



Materials for hydrogen storage

by Andreas Züttel

Hydrogen storage is a materials science challenge because, for all six storage methods currently being investigated, materials with either a strong interaction with hydrogen or without any reaction are needed. Besides conventional storage methods, i.e. high pressure gas cylinders and liquid hydrogen, the physisorption of hydrogen on materials with a high specific surface area, hydrogen intercalation in metals and complex hydrides, and storage of hydrogen based on metals and water are reviewed.

The goal is to pack hydrogen as close as possible, i.e. to reach the highest volumetric density by using as little additional material as possible. Hydrogen storage implies the reduction of an enormous volume of hydrogen gas. At ambient temperature and atmospheric pressure, 1 kg of the gas has a volume of 11 m³. To increase hydrogen density, work must either be applied to compress the gas, the temperature decreased below the critical temperature, or the repulsion reduced by the interaction of hydrogen with another material.

The second important criterion for a hydrogen storage system is the reversibility of uptake and release. Materials that interact with hydrogen, therefore, as well as inert materials, are important. The reversibility criterion excludes all covalent hydrogen-carbon compounds because hydrogen is only released if they are heated to temperatures above 800°C, or if the carbon is oxidized. Basically, six methods of reversible hydrogen storage with a high volumetric and gravimetric density are known today, listed in Table 1. This article reviews the various hydrogen storage methods and illustrates their advantages and the material challenges.

Storing hydrogen as a gas

Three isotopes of hydrogen are known, hydrogen or protium (H), deuterium (D), and the unstable tritium (T). All the isotopes of hydrogen form covalent molecules like H₂, D₂, and T₂, respectively, because of the single electron in the atom. Hydrogen has an ambivalent behavior towards other

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Table 1 The six basic hydrogen storage methods and phenomena. The gravimetric density ρ_m , the volumetric density ρ_v , the working temperature T , and pressure p are listed. RT stands for room temperature (25°C).

Storage method	ρ_m [mass%]	ρ_v [kg H ₂ m ⁻³]	T [°C]	p [bar]	Phenomena and remarks
High pressure gas cylinders	13	<40	RT	800	Compressed gas (molecular H ₂) in light weight composite cylinders (tensile strength of the material is 2000 MPa)
Liquid hydrogen in cryogenic tanks	size dependent	70.8	-252	1	Liquid hydrogen (molecular H ₂), continuous loss of a few % per day of hydrogen at RT
Adsorbed hydrogen	≈ 2	20	-80	100	Physisorption (molecular H ₂) on materials e.g. carbon with a very large specific surface area, fully reversible
Absorbed on interstitial sites in a host metal	≈ 2	150	RT	1	Hydrogen (atomic H) intercalation in host metals, metallic hydrides working at RT are fully reversible
Complex compounds	<18	150	>100	1	Complex compounds ([AlH ₄] ⁻ or [BH ₄] ⁻), desorption at elevated temperature, adsorption at high pressures
Metals and complexes together with water	<40	>150	RT	1	Chemical oxidation of metals with water and liberation of hydrogen, not directly reversible?

elements, occurring as an anion (H⁻) or cation (H⁺) in ionic compounds, forming covalent bonds, e.g. with carbon, or even behaving like a metal to form alloys or intermetallic compounds at ambient temperature.

The phase diagram of the hydrogen molecule H₂ is shown in Fig. 1. At low temperatures, hydrogen is a solid with a density of 70.6 kg·m⁻³ at -262°C, and a gas at higher temperatures with a density of 0.089886 kg·m⁻³ at 0°C and a pressure of 1 bar. Hydrogen is a liquid in a small zone between the triple and critical points with a density of 70.8 kg·m⁻³ at -253°C. At ambient temperature (298.15 K), hydrogen gas is described by the Van der Waals equation:

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2} \quad (1)$$

where p is the gas pressure, V the volume, T the absolute temperature, n the number of moles, R the gas constant, a is the dipole interaction or repulsion constant, and b is the volume occupied by the hydrogen molecules¹. The strong repulsive interaction between hydrogen is responsible for the low critical temperature ($T_c = 33$ K) of the gas.

High pressure gas cylinders

The most common storage system is high pressure gas cylinders, which are operated at a maximum pressure of 20 MPa. The wall thickness of a cylinder capped with two hemispheres is given by the following equation:

$$\frac{d_w}{d_o} = \frac{\Delta p}{2 \cdot \sigma_v + \Delta p} \quad (2)$$

where d_w is the wall thickness, d_o the outer diameter of the cylinder, Δp the overpressure, and σ_v the tensile strength of the material. The tensile strength of materials varies from 50 MPa for Al to more than 1100 MPa for high quality steel. Other materials like B have a tensile strength of up to 2410 MPa and a density of only 2370 kg·m⁻³. New lightweight composite cylinders have been developed that are able to withstand pressures up to 80 MPa, so that hydrogen can reach a volumetric density of 36 kg·m⁻³,

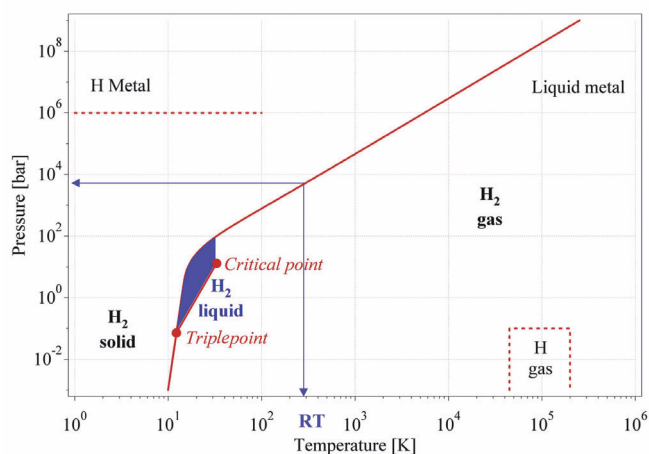


Fig. 1 Primitive phase diagram for hydrogen⁴⁶. Liquid hydrogen only exists between the solidus line and the line from the triple point at 21.2 K and the critical point at 32 K.

approximately half as much as in its liquid form at normal boiling point. The ideal material for a high pressure cylinder has a very high tensile strength (not necessarily isotropic), a low density, and does not react with hydrogen or allow hydrogen to diffuse into it. Most pressure cylinders to date have used austenitic stainless steel (e.g. AISI 316 and 304 and AISI 316L and 304L above 300°C to avoid carbon grain-boundary segregation²), Cu, or Al alloys, which are largely immune to hydrogen effects at ambient temperatures. Fig. 2 shows the volumetric density of hydrogen inside the cylinder and the ratio of the wall thickness to the outer diameter of the pressure cylinder for stainless steel with a tensile strength of 460 MPa. The volumetric density increases with pressure and reaches a maximum above 1000 bar, depending on the tensile strength of the material. However, the gravimetric density decreases with increasing pressure, and the maximum gravimetric density is found for zero overpressure! Therefore, the increase in volumetric storage density is sacrificed with the reduction of the gravimetric density in pressurized gas systems.

The safety of pressurized cylinders is a concern, especially in highly populated regions. It is envisaged that future pressure vessels will consist of three layers: an inner polymer liner over-wrapped with a carbon-fiber composite (which is the stress-bearing component) and an outer layer of an aramid-material capable of withstanding mechanical and corrosion damage. Industry has set itself a target of a 110 kg, 70 MPa cylinder with a gravimetric storage density of 6 mass% and a volumetric storage density of 30 kg·m⁻³.

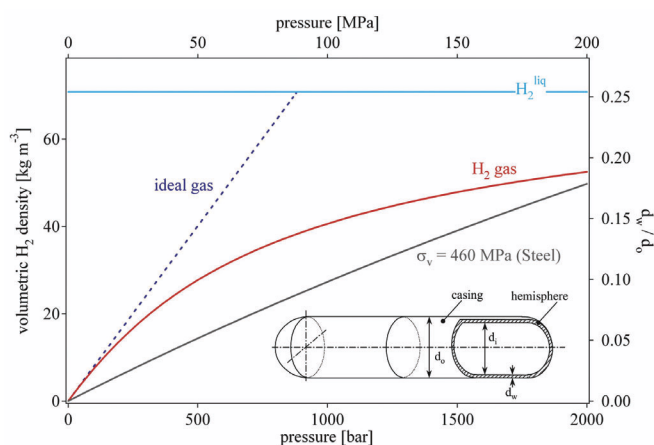


Fig. 2 Volumetric density of compressed hydrogen gas as a function of gas pressure, including the ideal gas and liquid hydrogen. The ratio of the wall thickness to the outer diameter of the pressure cylinder is shown on the right hand side for steel with a tensile strength of 460 MPa. A schematic drawing of the pressure cylinder is shown as an inset.

Hydrogen can be compressed using standard, piston-type mechanical compressors. The theoretical work for the isothermal compression of hydrogen is given by the equation:

$$\Delta G = R \cdot T \cdot \ln\left(\frac{p}{p_0}\right) \quad (3)$$

where R is the gas constant, T the absolute temperature, p and p_0 the end pressure and the starting pressure, respectively. The error of the work calculated with eq 3 in the pressure range of 0.1-100 MPa is less than 6%. The isothermal compression of hydrogen from 0.1-80 MPa therefore consumes 2.21 kWh·kg⁻¹. In a real process, the work consumption is significantly higher because compression is not isothermal. Compression ratios of greater than 20:1 are possible³ with final pressures >100 MPa.

The relatively low hydrogen density together with the very high gas pressures in the system are important drawbacks of this technically simple and, on the laboratory scale, well established high pressure storage method.

Liquid hydrogen storage

Liquid hydrogen is stored in cryogenic tanks at 21.2 K at ambient pressure. Because of the low critical temperature of hydrogen (33 K), the liquid form can only be stored in open systems, as there is no liquid phase existent above the critical temperature. The pressure in a closed storage system at room temperature (RT) could increase to ~10⁴ bar.

The simplest liquefaction cycle is the Joule-Thomson cycle (Linde cycle). The gas is first compressed and then cooled in a heat exchanger, before it passes through a throttle valve where it undergoes an isenthalpic Joule-Thomson expansion, producing some liquid. The cooled gas is separated from the liquid and returned to the compressor via the heat exchanger⁴. The Joule-Thomson cycle works for gases, such as nitrogen, with an inversion temperature above RT. Hydrogen, however, warms upon expansion at RT. For hydrogen to cool upon expansion, its temperature must be below its inversion temperature of 202 K. Hydrogen is usually precooled using liquid nitrogen (78 K), therefore, before the first expansion step occurs. The free enthalpy change⁵ between gaseous hydrogen at 300 K and liquid hydrogen at 20 K is 11640 kJ·kg⁻¹. The necessary theoretical energy (work) to liquefy hydrogen from RT is $W_{th} = 3.23$ kWh·kg⁻¹, the technical work⁶ is about 15.2 kWh·kg⁻¹, almost half of the lower heating value of hydrogen combustion.

The boil-off rate of hydrogen from a liquid storage vessel because of heat leaks is a function of its size, shape, and thermal insulation. Since boil-off losses as a result of heat leaks are proportional to the surface-to-volume ratio, the evaporation rate diminishes as the storage tank size increases. For double-walled, vacuum-insulated spherical dewars, boil-off losses are typically 0.4% per day for those with a storage volume of 50 m³, 0.2% for 100 m³ tanks, and 0.06% for 20 000 m³ tanks.

The large amount of energy necessary for liquefaction and the continuous boil-off of hydrogen limit the possible use of liquid hydrogen storage systems to applications where the cost of hydrogen is not an issue and the gas is consumed in a short time, e.g. air and space applications.

Physisorption of hydrogen

Resonant fluctuations in charge distributions, which are called dispersive or Van der Waals interactions, are the origin of the physisorption of gas molecules onto the surface of a solid. In this process, a gas molecule interacts with several atoms at the surface of a solid. The interaction is composed of two terms: an attractive term, which diminishes with the distance between the molecule and the surface to the power of -6, and a repulsive term, which diminishes with distance to the power of -12. The potential energy of the molecule, therefore, shows a minimum at a distance of approximately one molecular radius of the adsorbate. The energy minimum⁷ is of the order of 0.01-0.1 eV (1-10 kJ·mol⁻¹). Because of the weak interaction, significant physisorption is only observed at low temperatures (<273 K).

Once a monolayer of adsorbate molecules is formed, gaseous molecules interact with the surface of the liquid or solid adsorbate. The binding energy of the second layer of adsorbate molecules is, therefore, similar to the latent heat of sublimation or vaporization of the adsorbate. Consequently, a single monolayer is adsorbed at a temperature equal to or greater than the boiling point of the adsorbate at a given pressure⁸. To estimate the quantity of adsorbate in the monolayer, the density of the liquid adsorbate and the volume of the molecule is required. If the liquid is assumed to consist of a close-packed, face-centered cubic structure, the minimum surface area, S_{ml} , for one mole of adsorbate in a monolayer on a substrate can be calculated from the density of the liquid, ρ_{liq} and the molecular mass of the adsorbate, M_{ads} :

$$S_{ml} = \frac{\sqrt{3}}{2} \cdot \left(\sqrt{2 \cdot N_A} \cdot \frac{M_{ads}}{\rho_{liq}} \right)^{\frac{2}{3}} \quad (4)$$

where N_A is the Avogadro constant. The monolayer surface area for hydrogen is $S_{ml}(H_2) = 85\,917 \text{ m}^2 \cdot \text{mol}^{-1}$. The amount of adsorbate, m_{ads} , on a substrate material with specific surface area, S_{spec} is given by $m_{ads} = M_{ads} \cdot S_{spec} / S_{ml}$. In the case of carbon as the substrate and hydrogen as the adsorbate, the maximum specific surface area of carbon is $S_{spec} = 1315 \text{ m}^2 \cdot \text{g}^{-1}$ (single-sided graphene sheet) and the maximum amount of adsorbed hydrogen is $m_{ads} = 3.0 \text{ mass\%}$. From this approximation, we may conclude that the amount of adsorbed hydrogen is proportional to the specific surface area of the adsorbent with $m_{ads} / S_{spec} = 2.27 \times 10^{-3} \text{ mass\%} \cdot \text{m}^{-2} \text{ g}$, and can only be observed at very low temperatures.

Materials with a large specific surface area like activated or nanostructured carbon and carbon nanotubes (CNTs) are possible substrates for physisorption. The main difference between CNTs and high surface area graphite is the curvature of the graphene sheets and the cavity inside the tube. In microporous solids with capillaries, which have a width of less than a few molecular diameters, the potential fields from opposite walls overlap so that the attractive force acting upon adsorbate molecules is increased compared with that on a flat carbon surface⁹. This phenomenon is the main motivation for the investigation of the hydrogen-CNT interaction.

Most work on the theoretical absorption of hydrogen in carbon nanostructures uses the Feynman (semiclassical) effective potential approximation to calculate the adsorption potential¹⁰ or the grand canonical Monte Carlo simulation^{11,12}. The adsorption potential is 9 kJ mol⁻¹ (0.093 eV) for hydrogen molecules inside (13,0) zigzag CNTs with a diameter of 1.018 nm at 50 K – about 25% higher than the flat surface of graphite. The amount of absorbed hydrogen depends on the surface area of the sample, the maximum is 0.6 mass% (at $p = 6 \text{ MPa}$, $T = 300 \text{ K}$). The investigation of hydrogen absorption inside CNTs has shown that it is energetically more favorable for hydrogen atoms to recombine and form molecules¹³. Molecular dynamics simulations of hydrogen atom implantation¹⁴ with an energy of 20 eV through the sidewalls of a (5,5) single-walled carbon nanotube (SWNT) consisting of 150 atoms and a diameter of 0.683 nm has been performed. The hydrogen atoms

recombine to form molecules inside the tube and arrange themselves in a concentric pattern. The hydrogen pressure inside the SWNT increases with the number of injected atoms and reaches 35 GPa for 90 atoms (5 mass%). This simulation does not show condensation of hydrogen inside the nanotube. The critical temperature¹⁵ of hydrogen is 33.25 K. If we assume, that hydrogen behaves in a similar way to nitrogen¹⁶, it should only form one monolayer of liquid at the carbon surface at temperatures above its boiling point. Geometrical considerations of CNTs lead to the specific surface area and to the maximum amount of condensed hydrogen in a surface monolayer. Fig. 3 shows the maximum amount of hydrogen in mass% for the physisorption of hydrogen on CNTs¹⁷. The theoretical maximum amount of adsorbed hydrogen is 3.0 mass% for SWNTs with a specific surface area of $1315 \text{ m}^2 \text{ g}^{-1}$ at a temperature of 77 K.

A large variety of different nanostructured carbon samples have been investigated using a high-pressure microbalance^{18,19} at 77 K, electrochemical galvanostatic measurements at RT²⁰⁻²³, and volumetric (mass flow) gas phase measurements at 77 K. From adsorption–desorption experiments, it is evident that reversible physisorption takes place with all samples. The amount of adsorbed hydrogen correlates with the specific surface area of the sample (Fig. 3). The electrochemical hydrogen absorption is reversible. The maximum discharge capacity measured at

298 K is 2 mass% with a very small discharge current. A few electrochemical measurements are shown in Fig. 3 compared with calculated values. It is remarkable that measurements of hydrogen uptake in the gas phase at 77 K have the same value as electrochemical measurements at 298 K.

To summarize, the reversible hydrogen sorption process is based on physisorption. The amount of adsorbed hydrogen is proportional to the surface area of the nanostructured carbon sample. The amount of adsorbed hydrogen from the gas phase at 77 K and electrochemically at RT is $1.5 \times 10^{-3} \text{ mass}\% \cdot \text{m}^{-2} \text{ g}$. Together with the maximum specific surface area of carbon ($1315 \text{ m}^2 \text{ g}^{-1}$), the maximum measured absorption capacity of the nanostructured material is 2 mass%. The experimental results are in good agreement with theoretical estimations, if we take into account that the measurements were carried out at a temperature of 77 K. This is still far above the critical temperature of hydrogen, which means that the monolayer of hydrogen is not complete. There is no evidence that the geometric structure of nanostructured carbon influences the amount of adsorbed hydrogen. It is obvious that the curvature of nanotubes influences the adsorption energy, but not the amount of adsorbed hydrogen. All attempts to open nanotubes and absorb hydrogen inside do not show any increased absorption. Theoretical studies beyond the well-known physisorption routes lead to various maximum hydrogen absorption capacities. Most of the experiments were performed under special conditions, e.g. at 0 K or high-energy hydrogen atom implantation. No evidence has been found for a higher density of hydrogen in and on carbon nanostructures compared with liquid hydrogen at ambient conditions.

Besides carbon nanostructures, other nanoporous materials have been investigated for hydrogen absorption. Zeolites of different pore architecture and composition, e.g. A, X, and Y, have been analyzed²⁴ in the temperature range 293–573 K and at pressures of 2.5–10 MPa. In this work, hydrogen was absorbed at the desired temperature and pressure. Samples were cooled to RT and then evacuated. Hydrogen release upon heating of the samples to the absorption temperature was measured. The amount of hydrogen absorbed increased with temperature and absorption pressure. The maximum amount of desorbed hydrogen was found to be 0.08 mass% for a sample loaded at a temperature of 573 K and a pressure of 10 MPa. This behavior indicates that absorption is caused

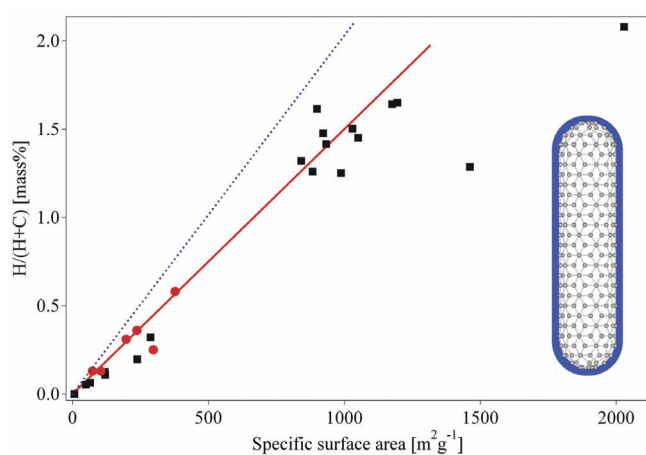


Fig. 3 Reversible amount of hydrogen adsorbed (electrochemical measurement at 298 K) versus the surface area (red circles) of a few CNT samples including two measurements on high surface area graphite (HSAG) samples together with the fitted line. Hydrogen gas adsorption measurements at 77 K from Nijkamp et al.¹⁹ (black squares) are included. The dotted line represents the calculated amount of hydrogen in a monolayer at the surface of the substrate.

by a chemical reaction rather than physisorption. At liquid nitrogen temperatures (77 K), zeolites physisorb hydrogen in proportion to the specific surface area of the material. A maximum of 1.8 mass% of adsorbed hydrogen was found²⁵ for a zeolite (NaY) with a specific surface area of 725 m²·g⁻¹. The low temperature physisorption (type I isotherm) of hydrogen in zeolites is in good agreement with the model for nanostructured carbon. The desorption isotherm follows the same path as adsorption²⁵, indicating that no pore condensation is occurring.

Recently, a microporous metal-organic framework of the composition Zn₄O(1,4-benzenedicarboxylate)₃ was proposed as a hydrogen storage material²⁶. The material was shown to absorb hydrogen at a temperature of 298 K in proportion to the applied pressure. The slope of the linear relationship between the gravimetric hydrogen density and the hydrogen pressure was found to be 0.05 mass%·bar⁻¹. No saturation of the hydrogen absorption was found, which is very unlikely for any kind of hydrogen absorption process. At 77 K, the amount of adsorbed hydrogen was 3.7 mass% at very low hydrogen pressures and showed an almost linear increase with pressure. This behavior is not a type I isotherm, as the authors claim, and the results should be taken with care.

The big advantages of physisorption for hydrogen storage are the low operating pressure, the relatively low cost of the materials involved, and the simple design of the storage system. The rather small gravimetric and volumetric hydrogen density on carbon, together with the low temperatures necessary, are significant drawbacks.

Metal hydrides

Hydrogen reacts at elevated temperatures with many transition metals and their alloys to form hydrides. The electropositive elements are the most reactive, i.e. Sc, Yt, lanthanides, actinides, and members of the Ti and Va groups. The binary hydrides of the transition metals are predominantly metallic in character and are usually referred to as metallic hydrides. They are good conductors, have a metallic or graphite-like appearance, and can often be wetted by Hg.

Many of these compounds, (MH_n), show large deviations from ideal stoichiometry ($n = 1, 2, 3$) and can exist as multiphase systems. The lattice structure is that of a typical metal with hydrogen atoms on the interstitial sites; and for this reason they are also called interstitial hydrides. This type

of structure is limited to the compositions MH, MH₂, and MH₃, with the hydrogen atoms fitting into octahedral or tetrahedral holes in the metal lattice, or a combination of the two. The hydrogen carries a partial negative charge, depending on the metal, but an exception²⁷ is PdH_{0.7}. Pt and Ru are able to adsorb considerable quantities of hydrogen, which becomes activated. These two elements, together with Pd and Ni, are extremely good hydrogenation catalysts, although they do not form hydrides²⁸.

Especially interesting are the metallic hydrides of intermetallic compounds, in the simplest case the ternary system AB_xH_n, because the variation of the elements allows the properties of these hydrides to be tailored. Element A is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. Element B is often a transition metal and forms only unstable hydrides. Some well defined ratios of B:A, where $x = 0.5, 1, 2, 5$, have been found to form hydrides with a hydrogen to metal ratio of up to two.

The reaction of hydrogen gas with a metal is called the absorption process and can be described in terms of a simplified one-dimensional potential energy curve²⁹ (Fig. 4). The hydrogen atoms contribute their electron to the band structure of the metal. At a small hydrogen to metal ratio

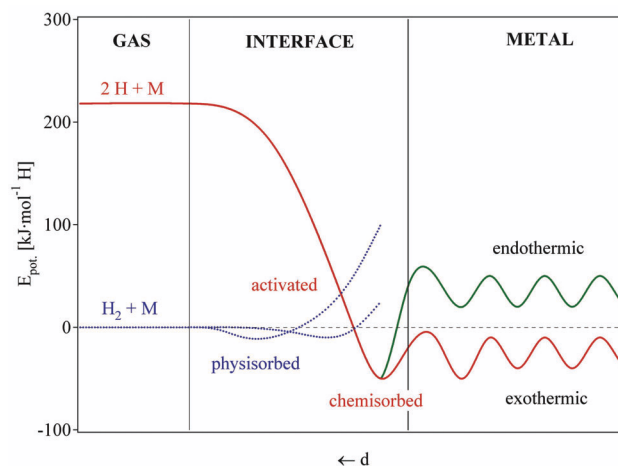


Fig. 4 Far from the metal surface, the potential of a hydrogen molecule and of two hydrogen atoms are separated by the dissociation energy ($H_2 \rightarrow 2H$, $E_D = 435.99 \text{ kJ mol}^{-1}$). The first attractive interaction of the hydrogen molecule approaching the metal surface is the Van der Waals force leading to the physisorbed state ($E_{\text{phys}} \approx 10 \text{ kJ mol}^{-1}$) approximately one hydrogen molecule radius ($\approx 0.2 \text{ nm}$) from the metal surface. Closer to the surface, the hydrogen has to overcome an activation barrier for dissociation and formation of the hydrogen metal bond. The height of the activation barrier depends on the surface elements involved. Hydrogen atoms sharing their electron with the metal atoms at the surface are then in the chemisorbed state ($E_{\text{chem}} \approx 50 \text{ kJ mol}^{-1} H_2$). The chemisorbed hydrogen atoms may have a high surface mobility, interact with each other, and form surface phases at sufficiently high coverage. In the next step, the chemisorbed hydrogen atom can jump in the subsurface layer and finally diffuse on the interstitial sites through the host metal lattice.

($H/M < 0.1$), the hydrogen is exothermically dissolved in the metal (solid-solution, α -phase). The metal lattice expands proportional to the hydrogen concentration by approximately $2\text{-}3 \text{ \AA}^3$ per hydrogen atom³⁰.

At greater hydrogen concentrations in the host metal ($H/M > 0.1$), a strong hydrogen-hydrogen interaction becomes important because of the lattice expansion, and the hydride phase (β -phase) nucleates and grows. The hydrogen concentration in the hydride phase is often found to be $H/M = 1$. The volume expansion between the coexisting α - and β -phases corresponds, in many cases, to 10-20% of the metal lattice. At the phase boundary, therefore, a large stress builds up and often leads to a decrepitation of brittle host metals such as intermetallic compounds. The final hydride is a powder with a typical particle size of 10-100 μm .

The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure-composition isotherms (Fig. 5). When solid solution and hydride phases coexist, there is a plateau in the isotherms, the length of which determines the amount of hydrogen stored. In the pure β -phase, the hydrogen pressure rises steeply with the concentration. The two-phase region ends in a critical point, T_c , above which the transition from the α - to β -phase is continuous. The equilibrium pressure, p_{eq} , is related to the changes ΔH and ΔS in enthalpy and entropy, respectively, as a function of temperature by the Van't Hoff equation:

$$\ln \left(\frac{p_{eq}}{p_{eq}^0} \right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R} \quad (5)$$

As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissolved solid hydrogen, it is approximately the standard entropy of hydrogen ($S_0 = 130 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$) and is, therefore, $\Delta S_f \approx -130 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}\text{H}_2$ for all metal-hydrogen systems. The enthalpy term characterizes the stability of the metal hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K, ΔH should amount to $39.2 \text{ kJ mol}^{-1}\text{H}_2$. The entropy of formation term for metal hydrides leads to a significant heat evolution $\Delta Q = T\Delta S$ (exothermal reaction) during hydrogen absorption. The same heat has to be provided to the metal hydride to desorb the hydrogen (endothermal reaction). If the hydrogen desorbs below RT , this heat can be delivered by the environment. However, if the desorption is carried out above RT , the necessary heat has to be delivered from an external source, such as the combustion of hydrogen. For a stable hydride like MgH_2 , the heat necessary for the desorption of hydrogen at 300°C and 1 bar is $\approx 25\%$ of the higher heating value of hydrogen.

Several empirical models allow the estimation of the stability and concentration of hydrogen in an intermetallic hydride. The maximum amount of hydrogen in the hydride phase is given by the number of interstitial sites in the intermetallic compound^{31,32}. As a general rule, it can be

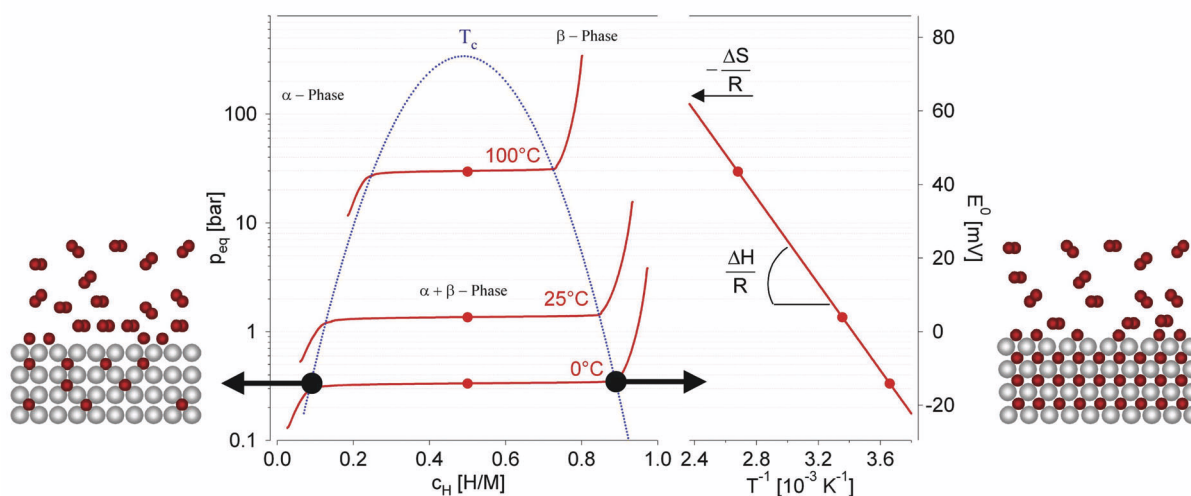


Fig. 5 Pressure composition isotherms for hydrogen absorption in a typical intermetallic compound on the left hand side. The solid solution (α -phase), the hydride phase (β -phase) and the region of the coexistence of the two phases are shown. The coexistence region is characterized by the flat plateau and ends at the critical temperature T_c . The construction of the Van't Hoff plot is shown on the right hand side. The slope of the line is equal to the enthalpy of formation divided by the gas constant and the intercept is equal to the entropy of formation divided by the gas constant.

stated that all elements with an electronegativity in the range of 1.35-1.82 do not form stable hydrides (hydride gap)³³. Here, the stability of a hydrogen atom on an interstitial site is the weighted average of the stability of the corresponding binary hydrides of the neighboring metallic atoms³⁴. More general is the Miedema model: the more stable an intermetallic compound is, the less stable the corresponding hydride and *vice versa*³⁵.

These semiempirical models allow estimation of the stability of binary hydrides as long as rigid band theory can be applied. However, the interaction of hydrogen with the electronic structure of the host metal is often more complicated. In many cases, the crystal structure of the host metal and, therefore, the electronic structure change upon the phase transition and the theoretical calculation of the stability of the hydride becomes very complex, if not impossible. The stability of metal hydrides is usually presented in the form of Van't Hoff plots according to eq 5 (Fig. 6). The most stable binary hydrides have enthalpies of formation of $\Delta H_f = -226 \text{ kJ}\cdot\text{mol}^{-1}\text{H}_2$, e.g. HoH_2 . The least stable hydrides are $\text{FeH}_{0.5}$, $\text{NiH}_{0.5}$ and $\text{MoH}_{0.5}$ with enthalpies of formation of $\Delta H_f = +20 \text{ kJ}\cdot\text{mol}^{-1}\text{H}_2$, $\Delta H_f = +20 \text{ kJ}\cdot\text{mol}^{-1}\text{H}_2$, and $\Delta H_f = +92 \text{ kJ}\cdot\text{mol}^{-1}\text{H}_2$, respectively³⁶.

Metal hydrides, because of this phase transition, can absorb large amounts of hydrogen at a constant pressure, i.e. the pressure does not increase with the amount of hydrogen absorbed. The characteristics of hydrogen absorption and desorption can be tailored by partial substitution of the constituent elements in the host lattice. Some metal hydrides

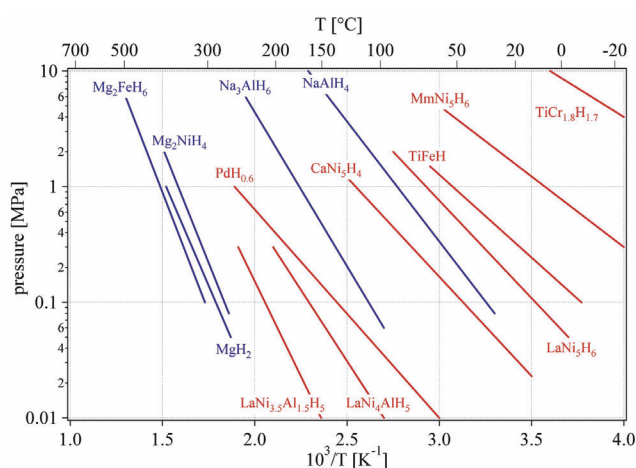


Fig. 6 Van't Hoff plots of some selected hydrides. The stabilization of the hydride of LaNi_5 by the partial substitution of Ni with Al in LaNi_5 is shown, as well as the substitution of La with mischmetal (e.g. 51% La, 33% Ce, 12% Nd, 4% Pr).

Table 2 The most important families of hydride-forming intermetallic compounds, including the prototype and the structure. Element A has a high affinity to hydrogen and element B has a low affinity to hydrogen.

Intermetallic compound	Prototype	Structure
AB_5 AB_2	LaNi_5 $\text{ZrV}_2, \text{ZrMn}_2, \text{TiMn}_2$	Haucke phases, hexagonal Laves phase, hexagonal or cubic
AB_3 A_2B_7 A_6B_{23}	$\text{CeNi}_3, \text{YFe}_3$ $\text{Y}_2\text{Ni}_7, \text{Th}_2\text{Fe}_7$ Y_6Fe_{23}	Hexagonal, PuNi_3 -typ Hexagonal, Ce_2Ni_7 -typ Cubic, $\text{Th}_6\text{Mn}_{23}$ -typ
AB A_2B	TiFe, ZrNi $\text{Mg}_2\text{Ni}, \text{Ti}_2\text{Ni}$	Cubic, CsCl- or CrB-typ Cubic, MoSi_2 - or Ti_2Ni -typ

absorb and desorb hydrogen at ambient temperature and close to atmospheric pressure. Several families of intermetallic compounds listed in Table 2 are interesting for hydrogen storage. They all consist of an element with a high affinity to hydrogen, element A, and a low affinity one, element B. The latter is often at least partially Ni, since it is an excellent catalyst for hydrogen dissociation.

One of the most interesting features of metallic hydrides is the extremely high volumetric density of hydrogen atoms present in the host lattice. The highest volumetric hydrogen density reported to date is $150 \text{ kg}\cdot\text{m}^{-3}$ in Mg_2FeH_6 and $\text{Al}(\text{BH}_4)_3$. Both hydrides belong to the complex hydrides family (see below). Metallic hydrides can reach a volumetric hydrogen density of $115 \text{ kg}\cdot\text{m}^{-3}$, e.g. LaNi_5 . Most metallic hydrides absorb hydrogen up to a hydrogen to metal ratio of $\text{H}/\text{M} = 2$. Greater ratios up to $\text{H}/\text{M} = 4.5$, e.g. for BaReH_9 , have been found³⁷. However, all hydrides with a hydrogen to metal ratio of more than two are ionic or covalent compounds and belong to the complex hydrides group.

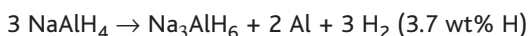
Metal hydrides are very effective at storing large amounts of hydrogen in a safe and compact way. All the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 mass%. It remains a challenge to explore the properties of the lightweight metal hydrides.

Complex hydrides

Group 1, 2, and 3 light metals, e.g. Li, Mg, B, and Al, give rise to a large variety of metal-hydrogen complexes. They are especially interesting because of their light weight and the number of hydrogen atoms per metal atom, which is two in many cases. The main difference between the complex and

metallic hydrides is the transition to an ionic or covalent compound upon hydrogen absorption. The hydrogen in the complex hydrides is often located in the corners of a tetrahedron with B or Al in the center. The negative charge of the anion, $[\text{BH}_4]^-$ and $[\text{AlH}_4]^-$, is compensated by a cation, e.g. Li or Na. The hydride complexes of borane, the tetrahydroborates $\text{M}(\text{BH}_4)$, and the tetrahydroaluminates $\text{M}(\text{AlH}_4)$ are interesting storage materials. They are known to be stable and decompose only at elevated temperatures, often above the melting point of the complex.

In 1996, Bogdanović and Schwickardi³⁸ showed, for the first time, adsorption and desorption pressure-concentration isotherms for catalyzed NaAlH_4 at temperatures of 180°C and 210°C. The isotherms, which have a nearly horizontal pressure plateau, do not show hysteresis. Furthermore, the catalyzed system reversibly absorbs and desorbs hydrogen of up to 4.2 mass%. The mechanism of the two-step reaction was also described. A more detailed study of NaAlH_4 with an improved catalyst has been conducted more recently³⁹. A desorption hydrogen pressure of 2 bar at 60°C was found and the enthalpy for the dissociation reaction was determined to be 37 $\text{kJ}\cdot\text{mol}^{-1}$ and 47 $\text{kJ}\cdot\text{mol}^{-1}$ for the first and second dissociation steps of Ti-doped NaAlH_4 , respectively, according to the reactions:



The equilibrium hydrogen pressure at RT, therefore, is approximately 1 bar. Furthermore, the reaction is reversible, a complete conversion to product was achieved at 270°C under 175 bar hydrogen pressure in 2-3 hours⁴⁰.

The compound with the highest gravimetric hydrogen density at RT known today is LiBH_4 (18 mass%). This complex hydride could, therefore, be the ideal hydrogen storage material for mobile applications. LiBH_4 desorbs three of the four hydrogens in the compound upon melting at 280°C and decomposes into LiH and B. The desorption process can be catalyzed by adding SiO_2 and significant thermal desorption has been observed⁴¹, starting at 100°C. The stability of metal tetrahydroborides has been discussed in relation to their percentage ionic character, and those compounds with less ionic character than diborane are expected to be highly unstable⁴². Steric effects have also been suggested to be important in some compounds^{43,44}. The special feature exhibited by covalent metal hydroborides is that the hydroboride group is bonded to the metal atom

by bridging hydrogen atoms, similar to the bonding in diborane, which may be regarded as the simplest of the so-called 'electron-deficient' molecules. Such molecules possess fewer electrons than apparently required to fill all the bonding orbitals, based on the criterion that a normal bonding orbital involving two atoms contains two electrons. The molecular orbital bonding scheme for diborane has been discussed⁴⁴.

Complex hydrides open a new field of hydrogen storage materials. While the alanates have been investigated extensively during the last six years, there is a whole field of new compounds ready to be explored. The borides are especially interesting because of their very high gravimetric and volumetric hydrogen density.

Storage via chemical reactions

Hydrogen can be generated by reacting metals and chemical compounds with water. The common experiment, seen in many chemistry classes, where a piece of Na floating on water produces hydrogen, demonstrates the process.

The Na transforms to NaOH in this reaction. The reaction is not directly reversible, but NaOH can be removed and reduced in a solar furnace back to metallic Na. Two Na atoms react with two H_2O molecules and produce one hydrogen molecule. The hydrogen molecule produces a H_2O molecule in combustion, which can be recycled to generate more hydrogen gas. However, the second H_2O molecule necessary for the oxidation of the two Na atoms has to be added. Therefore, Na has a gravimetric hydrogen density of 3 mass%. The same process carried out with Li leads to a gravimetric hydrogen density of 6.3 mass%. The major challenge of this storage method is reversibility and control of the thermal reduction process in order to produce the metal in a solar furnace. The process has been successfully demonstrated with Zn⁴⁵.

Conclusion

The materials science challenge of hydrogen storage is to understand the interaction of hydrogen with other elements better, especially metals. Complex compounds like $\text{Al}(\text{BH}_4)_3$ have to be investigated and new compounds of lightweight metals and hydrogen will be discovered. Hydrogen production, storage, and conversion has reached a technological level, although plenty of improvements and new discoveries are still possible.

Six different hydrogen storage methods have been described here. Alongside well-established, high-pressure cylinders for laboratory applications and liquid hydrogen storage methods for air and space applications, metal hydrides and complex hydrides offer a safe and efficient way to store hydrogen. Further research and technical development will lead to higher volumetric and gravimetric hydrogen density. The best materials known today show a volumetric storage density of $150 \text{ kg}\cdot\text{m}^{-3}$, which can still be improved by approximately 50% according to theoretical estimations. Fig. 7 shows the volumetric versus gravimetric hydrogen density for the various materials reviewed in this article. **MT**

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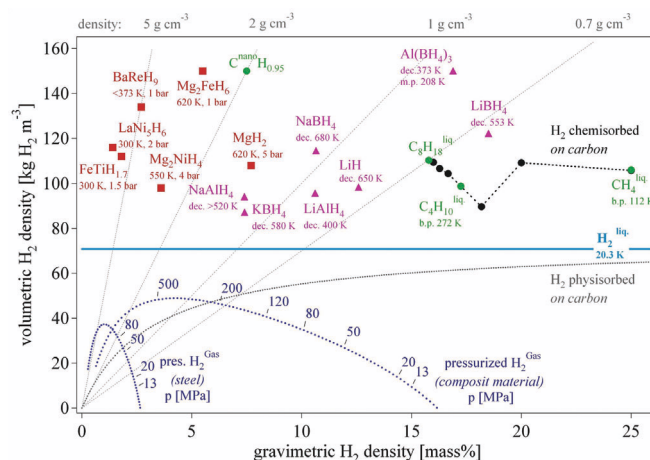


Fig. 7 Volumetric and gravimetric hydrogen density of some selected hydrides. Mg_2FeH_6 shows the highest known volumetric hydrogen density of $150 \text{ kg}\cdot\text{m}^{-3}$, which is more than double that of liquid hydrogen. BaReH_9 has the largest H/M ratio of 4.5, i.e. 4.5 hydrogen atoms per metal atom. LiBH_4 exhibits the highest gravimetric hydrogen density of 18 mass%. Pressurized gas storage is shown for steel (tensile strength $\sigma_v = 460 \text{ MPa}$, density $6500 \text{ kg}\cdot\text{m}^{-3}$) and a hypothetical composite material ($\sigma_v = 1500 \text{ MPa}$, density $3000 \text{ kg}\cdot\text{m}^{-3}$).

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