars, bus, and rail.

Figure 1 - Hydrogen Storage System Comparison: Reference Systems for Comparison to Hydrogen

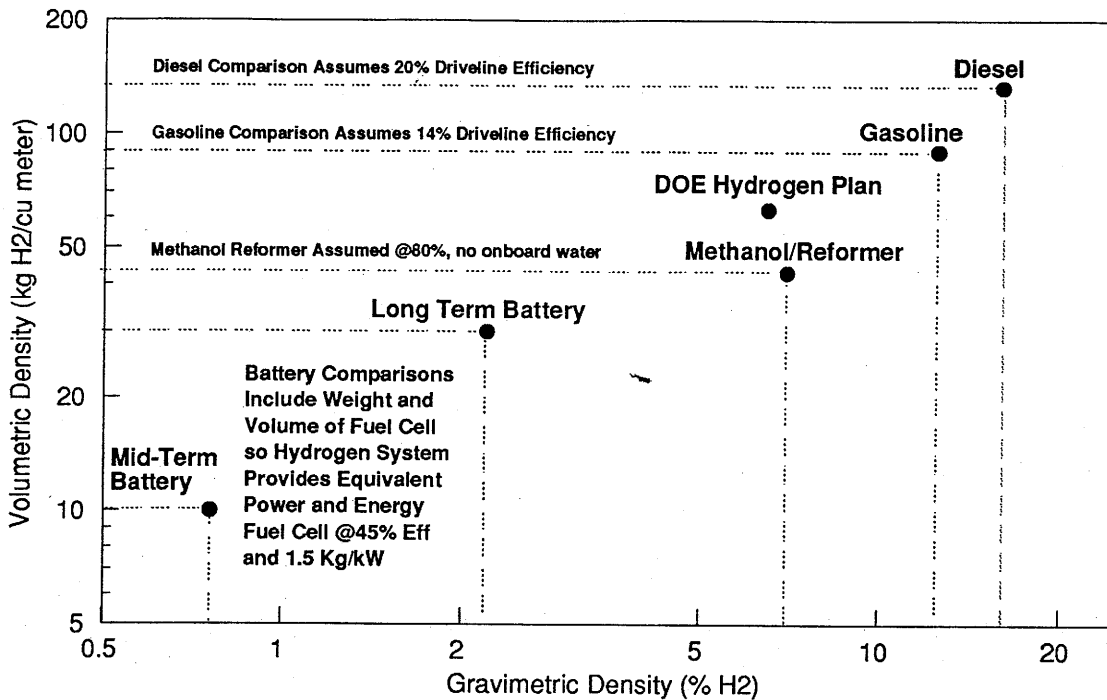


Figure 1 shows the tremendous difference in gravimetric density and volumetric density that exists between today's technologies (diesel and gasoline) and those technologies that are candidates to replace them. Note that even the DOE Hydrogen Plan does not propose to make hydrogen compete with diesel and gasoline on these bases. But hydrogen is expected to compare favorably to batteries, which represent the only competition to hydrogen for zero-emission vehicles.

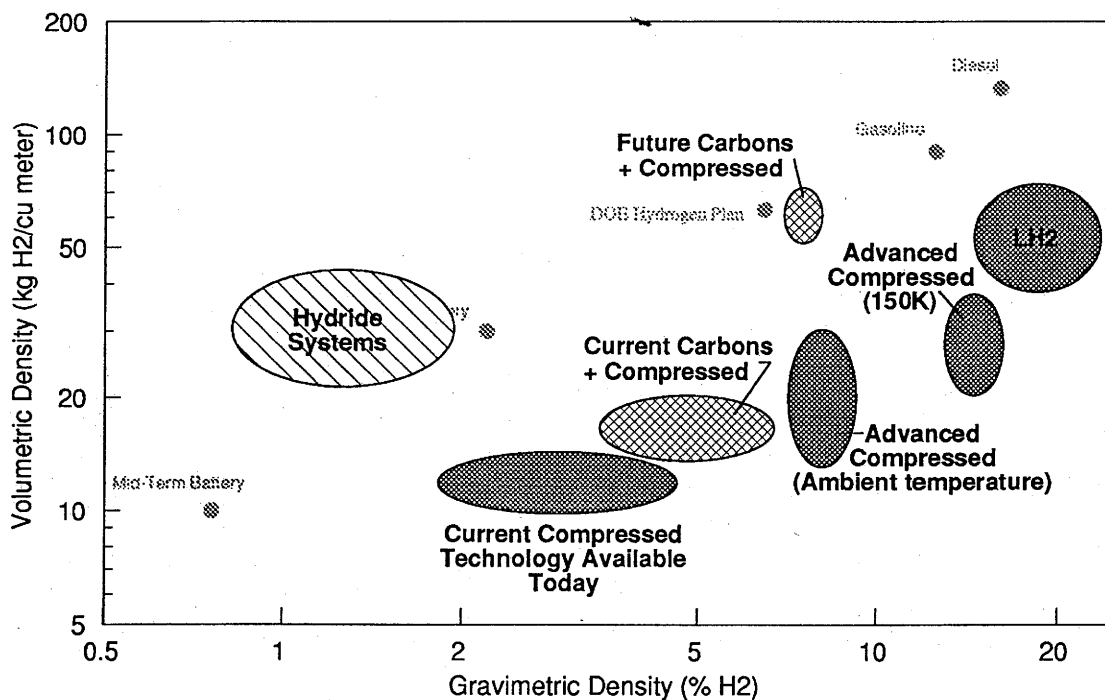
Figure 2 shows how several of the proposed hydrogen storage technologies compare to batteries, diesel/gasoline, and each other with respect to gravimetric and volumetric densities.

- A liquefied hydrogen, for example, has a higher gravimetric energy density than a diesel system, but takes up almost three times the volume for a given range.
- Today's lead-acid batteries, with 30 watt-hours/kg gravimetric energy density, do not even fit on these axes.
- Metal hydrides compare favorably to those batteries expected to be available by 2000 (e.g., sodium-sulfur); however, those batteries expected to be available in the next

century (e.g., lithium-polymer) will be just as compact as the metal hydrides and half as heavy.

- Compressed hydrogen gas using today's technology (aluminum tanks at 3000 psi) is as compact as the year-2000 battery, and weighs about 1/4 as much.
- Compressed hydrogen gas becomes more attractive if one uses advanced technologies for the pressure vessel, or cools the tank contents substantially, or both.

Figure 2 - Hydrogen Storage System Comparison: Summary of Current and Future Systems



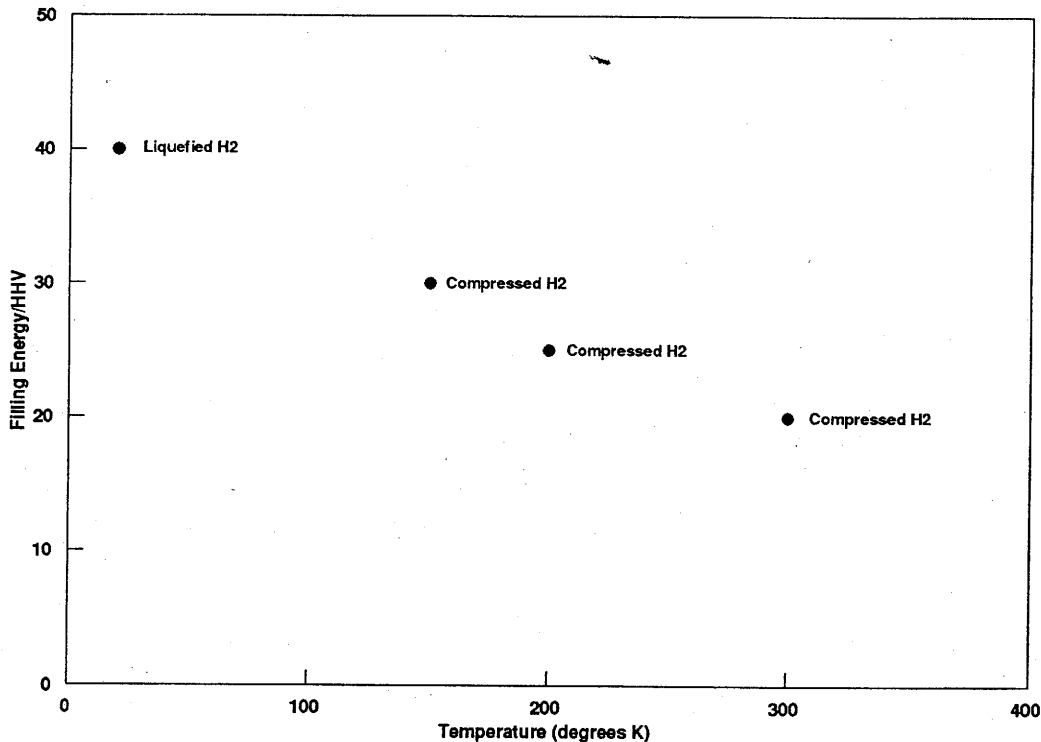
There are fundamentally two categories of hydrogen storage systems: those that contain hydrogen, and only hydrogen, within a vessel; and those that contain hydrogen associated with some other substance within a vessel.

## 2 Hydrogen-Only Storage Systems

One generally thinks of just two hydrogen-only storage systems: liquefied and compressed. One can actually consider a continuum of such systems, as indicated by Figure 3.

The characteristic that distinguishes all hydrogen-only storage systems from almost all bonded-hydrogen systems is that for the former, energy must be provided to the system when the tank is filled; rather than when the tank is discharged, as is the case for bonded-hydrogen systems. This filling energy comes from the infrastructure, and need not be carried on board the vehicle; this is no small advantage.

Figure 3 - Continuum of Hydrogen-Only Storage Systems



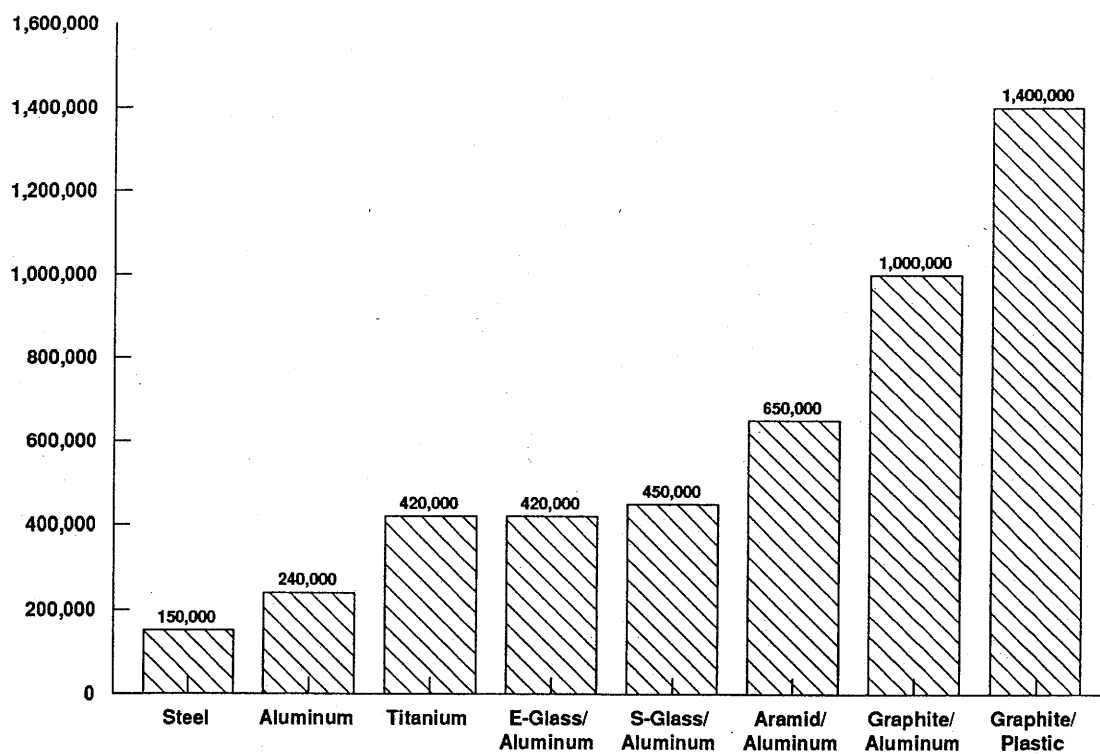
However, because no great effort is required to release hydrogen from such storage, there is concern over uncontrolled release due to vessel rupture, whether spontaneous or aggravated by vehicular mishap. This problem may be more perceived than real, but the nuclear industry can attest that empirically proven safety is no match for publicly perceived danger.

Liquefied hydrogen, favored by NASA for bulk storage and by industry for bulk transport, becomes less attractive as tanks get smaller and the surface-to-volume ratio gets large. Lockup time, or the time it takes a garaged cryogenically-fueled vehicle to reach its maximum design pressure, is short; a tank designed to hold liquefied natural gas for ten days will hold liquefied hydrogen for less than two.

The lockup problem could be solved by on-board magnetic refrigeration, but that would be costly. Magnetic liquefaction could reduce the high energy demand of liquefaction. Refueling and handling difficulties associated with the extreme temperature can be made more tractable through better component and system design.

The weight of compressed vapor systems can be reduced greatly by using advanced materials, such as carbon-graphite composite, for the storage cylinders. Figure 4 shows that the performance factor (*burst pressure • internal volume / weight*) for advanced designs, can reach nine times that of steel tanks and almost six times that of aluminum tanks.

**Figure 4 - Comparison of Tank Performance Factors for Various Materials/Technologies**



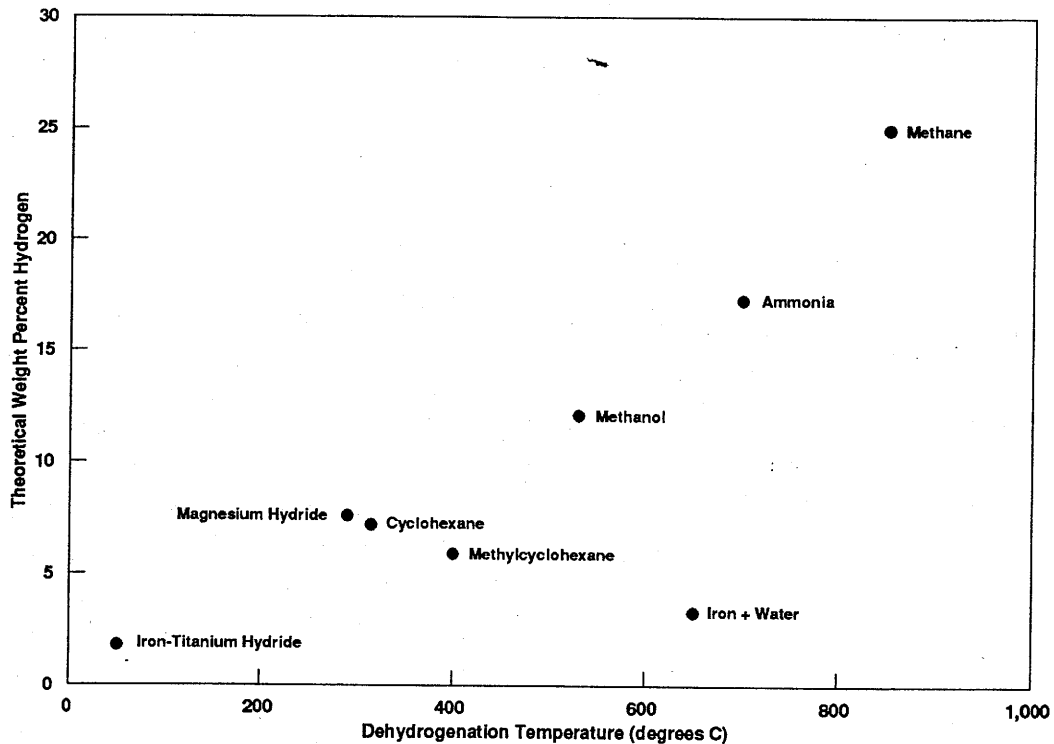
Furthermore, cold compressed vapor can easily have twice the density of ambient compressed vapor. It does so, however, at the cost of additional equipment at the refueling station: a multi-stage, intercooled compressor, a cascaded refrigeration system, and multiple high-pressure heat exchangers. Also, the vehicle tank must be both vacuum-insulated and capable of containing high-pressure.

### 3 Bonded-Hydrogen Storage Systems

Hydrogen atoms, or even hydrogen molecules, will bond to almost any element under appropriate conditions. Several hydrogen-containing compounds considered potential sources of hydrogen aboard vehicles are represented in Figure 5, which demonstrates that one price of high hydrogen weight percentage in a bonded-hydrogen storage system is high dissociation temperature. There are other prices, such as irreversibility and process complexity, to be paid for reforming methane or ammonia on board vehicles.

Let us look further at some of the technologies currently under development.

Figure 5 - The Price of High Hydrogen Weight Percentage is High Dissociation Temperature



#### 3.1 Metal Hydrides

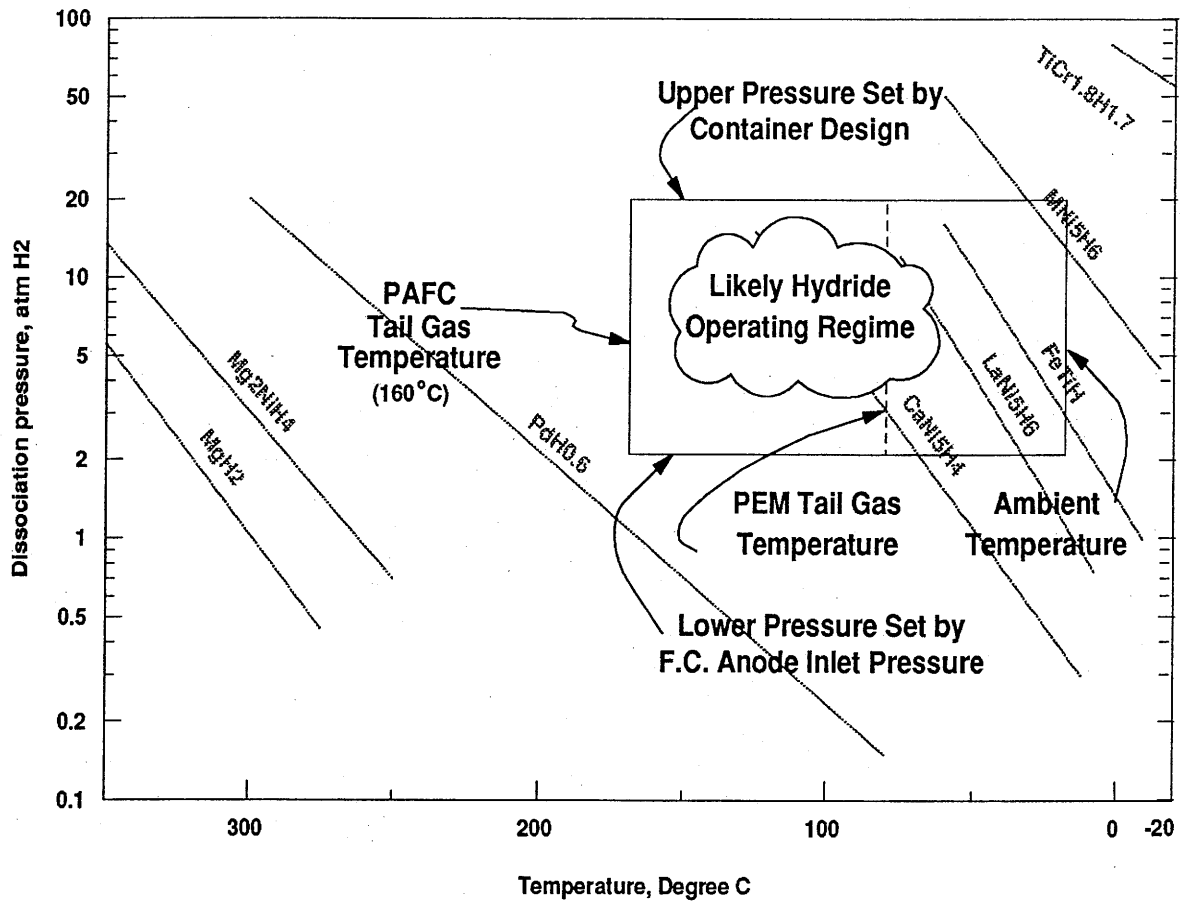
In theory, metal hydrides can store hydrogen at volumetric densities greater than that of liquid hydrogen. The volumetric densities of actual metal hydride storage systems, however, are somewhat lower, as

- a metal hydride system is burdened by a pressure vessel, by a heating system, and perhaps by thermal insulation; and
- not all of the hydrogen bound up in such a system is readily recoverable.

Figure 6 shows Van't Hoff plots for several of the commonly studied metal hydrides. These show the combinations of temperature and pressure at which the metal hydride is in equilibrium with hydrogen and the associated pure metal. These plots illustrate the conditions for which

- increasing the hydrogen pressure, or decreasing the metal/alloy temperature, favors the hydriding reaction (absorption of hydrogen); and
- decreasing the hydrogen pressure, or increasing the metal/alloy temperature, favors the de-hydriding reaction (release of hydrogen).

Figure 6 - Van't Hoff Plots for Various Metal Hydrides





Notice that these lines (called isochores) are gathered into two groupings:

- high-temperature hydrides, characterized by ionic bonds and by low molecular weights of the metals (which necessarily correspond to high hydrogen weight percentages); and
- low-temperature hydrides, characterized by covalent bonds and by high molecular weights of the metals (which necessarily correspond to low hydrogen weight percentages).

Were someone to succeed in creating intermediate-temperature hydrides, it is reasonable to suppose that they would have partly ionic, partly covalent bonds; and intermediate hydrogen weight percentages. That is to say, there is probably no metal hydride with high hydrogen weight percentage, low bonding energy, and low dissociation temperature waiting to be discovered. But hope springs eternal.

Only a few isochores on Figure 6 pass through the usable range of pressure and temperature, defined by

- pressures above atmospheric (to prevent oxidation due to inleakage), and
- temperatures within the range of waste heat available from either phosphoric acid or solid polymer electrolyte fuel cells;

all of these are low-temperature hydrides. Figure 7 presents the inefficiencies attendant to using some of the stored hydrogen to provide the dehydrating energy for high-temperature metal hydrides.

Internal combustion engines, with higher waste heat temperatures than fuel cells, could use the high-temperature hydrides, were weight the only problem. However, metal hydrides have other problems:

- Some are pyrophoric (especially high-temperature hydrides); others merely oxidize when exposed to air.
- Most are subject to irreversible poisoning by water, oxygen, and other common contaminants, or to segregation of species near the surface.
- Kinetics are often poor, especially at the interface, resulting in lengthy charging and discharging cycles.

Some of these secondary problems may be mitigated by creating nanocrystalline (crystal sizes  $<500 \text{ \AA}$ ) metal hydrides. Still, most metal hydrides under commercial development are low-temperature metal hydrides (see Table 1). However, the primary problems of high weight (plaguing all metal hydrides) and high cost (true of most metal hydrides) are inherent.

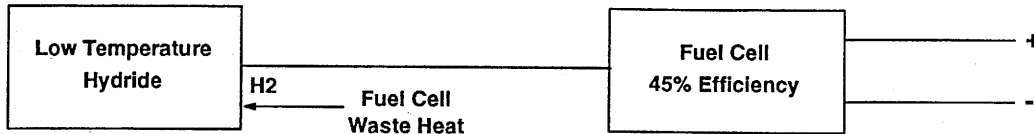
**Table 1 - Most Commercially Developing Metal Hydrides Are Low-Temperature Hydrides**

| Metal Hydride   | Gravimetric Density | Developer(s)   |
|---|---------------------|----------------|
| $\text{LaNi}_{4.6}\text{Al}_{0.4}\text{H}_{5.5}$  | 1.3%                | MITI; Ergenics |
| $\text{TiFeH}_{1.9}$  | 1.8%                | Billings       |
| $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{V}_{0.45}\text{Fe}_{0.10}\text{Cr}_{0.05}\text{H}_{3.4}$ | 2.1%                | Daimler        |

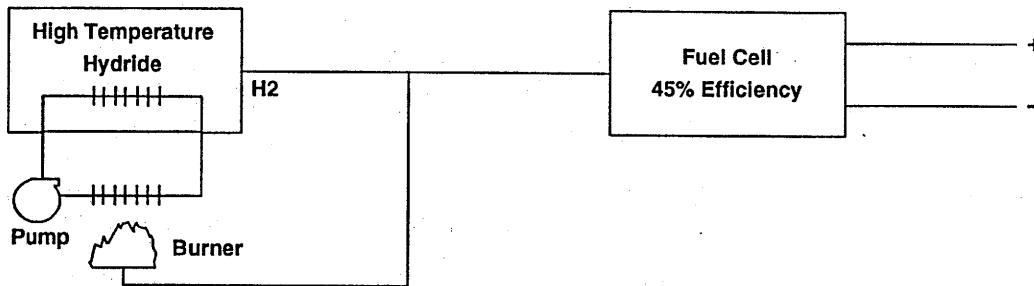
**Figure 7 - At Least 30% of the Hydrogen Stored as a High-Temperature Hydride Must Be Spent to Release the Hydrogen**

Percentage of Hydrogen Available for Useful Power

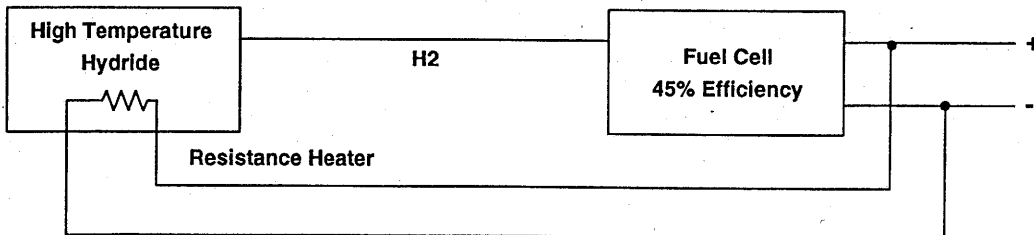
100%



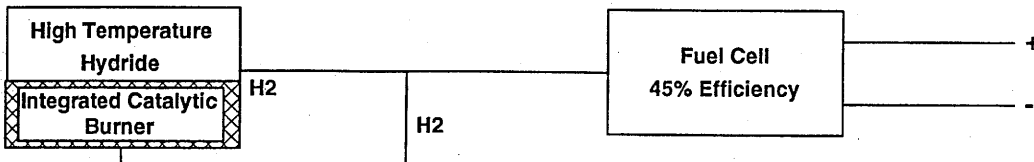
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46%



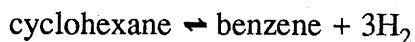
70%



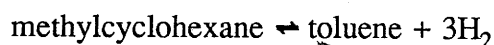
### 3.2 Liquid Hydrides

Certain hydrocarbons (naphthenes) can be reversibly transformed into other hydrocarbons (aromatics) with the same number of carbon atoms and a smaller number of hydrogen atoms. These naphthenes are variously referred to as recyclable liquid chemical carriers or liquid hydrides (something of a misnomer).

For example,



and



The first reaction has a slightly greater hydrogen weight percentage, but benzene is more carcinogenic than toluene, so the second reaction has received more attention.

The hydrogen weight storage density of methylcyclohexane is 5.9%, far better than those of most metal hydrides currently under development.

Releasing the hydrogen from liquid hydrides is not simply a matter of heating them or reducing the hydrogen overpressure. Cracking methylcyclohexane requires 10 atmospheres, 400 C, a platinum/rhenium catalyst, and 28% of the higher heating value of the released hydrogen. Therefore, required on-board equipment includes a catalytic reactor, a catalyst heater, a vaporizer, pumps, an air-cooled condenser, a gas-liquid separator, and a partitioned fuel tank.

A Swiss experiment, reported in 1984, used a diesel engine converted to spark-ignition to burn hydrogen cracked from methylcyclohexane on board a 17-ton truck. Their engine developed 197 hp, and the total weight of the cracking apparatus was 3500 pounds. It was determined that the exhaust heat was not enough to generate the hydrogen. We found no further references to Swiss experiments with methylcyclohexane in the literature.

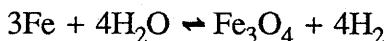
This technology may have applications in bulk transport. One need not transport the cracking equipment; it can remain at the receiving end, and it need not be built to withstand the rigors of perpetual transportation. On the other hand, if one uses stationary equipment to generate hydrogen for subsequent transport, there is no engine waste heat available at the site of the cracking process to apply to the cracking process. Therefore, overall energy efficiency suffers.

However unsuited liquid hydrides might be to vehicular IC engines, they are even less suited to fuel cell powered vehicles, as

- an engine has at least some waste heat above 400 C; a PAFC or a PEM fuel cell has none;
- the hydrogen will be accompanied by at least some toluene; an engine can tolerate this, but a fuel cell cannot; and
- an engine can cold-start with toluene as the fuel, until its waste heat is available to do most of the cracking; a fuel cell needs a full-sized heater for cracking both during startup and thereafter.

### 3.3 Iron and Water

H-Power has proposed to transport hydrogen in the form of water and to reduce that water to hydrogen by oxidizing iron, by means of the following reversible reaction:



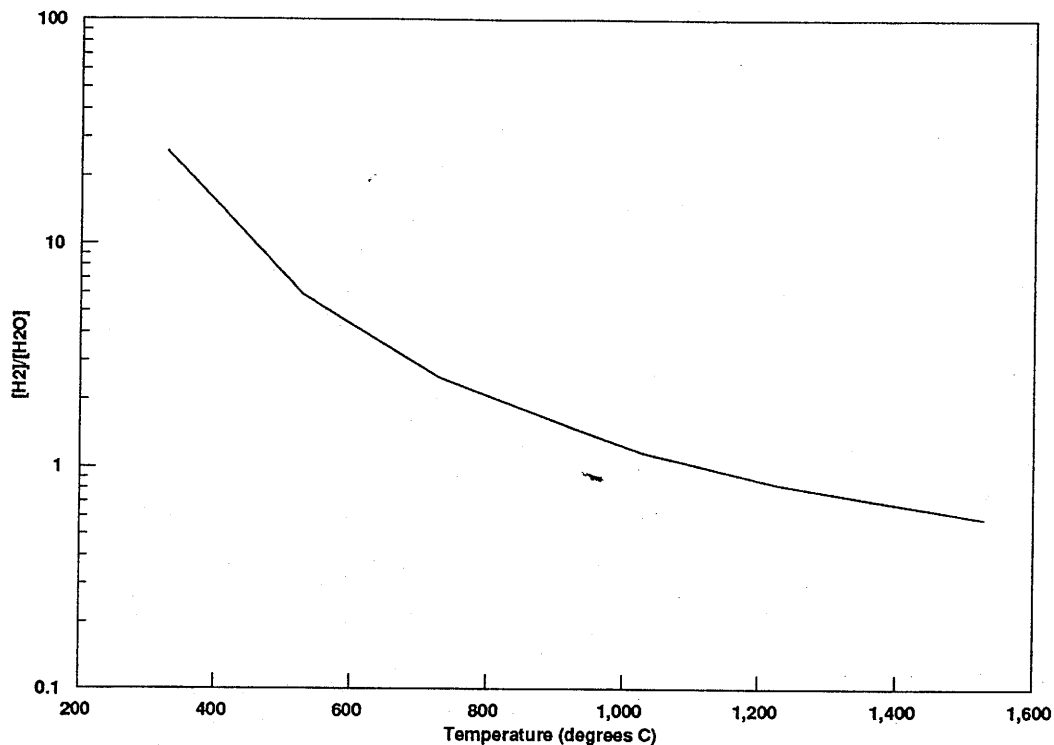
The forward reaction is familiar to all; indeed, it explains the appearance of my car. The reverse process is known to take place in blast furnaces, between magnetite ( $\text{Fe}_3\text{O}_4$ ) and the hydrogen in water gas ( $\text{H}_2 + \text{CO}$ ), which in turn comes from the reduction by coke of water vapor in the combustion air.

Neither reaction proceeds to completion. Figure 8 shows the ratio of the hydrogen concentration to the concentration of steam (at these temperatures water isn't liquid) as a function of temperature. Notice that the forward (hydrogen-generating) reaction is favored at temperatures below 1100 C (which is well beyond red hot), and that the reverse reaction cannot be called complete until well above the melting temperature of iron (1536 C).

Could one supply steam to this reaction from the cathode tail gas leaving the fuel cell? If the fuel cell is collocated with the reactor (as it is on a vehicle, but as it is not in a pipeline-feeding situation) one can do this, but this tail gas also has nitrogen. If you don't separate the nitrogen from the steam, it will be a diluent of ever-increasing concentration, eventually shutting down the fuel cell.

Could one separate the nitrogen from the steam with a regenerative condenser/boiler arrangement? Yes, but this equipment will be neither small, nor simple, nor inexpensive. Also, steam from the fuel cell is not available during startup.

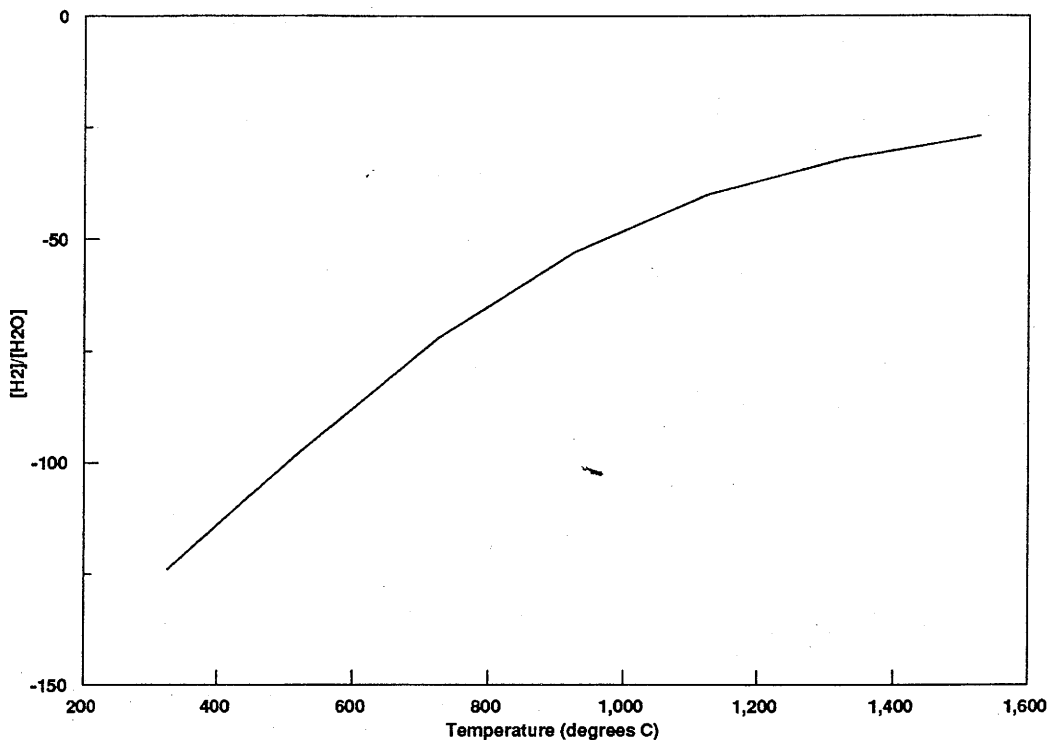
Figure 8 - The Reaction's Degree of Completion Depends on Temperature



The forward reaction is exothermic at all temperatures of interest aboard a vehicle, as shown by Figure 9. This would seem to be an advantage over both metal hydrides and liquid hydrides, the extraction of hydrogen from which is endothermic. However, the heat given off by generating each pound of hydrogen is not enough to boil and superheat the nine pounds of water required for each pound of hydrogen. Thus, the sum of the reactions on board the vehicle (that convert liquid water to gaseous hydrogen) is, sadly, endothermic.

Three percent of the released hydrogen's HHV is needed to heat up the reactant iron to the reaction temperature. If you only have to heat up that iron once, and if you don't have to heat up other iron that will never react, then this is tolerable. If you have to heat up the bed several times (say, because it cooled when the vehicle stopped operating), or if an appreciable fraction of the iron you carry will never react (more about this later), then it is quite possible that you will have to supply more energy (as heat) to the reactor than it will ever supply to the fuel cell (as hydrogen).

Figure 9 - The Reaction is Exothermic at All Temperatures of Interest



The positive slope of this curve indicates temperature stability. As long as water and heat are fed into the reactor, and hydrogen/steam is removed from it, at a steady rate, there will be a temperature at which the net heat gain balances the thermal losses. Were the reactor to get hotter, thermal losses would increase and the heat of reaction would decrease, thus making the reactor colder.

This reaction is **not** stable with respect to pressure. Were the withdrawal of hydrogen/steam from the reactor to be terminated and the supply of heat and water to it continued, pressure within the reactor would build up. Such a hydrogen pressure buildup would slow, and eventually stop, dehydrogenation from metal hydrides or liquid hydrides, but it would have no effect on this reaction; both sides of this reaction have the same number of moles of vapor, so it is insensitive to pressure.

How fast is this forward reaction, anyway? Fortunately for those of us who cross steel bridges and ride on steel ships, it is slow at ambient temperature. It does increase with temperature, though. In the past twelve years, this reaction has affected only a functionally insubstantial portion of my car's body, though it has wreaked aesthetic havoc; but it has, in that same time period, wiped out five mufflers.

We present no figure with reaction rate as a function of temperature alone. Such rates are calculable with homogeneous reactions, those in which everything is in solution and all reactants are plentiful and in intimate contact with each other. Such rates are not calculable with heterogeneous reactions, those in which reactants must diffuse through products of reaction to reach the reaction zone, for they depend on much more than temperature.

This reaction can take place **only** at the surface of the iron. As soon as any oxide forms on that surface, any subsequent reaction can only happen when the steam diffuses in through that oxide layer and when the hydrogen diffuses back out. This slows down the reaction considerably. The surface-to-volume ratio of the iron will determine what fraction of the iron will react before the reaction slows below the useful point.

Even with "sponge iron," most of the iron lies sufficiently far from the surface that it will never react within the few hours in which a vehicle must deplete its fuel tank. But this subsurface (unreactable) iron must be heated, along with the surface (reactable) iron, thus consuming more thermal energy than the hydrogen generated can provide.

Cannot one create lots of surface area by making very fine particles, and thus react almost all of the iron? Yes, but these would have to be very fine particles, and the steam would have to diffuse into, and the hydrogen out of, the very fine interstices between these very fine particles.

Unless, of course, one fluidizes these very fine particles, in which case one will have difficulty keeping them in the reactor and out of the fuel cell.

What happens to an iron particle as it reacts, or for that matter, to any fine structure made of iron? Iron oxide, formed in the presence of steam, is gelatinous and thus prone to agglomeration.

### 3.4 Dihydrides

Dihydrides (sometimes referred to as polyhydrides, a misnomer) are metal complexes (that is, metal atoms plus ligands) to which hydrogen molecules, rather than hydrogen atoms, attach. The ligands are coordination bonded to the metal atom. So far, researchers at the University of Hawaii have succeeded in storing hydrogen on iridium-phosphorus complexes. They are currently attempting to do the same with ruthenium (one row up on the periodic table), and plan to do the same with iron (another row up).

This is harder to do with iron than with iridium, for iron has fewer electrons and fewer electron states. However, unless one can do this with iron, this technology is commercially pointless, for both iridium and ruthenium are roughly as expensive as platinum. This technology is in its infancy, and there is no assurance that it will survive to the adolescence currently enjoyed by metal hydrides.

### 3.5 Carbon Adsorption of Hydrogen

Hydrogen molecules (not hydrogen atoms) can be made to adsorb onto carbon. Van der Waals forces account for this association, rather than electronic bonds, so comparatively little energy is needed to release the hydrogen. Methane can be similarly stored; indeed, more research energy is currently devoted to methane adsorption onto carbon than to hydrogen adsorption onto carbon.

Table 2 presents the experimental data and predictions that have been made available to us.

**Table 2 - Researchers Predict Vast Improvements in Carbon Adsorption**

| Source        | Temperature (K) | Pressure (psia) | Current Performance   |   | Goals   |   |
|---------------|-----------------|-----------------|---|---|---|---|
|               |                 |                 | Carbon Density $\left(\frac{g}{cc}\right)$<br>[skeletal density] <sup>1</sup> | Adsorption $\left(\frac{g H Adsorbed}{g Carbon}\right)$ | Carbon Density $\left(\frac{g}{cc}\right)$<br>[skeletal density] <sup>1</sup> | Adsorption $\left(\frac{g H Adsorbed}{g Carbon}\right)$ |
| Syracuse/YTI  | 150             | 810             | 0.32 [16%]  | 4%  | 0.80 [40%]  | 8.0%  |
| Allied Signal | 298             | 2000            | 0.32 [16%]  | 2%  | 0.80 [40%]  | 7.7%  |

<sup>1</sup>Skeletal density corresponds to fraction of internal volume taken up by solid carbon. Balance is assumed to be gaseous H<sub>2</sub>.

It is evident from Table 2 that even the goal of 40% skeletal density implies that the majority of the volume within the pressure vessel will be occupied by gaseous hydrogen.

Indeed, a pressure vessel with carbon-adsorbed hydrogen within it acts much as a pressure vessel without carbon in it; it just lasts longer. There is no need to supply much heat to desorb the hydrogen.

Carbons used for hydrogen adsorption differ from one another with respect to surface topology and doping materials. As is apparent from Table 2, some of these carbons work only at borderline cryogenic temperatures.

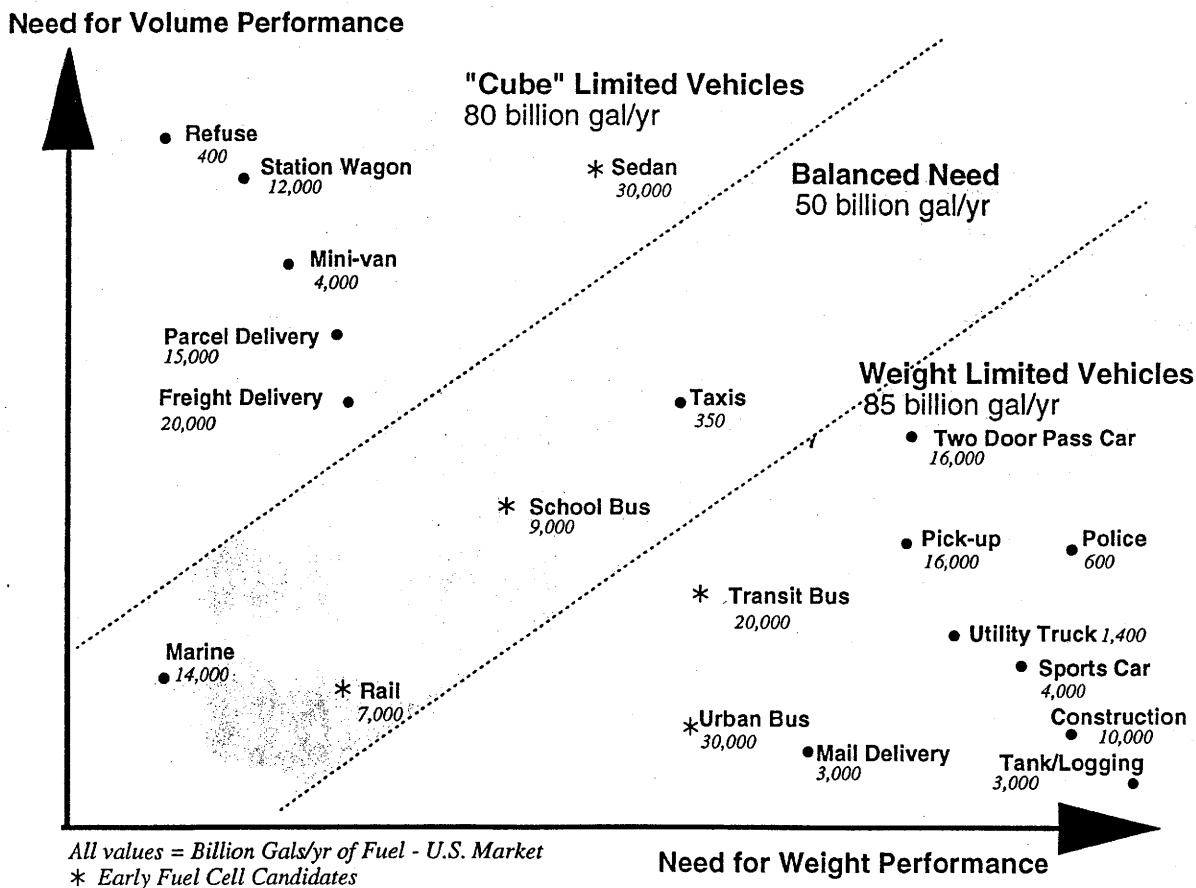


#### 4 Selecting Hydrogen Storage Technologies for Fuel Cell Powered Vehicle Applications

Each of the four primary candidates (liquefied hydrogen, metal hydrides, compressed vapor, and carbon adsorption) has its place within the diverse field of vehicles that could be powered by fuel cells. Figure 10 indicates that the literally dozens of vehicle types all differ with respect to their sensitivity to volumetric and gravimetric storage density.

For example, those vehicles (such as station wagons and refuse trucks) that are most sensitive to volumetric density would fare better with metal hydrides than with compressed vapor; the opposite would be true of vehicles (such as police vehicles and construction trucks) that are most sensitive to gravimetric density. Figure 2 suggests that carbon adsorption systems could be best for vehicles (such as taxis and school busses) with relatively balanced sensitivities.

Figure 10 - Needs Differ for Volume-Efficient and Weight-Efficient Hydrogen Storage



Liquefied hydrogen, with its exemplary storage densities, might well be restricted to applications in which professional operators and predictable schedules predominate; urban rail transit vehicles might be a good application for this technology.

## 5 Conclusions

1. *No hydrogen storage technology is best for all applications* - The relatively small tanks aboard vehicles permit high pressures more economically than do the relatively large tanks of bulk storage/transport. On the other hand, the large tanks of bulk storage/transport have relatively low ratios of surface area to volume, and thus contain liquefied hydrogen with tolerable losses.
2. *No hydrogen storage technology is obviously favored for fuel cell powered vehicles* - For example, different fuel cell powered vehicles rank volumetric and gravimetric densities differently, as shown in Figure 10.
3. *Metal hydride systems are a near-term solution* - They offer better volumetric and gravimetric density than do today's lead-acid batteries, but they will probably be overtaken eventually in those respects by lithium solid polymer electrolyte batteries and even more so by carbon adsorption systems. This prediction remains likely even if all secondary problems (oxidation, poisoning, decrepitation) are resolved.
4. *Carbon adsorption is the only developing technology likely to meet the goals of the DOE Hydrogen Plan for smaller fuel cell powered vehicles* - Metal hydrides have inherent storage density limitations (one fifth the gravimetric density, one half the volumetric density). Even the best compressed hydrogen gas technology will fall short of the volumetric density goal. Liquefied hydrogen's problems with lockup and handling make it impractical for general use.
5. *Liquefied hydrogen could be made to work for urban rail transport* - Trains have predictable loads, so lockup issues can be rendered moot. Difficulties in handling are resolvable, at least within the context of trained operators.
6. *The hydrogen industry would be wise to address the safety problems (including the public perception thereof) of the compressed gas and carbon adsorption technologies* - Uncontrolled release of compressed hydrogen gas can be made less likely than the uncontrolled release of gasoline (which is a risk the public accepts) through proper engineering. Also, the consequences of uncontrolled releases can be mitigated, again through proper engineering.