

# Hydrogen-storage materials for mobile applications

Louis Schlapbach\*† & Andreas Züttel†

\*EMPA, Swiss Federal Laboratories for Materials Research and Testing, CH-8600 Dübendorf, Switzerland

†University of Fribourg, Physics Department, CH-1700 Fribourg, Switzerland (e-mail: andreas.zuetzel@unifr.ch)

Mobility — the transport of people and goods — is a socioeconomic reality that will surely increase in the coming years. It should be safe, economic and reasonably clean. Little energy needs to be expended to overcome potential energy changes, but a great deal is lost through friction (for cars about 10 kWh per 100 km) and low-efficiency energy conversion. Vehicles can be run either by connecting them to a continuous supply of energy or by storing energy on board. Hydrogen would be ideal as a synthetic fuel because it is lightweight, highly abundant and its oxidation product (water) is environmentally benign, but storage remains a problem. Here we present recent developments in the search for innovative materials with high hydrogen-storage capacity.

**E**nergy can be stored in different forms: as mechanical energy (for example, potential energy or rotation energy of a flywheel); in an electric or magnetic field (capacitors and coils, respectively); as chemical energy of reactants and fuels (batteries, petrol or hydrogen); or as nuclear fuel (uranium or deuterium). Chemical and electric energy can be transmitted easily because they both involve electronic Coulomb interaction. Chemical energy is based on the energy of unpaired outer electrons (valence electrons) eager to be stabilized by electrons from other atoms. The hydrogen atom is most attractive because its electron (for charge neutrality) is accompanied by only one proton. Hydrogen thus has the best ratio of valence electrons to protons (and neutrons) of all the periodic table, and the energy gain per electron is very high.

Hydrogen is the most abundant element on Earth, but less than 1% is present as molecular hydrogen gas  $H_2$ . The overwhelming majority is chemically bound as  $H_2O$  in water and some is bound to liquid or gaseous hydrocarbons. The clean way to produce hydrogen from water is to use sunlight in combination with photovoltaic cells and water electrolysis (see review in this issue by Grätzel, pages 338–344). Other forms of primary energy and other water-splitting processes are also used: the hydrogen consumed today as a chemical raw material (about  $5 \times 10^{10}$  kg per year worldwide) is to a large extent produced using fossil fuels and the reaction of hydrocarbon chains ( $-CH_2-$ ) with  $H_2O$  at high temperatures, which produces  $H_2$  and  $CO_2$ . Direct thermal dissociation of  $H_2O$  requires temperatures higher than 2,000 °C (>900 °C with a Pt/Ru catalyst).

The chemical energy per mass of hydrogen (142 MJ kg<sup>-1</sup>) is at least three times larger than that of other chemical fuels (for example, the equivalent value for liquid hydrocarbons is 47 MJ kg<sup>-1</sup>). Once produced, hydrogen is a clean synthetic fuel: when burnt with oxygen, the only exhaust gas is water vapour, but when burnt with air, lean mixtures have to be used to avoid the formation of nitrogen oxides. Whether hydrogen can be considered a clean form of energy on a global scale depends on the primary energy that is used to split water<sup>1</sup>.

The availability of free energy is often unsafe. The mechanical energy of a 1,000-kg car running out of control

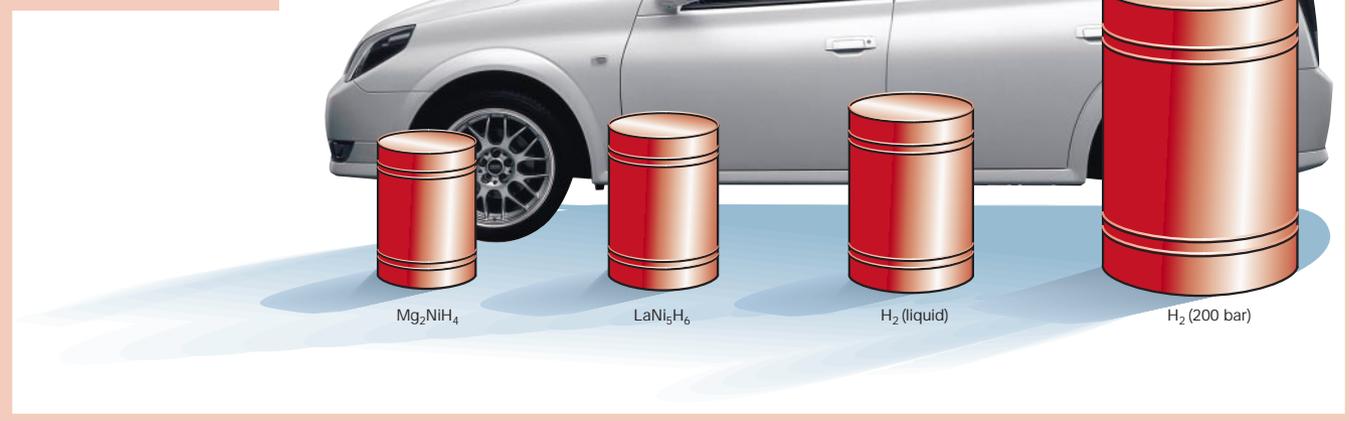
at 40 km h<sup>-1</sup> can kill pedestrians. The process of burning hydrogen can be done in an efficient and controlled way to liberate energy at a desirable rate, or in an uncontrolled way with the potential to cause damage. For historical reasons hydrogen has a bad reputation, which is not altogether justified: a more recent analysis<sup>2</sup> of the *Hindenburg* catastrophe shows that the air ship caught fire because of a highly flammable skin material and not because of the hydrogen gas it contained. The safety of hydrogen relies on its high volatility and non-toxicity.

Today, many scientists and engineers, some companies, governmental and non-governmental agencies and even finance institutions are convinced that hydrogen's physical and chemical advantages will make it an important synthetic fuel in the future. After the successful use of hydrogen for space technology, national hydrogen associations were created and joint ventures started. Examples are fuel-cell development projects, the Shell-GfE-Hydro-Québec joint venture<sup>3</sup>, the International Hydrogen Energy Association and its technical-economic conferences, and solar hydrogen R&D programmes. But are these ventures aimed at mobility?

There are essentially two ways to run a road vehicle on hydrogen. In the first, hydrogen in an internal combustion engine is burnt rapidly with oxygen from air. The efficiency of the transformation from chemical to mechanical through thermal energy is limited by the Carnot efficiency and is slightly higher for hydrogen–air mixtures (around 25%) than for petrol–air mixtures. When a lean mixture is used, the exhaust gas contains nothing but water vapour; richer mixtures also produce  $NO_x$ . In the second method, hydrogen is 'burnt' electrochemically with oxygen from air in a fuel cell, which produces electricity (and heat) and drives an electric engine (see review in this issue by Steele and Heinzl, pages 345–352). Here, the efficiency of the direct process of electron transfer from oxygen to hydrogen is not limited by the Carnot efficiency; it can reach 50–60%, twice as much as the thermal process.

For on-board energy storage, vehicles need compact, light, safe and affordable containment. A modern, commercially available car optimized for mobility and not prestige with a range of 400 km burns about 24 kg of petrol in a combustion engine; to cover the same range, 8 kg hydrogen

**Figure 1** Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)



are needed for the combustion engine version or 4 kg hydrogen for an electric car with a fuel cell.

Hydrogen is a molecular gas. At room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of 45 m<sup>3</sup>. This corresponds to a balloon of 5 m diameter — hardly a practical solution for a vehicle (Table 1). In the following we will focus on the question of compacting hydrogen, looking at the materials, technology and safety aspects (Fig. 1).

### Conventional hydrogen storage

Classical high-pressure tanks made of fairly cheap steel are tested up to 300 bar and regularly filled up to 200 bar in most countries. To store our 4 kg hydrogen still requires an internal volume of 225 litres (about 60 gallons) or 5 tanks of 45 litres each. Novel high-pressure tanks made of carbon-fibre-reinforced composite materials are being developed; these are tested up to 600 bar and filled up to 450 bar for regular use. But they need a special inert inner coating to prevent the high-pressure hydrogen reacting with the polymer. Consequently, another approach is to use hydrogen-inert aluminium tanks and to strengthen them with external carbon-fibre coatings. Spherical containers slightly smaller than 60 cm in diameter would be able to carry our 4 kg, but for practical fabrication a cylindrical shape is preferred.

These high-pressure containers, when full, would contain about 4% hydrogen by mass, but with significant disadvantages: the fuel would be available at a pressure dropping from 450 bar to zero overpressure, so additional pressure control would be essential. High-pressure vessels present a considerable risk — the compression itself is the most dangerous and complicated part. In Japan such vessels are prohibited on the roads in ordinary cars.

Condensation into liquid or even solid hydrogen is, of course, particularly attractive from the point of view of increasing the mass

per container volume. The density of liquid hydrogen is 70.8 kg m<sup>-3</sup> (70.6 kg m<sup>-3</sup> for solid hydrogen). But the condensation temperature of hydrogen at 1 bar is -252 °C and the vaporization enthalpy at the boiling point amounts to 452 kJ kg<sup>-1</sup>. As the critical temperature of hydrogen is -241 °C (above this temperature hydrogen is gaseous), liquid hydrogen containers are open systems to prevent strong overpressure. Therefore, heat transfer through the container leads directly to the loss of hydrogen. Larger containers have a smaller surface to volume ratio than small containers, so the loss of hydrogen is smaller. The continuously evaporated hydrogen may be catalytically burnt with air in the overpressure safety system of the container or collected again in a metal hydride. (Solid hydrogen is a molecular insulating solid; under high pressure it transforms into metallic, possibly even superconducting hydrogen<sup>4</sup> with  $T_c$  of 200–300 °C.)

Cryotechniques for cooling and superinsulated low temperature storage units were developed and proven in space technology. Liquid hydrogen is a fuel in the launching process of the Space Shuttle and in *Ariane*. A Lockheed military-type aircraft and a Tupolev supersonic aircraft have been flown with engines fuelled by liquid hydrogen. BMW have built an automated liquid-hydrogen filling station, and developed and tested several cars running with hydrogen in newly designed vessels to reduce losses by evaporation to below 1.5 mass% per day (BMW, personal communication).

Hydrocarbons with a molecular mass of at least 60 g mol<sup>-1</sup> are liquid at room temperature with a density close to 1,000 kg m<sup>-3</sup>. The number of hydrogen atoms per carbon atom can vary in hydrocarbons owing to their ability to change from  $\sigma$ -bonds to  $\pi$ -bonds. Hydrocarbons can be burnt completely by oxidation of carbon into CO<sub>2</sub> and of hydrogen into H<sub>2</sub>O; some can also be considered as a liquid storage medium for hydrogen if they can be hydrogenated and dehydrogenated; that is, if their ratio of hydrogen to carbon atoms can be adapted reversibly. Cyclohexane (C<sub>6</sub>H<sub>12</sub>), for example, reversibly desorbs six hydrogen atoms (7.1 mass%) and forms benzene (C<sub>6</sub>H<sub>6</sub>). Stationary hydrogenation and dehydrogenation under steady-state conditions are managed in numerous chemical plants, but the on-board process under variable conditions is another matter. We do not consider hydrogen storage in NH<sub>3</sub> (5.9 mass%) to be realistic, owing to the corrosive nature of ammonia.

### Hydrogen adsorption on solids of large surface area

Hydrogen adsorbs at solid surfaces depending on the applied pressure and the temperature. The variation of attractive surface forces as a function of distance from the surface decides whether van der

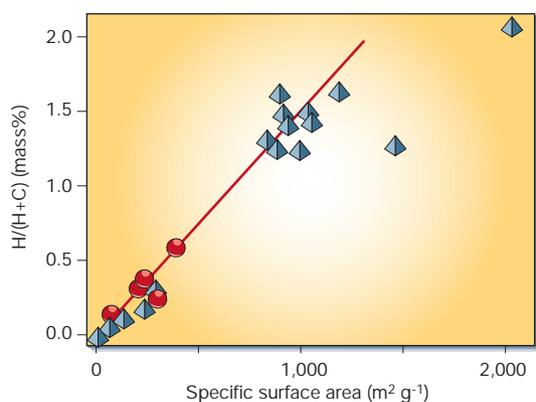
**Table 1** Physical and chemical properties of hydrogen, methane and petrol

Properties	Hydrogen (H <sub>2</sub> )	Methane (CH <sub>4</sub> )	Petrol (–CH <sub>2</sub> –)
Lower heating value (kWh kg <sup>-1</sup> )	33.33	13.9	12.4
Self-ignition temperature (°C)	585	540	228–501
Flame temperature (°C)	2,045	1875	2,200
Ignition limits in air (Vol%)	4–75	5.3–15	1.0–7.6
Minimal ignition energy (mW s)	0.02	0.29	0.24
Flame propagation in air (m s <sup>-1</sup> )	2.65	0.4	0.4
Diffusion coefficient in air (cm <sup>2</sup> s <sup>-1</sup> )	0.61	0.16	0.05
Toxicity	No	No	High

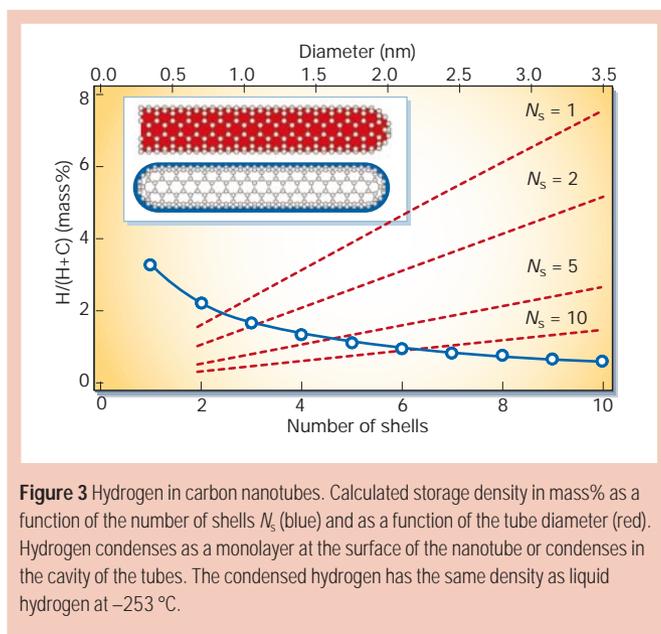
Waals-type weak physisorption of molecular hydrogen occurs, or whether dissociation and chemisorption of atomic hydrogen takes place. Owing to the attractive forces, the most stable position for an adsorbed molecule is with its centre at about 1 molecular radius from the surface, and the attractive field rapidly diminishes at greater distances. Once a monolayer of adsorbate molecules or atoms has formed, the gaseous species interacts with the liquid or solid adsorbate. Therefore, the binding energy of the second layer of adsorbates is similar to the latent heat of sublimation or vaporization of the adsorbate. Consequently, adsorption at a temperature at or above the boiling point of the adsorbate at a given pressure leads to the adsorption of a single monolayer. For storage purposes, the adsorption of hydrogen has been studied on carbon species only. Other light and reasonably cheap materials of high surface area may prove to be attractive as well.

The condensation of a monolayer of hydrogen on a solid leads to a maximum of  $1.3 \times 10^{-5} \text{ mol m}^{-2}$  of adsorbed hydrogen. In the case of a graphene sheet with a specific surface area of  $1,315 \text{ m}^2 \text{ g}^{-1}$  as adsorbent, the maximum theoretical concentration is 0.4 H atoms per surface carbon atom or 3.3 mass% hydrogen on sheets with hydrogen atoms on one side. On active carbon with the specific surface area of  $1,315 \text{ m}^2 \text{ g}^{-1}$ , 2 mass% hydrogen is reversibly adsorbed at a temperature of 77 K (ref. 4). On nanostructured graphitic carbon at 77 K (liquid nitrogen temperature), the reversibly adsorbed quantity of hydrogen correlates with the specific surface area of the sample. It amounts to 1.5 mass% per  $1,000 \text{ m}^2 \text{ g}^{-1}$  of specific surface area (Fig. 2), in agreement with the calculation shown in Fig. 3. Nanostructured graphite produced by ball milling for 80 h in a 1-MPa hydrogen atmosphere contains up to 0.95 H atoms per carbon atom or 7.4 mass%. Eighty per cent of this hydrogen desorbs at a temperature of over 600 K. Evidently, moderately high hydrogen absorption can be realized with planar graphitic structures at low temperature<sup>7,8</sup>.

Are curved structures more attractive? In microporous solids with capillaries which have a width not exceeding a few molecular diameters (the diameter of  $\text{H}_2$  is 0.41 nm), the potential fields from opposite walls overlap so that the attractive force acting on hydrogen molecules is greater than that on an open flat surface. The effect of nanotube curvature on the adsorption energy for hydrogen has been investigated theoretically by Stan and Cole<sup>9</sup>. The Feynman (semiclassical) effective potential approximation was used to calculate the adsorption potential and the amount of hydrogen adsorbed on a (13,0) zigzag nanotube. The adsorption potential was found to be  $9 \text{ kJ mol}^{-1}$  for hydrogen molecules inside the nanotubes at 50 K, about 25% higher than on the flat surface of graphite. The increase arises



**Figure 2** Reversibly stored amount of hydrogen on various carbon materials versus the specific surface area of the samples. Circles represent nanotube samples (best-fit line indicated), triangles represent other nanostructured carbon samples<sup>17</sup>.



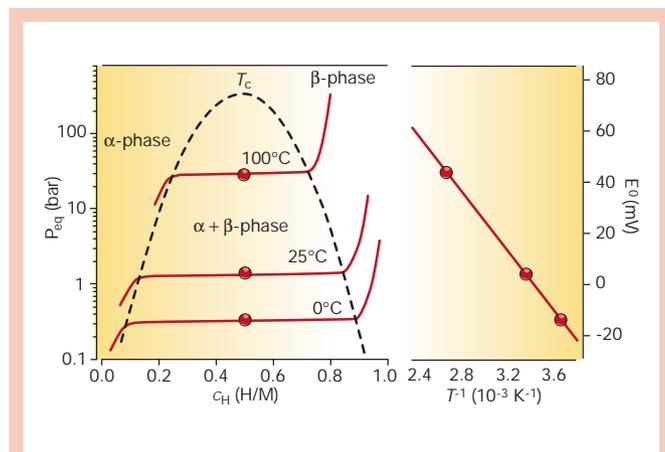
**Figure 3** Hydrogen in carbon nanotubes. Calculated storage density in mass% as a function of the number of shells  $N_s$  (blue) and as a function of the tube diameter (red). Hydrogen condenses as a monolayer at the surface of the nanotube or condenses in the cavity of the tubes. The condensed hydrogen has the same density as liquid hydrogen at  $-253 \text{ }^\circ\text{C}$ .

from the curvature of the surface and the related higher number of carbon atoms interacting with the hydrogen molecule. At low temperatures, far more hydrogen can be adsorbed in the tube than on a flat surface; but the ratio decreases strongly with increasing temperature, from 55 at 50 K to 11 at 77 K.

Conflicting results have been published concerning the reversible storage of hydrogen in carbon nanotubes (see refs 8, 9 for detailed reviews). To a large extent the controversy is caused by insufficient characterization of the carbon material used. It is often a mixture of opened and unopened, single-walled and multi-walled tubes of various diameters and helicities together with other carbonaceous species, just a few of which will be analysed in transmission electron micrographs. To our knowledge, the 'fantastic' results of the Northwestern University group<sup>10</sup> (more than 60 mass% hydrogen in specific carbon fibres) have not been reproduced elsewhere. Heben *et al.*<sup>11,12</sup> still claim to reach 6–8 mass% reversible storage (cooling at 1 bar down to liquid nitrogen temperature) in high-purity single-walled tubes opened by sonication. But Hirscher *et al.*<sup>13</sup> revealed that a sonication bar made of titanium alloy results in hydrogen-storing titanium alloy particles in the nanotube material; storage was below 1 mass% when stainless steel sonication bars were used. Zuetzel *et al.*<sup>14</sup> showed by thermal desorption mass spectroscopy that after reaction of carbon nanotubes with hydrogen at elevated temperatures, hydrocarbons are desorbed. The large mass increase observed by Chen *et al.*<sup>15</sup> when carbon nanotubes filled with alkaline metals were exposed to hydrogen has been attributed to hydroxide formation<sup>16</sup>.

Nijkamp *et al.*<sup>17</sup> have surveyed the storage capacities of a large number of different carbonaceous adsorbents for hydrogen at 77 K and 1 bar. They concluded that microporous adsorbents, for example zeolites and activated carbons, have appreciable sorption capacities. Optimization of sorbent and adsorption conditions is expected to lead to adsorption of  $560 \text{ ml STP g}^{-1}$ , close to targets set for practical use in vehicles. Zuetzel *et al.*<sup>18</sup> concluded that charging of carbon nanotubes with hydrogen at liquid nitrogen temperature (77 K), or cathodically at ambient conditions, is due to physisorption. The amount of adsorbed hydrogen is proportional to the specific surface area of the carbon nanotube material and limited to 2 mass% for carbon materials (Fig. 2).

Taking all these results together, we consider it to be scientifically interesting and challenging to continue research on the interaction of hydrogen with different and well-characterized carbon nanostructures. Whether a hydrogen-storage material will emerge from it, however, remains an open question.



**Figure 4** Pressure–concentration–temperature plot and a van't Hoff curve (logarithm of the equilibrium or plateau pressure against the reciprocal temperature); values are for  $\text{LaNi}_5$ . The vertical axes indicate the corresponding hydrogen pressure or the equivalent electrochemical potential. From the slope of the van't Hoff plot, experimental values of the enthalpy of hydride formation  $\Delta H$  can be evaluated. The plateau pressure  $p_{\text{eq}}(T)$  as a function of temperature is related to the changes  $\Delta H$  and  $\Delta S$  of enthalpy and entropy, respectively, by the van't Hoff equation:  $\ln(p_{\text{eq}}/p_{\text{eq}}^0) = (-\Delta H/R)(1/T) + \Delta S/R$ .

In an interesting sideline to work<sup>19</sup> — addressing the potential of metallization and superconductivity of hydrogen, rather than its storage — some hydrogen was reported to be sorbed into graphite intercalation compounds made of alkaline metals between graphene sheets. Intercalation of hydrogen alone between the graphene layers in macroscopic structures has never been reported. The dynamic diameter of a free hydrogen molecule ( $d = 0.4059$  nm) is larger than the interlayer distance in graphite ( $d = 0.3355$  nm), so a significant size mismatch would have to be accommodated upon entry.

### Hydrogen storage by metal hydrides

Many metals and alloys are capable of reversibly absorbing large amounts of hydrogen. Charging can be done using molecular hydrogen gas or hydrogen atoms from an electrolyte. Molecular hydrogen is dissociated at the surface before absorption; two H atoms recombine to  $\text{H}_2$  in the desorption process. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure–composition isotherms (Fig. 4). The host metal initially dissolves some hydrogen as a solid solution ( $\alpha$ -phase). As the hydrogen pressure together with the concentration of H in the metal is increased, interactions between hydrogen atoms become locally important, and we start to see nucleation and growth of the hydride ( $\beta$ ) phase. While the two phases coexist, the isotherms show a flat plateau, the length of which determines how much  $\text{H}_2$  can be stored reversibly with small pressure variations. In the pure  $\beta$ -phase, the  $\text{H}_2$  pressure rises steeply with the concentration. At higher  $\text{H}_2$  pressure, further plateaux and further hydride phases may be formed. The two-phase region ends in a critical point  $T_c$ , above which the transition from  $\alpha$  to  $\beta$ -phase is continuous. The plateau or equilibrium pressure depends strongly on temperature and is related to the changes  $\Delta H$  and  $\Delta S$  of enthalpy and entropy, respectively. As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissolved hydrogen, it is roughly  $130 \text{ J K}^{-1} \text{ mol}^{-1}$  for all metal–hydrogen systems under consideration. The enthalpy term characterizes the stability of the metal–hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K,  $\Delta H$  should amount to  $19.6 \text{ kJ mol H}^{-1}$  (ref. 20). The operating temperature of a metal hydride system is fixed by the plateau pressure in thermodynamic equilibrium and by the overall reaction kinetics<sup>21</sup>.

Hydrogen is located in the form of atoms, never molecules, on interstitial sites of the host metal lattice. The lattice expands during

hydrogen sorption, often losing some of its high symmetry. As a consequence of the coexistence of the non-expanded  $\alpha$ -phase and anisotropically expanded  $\beta$ -phase, lattice defects and internal strain fields are formed, which end in a decrepitation of brittle host metals such as intermetallics. The H atoms vibrate about their equilibrium position, and perform local motions and long-range diffusion.

In terms of electronic structure, the proton acts as an attractive potential to the host metal electrons; electronic bands are lowered in energy and form low-lying bands by hybridization with the hydrogen band, 6–8 eV below the Fermi level. The Fermi level itself is shifted, and various phase transitions (metal–semiconductor, magnetic–non-magnetic, reflecting–transparent, order–disorder) may occur. The metal–hydrogen bond offers the advantage of very high hydrogen density at moderate pressure and desorption of all stored hydrogen at the same pressure.

Which metallic systems are appropriate for hydrogen storage? Many elemental metals form hydrides, for example  $\text{PdH}_{0.6}$ , rare earth  $\text{REH}_2$ ,  $\text{REH}_3$  or  $\text{MgH}_2$ , none of which are in the pressure and temperature range attractive for mobile storage (1–10 bar, 0–100 °C, corresponding to an enthalpy change between 15 and  $24 \text{ kJ mol H}^{-1}$ ). The discovery of hydrogen sorption by intermetallic compounds created great hopes and stimulated R&D efforts worldwide. Well-known compounds and their properties are summarized in Table 2 (ref. 22).

Alloys derived from  $\text{LaNi}_5$  show some very promising properties, including fast and reversible sorption with small hysteresis, plateau pressure of a few bars at room temperature and good cycling life. The volumetric hydrogen density (crystallographically) of  $\text{LaNi}_5\text{H}_{6.5}$  at 2 bar equals that of gaseous molecular hydrogen at 1,800 bar; but advantageously, all the hydrogen desorbs at a pressure of 2 bar. The density for practical purposes is reduced by the packing fraction of  $\text{LaNi}_5$  powder, but is still above that of liquid hydrogen (Fig. 5). Storage in these intermetallics allows very safe hydrogen handling. But as lanthanum and nickel are large elements, the proportion of hydrogen in  $\text{LaNi}_5\text{H}_{6.5}$  remains below 2 mass%. This is attractive for electrochemical hydrogen storage in rechargeable metal hydride electrodes, reaching a capacity of  $330 \text{ mA h g}^{-1}$ , and produced and sold in more than a billion  $\text{AB}_5$ -type metal hydride batteries per year<sup>23–25</sup>.

For gaseous hydrogen fuel tanks to be used in vehicles, however, this is not enough. We need some 4–5 mass% (indeed, 6.5 mass% and  $62 \text{ kg H}_2 \text{ m}^{-3}$  are the targets of the US Department of Energy). This low mass density is the general weakness of all known metal hydrides working near room temperature (Fig. 6). Of course, many intermetallic compounds and alloys are known that form hydrides with up to 9 mass% hydrogen (such as  $\text{Li}_3\text{Be}_2\text{H}_7$ ; ref. 26) and 4.5 H atoms per metal atom ( $\text{BaReH}_9$ ; ref. 27), but they are not reversible within the required range of temperature and pressure.

When reaction kinetics rather than thermodynamic equilibrium conditions limit the hydride formation and decomposition, various physical and chemical pretreatments can be applied. Ball milling has the benefits of reducing the grain size, increasing the defect concentration and shortening the diffusion path. Fluorination treatments<sup>28</sup> are well suited to render the surface active, apparently by means of the formation of surface nickel precipitates, the role of which is well known in the hydrogen dissociation process.

Many promising new ideas are under investigation with the clear goal of enhancing the mass density. For example, new families of

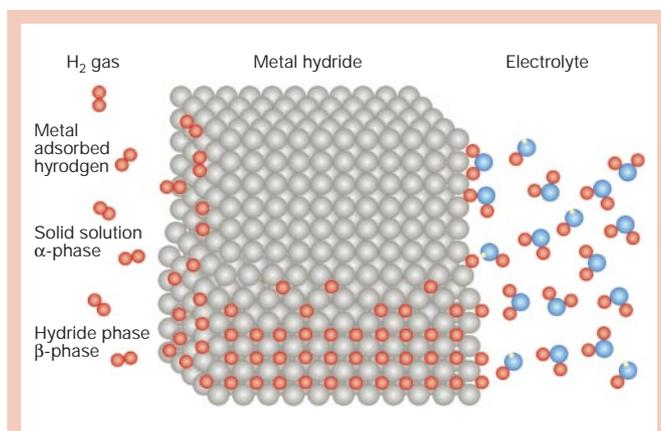
**Table 2** Intermetallic compounds and their hydrogen-storage properties<sup>22</sup>

Type	Metal	Hydride	Structure	mass%	$p_{\text{eq}}, T$
Elemental	Pd	$\text{PdH}_{0.6}$	$Fm\bar{3}m$	0.56	0.020 bar, 298 K
$\text{AB}_5$	$\text{LaNi}_5$	$\text{LaNi}_5\text{H}_6$	$P6/mmm$	1.37	2 bar, 298 K
$\text{AB}_2$	$\text{ZrV}_2$	$\text{ZrV}_2\text{H}_{6.5}$	$Fd\bar{3}m$	3.01	$10^{-8}$ bar, 323 K
AB	FeTi	$\text{FeTiH}_2$	$Pm\bar{3}m$	1.89	5 bar, 303 K
$\text{A}_2\text{B}$	$\text{Mg}_2\text{Ni}$	$\text{Mg}_2\text{NiH}_4$	$P6222$	3.59	1 bar, 555 K
Body-centred cubic	$\text{TiV}_2$	$\text{TiV}_2\text{H}_4$	b.c.c.	2.6	10 bar, 313 K

alloys are being studied in several Japanese laboratories<sup>29–31</sup> and are included into the national 'Protium' programme. They are based on vanadium, zirconium and titanium as rather electropositive components combined with 3*d* and 4*d* transition metals. Reversible hydrogen-storage capacities approaching 3 mass% around room temperature have been reported.

A higher mass density is reachable only with light elements such as calcium and magnesium. In fact, Mg forms ionic, transparent MgH<sub>2</sub> containing 7.6 mass% hydrogen. But its formation from bulk Mg and gaseous hydrogen is extremely slow, and in thermodynamic equilibrium a plateau pressure of 1 bar requires not room temperature but 300 °C. Different processes have been tried to obtain micro- or nanostructured Mg: precipitations from metal-organic solutions or high-energy ball milling of Mg have proved successful ways to obtain good charging or discharging kinetics at 150 °C, and the thermodynamics evidently are not affected<sup>26,29–31</sup>. Alloying Mg before the hydride formation is another approach: Mg<sub>2</sub>Ni forms a ternary complex hydride Mg<sub>2</sub>NiH<sub>4</sub>, which still contains 3.6 mass% hydrogen. The hydride forms fairly rapidly, probably owing to the presence of Ni as catalyst for the dissociation of molecular hydrogen, but thermodynamically it still requires 280 °C for 1 bar hydrogen. The alloys Mg<sub>2</sub>Cu, Mg<sub>17</sub>La<sub>2</sub> and MgAl, and some other known alloys or intermetallic compounds of Mg, react readily (MgAl after ball milling) with hydrogen and decompose into MgH<sub>2</sub> and another compound or hydride. One example is Mg<sub>2</sub>Cu + H<sub>2</sub> which decomposes to MgH<sub>2</sub> + MgCu<sub>2</sub>. The reactions are reversible at high temperature.

In addition to the enthalpy change of the hydrogen sorption reaction, we now also have to consider the enthalpy change of the host metal system. Could this make Mg-based storage alloys more attractive? If the transformation of the host metal system that accompanies hydrogen desorption is exothermic itself, the net enthalpy of hydrogen desorption becomes smaller. In the systems studied so far (Mg–Cu, Mg–Al), the temperature for 1 bar equilibrium pressure could be lowered from 300 °C to 280 °C. This is not a large improvement, and it has the penalty that the mass density is thereby reduced as well. Magnesium does not form a binary intermetallic compound with iron, but in the presence of hydrogen it is possible to synthesize the rather stable ternary hydride Mg<sub>2</sub>FeH<sub>6</sub> with 5.5 mass% hydrogen<sup>26</sup>.



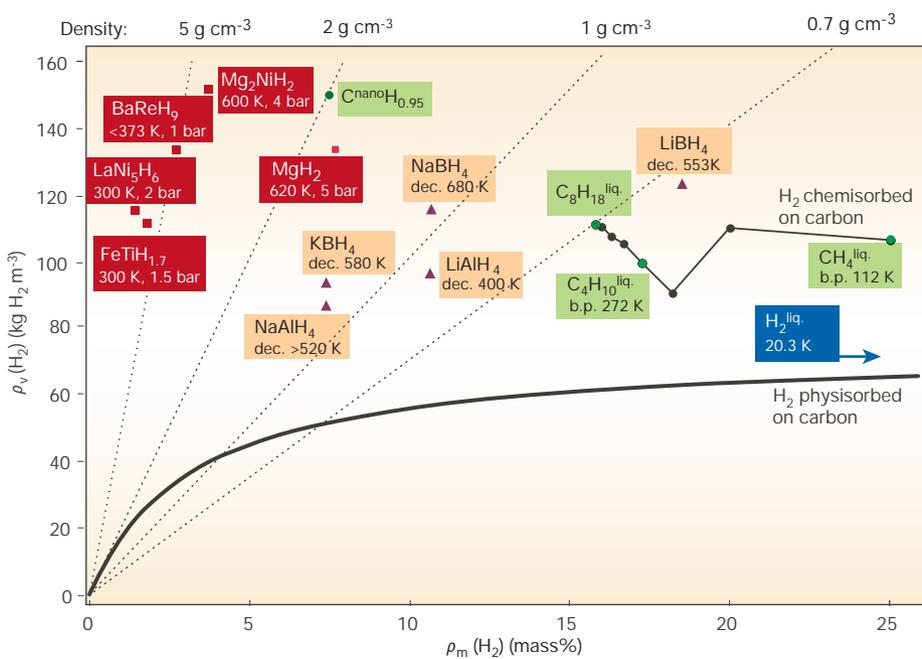
**Figure 5** Schematic model of a metal structure with H atoms in the interstices between the metal atoms, and H<sub>2</sub> molecules at the surface. Hydrogen atoms are from physisorbed hydrogen molecules on the left-hand side and from the dissociation of water molecules on the right-hand side.

A different approach is to use composite materials, in which attractive properties of two components are combined to overcome their weaknesses. For instance, magnesium has been ball milled with graphitic carbon or mixed with hydrides showing fast kinetics, such as LaNi<sub>5</sub> or Mg<sub>2</sub>Ni. It comes as no surprise that the capacities reached values between those of the components<sup>5,26,32</sup>.

### Alanes and other light hydrides

Some of the lightest elements in the periodic table, for example lithium, boron, sodium and aluminium, form stable and ionic compounds with hydrogen. The hydrogen content reaches values of up to 18 mass% for LiBH<sub>4</sub>. However, such compounds desorb the hydrogen only at temperatures from 80 °C up to 600 °C, and the reversibility of the reaction is not yet clear for all systems. Bogdanovic and Schwickardi<sup>33</sup> showed in 1996 that the decomposition temperature of NaAlH<sub>4</sub> can be lowered by doping the hydride with TiO<sub>2</sub>. The same group showed the reversibility of the reaction

**Figure 6** Stored hydrogen per mass and per volume. Comparison of metal hydrides, carbon nanotubes, petrol and other hydrocarbons.



for several desorption/absorption cycles. This is a good example of the potential of such hydrides, which were discovered more than 50 years ago. But several points have to be clarified. First, is the high desorption temperature due to the poor kinetics of the system or due to the thermodynamic stability of the compound? The kinetics can be improved by applying an appropriate catalyst to the system and apparently also by ball milling and the introduction of defects. Second, what are the conditions for a reversible reaction — for example, formation and stabilization of clusters of an intermetallic compound of the remaining metals on desorption? Third, what is the desorption reaction and what are the intermediate reaction products (decomposition in several steps)?

Assuming that these questions can be answered, what would be the role of light hydrides in an on-board fuel cell? The exhaust gas of a fuel cell is water vapour, which could be collected and reused for on-board hydrogen production. The common experiment — shown in many chemistry classes — where a small piece of sodium floating on water produces hydrogen, demonstrates such a process. The sodium is transformed to sodium hydroxide in this reaction. The reaction is not reversible, but the sodium hydroxide could later be removed and reduced in a solar furnace back to sodium. Each sodium atom produces one hydrogen atom, so the corresponding gravimetric hydrogen density of the sodium reaction is slightly more than 4 mass%. Lithium used in the same way would deliver up to 14 mass% of hydrogen. The alkali metals as a hydrogen source are easy to handle, and a car could be refilled within a few minutes. To deliver the necessary 4 kg of hydrogen using the water produced in the fuel cell would take 28 kg of lithium. After using up all the hydrogen the tank would contain 99 kg of lithium hydroxide, ready to be recycled.

### Visions for the future

Road traffic is likely to increase even more. Must road vehicles have to satisfy human prestige, and do we need a strong and heavy vehicle cage to protect drivers and passengers from being injured in case of inevitable mistakes? As soon as wireless, electronic control systems are installed to help to avoid crashes, much lighter and more energy-efficient vehicles will be built in countries that do not consider energy availability to be unlimited. In Europe and Japan, there are already small and lightweight cars available with a combustion engine using as little as 3 l of petrol per 100 km (that is, less than half the amount used by conventional, widely used cars). Four kilograms of hydrogen are enough to run 400 km with a combustion engine, and only 2 kg hydrogen for a modern car driven by a fuel cell.

The new joint venture of Shell, GfE and Hydro-Québec<sup>3</sup> on hydrogen storage using metal hydrides, and the fact that no comparable economic effort on hydrogen storage in carbon nanostructures exists, can be taken as clear signs in favour of the metal–hydrogen systems. There is reason for hope that one day much better hydrogen-storage materials will be discovered and developed, rather as we have seen a revolution in high-temperature superconducting materials or hard permanent magnets. We must bear in mind that to develop a sustainable future energy policy requires us to focus not only on the scientific and technical challenge, but also on vital adaptations by the socioeconomic system and a change in attitudes to energy. Sustainability — and humanity — will profit if the price we

pay for energy includes costs for long-term production, transport and distribution of energy, materials, and restoration of the damaged environment. □

1. Winter, C. J. & Nitsch, J. *Hydrogen as an Energy Carrier: Technologies, Systems, Economy* (Springer, 1988).
2. Bain, A. & Van Vorst, W. D. *Int. J. Hydrogen Energy* **24**, 399–403 (1999).
3. Shell Hydrogen, Hydro-Québec (HQ) & Gesellschaft für Elektrometallurgie (GfE). Hydrogen storage joint venture to be established. < http://www.shell.com > Press release (12-07-2001).
4. Nellis, W. J., Louis, A. A. & Ashcroft, N. W. Metallization of fluid hydrogen. *Phil. Trans. R. Soc. Lond. A* **356**, 119–135 (1998).
5. Orimo, S.-I. *et al.* Hydrogen in the mechanically prepared nanostructured graphite. *Appl. Phys. Lett.* **75**, 3093 (1999).
6. Orimo, S., Matsushima, T., Fujii, H., Fukunaga, T. & Majer, G. Defective carbon for hydrogen storage—thermal desorption property of the mechanically prepared nanostructured graphite. *J. Appl. Phys.* (in the press).
7. Stan, G. & Cole, M. W. Hydrogen adsorption in nanotubes. *J. Low Temp. Phys.* **110**, 539–544 (1998).
8. Hirscher, M. (ed.) Hydrogen storage in nanoscale carbon and metals. *Appl. Phys. A* (special issue) **72**, 2 (2001).
9. Sholl, C. A. & Gray, E. MacA. (eds) Proc. Int. Symp. Metal Hydrogen Systems—Fundamentals and Applications, Noosa, Australia, 1–6 October 2000. *J. Alloys Compounds* (in the press).
10. Chambers, A., Park, C., Baker, R. T. K. & Rodriguez, N. M. Hydrogen storage in graphite nanofibers. *Phys. Chem. B* **102**, 4253–4256 (1998).
11. Dillon, A. C. *et al.* Storage of hydrogen in single-walled carbon nanotubes. *Nature* **386**, 377–379 (1997).
12. Dillon, A. C. *et al.* Carbon nanotube materials for hydrogen storage. Proc. 2000 DOE/NREL Hydrogen program review, 8–10 May 2000.
13. Hirscher, M. *et al.* Hydrogen storage in sonicated carbon materials. *Appl. Phys. A* **72**, 129–132 (2001).
14. Züttel, A. *et al.* Hydrogen sorption by carbon nanotubes and other carbon nanostructures. *J. Alloys Compounds* (in the press).
15. Chen, P., Wu, X., Lin, J. & Tan, K. L. High H<sub>2</sub> uptake by alkali-doped carbon nanotubes under ambient pressure and moderate temperatures. *Science* **285**, 91–93 (1999).
16. Hirscher, M. *et al.* Hydrogen storage in carbon nanostructures. *J. Alloys Compounds* (in the press).
17. Nijkamp, M. G., Raaymakers, J. E. M. J., Van Dillen, A. J. & De Jong, K. P. Hydrogen storage using physisorption—materials demands. *Appl. Phys. A* **72**, 619–623 (2001).
18. Züttel, A. *et al.* Hydrogen storage in carbon nanostructures. *Int. J. Hydrogen Energy* (in the press).
19. Enoki, T., Shindo, K. & Sakamoto, N. Electronic properties of alkali-metal-hydrogen-graphite intercalation compounds. *Z. Phys. Chem.* **181**, 75–82 (1993).
20. Schlögl, L. (ed.) *Hydrogen in Intermetallic Compounds I. Electronic, Thermodynamic, and Crystallographic Properties, Preparation* (Topics in Applied Physics Vol. 63) (Springer, 1988).
21. Schlögl, L. (ed.) *Hydrogen in Intermetallic Compounds II. Surface and Dynamic Properties, Applications* (Topics in Applied Physics Vol. 67) (Springer, 1992).
22. Sandrock, G. & Thomas, G. The IEA/DOC/SNL on-line hydride databases. *Appl. Phys. A* **72**, 153–155 (2001).
23. Sakai, T., Natsuoka, M. & Iwakura, C. Rare earth intermetallics for metal–hydrogen batteries. *Handb. Phys. Chem. Rare Earths* **21**, 135–180 (1995).
24. Lacroche, M., Percheron-Guegan, A. & Chabre, Y. Influence of cobalt content in MmNi<sub>(1-x)</sub>Mn<sub>0.3</sub>Al<sub>0.7</sub>Co<sub>x</sub> alloy (x = 0.36 and 0.69) on its electrochemical behaviour studied by in situ neutron diffraction. *J. Alloys Compounds* **295**, 637–642 (1999).
25. Schlögl, L., Felix Meli, F., Züttel, A., Westbrook, J. H. & Fleischer, R. L. (eds) in *Intermetallic Compounds: Principles and Practice* Vol. 2, Ch. 22 (Wiley, 1994).
26. Zaluska, A., Zaluski, L. & Stroem-Olsen, J. O. Structure, catalysis and atomic reactions on the nanoscale: a systematic approach to metal hydrides for hydrogen storage. *Appl. Phys. A* **72**, 157 (2001).
27. Yvon, K. Complex transition metal hydrides. *Chimia* **52**, 613–619 (1998).
28. Liu, F. J. & Suda, S. A method for improving the long-term storability of hydriding alloys by air water exposure. *J. Alloys Compounds* **231**, 742–750 (1995).
29. Akiba, E. & Iba, H. Hydrogen absorption by Laves phase related BCC solid solution. *Intermetallics* **6**, 461–470 (1998).
30. Kuriwa, T. *et al.* New V-based alloys with high protium absorption and desorption capacity. *J. Alloys Compounds* **295**, 433–436 (1999).
31. Tsukahara, M. *et al.* Hydrogen storage and electrode properties of V-based solid solution type alloys prepared by a thermic process. *J. Electrochem. Soc.* **147**, 2941–2944 (2000).
32. Inoue, H. *et al.* Effect of ball-milling with Ni and Raney Ni on surface structural characteristics of TiV<sub>2</sub>1Ni<sub>0.3</sub> alloy. *J. Alloys Compounds* **325**, 299–303 (2001).
33. Bogdanovic, B. & Schwickardi, M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. *J. Alloys Compounds* **253**, 1–9 (1997).

### Acknowledgements

We thank the Swiss Federal Office of Energy (BFE), in contract with IEA, the Swiss Federal Office of Education and Science (BBW), and the University of Fribourg and EMPA for support of our hydrogen-storage research projects.