# Hydrogen Effects on Materials for the Hydrogen Economy

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Hydrogen-materials compatibility will be a primary issue in just about every aspect of the hydrogen economy from production to use. Hydrogen is currently produced by reforming natural gas but to reduce dependence on foreign oil and to reduce greenhouse gases alternative hydrogen production methods must be developed. High temperature electrolysis is one such technique that looks promising as are chemical routes such as the S-I process. Both of these production methods will be greatly aided by a high temperature nuclear reactor. Materials that are compatible with the high temperature electrolysis or chemical processes will be critical to this production method and hydrogen compatibility is a key factor in their performance. If hydrogen is produced in central plant, it must be distributed to the end user. One method being considered is through pipelines such as natural gas pipelines in a mixture of natural gas and hydrogen. Success of this distribution method will depend on the development of a low cost, low hydrogen permeation barrier that can be applied to the interior of these pipes. Natural gas pipelines currently fail by stress corrosion cracking from the outer diameter because of water ingress beneath the protective coatings. Uptake of hydrogen from the interior will only exacerbate their durability. Once hydrogen is delivered to a fueling station it must be stored on-site, vehicles fueled (for hydrogen storage concepts except chemical hydrides) and stored on-board the vehicle. On-site storage can be accomplished with current technology as compressed hydrogen, but on-board storage has some very stringent volummetric and gravimetric density requirements for which there is no material that meets these requirements. On-board storage concepts include liquid hydrogen, compressed hydrogen, adsorption on carbon, complex hydrides, chemical hydrides and a wide variety of novel new ideas being explored. Safety is a stringent requirement for all aspect of the hydrogen economy but especially where it interfaces closely with the consumer. A central hydrogen generation facility could be removed from the public but distribution systems and on-site and on-board storage systems must meet higher safety standards then the current commercial hydrogen industry. Hydrogen for transportation will likely utilize internal combustion, or PEM fuel cells while stationary power could also make use of high-temperature solid oxide fuel cells. Hydrogen-materials compatibility issues for internal combustion includes fuel injectors, valves, pistons, and rings. Aluminum is known to absorb hydrogen from water vapor at temperatures consistent with internal combustion chambers. Hydrogen bubbles have been observed to form in their grain boundaries. Also, it is known that the hydrogen diffusivity in metallic aluminum is fairly high but that permeation is reduced because of the aluminum oxide on its surface. Anything that disrupts this oxide layer will allow hydrogen uptake directly from hydrogen gas so there are two ways for aluminum components to be embrittled in internal combustion engines. Ferritic stainless steels are used as interconnects in solid oxide fuel cells because of their corrosion resistance and relatively low cost. However, it has been found that the high-temperature oxidation resistance is accelerated when the opposite side of the material is exposed to hydrogen. Hydrogen permeation to the oxidation side is thought to be the cause. This hydrogen permeation could also contribute to structural degradation as well.

## Hydrogen Transport in Pipelines

One concept for distributing hydrogen is to transport it through natural gas pipelines as a mixture of natural gas + hydrogen. The hydrogen and natural gas would be separated at the delivery point. Natural gas pipeline steels are not generally susceptible to hydrogen induced cracking or hydrogen embrittlement because they are relatively low strength. However, one consideration that must be considered is the uptake of hydrogen and its impact on stress corrosion cracks growing from the exterior of the pipe. The diffusivity of hydrogen in steel is relatively fast on the order of $10^{-9}$ to $10^{-6}$ $cm^2/s$, depending on the material chemistry and microstructure, so it will not take long for any hydrogen that is absorbed in the steel to reach the outer diameter. Stress corrosion cracking of gas pipeline materials occurs in one of two environments: 1) high pH carbonate/bi-carbonate and 2) a near neutral pH environment. Hydrogen effects are unlikely in the high pH environment but are possible in the low pH environment. However, with the supply of hydrogen from the inside of the pipe, stress corrosion cracking in both environments could be affected by hydrogen.

Stress corrosion cracking is a form of subcritical cracking that exhibits features very similar to that observed with hydrogen induced subcritical cracking, i.e. threshold stress intensity and stage I, II and III regions. Some differences between stress corrosion and hydrogen induced cracking are: 1) the threshold stress intensities for hydrogen induced cracking are generally lower than for stress corrosion cracking and 2) hydrogen can decrease the fracture toughness of the material while stress corrosion cracking does not. This has the affect of shifting the entire da/dt vs K curve to lower stress intensities in the case of hydrogen induced cracking. Clearly, this suggests that hydrogen penetration from the inside of the pipe to where stress corrosion cracks are initiating and growing could be a serious concern.

## Hydrogen Storage Materials:

In his January 2003 State of the Union Address, President Bush announced the Hydrogen Fuel Initiative – “so that America can lead the world in developing clean, hydrogen-powered automobiles.” Hydrogen storage technology - the ability to carry enough hydrogen on-board a vehicle to enable 300-mile vehicle range - is critical to the success of the President’s initiative.

The overall goal of the DOE hydrogen storage activity is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications. The objectives are:

- By 2005, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 wt%), 1.2 kWh/L, and $6/kWh.
- By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh.
- By 2015, develop and verify on-board hydrogen storage systems achieving 3 kWh/kg (9 wt%), 2.7 kWh/L, and $2/kWh.
- By 2015, develop and verify low-cost, compact hydrogen storage systems, as required for hydrogen infrastructure needs and portable/stationary power systems.

There is a high incentive for moving away from hydrocarbon fuels to a hydrogen economy because of the impact of oxides of carbon on global warming and diminishing supply of hydrocarbon fuels. An increased use of hydrogen as a fuel will require new production methods, preferably without use of hydrocarbon fuels, transportation, storage and utilization technologies. The challenge of the DOE goals is illustrated by the data in Figure 1. Only those materials within the rectangular box meet even the 2010 goals while a 50% increase is needed to meet the 2015 goals.

Volumetric density (kg H/m$^3$) and mass density (mass% H) are two parameters that characterize the practicality of various storage concepts for transportation needs. A low volumetric density requires too large a container to hold the needed fuel while a low mass density results in a weight penalty for the vehicle for a fixed quantity of fuel. Metal hydrides such as $MgH_2$, $MgNiH_4$ and $LaNi_5H_6$ have high volumetric densities but low mass densities. Several of the complex hydrides have both volumetric and mass densities that exceed the DOE goals and the automotive manufacturer's goals. These include $LiBH_4$, $NaBH_4$, and $LiAlH_4$ with volumetric and mass densities of about 120 and 18, 120 and 10 and 90 and 10 respectively, Figure 1. The one reversible complex hydride, $NaAlH_4$, has a volumetric density of about 80 kg H/m3 and a mass density of about 8 wt%. However, decomposition occurs through several steps with an intermediate step of NaH and Al. It is impractical to recover the H from the NaH because of the high dissociation temperature, therefore, the practical densities are 60 and 5.6, respectively.

Among the metallic materials that are capable of reversibly absorbing hydrogen, the family of $LaNi_5$ intermetallic-derived compositions display appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption), relatively fast kinetics (quick uptake and release), and good cycle life [1,2]. However, because of the use of heavy elements, the gravimetric hydrogen storage capacity of $LaNi_5$ is below 1.5wt% that is of particular concern with respect to transportation applications. The same issue is also found in compounds or alloys containing transition metal elements as a major component and mainly in types of $AB_5$, AB, $AB_2$, and $A_2B$, all of which typically possess the effective hydrogen absorbing capacity of less than 3.6 wt% [3-6]. It should be noted that the hydrogen storage capabilities of these metal hydrides in general are a factor of about 3 lower than DOE's FreedomCAR requirements. In contrast, the hydrides or compounds with the light elements as their major components can have a favorable gravimetric and volumetric capacity. For example, Mg is capable of storing hydrogen with a gravimetric capacity of 7.6% [4]. A common issue of these light metal-based hydrides is that charging and especially discharging cannot be achieved reversibly under a reasonable temperature and pressure, i.e. around ambient ones [5,6]. However, some improvements in the kinetics have been achieved recently by microstructural refining and adding catalysts [7].

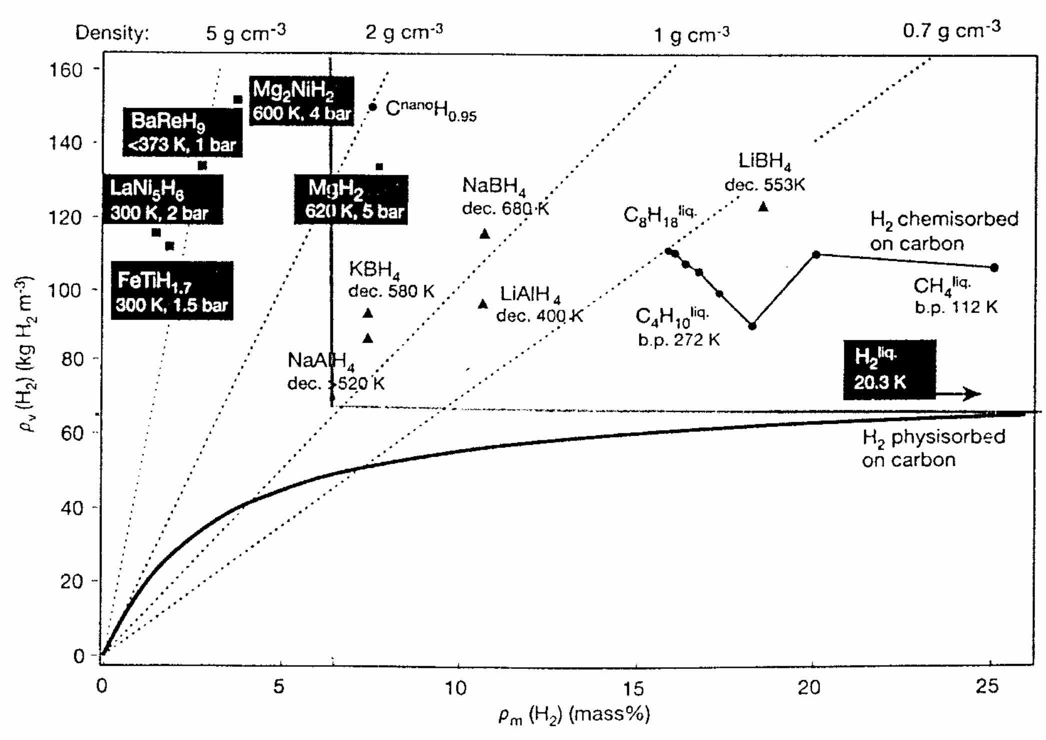

Figure 1 Summary of hydrogen storage capacities for various material

In additional to metal hydrides, complex hydrides, carbon nanotubes and chemical hydrides have also been widely studied. Like light metal hydrides, the complex hydrides in which hydrogen encapsulates a metal element have the potential to produce both high gravimetric and volumetric capacities. But Ti doped $NaAlH_4$ is so far the only one found reversible, which releases hydrogen in two step reactions with a total capacity of 5.6 wt% [8-10]. Nano-carbon tubes that store hydrogen by adsorption of molecular hydrogen on their high surface area and microporosity, are considered as promising hydrogen storage materials. But experimental results have been controversial and irreproducible and significant storage is only realized at cryogenic temperatures in combination with high pressure [11]. Two chemical hydrides have been taken to the demonstration stage of powering a vehicle. These are: 1) $NaBH_4$ and 2) LiH. The chemical hydrides, $NaBH_4$ and and LiH were used in a demonstrations by Millenium Cell and Safe Hydrogen, Inc, respectively. While these accomplishments are noteworthy, the issue of reprocessing of the reaction product remains a major issue. Overall, none of the existing storage technology and materials that have been developed and found so far can completely satisfy the DOE targets for on board applications.

## Internal Combustion

There are a number of components in an internal combustion engine that could be affected by the combustion of H2. The hydrogen embrittlement of aluminum alloys is not generally considered an issue but there is clear evidence now that these alloys are affected by H induced cracking and embrittlement. There have been a number of observations of H uptake in aluminum during corrosion and stress corrosion testing as measured by thermal desorption following exposure. While these observations are less quantifiable than permeation measurements they do provide direct evidence of H uptake during specific corrosion conditions. Several methods have been used to monitor H uptake during corrosion including: 1) thermal desorption, 2) transmission electron microscopy (TEM) of bubbles and 3) resistivity change. E. Charitidou et al. (12) and Haidemenopoulos et al. (13) measured the thermal desorption of H from 2024 Al that had been exposed to the exfoliation corrosion solution according to ASTM G 34-90. Charitidou et al. (12) found that the alloy had absorbed over 1200 wt ppm after exposure for 40 hr following thermal desorption at 600 C but only about 30 wt ppm was released at 100°C. Haidemenopoulus et al. (13) measured a H release corresponding to 90 wt ppm following 216 h exposure to the ASTM G34-90 solution when the H extraction was done at 100°C. These two results are very similar considering the longer exposure time in the latter measurement. The H uptake during these tests are significantly greater than that expected in a 3.5% NaCl solution because the G34 solution is extremely aggressive.

The observation of bubbles in Al and Al alloys exposed to water vapor is an indirect method of evaluating H uptake (14-16). Scamans and Rehal (14) found bubbles that they identified as H bubbles, in pure aluminum and aluminum alloys. The authors do not directly measure H in these bubbles but seem to infer that they are H filled based on the reaction of Al with $H_2O$ to produce H. In an Al-Mg alloy they noted bubbles on grain boundaries and dislocations following only 10 min exposure to water vapor at 70°C. Alani and Swann (16) also observed bubbles in Al-Zn-Mg alloys exposed to water vapor at 80°C. They proposed that the bubbles were the result of the precipitation of molecular hydrogen and that the cracks observed to emanate from the bubbles resulted from the pressure in the bubbles. However, they also proposed that it was the atomic H dissolved along the grain boundaries that was most embrittling. Scully and Young (17) evaluated the kinetics of crack growth of a low Cu AA 7050 in a 90% relative humidity environment and concluded that crack growth was controlled by H environment assisted cracking over temperatures of 25 to 90°C.

## Hydrogen Effects on Solid Oxide Fuel Cells

The oxidation of ferritic stainless steel was evaluated under dual exposure conditions typical of solid oxide fuel cells (18). The material was exposed to simultaneous oxidation on one side and moist hydrogen on the other side. When both sides are exposed to the same environment whether, oxidation on both sides or moist hydrogen on both sides the oxidation behavior was identical on both sides but when the exposures are mixed the oxide growth rate on the oxidation side was greatly altered. This anomalous oxidation was dependent on the alloy composition and the thermal history. For instance, AISI 430, with 17% Cr, experienced localized attack via formation of $Fe_2O_3$ hematite-rich nodules on the air side of the dual exposure samples. For Crofer22, with 23% Cr, the outer layer was spinel enriched with iron while for E-brite, which has 27% Cr, no unusual phases were found on the airside. Increasing the temperature and thermal cycling both accelerated the anomalous oxidation. Clearly, hydrogen has the possibility of altering the oxidation behavior but there is also the possibility that hydrogen could alter the structural integrity of the interconnect component in a solid oxide fuel cell.

## Summary

The performance of a wide range of materials in the presence of hydrogen will be a critical factor in the success of the hydrogen economy. These materials must perform in the production, distribution, storage and utilization of hydrogen. Issues in the performance of materials in hydrogen include structural, chemical and corrosion behavior. The structural performance of pipelines used to transport hydrogen and components used for internal combustion of hydrogen, the chemical properties in terms of hydrogen uptake and release kinetics and storage capacity of a hydrogen storage material and the oxidation rate of metallic interconnect in the presence of hydrogen will all play a critical role in the success of the hydrogen economy.

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