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Hydrogen Storage Materials: Properties and Possibilities

R. L. Cohen and J. H. Wernick

Summary. The physics, chemistry, and possible applications of the storage of hydrogen in intermetallic reservoirs are discussed. Storage in the form of intermetallic hydrides can be safe and, where hydrogen has some special value as a fuel, economical. New pumps and refrigerators based on the heat of sorption of the hydrogen into the intermetallic are approaching commercial viability.

The use of hydrogen as a source of energy and as a means of transmitting energy from one place to another requires pumps, transmission lines, and storage facilities analogous to those used for liquid fuels and natural gas. Pumps and transmission lines similar to those used for natural gas can be used for hydrogen, but storage facilities, both for stationary and for mobile applications, must be quite different. The very low boiling point of hydrogen (20.4 K at 1 atmosphere) and its low density (0.071 kilogram per liter) make it difficult to store as a liquid. The liquefaction is also costly in terms of energy, using substantially more than 30 percent of the energy content of the gas; this cost is not normally retrievable on reconversion to gas. Inadvertent exposure of liquid hydrogen to air results in violent boiling of the liquid as it condenses nitrogen and oxygen out of the air, and the evaporated hydrogen forms a dangerously explosive mixture with the air.

Storage of hydrogen at high pressures at ambient temperature yields discouragingly small amounts of hydrogen per unit mass or per unit volume of container. First-order scaling laws show that the container mass required to store a certain hydrogen mass is essentially independent of the pressure and container volume, so there is little hope of improvement by going away from the standard 150-atmosphere storage tanks commonly used. Further, accidental rupture of the container is always a concern because of the wide range over which hydrogen-air mixtures are explosive. The "*Hindenburg* syndrome" is still widely felt.

Despite these problems, hydrogen is a widely used industrial commodity. It is too expensive to use as a normal fuel (the cost per unit of energy is about two to eight times that of natural gas), but it is widely used as an intermediate in petroleum refining and ammonia manufacture, as the most powerful rocket fuel, and to produce high-temperature flames. The main engines of the space shuttle *Columbia* are fueled with liquid hydrogen.

Much of the interest in hydrogen as an energy source—the "hydrogen economy" vision—is based on the idea that very cheap and abundant electrical energy (from nuclear fission or fusion, or, more recently, from solar photovoltaic or solar power satellite sources) could be used to electrolyze water to produce hydrogen, which could then be economically transmitted over long distances. For the past 5 years this vision has been dimming. However, an alternative possibility has arisen. Hydrogen is now generated commercially primarily from natural gas or petroleum refining, with a small additional quantity obtained as a by-product of electrochemical processes. As stated above, it is more expensive (per joule) than other forms of energy. However, a standard first step in making liquid synfuels is reacting coal with steam to make synthesis gas, a mixture of H_2 and CO (*1*). One could elect to use the H_2 directly as a fuel, rather than converting it to a liquid, if appropriate storage and transmission arrangements were made. Energetically, this would be a more efficient process than making liquid synfuels, which requires additional energy-consuming chemical steps. Thus there is still some possibility that hydrogen could become economically competitive with the major fuel sources.

In the past few years there has been increasing interest in using fundamentally different techniques for storage of hydrogen (*2–4*). The leading contender is the use of intermetallic compounds that reversibly absorb hydrogen at convenient temperatures and pressures. The properties and possible applications of these materials form the main subject of this article. In addition to use for storage, these materials can be used for a new class of compressors and heat pumps, and these applications are also discussed. We do not cover the use of these intermetallics as electrodes in electrochemical cells (that is, a protonic battery) or in combination with hydrogen fuel cells; these applications are discussed in (*5*, *6*).

The use of glass Microballoons to store hydrogen at very high pressures has also been proposed (*6*). It has been suggested that in some respects Microballoon storage would be competitive with storage in metal hydrides. Microballoon storage would require use of elevated temperatures to release the hydrogen and would not allow any of the heat engine applications discussed below. Swisher and Johnson (*6*) provide an excellent review of this area and a number of other competing storage possibilities.

The authors are members of the technical staff of Bell Laboratories, Murray Hill, New Jersey 07974.

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Intermetallics for Hydrogen Storage

Ideally, a metallic hydrogen storage material will have a low atomic weight to decrease the reservoir mass, be inexpensive, have rapid kinetics for absorbing and desorbing H_2, and store large quantities of hydrogen reversibly with an equilibrium pressure of about 1 atmosphere at room temperature. Available materials (see Table 1 and below) fail to fulfill all these requirements.

Table 1 shows the properties and specific energy densities available with various means of storage. The intermetallics $LaNi_5$ and FeTi (and their pseudobinary alloys) are the principal materials now being considered for hydrogen storage. Although they have far less specific energy content than liquid hydrocarbon fuels, they provide higher specific energy values than storage in currently available electrochemical batteries. Although MgH_2 provides an attractive figure of merit, it is impractical for most applications, as discussed below.

The feature of $LaNi_5$ and FeTi that makes them so attractive for this application, besides their ability to store relatively large quantities of hydrogen, is that the hydrogen can be added to or removed from the intermetallic very rapidly at convenient pressures and temperatures (Fig. 1). In both materials, there is a heat of absorption of about 30 kilojoules per mole of H_2 (about 10 percent of the heat of combustion of the H_2). This heat of absorption complicates the use of these materials, because it must be removed while hydrogen is being absorbed and must be supplied to desorb the hydrogen. For large reservoirs, these heat flow considerations limit the absorption and desorption rates that can be obtained and complicate container design considerably. The existence of the heat of absorption, however, makes possible several new types of heat engines and compressors based on the temperature dependence of the absorption isotherm.

The modest pressures at which hydrogen is stored and the requirement that significant heat be supplied to desorb it from the intermetallic are important safety features. First, there is no large volume of hydrogen at high pressures to rush out if the container is ruptured. Second, the cooling of the intermetallic hydride as the hydrogen "evaporates" reduces the equilibrium pressure and thus greatly reduces the hydrogen evolution rate if there is a break in the system.

The strong dependence of the plateau pressure (Figs. 1 and 2) on temperature offers another interesting possibility. The hydrogen can be absorbed into the intermetallic at a low temperature (and therefore a low pressure), but if the hydrided intermetallic is then heated, it is possible to desorb the hydrogen at a very high pressure. This approach not only can be useful as a convenient source of high-pressure hydrogen, but can be used to make a hydrogen pump. With suitable valving and two or three reservoirs heated cyclically, high-pressure hydrogen can be supplied continuously without pistons or rotating seals. The hydrogen supplied by such a pump is extremely pure. Such a compressor has been built by the Philips Company (*7*), which has pioneered in intermetallic hydrogen storage studies.

The compressor operates on the following cycle (see Fig. 1). Hydrogen is absorbed into the material (for instance, $LaNi_5$) at 20°C, going from point A to point B on the diagram, while the heat of absorption is removed and passed to a sink at or below 20°C. After the intermetallic is loaded (point B), the low-pressure hydrogen input line is valved off, the hydride heated to 140°C (point C), and hydrogen desorbed at about 50 atm until point D is reached. Heat at 140°C must be supplied to replace the heat of desorption. When the hydrogen has been desorbed, the intermetallic is cooled to point A and is ready for another cycle. This type of compressor has the advantage that it can use relatively low-temperature "waste" heat or, possibly, heat from a solar collector.

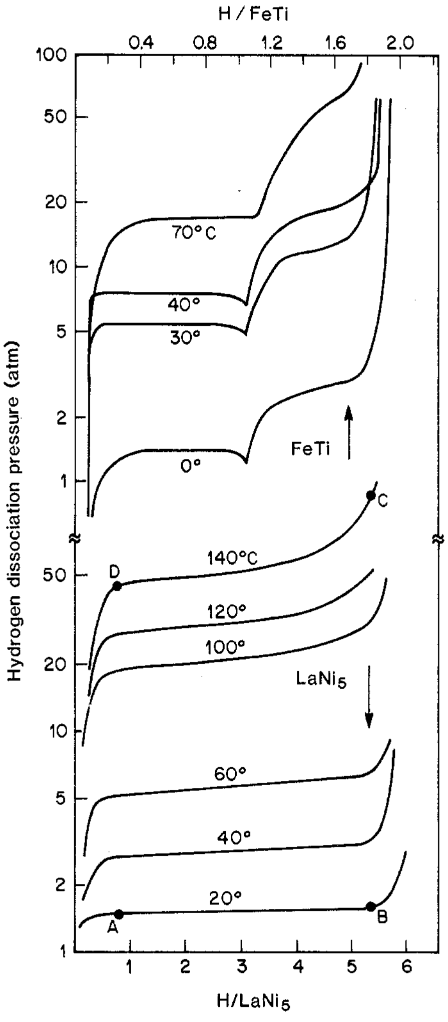

Fig. 1. Pressure-hydrogen content isotherms for $LaNi_5$. The flat region between $H/LaNi_5$ ~ 0.5 and 5.5 is generally referred to as the "plateau." Isotherms for FeTi are also shown. Points A to D are referred to in the text. [Data are from (*7*, *26*)]

Thermodynamics of Intermetallic Storage Materials

As noted above, the ideal technical material for hydrogen storage is one that absorbs and releases hydrogen easily near room temperature and 1 atm of hydrogen. As shown in Fig. 1 the absorption-desorption isotherm generally has a plateau pressure, and for the purposes of the following discussion the hydride is assumed to coexist with the "unhydrided" intermetallic. A measure of the possible utility of a material for hydrogen storage can be obtained from thermodynamic arguments, neglecting kinetic effects such as the rate of decomposition of H_2 to 2H at the gas-solid interface (*8*).

Consider the following hydrogen absorption-desorption reaction for the intermetallic A_xB_y:

$$A_xB_y \text{ (s)} + mH_2 \text{ (g)} \rightleftarrows A_xB_yH_{2m} \text{ (s)} \qquad (1)$$

where (s) and (g) denote solid and gas, respectively.

The relation between the equilibrium hydrogen pressure (P_{H_2}) and standard entropy (ΔS^0) and enthalpy (ΔH^0) changes for reaction 1 is

$$\ln P_{H_2} = \frac{-\Delta S^0}{mR} + \frac{\Delta H^0}{mRT} \qquad (2)$$

where R is the gas constant and T is absolute temperature. Van Mal *et al.* (*9*) used this relation for comparing the hydrogen storage effectiveness of various intermetallics to arrive at thermodynamic quantities that can be used as a guide to search for and evaluate materials. The decrease in entropy for the sorption reaction is nearly entirely due to the transition of H_2 gas to the solid phase (hydride). From an examination of thermodynamic data for many reactions of this type by van Mal *et al.*, $\Delta S^0 \approx -30 \pm 6$ calories per degree per mole of H_2. Thus ΔH^0 is the more important quantity in the consideration of sorption-desorption reactions. For a plateau pressure of 1 atm, ΔH^0 for the hydride reaction is approximately −9 kcal per mole of H_2 at room temperature. Thus absorption reactions with a ΔH^0 of approximately −9 kcal/mole at room temperature are sought for materials used at room temperature. Figure 2 shows the range of dissociation pressures available for a number of intermetallic hydrides.

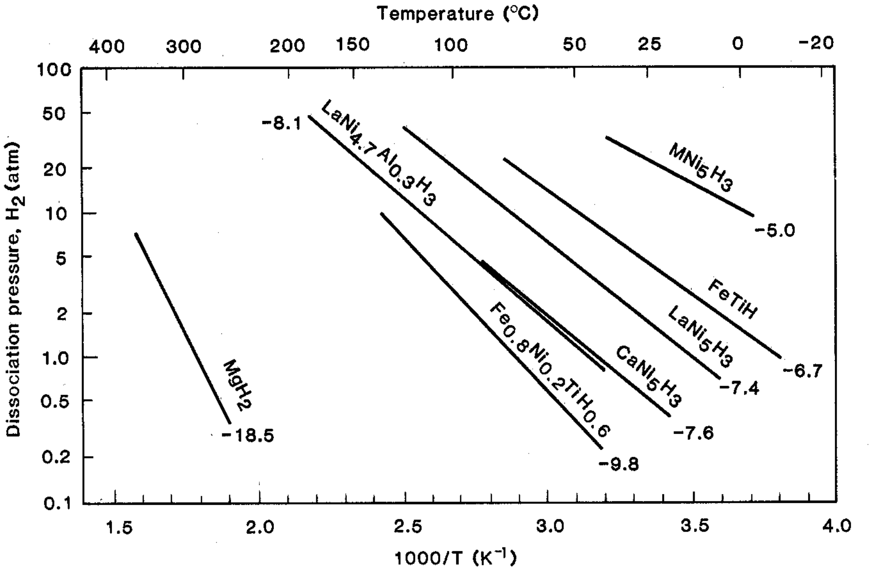

Fig. 2. Hydrogen dissociation pressures versus temperature for a number of commerical storage intermetallics (*32*). Midplateau values are shown. The numbers are the heats of formation of the hydrides in kilocalories per mole of H_2; M denotes misch metal, an inexpensive mixture of rare earths. [Figure from (*32*)]

The stability of an intermetallic relative to its hydride was mentioned above in terms of the heat of formation, ΔH_f^0, of the intermetallic. According to Eq. 1, an intermetallic with a very large negative ΔH_f^0 would lead to an unstable hydride; P_{H_2} would be large and the hydride would have a large dissociation pressure. Conversely, a relatively unstable intermetallic (small negative ΔH_f^0) would lead to a stabler hydride (lower plateau pressure) and perhaps a larger storage capacity. Van Mal *et al.* (*9*) showed that the formation of a ternary solid solution from binary intermetallics of the type RM_5, where R is a rare earth and M is a 3*d* transition element, in order to alter ΔH_f^0 to an intermediate value, could lead to a more attractive alloy for hydrogen storage. As another example (*10*), consider the two isostructural Laves phases $ZrCr_2$ and $ZrFe_2$. Whereas $ZrCr_2$ (calculated $\Delta H_f^0 \approx -3.9$ kcal/mole) has a low hydrogen plateau pressure (~ 0.01 atm) at 50°C, $ZrFe_2$ (calculated $\Delta H_f^0 \approx -8.05$ kcal/mole) has a plateau pressure greater than 10 atm at 50°C. When Cr is replaced with Fe, the ΔH_f^0 of $Zr(Fe_xCr_{1-x})_2$ moves toward a value more negative than that of $ZrCr_2$ and a hydride of practical interest results. For the alloy $ZrFe_{0.4}Cr_{0.6}$, the plateau pressure is ~ 1 atm at 50°C. If experimental heats of formation are not available for analyses of this type, estimates can sometimes be made by use of the theory of Miedema and co-workers (*11*).

Hydride heats and free energies of formation at 40°C for the two best intermetallics, $LaNi_5$ and FeTi, are given in Table 2 to illustrate the points made above. The small positive standard free energies of formation are a good measure of the instability of the hydrides. Also shown is the ΔH_f^0 for MgH_2, a very poor material for room-temperature hydrogen storage, and $LaCu_5$, a very poor hydride former.

The large negative ΔH_f^0 for MgH_2 shows why it is not useful as a general-purpose storage material; it must be heated to about 300°C before the dissociation pressure is useful. Large amounts of heat must be provided to desorb the hydrogen, and it must be provided at 300°C, so that it would be difficult to use waste heat for this function. The kinetics of absorption and desorption are very slow, even at this temperature (*12*). Some improvement can be made in the kinetics by adding several percent nickel, but that does not improve the dissociation pressure significantly. Thus we cannot take advantage of the high hydrogen weight content (Table 1) and low cost of magnesium as a storage material. A number of other intermetallics based on magnesium have been investigated (*12*), but in general the higher their magnesium content, the lower the hydrogen dissociation pressure, so that at this time there appears to be no material competitive with $LaNi_5$ or FeTi.

An important feature of $LaNi_5$ and its analogs is that they can be doped—for instance, with other 3*d* or group IIIA or IVA metals at the nickel site, or with other rare earths or calcium at the lanthanum site. Doping causes the plateau pressure to vary a wide range. For example, at room temperature $LaNi_4Al$ has a plateau pressure of about 0.002 atm, while $GdNi_5$ has a plateau pressure of 150 atm. Thus it is possible to design a material for heat engine applications at a specific temperature and pressure. Low levels of doping tend to leave the plateau relatively flat, which is desirable for compressor and refrigeration applications. Use of calcium, or inexpensive rare earth combinations, produces material of much lower cost than pure $LaNi_5$. However, the plateau is not as flat, and calcium alloys appear to be especially susceptible to degradation (*13*).

Table 1. Energies, energy densities, and capital costs for various forms of energy storage for a reservoir with a total mass of 50 kg.

Form	Volume (liters)	Energy (MJ)	Energy density (MJ/kg)	Estimated capital cost (MJ per $1000)
Gasoline (35 kg, 13 gal)	60	1,620	33	20,000
Hydrogen gas cylinder at 150 atm	60	63	1.3	600
MgH_2 at 300°C (35 kg of MgH_2 + 15-kg tank)	30	290	5.9	
$FeTiH_{1.7}$ (40 kg of FeTi + 10-kg tank)	15	64	1.3	65*
$LaNi_5H_{6.7}$ (40 kg of $LaNi_5$ + 10-kg tank)	15	50	1.0	20†
Liquid hydrogen (5 kg, 75 liters)	150	750	5.0	1,000
Lead acid battery	30	9	0.18	72
ZnCl battery/fuel cell			0.5	75‡

*Includes $15 per kilogram for FeTi plus $10 per kilogram for the tank, heat exchanger, and activation. †Includes $50 per kilogram for $LaNi_5$ plus $10 per kilogram for the tank, heat exchanger, and activation. ‡Developmental; values are very uncertain.

Physics and Chemistry of Hydrogen Absorption

Extensive studies of the chemistry and physics of the absorption of hydrogen in intermetallics have been carried out. For $LaNi_5$, hydrogen absorption occurs at a constant pressure, suggesting that there is an almost unhydrided (alpha) phase, $LaNi_5$, and a fully hydrided (beta) phase, $LaNi_5H_{6.7}$, and that increasing the stored hydrogen produces more beta phase and less alpha phase. This picture has been confirmed by Mössbauer spectroscopy (*14, 15*) and x-ray and neutron diffraction studies, which have shown that, for samples which contain less H than the saturation value, the spectra or diffraction patterns can be fitted with one component from the alpha phase and another component from the beta phase.

X-ray diffraction studies show that the metal ion positions in the beta phase are similar to those in the alpha phase, but the lattice volume is expanded by about 25 percent. Since the protons do not scatter x-rays significantly, their positions cannot be determined by x-ray techniques. Neutron scattering on $LaNi_5D_{6.7}$ originally showed (*16, 17*) that the deuterium occupied two inequivalent interstitial sites of the $LaNi_5$ lattice, but recent studies indicate a much more complex structure (*18*).

Activation

Bulk samples of intermetallics do not absorb hydrogen readily. They must first be "activated" by being forced through one or more charge-discharge cycles. It has been found that both the kinetics and the amount of stored hydrogen increase greatly during this treatment (Fig. 3). One can activate $LaNi_5$ simply by exposing it to hydrogen at a pressure of a few atmospheres for some time (seconds to hours, depending on the history of the sample) at room temperature. The $LaNi_5$ begins to crack and splinter vigorously, because the large lattice volume change that occurs when hydrogen is absorbed into the outer layers induces very large strains, which lead to violent disintegration of the material. After hydrogen has been absorbed and desorbed through a few cycles, the $LaNi_5$ is reduced to a powder of particle size 10 to 100 micrometers (Fig. 4). It is generally much harder to activate FeTi; normally, the initial exposure to hydrogen is at 200° to 400°C and considerable overpressures of hydrogen are required for the initial absorption. Clearly, one purpose of these activation steps is to increase the surface-to-volume ratio of the intermetallics to provide a greater area for hydrogen absorption.

Until recently the microscopic processes that occur during activation of the intermetallics were not understood. With $LaNi_5$ this lack of knowledge was not a problem, because it is normally easily activated. With FeTi, however, long exposure of the material to elevated temperatures was required, and many batches of FeTi proved to be very recalcitrant. Impurities, especially oxygen, have frequently been blamed for sluggish activation.

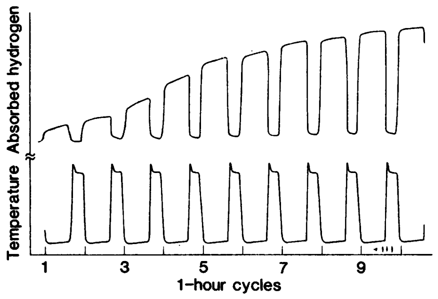

Fig. 3. Activation of $LaNi_5$ by successive hydrogen absorption-desorption cycles immediately after exposure of new material to hydrogen. In this case, the absorption-desorption cycles are carried out by keeping the hydrogen pressure constant and heating and cooling the sample cyclically.

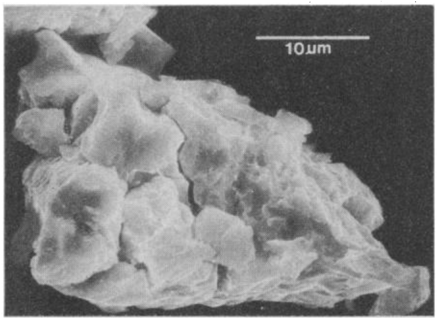

Fig. 4. Scanning electron micrograph of a 30-μm-long $LaNi_5$ particle produced by cyclically absorbing and desorbing hydrogen. The deep cracks result from strain produced by the expansion of $LaNi_5$ as it absorbs hydrogen.

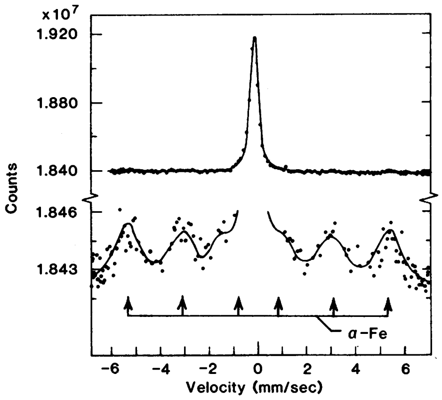

Fig. 5. Mössbauer spectrum of ^{57}Fe at the surface of FeTi powder after 51 hydriding cycles (*19*). Weak lines due to iron metal are visible.

Recently, several experiments have shown that the activation produces microcrystals of the 3*d* metal at the surface of the particles. For FeTi, Mössbauer measurements (*19, 20*) (Fig. 5) directly showed the presence of iron metal at the surface of the activated material, and these measurements have been supported by magnetic susceptibility data suggesting the presence of iron (FeTi itself is almost nonmagnetic, so even a very small amount of metallic iron strongly changes the magnetic behavior). For $LaNi_5$, x-ray photoelectric spectroscopy (*21*) shows some lines in the 3*d* band structure which appear to coincide with those of nickel and which were not present before the intermetallic was exposed to hydrogen. Magnetization data for $LaNi_5$ also support the idea that ferromagnetic nickel is generated by absorption-desorption cycling with hydrogen (*21*).

The role of these metallic clusters was suggested by recent experiments (*8*) in which the "sticking coefficient" of hydrogen on various surfaces was determined. A clean niobium surface rapidly accumulated a layer of hydrogen, which stayed on the surface despite the large diffusivity of protons in niobium. When the surface was coated with a thin layer of palladium, however, hydrogen incident on the palladium was immediately "conducted" into the niobium substrate. The implication was that the palladium layer acted as a catalyst to enhance the dissociation of H_2 to 2H at the surface of the palladium, and that the H could then diffuse rapidly into the niobium. For $LaNi_5$ and FeTi as well, the role of the 3*d* metallic clusters at the surface could be to dissociate the H_2. Once it is dissociated, the protons are known to diffuse very rapidly in $LaNi_5$.

Limitations

There are five significant problems in the use of these materials for storage or for heat engine applications. First, the absorption of hydrogen liberates large quantities of heat, which must be conducted away from the powder. Similarly, removal of hydrogen requires that heat be added to the powder bed, or else the powder temperature will fall and the equilibrium pressure over the powder will decrease (see Fig. 1). For reservoirs containing less than 100 grams of intermetallic, or for very slow absorption-desorption cycles, no special precautions need be taken, but for larger tanks careful attention must be paid to heat transfer. One approach is to incorporate the powder in a macroscopically porous metallic host (for example, aluminum) with high thermal conductivity (*22*), which makes it easier to get heat into and out of the powder.

Second, the powder is fine enough to be carried along with the hydrogen stream and clog valves, pile up at sharp bends in the piping, and so on. The use of graded filters is effective in constraining the powder to its reservoir, but again careful design is necessary.

Third, the repeated swelling and shrinking of the powder as it absorbs and desorbs hydrogen leads to packing under the action of gravity. As the powder settles toward the bottom of a container it is increasingly compacted. Eventually, the swelling during absorption of hydrogen begins to stretch the container horizontally and can lead to rupture of the vessel after extensive cycling. Here, the remedy is to use horizontal tanks which have a small diameter or contain small subcompartments so that the volume increase can be relieved by vertical expansion.

The fourth and fifth problems are fundamentally more difficult to deal with. We consider the fourth problem to be degradation of the surface of the absorbing powder due to the presence of carbon monoxide water, or other reactive species in the hydrogen, even in trace amounts. The intermetallics generally used for hydrogen storage are sensitive to these species, which are common in commercial hydrogen. A concentration of only 300 parts per million CO leads to a 50 percent loss of absorption capacity after a few absorption-desorption cycles (*23*). This sensitivity apparently results from the fact that as soon as the surface sites that catalyze $H_2 \Leftrightarrow 2H$ are poisoned by the reactive contaminant, the absorption and desorption rates are greatly decreased. In general, the damage is only to the surface of the particles, and the material can be "reformed" by going through a reactivation process. The intermetallic $LaNi_5$ is somewhat immune to poisoning by H_2O; this is believed to occur because a protective layer of $La(OH)_3$ is formed (*24*) and the Ni catalyst particles project through the layer.

This sensitivity of the intermetallics to impurities will be a problem in the large-scale use of hydrogen fuel with intermetallic storage. The most attractive source of low-cost hydrogen, coal gasification, produces a gas rich in CO and H_2O, which would have to be purified to be usable with intermetallics. In general, boil-off gas from liquid hydrogen is clean enough to avoid poisoning problems, but substantial extra energy and capital costs are incurred by going through the liquid state. A number of schemes have been proposed to protect the particles, such as covering them with a thin nickel film, but, as far as we know, little success has been demonstrated.

Table 2. Experimental standard heats and free energies of formation (ΔH_f^0 and ΔG_f^0) of some intermetallics and hydrides at 40°C (*9–11, 26*).

Compound	ΔH_f^0 (kcal/ mole)	ΔH_f^0 (kcal/ mole H_2)	ΔG_f^0 (kcal/ mole H_2)
$LaNi_5$ hydride		−7.4	0.7
$LaNi_5$	−14.4		
$LaCu_5$	−24.2		
FeTi	− 9.45		
MgH_2	−18.5		
FeTi hydride		−6.7	1.25

The fifth problem, which has only recently been discovered in practical storage intermetallics (*25*), may be termed "intrinsic" degradation, in contrast with the extrinsic degradation produced by reactive gases. Intrinsic degradation is a problem in closed systems that are cycled hundreds or thousands of times. It results from the fact that the "reversible" hydrogen storing material, such as $LaNi_5H_x$, is metastable with respect to LaH_2 and Ni. While for tens or even hundreds of absorption-desorption cycles the hydrogen appears to be reversibly absorbed and desorbed, eventually a phase separation begins, and the amount of hydrogen that can be reversibly stored begins to decrease as the $LaNi_5$ is converted to LaH_2 and Ni metal (Fig. 6). The storage material can be readily reformed by mild annealing under vacuum, but this degradation represents an additional complication which must be accounted for in system design. Intrinsic degradation will not be significant unless temperatures greater than 100°C or hundreds of thousands of absorption-desorption cycles are required. The FeTi hydride is also metastable with respect to TiH and Fe, but it appears to be immune to intrinsic degradation (*26*). However, it is not likely to be useful in applications (such as absorption air conditioning) involving frequent cycling, because the break in the absorption plateau (Fig. 1) makes it difficult to use where thermodynamic efficiency is important.

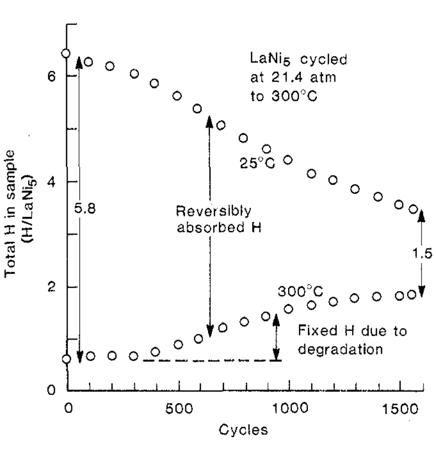

Fig. 6. Loss of reversible hydrogen-storage capacity due to intrinsic degradation after extended absorption-desorption cycling of $LaNi_5$. Hydrogen is desorbed (see Fig. 1) at 300°C and 21.4 atm and absorbed at the same pressure at room temperature.

Applications

There is a large disparity between the applications that have been proposed for intermetallic storage materials and the applications that appear to be economical. At this time, the range of applications that are technically feasible far exceeds the range for which hydride storage is the most effective solution.

A good example of an effective use of hydride storage is a storage cell using $LaNi_5$ to supply ultrapure hydrogen for gas chromatographs and other instrumentation applications (*27*). The entire unit weighs about 6 kg, including the heater, case, and controls, and stores about 200 liters of hydrogen at standard temperature and pressure (STP). [A standard 1.5-meter-high gas cylinder (50 kg, 150 atm) stores about 6000 liters STP.] The $LaNi_5$ cell can be easily recharged from an electrolyzer and can remain permanently connected to the system it supplies. Hydrogen desorbed from $LaNi_5$ is extremely pure, since the $LaNi_5$ is a good getter for most contaminants. In this application, the convenience and assured purity of this hydrogen source, the elimination of the need to handle and connect bulky gas cylinders, and the reduction in explosion hazard are strong advantages, and the actual cost of the hydrogen is insignificant.

An intriguing operation based on the heat of desorption of hydrogen is the HYCSOS cooling cycle, which has been studied at Argonne National Laboratory for a number of years (*13, 28*). This system (Fig. 7) has two different reservoirs, filled with materials that require different temperatures for the same plateau pressure—for instance, $LaNi_5$ and $CaNi_5$ (Fig. 2). Hydrogen is desorbed at a high temperature from the $CaNi_5$ and

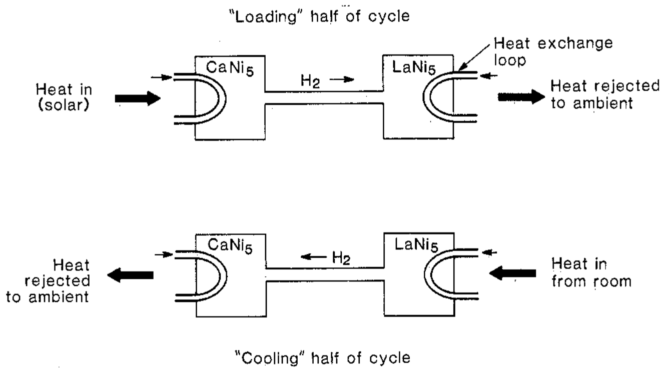

Fig. 7. HYCSOS scheme implemented for building air conditioning. Two reservoirs containing different intermetallics are used. The heat pump action is obtained from the heat of absorption of the hydrogen into the intermetallics as it is pumped back and forth between the reservoirs by varying the temperatures.

absorbed into the $LaNi_5$, with the heat of absorption being removed to a heat sink at ~ 30°C. After the $LaNi_5$ reservoir is emptied, it is cooled to 30°C, and the hydrogen is then desorbed from the $LaNi_5$ reservoir. If this half of the cycle is performed at ≤ 0.5 atm, cooling at ~ 0°C will be available from the $LaNi_5$ reservoir as the hydrogen is desorbed from it. This approach can be used to build a hydrogen absorption refrigerator whose sole energy source is heat at 100° to 150°C, so that it is ideally suited for solar-powered air conditioning. Continuous cooling can be achieved by using two sets of reservoirs, with one providing cooling while the other is being loaded with hydrogen. Estimates indicate that cost would be competitive with those of conventional absorption-type refrigerators (*13*).

Intermetallic storage of hydrogen fuel has also been used for a hydrogen-powered tractor for underground mines. In this application the mass of the hydride reservoir is not a problem and the amounts of energy required are not enormous. The inherent safety of the hydride storage system and the fact that the exhaust of the internal combustion engine consists of only water are commanding advantages.

In the United States, the word energy is closely associated with the use of automobiles, and considerable effort has been expended to develop hydride storage for motor vehicles. The most ambitious such effort has been made by Daimler-Benz, which has equipped several dozen standard passenger cars with hydride reservoirs as a demonstration project (*29*). A vehicle with a 260-kg hydride storage container (FeTi or equivalent) has a range of about 150 km. Some vehicles have been built with an additional hydrocarbon fuel system to provide increased range; the idea is that the low-pollution hydrogen fuel could be used in densely populated areas and the hydrocarbon burned for long intercity runs. Commendably, Daimler-Benz has taken an integrated view of the energy system (*30*). The company has constructed some hydrogen "filling stations"; it has considered using the heat liberated when the intermetallic is hydrided to heat buildings or produce hot water; and it has built a van in which the cooling effect of the desorption of hydrogen from the intermetallic is used to cool air for air conditioning.

In our opinion, however, intermetallic hydrogen storage for cars is not likely to be a strong contender for wide use. There are obviously severe range limitations, and even modest reservoirs have enough mass that they cut into performance and energy efficiency. But rather than looking at absolute indices, it is instructive to compare the values for hydride storage and for electrochemical storage in Table 1. While the hydride storage is clearly superior in joules per kilogram, the electrical output of the battery can be converted to motive power three to four times more effectively than burning hydrogen in an internal combustion engine can, and this consideration removes much of the apparent advantages of the hydride. Further, while the hydride storage systems are essentially at the theoretical limit of their energy density and little improvement is in prospect, current electrochemical systems achieve only 1 to 10 percent of their theoretical energy densities. Thus there is the possibility of great improvement in the electrochemical systems, but little prospect of fundamental large improvement in room temperature hydride systems. The use of magnesium hydrides at high temperature (~ 300°C) would provide a large improvement, but then one would have to consider competition from the sodium-sulfur battery (which is still not a commercial item), which functions at approximately 400°C and has a very high specific stored energy.

The outlook for hydride fuel storage is much more attractive for heavy long-distance trucks and buses. For these vehicles a heavy reservoir is not as severe a drawback, and the operating cycle would allow the use of magnesium hydride storage, since the hydride could be kept at 300°C for long times while the vehicle was running. Ultimately, the practicality of this approach will be decided by the costs of hydrogen and the progress of attempts to find new hydrides or to improve the kinetics of the absorption and desorption of hydrogen from magnesium.

Until recently, each of the intermetallic storage applications discussed above was carried out with a specially designed and fabricated package. All the engineering problems discussed above were dealt with almost anew for each project, resulting in extremely high development costs and slow and painful development. Problems that appear trivial before construction has begun (in this case, the heat transfer, powder containment, and packing/swelling problems) are often extremely difficult to overcome without experience. An important recent development has been the design (*13, 31*) of small modular capsules, conveniently arranged for heat transfer and with filters to confine the powder. With these modules (about the size of a finger) it should be possible to construct storage reservoirs for many projects without having to go through a long design and debugging process. The existence of such standardized units is a sign that the range of commercial applications will be expanding in the immediate future.

Conclusions

Currently, the high cost of hydrogen in comparison to hydrocarbon fuels is a severe limitation in its use as a primary fuel. Where hydrogen has some special value or virtue as a fuel, storage in the form of intermetallic hydrides can be useful and economical. Many heat engine devices using the heat of sorption of the hydrogen into the intermetallic storage system have been built. None has yet become a commercial item, but the prospects for successful application in the near future are good.

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The World Food Situation and Global Grain Prospects

Terry N. Barr

As we proceed further into the 1980's, a review of the world food situation and global grain prospects is timely. The public tendency to view world food problems only in terms of crisis has done a profound disservice to the world's hungry. Peaks and troughs of such public interest do not provide an environment conducive to productive assessment of the basic problems. Food crises do occur but they often are only warning episodes of a critical underlying trend (*1–5*). Today's world is not without a food crisis—witness the recent effects of weather-reduced production and rapid population growth in Africa. However, the magnitude of weather-related fluctuations and the resulting problems should not obscure the basic facts underlying developments in the world food situation in the past three decades.

Summary. The basic realities of the distribution of the world's population, wealth, and agricultural production base are not conducive to an automatic stabilizing process for the world's hungry. Increasing volatility in world grain production in the 1980's could create a problem of major proportions. By 1990, the developed world will account for 24 percent of the world's population, 85 percent of the world's economic activity, and around 50 percent of the world's grain production and consumption. On a per capita basis, the developed world will consume nearly three times as much grain as the developing countries which account for three-fourths of the world's population. Increased food aid, which is essential, is not the solution to the basic problem. The low-income countries need a massive infusion of capital investment, research support, and education if they are to build infrastructures that have the capacity to produce, distribute, and market food supplies. Other options serve only to prolong and aggravate the current disparities.

From 1950 to 1980, world food production doubled, with the increase in the developing countries actually exceeding that of the developed countries (Table 1). At the same time, population in developing countries grew at more than twice the rate evidenced in the developed world. In developed countries, food production nearly doubled whereas population increased around a third. As a result, per capita food production increased nearly 50 percent. In developing countries, where food production increased nearly 120 percent since the early 1950's, population almost doubled and gains in per capita food production were limited (*6*). Although food production in the developing world grew at a compound rate nearly 15 percent higher than the developed world over the past three decades, the disparity in population growth rates permitted the developed countries to increase per capita food production nearly three times faster than the developing countries.

Food production has doubled since 1950, and during the same period world food trade has increased fourfold. Since 1970, the annual rate of growth in food trade was about three times faster in the developing countries than the developed world, with the developed world acting as the major supplier of the world food trade. The developing countries, through increased food trade, have considerably narrowed the gaps with the developed world in per capita food consumption.

The Food and Agriculture Organization of the United Nations (FAO) estimates that on a per capita basis, levels of calorie and protein intake from vegetable products were very similar among the three major economic classes in 1977 (Table 2). The per capita intake of 2016 calories from vegetable products in the developing countries was only 264 calories or 13 percent less than in the developed world, but the protein intake of 42.9 grams from these vegetable products was nearly 10 percent higher. The major difference in nutritional levels among the developed, developing, and

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The author is acting chairman of the World Agricultural Outlook Board, U.S. Department of Agriculture, Washington, D.C. 20250.

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