

# Thermodynamics of Metal Hydrides: Tailoring Reaction Enthalpies of Hydrogen Storage Materials

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## 1. Introduction

Considering the increasing pollution and exploitation of fossil energy resources, the implementation of new energy concepts is essential for our future industrialized society. Renewable sources have to replace current energy technologies. This shift, however, will not be an easy task. In contrast to current nuclear or fossil power plants renewable energy sources in general do not offer a constant energy supply, resulting in a growing demand of energy storage. Furthermore, fossil fuels are both, energy source as well as energy carrier. This is of special importance for all mobile applications. Alternative energy carriers have to be found. The hydrogen technology is considered to play a crucial role in this respect. In fact it is the ideal means of energy storage for transportation and conversion of energy in a comprehensive clean-energy concept. Hydrogen can be produced from different feedstocks, ideally from water using regenerative energy sources. Water splitting can be achieved by electrolysis, solar thermo-chemical, photoelectrochemical or photobiological processes. Upon reconversion into energy, by using a fuel cell only water vapour is produced, leading to a closed energy cycle without any harmful emissions. Besides stationary applications, hydrogen is designated for mobile applications, e.g. for the zero-emission vehicle. In comparison to batteries hydrogen storage tanks offer the opportunity of fast recharging within a few minutes only and of higher storage densities by an order of magnitude. Hydrogen can be produced from renewable energies in times when feed-in into the electricity grid is not possible. It can be stored in large caverns underground and be utilized either to produce electricity and be fed into the electricity grid again or directly for mobile applications.

However, due to the very low boiling point of hydrogen (20.4 K at 1 atm) and its low density in the gaseous state ( $90 \text{ g/m}^3$ ) dense hydrogen storage, both for stationary and mobile applications, remains a challenging task. There are three major alternatives for hydrogen storage: compressed gas tanks, liquid hydrogen tanks as well as solid state hydrogen storage such as metal hydride hydrogen tanks. All of these three main techniques have their special advantages and disadvantages and are currently used for different applications. However, so far none of the respective tanks fulfils all the demanded technical requirements in terms of gravimetric storage density, volumetric storage density, safety,

free-form, ability to store hydrogen for longer times without any hydrogen losses, cyclability as well as recyclability and costs. Further research and development is strongly required. One major advantage of hydrogen storage in metal hydrides is the ability to store hydrogen in a very energy efficient way enabling hydrogen storage at rather low pressures without further need for liquefaction or compression. Many metals and alloys are able to absorb large amounts of hydrogen. The metal-hydrogen bond offers the advantage of a very high volumetric hydrogen density under moderate pressures, which is up to 60% higher than that of liquid hydrogen (Reilly & Sandrock, 1980).

Depending on the hydrogen reaction enthalpy of the specific storage material during hydrogen uptake a huge amount of heat (equivalent to 15% or more of the energy stored in hydrogen) is generated and has to be removed in a rather short time, ideally to be recovered and used as process heat for different applications depending on quantity and temperature. On the other side, during desorption the same amount of heat has to be applied to facilitate the endothermic hydrogen desorption process – however, generally at a much longer time scale. On one side this allows an inherent safety of such a tank system. Without external heat supply hydrogen release would lead to cooling of the tank and finally hydrogen desorption necessarily stops. On the other side it implies further restrictions for the choice of suitable storage materials. Highest energy efficiencies of the whole tank to fuel combustion or fuel cell system can only be achieved if in case of desorption the energy required for hydrogen release can be supplied by the waste heat generated in case of mobile applications on-board by the hydrogen combustion process and the fuel cell respectively.

## 2. Basics of hydrogen storage in metal hydrides

Many metals and alloys react reversibly with hydrogen to form metal hydrides according to the reaction (1):



Here, Me is a metal, a solid solution, or an intermetallic compound,  $\text{MeH}_x$  is the respective hydride and  $x$  the ratio of hydrogen to metal,  $x=c_H [\text{H}/\text{Me}]$ ,  $\text{Q}$  the heat of reaction. Since the entropy of the hydride is lowered in comparison to the metal and the gaseous hydrogen phase, at ambient and elevated temperatures the hydride formation is exothermic and the reverse reaction of hydrogen release accordingly endothermic. Therefore, for hydrogen release/desorption heat supply is required.

Metals can be charged with hydrogen using molecular hydrogen gas or hydrogen atoms from an electrolyte. In case of gas phase loading, several reaction stages of hydrogen with the metal in order to form the hydride need to be considered. Fig. 1 shows the process schematically.

The first attractive interaction of the hydrogen molecule approaching the metal surface is the Van der Waals force, leading to a physisorbed state. The physisorption energy is typically of the order  $E_{\text{Phys}} \approx 6 \text{ kJ/mol H}_2$ . In this process, a gas molecule interacts with several atoms at the surface of a solid. The interaction is composed of an attractive term, which diminishes with the distance of the hydrogen molecule and the solid metal by the power of 6, and a repulsive term diminishing with distance by the power of 12. Therefore, the potential energy of the molecule shows a minimum at approximately one molecular radius. In addition to hydrogen storage in metal hydrides molecular hydrogen adsorption is a second technique to store hydrogen. The storage capacity is strongly related to the temperature and the specific

surface areas of the chosen materials. Experiments reveal for carbon-based nanostructures storage capacities of less than 8 wt.% at 77 K and less than 1wt.% at RT and pressures below 100 bar (Panella et al., 2005; Schmitz et al., 2008).

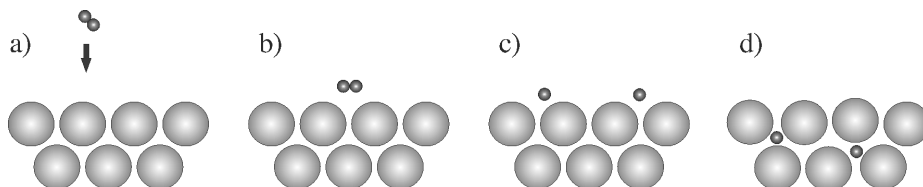


Fig. 1. Reaction of a  $H_2$  molecule with a storage material: a)  $H_2$  molecule approaching the metal surface. b) Interaction of the  $H_2$  molecule by Van der Waals forces (physisorbed state). c) Chemisorbed hydrogen after dissociation. d) Occupation of subsurface sites and diffusion into bulk lattice sites.

In the next step of the hydrogen-metal interaction, the hydrogen has to overcome an activation barrier for the formation of the hydrogen metal bond and for dissociation, see Fig. 1c and 2. This process is called dissociation and chemisorption. The chemisorption energy is typically in the range of  $E_{\text{Chem}} \approx 20 - 150 \text{ kJ/mol } H_2$  and thus significantly higher than the respective energy for physisorption which is in the order of  $4-6 \text{ kJ/mol } H_2$  for carbon based high surface materials (Schmitz et al., 2008).

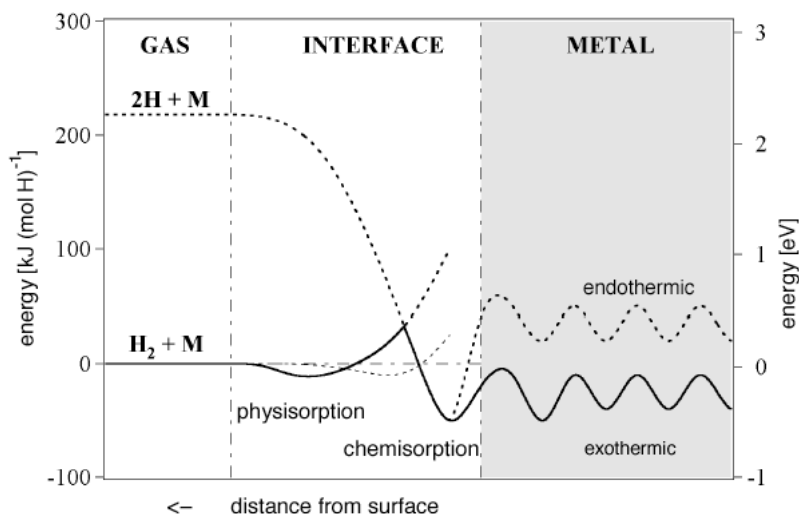


Fig. 2. Schematic of potential energy curves of hydrogen in molecular and atomic form approaching a metal. The hydrogen molecule is attracted by Van der Waals forces and forms a physisorbed state. Before diffusion into the bulk metal, the molecule has to dissociate forming a chemisorbed state at the surface of the metal (according to Züttel, 2003).

After dissociation on the metal surface, the H atoms have to diffuse into the bulk to form a M-H solid solution commonly referred to as  $\alpha$ -phase. In conventional room temperature metals / metal hydrides, hydrogen occupies interstitial sites - tetrahedral or octahedral - in the metal host lattice. While in the first, the hydrogen atom is located inside a tetrahedron formed by four metal atoms, in the latter, the hydrogen atom is surrounded by six metal atoms forming an octahedron, see Fig. 3.

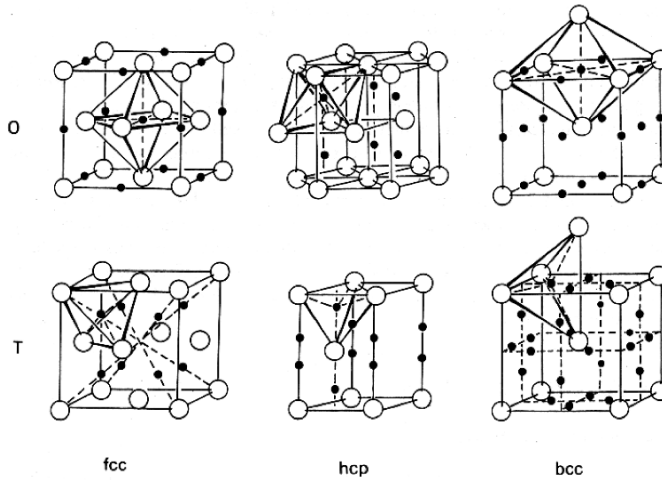


Fig. 3. Octahedral (O) and tetrahedral (T) interstitial sites in fcc-, hcp- and bcc-type metals. (Fukai, 1993).

In general, the dissolution of hydrogen atoms leads to an expansion of the host metal lattice of 2 to 3  $\text{\AA}^3$  per hydrogen atom, see Fig. 4. Exceptions of this rule are possible, e.g. several dihydride phases of the rare earth metals, which show a contraction during hydrogen loading for electronic reasons.

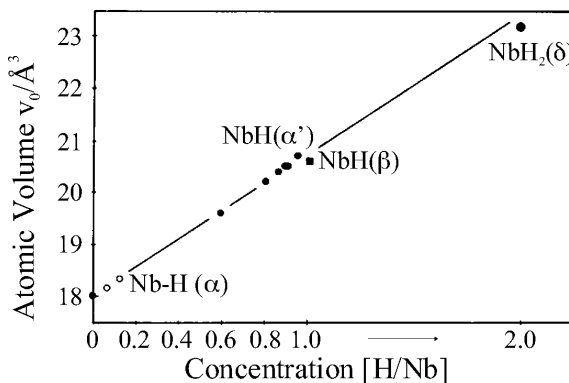


Fig. 4. Volume expansion of the Nb host metal with increasing H content. (Schober & Wenzl, 1978)

In the equilibrium the chemical potentials of the hydrogen in the gas phase and the hydrogen absorbed in the metal are the same:

$$\frac{1}{2} \mu_{gas} = \mu_{metal} \quad (2)$$

Since the internal energy of a hydrogen molecule is  $7/2 kT$  the enthalpy and entropy of a hydrogen molecule are

$$h_{gas} = \frac{7}{2} \cdot k \cdot T - E_{Diss} \quad (3)$$

and

$$s_{gas} = \frac{7}{2} \cdot k - k \cdot \ln \frac{p}{p_0(T)} \quad \text{with} \quad p_0(T) = \frac{8(\pi k T)^{\frac{7}{2}} \cdot M_{H-H}^{\frac{5}{2}} \cdot r_{H-H}^2}{h^5} \quad (4)$$

Here  $k$  is the Boltzmann constant,  $T$  the temperature,  $p$  the applied pressure,  $E_{Diss}$  the dissociation energy for hydrogen ( $E_{Diss} = 4.52 \text{ eV}$   $\text{eV}/\text{H}_2$ ),  $M_{H-H}$  the mass of the  $\text{H}_2$  molecule,  $r_{H-H}$  the interatomic distance of the two hydrogen atoms in the  $\text{H}_2$  molecule.

Consequently the chemical potential of the hydrogen gas is given by

$$\mu_{gas} = k \cdot T \cdot \ln \frac{p}{p_0(T)} - E_{Diss} = k \cdot T \cdot \ln \frac{p}{p_0} + \mu_{gas_0} \quad (5)$$

with  $p_0 = 1.01325 \cdot 10^5 \text{ Pa}$ .

In the solid solution ( $\alpha$ -phase) the chemical potential is accordingly

$$\mu_{\alpha} = h_{\alpha} - T s_{\alpha} \quad \text{mit} \quad s_{\alpha} = s_{\alpha,conf} + s_{\alpha,vibr,electr} \quad (6)$$

Here,  $s_{\alpha,conf}$  is the configuration entropy which is originating in the possible allocations of  $N_H$  hydrogen atoms on  $N_{is}$  different interstitial sites:

$$S_{\alpha,conf} = k \cdot \ln \frac{N_{is}!}{N_H!(N_{is} - N_H)!} \quad (7)$$

and accordingly for small  $c_H$  using the Stirling approximation we get

$$s_{\alpha,conf} = -k \cdot \ln \frac{c_H}{n_{is} - c_H} \quad (8)$$

with  $n_{is}$  being the number of interstitial sites per metal atom:  $n_{is} = N_{is}/N_{Me}$  and  $c_H$  the number of hydrogen atoms per metal atom:  $c_H = N_H/N_{Me}$ .

Therefore the chemical potential of hydrogen in the solid solution ( $\alpha$ -phase) is given by

$$\mu_{\alpha} = h_{\alpha} - T \cdot \left( s_{\alpha,vibr,electr} - k \cdot \ln \frac{c_H}{n_{is} - c_H} \right) \quad (9)$$

Taking into account the equilibrium condition (2) the hydrogen concentration  $c_H$  can be determined via

$$\frac{c_H}{n_{is} - c_H} = \sqrt{\frac{p}{p_0(T)}} \cdot e^{-\frac{\Delta G_s}{k \cdot T}} \quad \text{with} \quad \Delta G_s = h_\alpha - T \cdot s_{\alpha_{vibr}} + \frac{1}{2} \mu_{g_0} \quad (10)$$

or

$$\frac{c_H}{n_{is} - c_H} = \sqrt{\frac{p}{p_0(T)}} \cdot e^{-\frac{\Delta G_s}{R \cdot T}} \quad \text{with} \quad \Delta G_s = \Delta H_s - T \Delta S. \quad (11)$$

Here  $\mu_{g_0}$  is the chemical potential of the hydrogen molecule at standard conditions and  $R$  being the molar gas constant.

For very small hydrogen concentrations  $c_H|_{cH} \ll n_{is}$  in the solid solution phase  $\alpha$  the hydrogen concentration is directly proportional to the square root of the hydrogen pressure in the gas phase. This equation is also known as the **Sievert's law**, i.e.

$$c_H = \frac{1}{K_S} \sqrt{p} \quad (12)$$

with  $K_S$  being a temperature dependent constant. As the hydrogen pressure is increased, saturation occurs and the metal hydride phase  $MeH_{c_\beta}$  starts to form.

For higher hydrogen pressures/concentrations metal hydride formation occurs.

The conversion from the saturated solution phase to the hydride phase takes place at constant pressure  $p$  according to:



In the equilibrium the chemical potentials of the gas phase, the solid solution phase  $\alpha$  and the hydride phase  $\beta$  coincide:

$$\mu_\alpha(p, T, c_\alpha) = \mu_\beta(p, T, c_\beta) = \frac{1}{2} \mu_{gas}(p, T) = \frac{1}{2} \cdot k \cdot T \cdot \ln \left( \frac{p_{eq}(T)}{p_0} \right) + \frac{1}{2} \mu_{gas_0}. \quad (14)$$

Following Gibb's Phase Rule  $f=c-p+2$  with  $f$  being the degree of freedom,  $k$  being the number of components and  $p$  the number of different phases only one out of the four variables  $p, T, c_\alpha, c_\beta$  is to be considered as independent. Therefore for a given temperature all the other variables are fixed.

Therefore the change in the chemical potential or the Gibbs free energy is just a function of one parameter, i.e. the temperature  $T$ :

$$\Delta G = \frac{1}{2} \cdot R \cdot T \cdot \ln \left( \frac{p(T)}{p_0} \right). \quad (15)$$

From this equation follows the frequently-used **Van't Hoff equation** (16):

$$\frac{1}{2} \cdot \ln \frac{p}{p_0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{16}$$

The temperature dependent plateau pressure of this two phase field is the equilibrium dissociation pressure of the hydride and is a measure of the stability of the hydride, which commonly is referred to as  $\beta$ -phase. After complete conversion to the hydride phase, further dissolution of hydrogen takes place as the pressure increases, see Fig. 5.

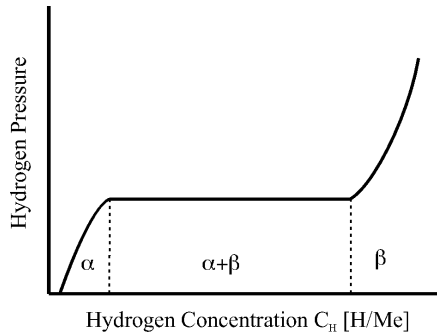


Fig. 5. Schematic Pressure/Composition Isotherm. The precipitation of the hydride phase  $\beta$  starts when the terminal solubility of the  $\alpha$ -phase is reached at the plateau pressure.

Multiple plateaus are possible and frequently observed in composite materials consisting of two hydride forming metals or alloys. The equilibrium dissociation pressure is one of the most important properties of a hydride storage material. If the logarithm of the plateau pressure is plotted vs  $1/T$ , a straight line is obtained (van't Hoff plot) as seen in Fig. 6.

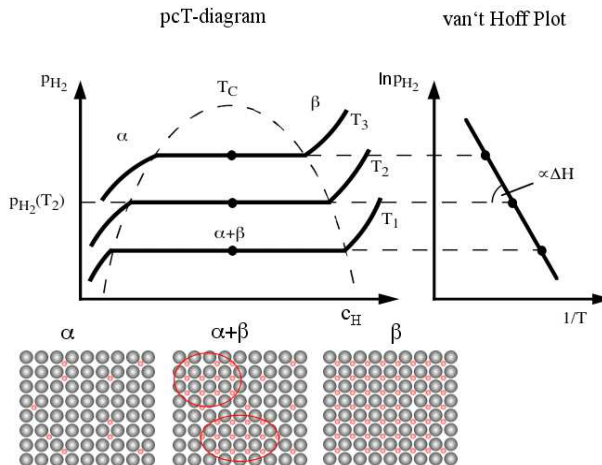


Fig. 6. Schematic  $pcT$ -diagram and van't Hoff plot. The  $\alpha$ -phase is the solid solution phase, the  $\beta$ -phase the hydride phase. Within the  $(\alpha - \beta)$  two phase region both the metal-hydrogen solution and the hydride phase coexist.

## 2.1 Conventional metal hydrides

Fig. 7 shows the Van't Hoff plots of some selected binary hydrides. The formation enthalpy of these hydrides  $H^0_f$  determines the amount of heat which is released during hydrogen absorption and consequently is to be supplied again in case of desorption. To keep the heat management system simple and to reach highest possible energy efficiencies it is necessary to store the heat of absorption or to get by the waste heat of the accompanying hydrogen utilizing process, e.g. energy conversion by fuel cell or internal combustion system. Therefore the reaction enthalpy has to be as low as possible. The enthalpy and entropy of the hydrides determine the working temperatures and the respective plateau pressures of the storage materials. For most applications, especially for mobile applications, working temperatures below 100°C or at least below 150°C are favoured. To minimize safety risks and avoid the use of high pressure composite tanks the favourable working pressures should be between 1 and 100 bar.

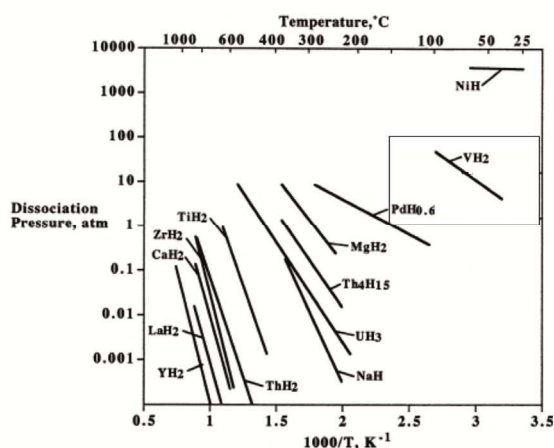


Fig. 7. Van't Hoff lines (desorption) for binary hydrides. Box indicates 1-100 atm, 0-100 °C ranges, taken from Sandrock et al. (Sandrock, 1999).

However, the Van't Hoff plots shown in Fig. 7 indicate that most binary hydrides do not have the desired thermodynamic properties. Most of them have rather high thermodynamic stabilities and thus release hydrogen at the minimum required pressure of 1 bar only at rather high temperatures ( $T > 300^\circ\text{C}$ ). The values of their respective reaction enthalpies are in the range of 75 kJ/(mol H<sub>2</sub>) (MgH<sub>2</sub>) or even higher. Typical examples are the hydrides of alkaline metals, alkaline earth metals, rare earth metals as well as transition metals of the Sc-, Ti- and V-group. The strongly electropositive alkaline metals like LiH and NaH and CaH<sub>2</sub> form saline hydrides, i.e. they have ionic bonds with hydrogen. MgH<sub>2</sub> marks the transition between these predominantly ionic hydrides and the covalent hydrides of the other elements in the first two periods.

Examples for high temperature hydrides releasing the hydrogen at pressures of 1 bar at extremely high temperatures ( $T > 700^\circ\text{C}$ ) are ZrH<sub>2</sub> and LaH<sub>2</sub> (Dornheim & Klassen, 2009). ZrH<sub>2</sub> for example is characterized by a high volumetric storage density  $N_{\text{H}}$ .  $N_{\text{H}}$  values larger than  $7 \times 10^{22}$  hydrogen atoms per cubic centimetre are achievable. This value corresponds to



58 mol H<sub>2</sub>/l or 116 g/l and has to be compared with the hydrogen density in liquid hydrogen (20 K):  $4.2 \times 10^{22}$  (35 mol H<sub>2</sub>/l or 70 g/l) and in compressed hydrogen (350 bar / 700 bar):  $1.3 / 2.3 \times 10^{22}$  atoms/cm<sup>3</sup> ( 11 mol H<sub>2</sub>/l or 21 g/l and 19 mol H<sub>2</sub>/l or 38 g/l respectively) . The hydrogen density varies a lot between different hydrides. VH<sub>2</sub> for example has an even higher hydrogen density which amounts to  $11.4 \times 10^{22}$  hydrogen atoms per cubic centimetre and accordingly 95 mol H<sub>2</sub>/l or 190 g/l. As in the case of many other transition metal hydrides Zr has a number of different hydride phases ZrH<sub>2-x</sub> with a wide variation in the stoichiometry (Hägg, 1931). Their compositions extend from about ZrH<sub>1.33</sub> up to the saturated hydride ZrH<sub>2</sub>. Because of the limited gravimetric storage density of only about 2 wt.% and the negligibly low plateau pressure within the temperature range of 0 - 150 °C Zr as well as Ti and Hf are not suitable at all as a reversible hydrogen storage material. Thus, they are not useful for reversible hydrogen storage if only the pure binary hydrides are considered (Dornheim & Klassen, 2009). Libowitz et al. (Libowitz et al., 1958) could achieve a breakthrough in the development of hydrogen storage materials by discovering the class of reversible intermetallic hydrides. In 1958 they discovered that the intermetallic compound ZrNi reacts reversibly with gaseous hydrogen to form the ternary hydride ZrNiH<sub>3</sub>. This hydride has a thermodynamic stability which is just in between the stable high temperature hydride ZrH<sub>2</sub> ( $\Delta_f H^\circ = -169$  kJ/mol H<sub>2</sub>) and the rather unstable NiH ( $\Delta_f H^\circ = -8.8$  kJmol<sup>-1</sup>H<sub>2</sub>). Thus, the intermetallic Zr-Ni bond exerts a strong destabilizing effect on the Zr-hydrogen bond so that at 300°C a plateau pressure of 1bar is achieved which has to be compared to 900°C in case of the pure binary hydride ZrH<sub>2</sub>. This opened up a completely new research field. In the following years hundreds of new storage materials with different thermodynamic properties were discovered which generally follow the well-known semi-empirical rule of Miedema (Van Mal et al., 1974):

$$\Delta H(A_n B_m H_{x+y}) = \Delta H(A_n H_x) + \Delta H(B_m H_y) - \Delta H(A_n B_m) \quad (17)$$

Around 1970, hydrides with significantly lowered values of hydrogen reaction enthalpies, such as LaNi<sub>5</sub> and FeTi but also Mg<sub>2</sub>Ni were discovered. While 1300 °C are necessary to reach a desorption pressure of 2 bar in case of the pure high temperature hydride LaH<sub>2</sub>, in case of LaNi<sub>5</sub>H<sub>6</sub> a plateau pressure of 2 bar is already reached at 20 °C only. The value of the hydrogen reaction enthalpy is lowered to  $|\Delta H_{LaNi_5H_6}| = 30.9$  kJmol<sup>-1</sup>H<sub>2</sub>. The respective values for NiH are  $|\Delta H_{NiH}| = 8.8$  kJmol<sup>-1</sup>H<sub>2</sub> and  $P_{diss, NiH, RT} = 3400$  bar.

In the meantime, several hundred other intermetallic hydrides have been reported and a number of interesting compositional types identified (table 1). Generally, they consist of a high temperature hydride forming element A and a non hydride forming element B, see fig. 8.

COMPOSITION	A	B	COMPOUNDS
A <sub>2</sub> B	Mg, Zr	Ni, Fe, Co	Mg <sub>2</sub> Ni, Mg <sub>2</sub> Co, Zr <sub>2</sub> Fe
AB	Ti, Zr	Ni, Fe	TiNi, TiFe, ZrNi
AB <sub>2</sub>	Zr, Ti, Y, La	V, Cr, Mn, Fe, Ni	LaNi <sub>2</sub> , YNi <sub>2</sub> , YMn <sub>2</sub> , ZrCr <sub>2</sub> , ZrMn <sub>2</sub> , ZrV <sub>2</sub> , TiMn <sub>2</sub>
AB <sub>3</sub>	La, Y, Mg	Ni, Co	LaCo <sub>3</sub> , YNi <sub>3</sub> , LaMg <sub>2</sub> Ni <sub>9</sub>
AB <sub>5</sub>	Ca, La, Rare Earth	Ni, Cu, Co, Pt, Fe	CaNi <sub>5</sub> , LaNi <sub>5</sub> , CeNi <sub>5</sub> , LaCu <sub>5</sub> , LaPt <sub>5</sub> , LaFe <sub>5</sub>

Table 1. Examples of intermetallic hydrides, taken from Dornheim et al. (Dornheim, 2010).

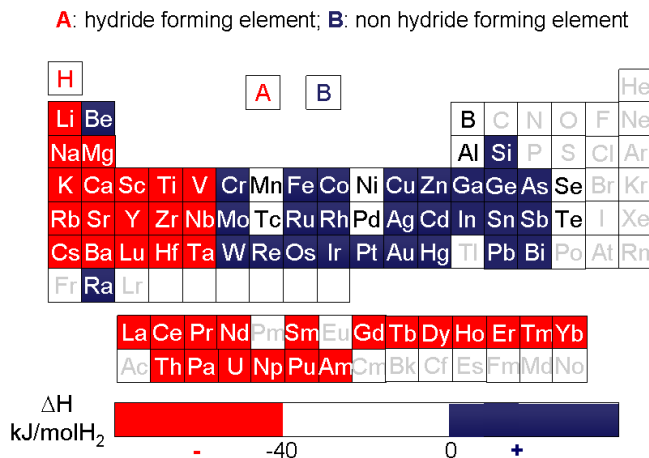


Fig. 8. Hydride and non hydride forming elements in the periodic system of elements.

Even better agreement with experimental results than by use of Miedema's rule of reversed stability is obtained by applying the semi-empirical band structure model of Griessen and Driessen (Griessen & Driessen, 1984) which was shown to be applicable to binary and ternary hydrides. They found a linear relationship of the heat of formation  $\Delta H = H^0_f$  of a metal hydride and a characteristic energy  $\Delta E$  of the electronic band structure of the host metal which can be applied to simple metals, noble metals, transition metals, actinides and rare earths:

$$\Delta H = \alpha \cdot \Delta E + \beta \quad (18)$$

with  $\Delta E = E_F - E_S$  ( $E_F$  being the Fermi energy and  $E_S$  the center of the lowest band of the host metal,  $\alpha = 59.24 \text{ kJ (eV mol H}_2\text{)}^{-1}$  and  $\beta = -270 \text{ kJ (mol H}_2\text{)}^{-1}$  and  $\Delta E$  in eV.

As described above, most materials experience an expansion during hydrogen absorption, wherefore structural effects in interstitial metal hydrides play an important role as well. This can be and is taken as another guideline to tailor the thermodynamic properties of interstitial metal hydrides. Among others Pourarian et al. (Pourarian, 1982), Fujitani et al. (Fujitani, 1991) and Yoshida & Akiba (Yoshida, 1995) report about this relationship of lattice parameter or unit cell volume and the respective plateau pressures in different material classes.

Intensive studies led to the discovery of a huge number of different multinary hydrides with a large variety of different reaction enthalpies and accordingly working temperatures. They are not only attractive for hydrogen storage but also for rechargeable metal hydride electrodes and are produced and sold in more than a billion metal hydride batteries per year. Because of the high volumetric density, intermetallic hydrides are utilized as hydrogen storage materials in advanced fuel cell driven submarines, prototype passenger ships, forklifts and hydrogen automobiles as well as auxiliary power units.

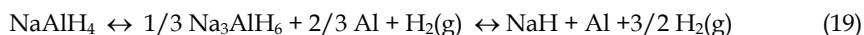
## 2.2 Hydrogen storage in light weight hydrides

Novel light weight hydrides show much higher gravimetric storage capacities than the conventional room temperature metal hydrides. However, currently only a very limited number of materials show satisfying sorption kinetics and cycling behaviour. The most prominent ones are magnesium hydride ( $\text{MgH}_2$ ) and sodium alanate ( $\text{NaAlH}_4$ ). In both cases a breakthrough in kinetics could be attained in the late 90s of the last century / the early 21<sup>st</sup> century.

Magnesium hydride is among the most important and most comprehensively investigated light weight hydrides.  $\text{MgH}_2$  itself has a high reversible storage capacity, which amounts to 7.6 wt.%. Furthermore, magnesium is the eighth most frequent element on the earth and thus comparably inexpensive. Its potential usage initially was hindered because of rather sluggish sorption properties and unfavourable reaction enthalpies. The overall hydrogen sorption kinetics of magnesium-based hydrides is as in case of all hydrides mainly determined by the slowest step in the reaction chain, which can often be deduced e.g. by modelling the sorption kinetics (Barkhordarian et al, 2006; Dornheim et al., 2006). Different measures can be taken to accelerate kinetics. One important factor for the sorption kinetics is the micro- or nanostructure of the material, e.g. the grain or crystallite size. Because of the lower packing density of the atoms, diffusion along grain boundaries is usually faster than through the lattice. Furthermore, grain boundaries are favourable nucleation sites for the formation and decomposition of the hydride phase. A second important parameter is the outer dimension of the material, e.g. in case of powdered material, its particle size. The particle size (a) determines the surface area, which is proportional to the rate of the surface reaction with the hydrogen, and (b) is related to the length of the diffusion path of the hydrogen into and out of the volume of the material. A third major factor by which hydrogen sorption is improved in many hydrogen absorbing systems is the use of suitable additives or catalysts. In case of  $\text{MgH}_2$  it was shown by Oelerich et al. (Oelerich et al., 2001; Dornheim et al., 2007) that already tiny amounts of transition metal oxides have a huge impact on the kinetics of hydrogen sorption. Using such additives Hanada et al. (Hanada et al., 2007) could show that by using such additives hydrogen uptake in Mg is possible already at room temperature within less than 1 min. The additives often do not just have one single function but multiple functions. Suitable additives can catalyze the surface reaction between solid and gas. Dispersions in the magnesium-based matrix can act as nucleation centres for the hydride or the dehydrogenated phase. Furthermore, different additives, such as liquid milling agents and hard particles like oxides, borides, etc. , can positively influence the particle size evolution during the milling process (Pranzas et al., 2006; Pranzas et al., 2007; Dornheim et al, 2007) and prevent grain i.e. crystallite growth. More detailed information about the function of such additives in  $\text{MgH}_2$  is given in (Dornheim et al., 2007). Beyond that, a preparation technique like high-energy ball milling affects both the evolution of certain particle sizes as well as very fine crystallite sizes in the nm range and is also used to intermix the hydride and the additives/catalysts. Thus, good interfacial contact with the light metal hydride as well as a fine dispersion of the additives can be achieved.

As in case of  $\text{MgH}_2$  dopants play also an important role in the sorption of Na-Al-hydride, the so-called Na-alanate. While hydrogen liberation is thermodynamically favorable at moderate temperatures, hydrogen uptake had not been possible until in 1997 Bogdanovic et al. demonstrated that mixing of  $\text{NaAlH}_4$  with a Ti-based catalyst leads to a material, which can be reversibly charged with hydrogen (Bogdanovic, 1997). By using a tube vibration mill

of Siebtechnik GmbH Eigen et al. (Eigen et al., 2007; Eigen et al., 2008) showed that upscaling of material synthesis is possible: After only 30 min milling under optimised process conditions in such a tube vibration mill in kg scale, fast absorption and desorption kinetics with charging/discharging times of less than 10 min can be obtained. The operation temperatures of this complex hydride are much lower than compared to  $\text{MgH}_2$  and other light weight hydrides. Fast kinetics is achieved at 100 °C to 150 °C which is much less than what is required in case of  $\text{MgH}_2$ , however, still significantly higher than in case of the conventional hydrides which show only a very limited storage capacity. Such hydride working temperatures offer the possibility for combinations of metal hydride tanks based on these complex hydrides with e. g. combustion engines, high temperature PEM fuel cells or other medium to high temperature fuel cells. However, compared to  $\text{MgH}_2$  the gravimetric hydrogen storage capacity is significantly reduced. Having a maximum theoretical storage capacity of about 5.6 wt. %  $\text{NaAlH}_4$  exhibits a long term practical storage capacity of 3.5-4.5 wt. %  $\text{H}_2$  only. Furthermore, in difference to  $\text{MgH}_2$   $\text{NaAlH}_4$  decomposes in two reaction steps upon dehydrogenation which implies two different pressure plateaus instead of just one:



The first decomposition step has an equilibrium pressure of 0.1 MPa at 30 °C, the second step at about 100 °C (Schüth et al., 2004). A maximum of 3.7 wt.%  $\text{H}_2$  can be released during the first desorption step, 5.6 wt.% in total. The remaining hydrogen bonded to Na is technically not exploitable due to the high stability of the respective hydride.

While the reaction kinetics was optimized significantly, the desorption enthalpy of  $\text{NaAlH}_4$  of 37 kJ/mol $\text{H}_2$  and  $\text{Na}_3\text{AlH}_6$  of 47 kJ/mol  $\text{H}_2$  respectively remains a challenge. For many applications even this value which is much below that of  $\text{MgH}_2$  is still too large.

### 3. Tailoring thermodynamics of light weight metal hydrides

While there are plenty of known hydrides with suitable thermodynamics for hydrogen uptake and release at ambient conditions (several bar equilibrium pressure at or nearby room temperature) currently no hydride is known which combines suitable thermodynamics and kinetics with such a high gravimetric storage capacity that a hydrogen storage tank based on such a material could compete with a 700 bar compressed composite vessel in regard to weight. Depending on the working temperature and pressure as well as the reversible gravimetric storage capacity of the selected hydride the achievable capacity of a metal hydride based storage tank is usually better than half of the capacity of the metal hydride bed itself (Buchner & Povel, 1982). Since modern composite pressurized gas tanks meanwhile show gravimetric hydrogen storage capacities of around 4 wt.% according to conservative extrapolations the possible choice of hydrides should be limited to those having the ability to reversibly store at least 6 wt.% $\text{H}_2$ . All currently known high capacity hydrides, however, show either too small values of the respective reaction enthalpy and are therefore not reversible or would require several thousand bar hydrogen pressure or alternatively electrochemical loading or on the other hand are too stable and have an equilibrium pressure which around room temperature is much below the required pressures. The value of reaction enthalpy aimed at is between 20 and 30 kJ/mol  $\text{H}_2$ . Fig. 9 shows the potentially available hydrogen content of some well known hydrides plotted against their hydrogen reaction enthalpies.

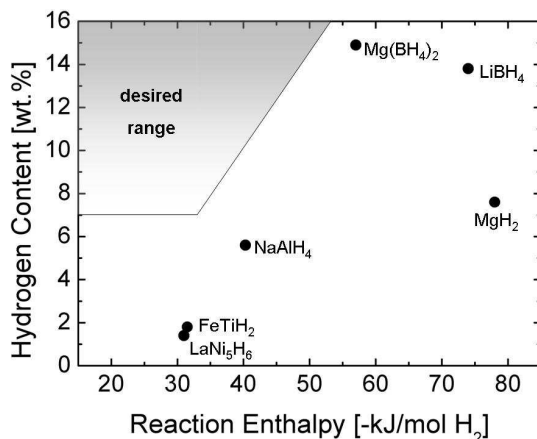


Fig. 9. Theoretically achievable reversible storage capacities and reaction enthalpies of selected hydrides. LaNi<sub>5</sub>H<sub>6</sub> and FeTiH<sub>2</sub> are taken as examples for conventional room temperature hydrides. The reaction enthalpies and achievable hydrogen storage capacities are  $\Delta H = -31$  kJ/mol H<sub>2</sub>,  $C_{H,max} = 1.4$  wt.% for LaNi<sub>5</sub>H<sub>6</sub> and for the Fe-Ti system  $\Delta H = -31.5$  kJ/mol H<sub>2</sub>,  $C_{H,max} = 1.8$  wt.% (average over two reaction steps with  $\Delta H(\text{FeTiH}_2) = -28$  kJ/mol H<sub>2</sub> and  $\Delta H(\text{FeTiH}) = -35$  kJ/mol H<sub>2</sub> respectively) (Buchner, 1982). The respective values for NaAlH<sub>4</sub> are  $\Delta H = -40.5$  kJ/mol H<sub>2</sub>,  $C_{H,max} = 5.6$  wt.% (average over two reaction steps with  $\Delta H(\text{NaAlH}_4) = -37$  kJ/mol H<sub>2</sub> and  $\Delta H(\text{NaAl}_3\text{H}_6) = -47$  kJ/mol H<sub>2</sub> (Bogdanovic et al., 2009)), for MgH<sub>2</sub>:  $\Delta H = -78$  kJ/mol H<sub>2</sub> (Oelerich, 2000) and  $C_{H,max} = 7.6$  wt.%, for LiBH<sub>4</sub>:  $\Delta H = -74$  kJ/mol H<sub>2</sub> (Mauron, 2008) and  $C_{H,max} = 7.6$  wt.%, for Mg(BH<sub>4</sub>)<sub>2</sub>:  $\Delta H = -57$  kJ/mol H<sub>2</sub> (Li, 2008) and  $C_{H,max} = 14.9$  wt.%.

As shown in Fig. 9 none of the plotted hydrides, neither the conventional room temperature hydrides with their rather low gravimetric capacity nor the sophisticated novel chemical hydrides with their unsuitable reaction enthalpy, show the desired combination of properties. Therefore the tailoring of the thermodynamic properties of high capacity light weight and complex hydrides is a key issue, an imperative for future research in the area of hydrides as hydrogen storage materials.

### 3.1 Thermodynamic tuning of single phase light weight hydrides

The traditional way of tailoring the thermodynamic properties of metal hydrides is by formation of alloys with different stabilities as described in chapter 2.1. Thereby the value of reaction enthalpy can be reduced by stabilising the dehydrogenated state and/or destabilising of the hydride state, see Fig. 10 a. Accordingly, the total amount of reaction enthalpy is increased by destabilising the dehydrogenated state and/or stabilising the hydride, see Fig. 10 b.

This approach has been successfully applied to light weight metal hydrides also.

#### Mg-based hydrides

One of the first examples using this approach for tuning the thermodynamic properties of light weight metal hydrides was the discovery of the Mg-Ni -system as potential hydrogen storage system by Reilly and Wiswall (Reilly & Wiswall, 1968). Mg<sub>2</sub>Ni has a negative heat of

Products of dehydrogenation reactions:  $A + x H_2$

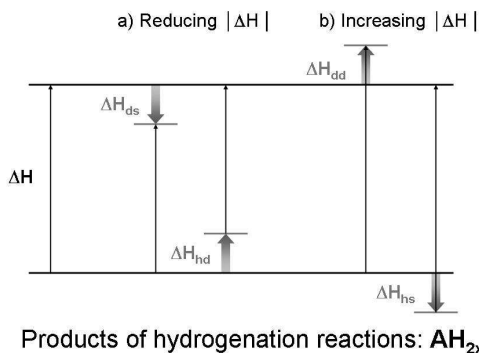


Fig. 10. Tailoring of the reaction enthalpy by altering the stability of the hydrogenated or dehydrogenated state of the metal hydrides: a) Reduction of total reaction enthalpy by stabilising the dehydrogenated phase by  $\Delta H_{ds}$  or destabilising the hydride phase by  $\Delta H_{hd}$ . b) Increase of total reaction enthalpy by destabilising the dehydrogenated state by  $\Delta H_{dd}$  or stabilising the hydrogenated state by  $\Delta H_{hs}$ .

formation of  $H^0(Mg_2Ni) = -42$  kJ/mol. Therefore, compared to pure Mg the dehydrogenated state is stabilised by  $\Delta H_{ds} = -21$  kJ/(mol Mg). The enthalpy of formation of  $Mg_2NiH_4$  is  $H^0_f(Mg_2NiH_4) = -176$  kJ/mol (= -88 kJ/(mol Mg)), wherefore the hydride phase is stabilised by  $\Delta H_{hd} = -10$  kJ/(mol Mg) if compared to pure  $MgH_2$ . In total the hydrogen reaction enthalpy of  $Mg_2Ni$

$$\left| \Delta H_{Mg_2Ni-H} \right| = \left| \Delta H_{Mg-H} \right| + \Delta H_{ds} - \Delta H_{hd} \quad (20)$$

is reduced by 11 kJ/mol  $H_2$  to about  $\left| \Delta H(Mg_2Ni-H) \right| = 67$  kJ/mol  $H_2$ . While pure  $MgH_2$  exhibits a hydrogen plateau pressure of 1 bar around 300 °C, in case of  $Mg_2NiH_4$  such a plateau pressure is reached already at around 240 °C and in case of further alloying and substituting Ni by Cu at around 230 °C in  $Mg_2Ni_{0.5}Cu_{0.5}$  (Klassen et al., 1998). Unfortunately, the gravimetric storage capacity of  $Mg_2NiH_4$  is reduced to 3.6 wt.%  $H_2$  only and thus is less than half the respective value in the  $MgH_2$  system. Darnaudery et al. (Darnaudery et al., 1983) were successful to form several quaternary hydrides by hydrogenating  $Mg_2Ni_{0.75}M_{0.25}$  with different 3d elements  $M \in \{V, Cr, Fe, Co \text{ and } Zn\}$  showing stabilities very similar  $Mg_2NiH_4$ .

Increasing the amount of 3d metals Tsushio et al. (Tsushio et al., 1998) investigated the hydrogenation of  $MgNi_{0.86}M_{0.03}$  with  $M \in \{Cr, Fe, Co, Mn\}$ . Consequently, they observed a dramatic decrease in hydrogen storage capacity to 0.9 wt.% and in hydrogen reaction enthalpy which amounts to 50 kJ/(mol  $H_2$ ) for  $MgNi_{0.86}Cr_{0.03}$ . This reaction enthalpy value is in very good agreement with the value 54 kJ/(mol  $H_2$ ) given by Orimo et al. for amorphous  $MgNi$  (Orimo et al., 1998).

Lowering even more the content of Mg Terashita et al. (Terashita et al., 2001) found  $(Mg_{1-x}Ca_x)Ni_2$  based alloys desorbing hydrogen at room temperature. They determined the hydride formation enthalpy and entropy of  $(Mg_{0.68}Ca_{0.32})Ni_2$  to be  $H = -37$  kJ/(mol  $H_2$ ) and  $S = -94$  J/(mol  $H_2$  K) respectively, which is already quite near to the envisioned target.

Unfortunately, with lowering the Mg content the hydrogen storage capacity dropped down to 1.4 wt.% only.

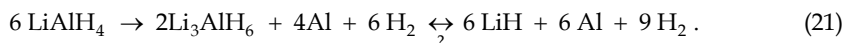
On the other side, as schematically shown in Fig. 10b the absolute value of reaction enthalpy can be increased by either stabilising the hydride phase or destabilising the dehydrogenated phase. In case of Mg-based hydrogen absorbing alloys this is not at all of interest for hydrogen storage itself since  $\text{MgH}_2$  is too stable for most hydrogen storage applications, however, this is of interest for other applications like the storage of thermal energy (Dornheim & Klassen, 2009).  $\text{Mg}_2\text{FeH}_6$  is an example of such materials with increased amount of reaction enthalpy. Furthermore, it is the one with the highest known volumetric hydrogen density which amounts to  $150 \text{ kg m}^{-3}$ . This enormously high hydrogen density is more than double the value found in case of liquid hydrogen at 20 K and moderate pressures of up to 20 bar (Klell, 2010). The gravimetric storage capacity is 5.6 wt.% and thus still rather high. Since Mg and Fe are immiscible the dehydrogenated state is destabilised compared to pure Mg:  $\Delta H_{\text{dd}} > 0 \text{ kJ}/(\text{mol H}_2)$ . Accordingly the hydride phase is more difficult to be synthesised and reversibility as well as long term stability is more difficult to be accomplished.

Nevertheless, hydrogenation is possible at hydrogen pressures of at least 90 bar and temperatures of at least  $450 \text{ }^\circ\text{C}$  (Selvam & Yvon, 1991). Bogdanovic et al. (Bogdanovic et al., 2002) achieved very good reversibility and cycling stability with the hydrogen storage capacities remaining unchanged throughout 550-600 cycles at a level of 5-5.2 wt.%  $\text{H}_2$ . The reaction enthalpy value is reported to be in between  $77 \text{ kJ}/(\text{mol H}_2)$  and  $98 \text{ kJ}/(\text{mol H}_2)$  (Bogdanovic et al., 2002), (Konstanchuk et al, 1987), (Puszkiel et al., 2008), (Didisheim et al., 1984).

The large reaction enthalpies of  $\text{MgH}_2$  and  $\text{Mg}_2\text{FeH}_6$  lead to weight and volume related heat storage densities in the temperature range of  $500 \text{ }^\circ\text{C}$  which are many times higher than that of the possible sensible or latent heat storage materials (Bogdanovic et al., 2002). The calculated and experimental heat storage densities to weight given by Bogdanovic et al. are  $2814 \text{ kJ}/\text{kg}$  and  $2204 \text{ kJ}/\text{kg}$  for the  $\text{MgH}_2$ -Mg system and  $2106$  and  $1921 \text{ kJ}/\text{kg}$  for the  $\text{Mg}_2\text{FeH}_6 - 2\text{Mg} + \text{Fe}$  system respectively. The corresponding calculated and experimental values for the volumetric thermal energy storage density are  $3996 \text{ kJ}/\text{dm}^3$  and  $1763 \text{ kJ}/\text{dm}^3$  for the  $\text{MgH}_2$ -Mg system and  $5758 \text{ kJ}/\text{dm}^3$  and  $2344 \text{ kJ}/\text{dm}^3$  respectively (Bogdanovic et al., 2002). These thermal energy densities ought not to be mistaken with the energy stored in the hydrogen (lower heating value) which is more than a factor of three larger.

### Aluminum-based complex hydrides

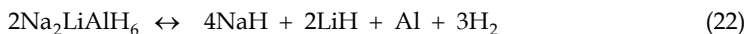
As  $\text{Mg}_2\text{FeH}_6$  decomposes during hydrogen release into 2 Mg, Fe and 3  $\text{H}_2$   $\text{LiAlH}_4$  decomposes during hydrogen release in  $1/3 \text{ Na}_3\text{AlH}_6 + 2/3 \text{ Al} + \text{H}_2$  and finally  $\text{NaH} + \text{Al} + 3/2 \text{ H}_2$ . As written in chapter 2.2 while much lower than those of the Mg-based hydrides the reaction enthalpies of  $|\Delta H| = 37 \text{ kJ}/(\text{mol H}_2)$  and  $|\Delta H| = 47 \text{ kJ}/(\text{mol H}_2)$  are still too high for many applications especially for the usage in combination with low temperature PEM fuel cells.  $\text{LiAlH}_4$  on the other hand is much less stable. It decomposes in two steps as is the case of the  $\text{NaAlH}_4$ :



The first reaction step, however, the decomposition of  $\text{LiAlH}_4$  is found to be exothermic with  $\Delta H_{\text{decomposition}} = -10 \text{ kJ}/(\text{mol H}_2)$ . Since the entropy of decomposition is positive.

Rehydrogenation is not possible at all. The second reaction step, the decomposition of  $\text{Li}_3\text{AlH}_6$  is endothermic with  $\Delta H_{\text{decomposition}} = 25 \text{ kJ}/(\text{mol H}_2)$ . The decomposition of  $\text{LiH}$  itself takes place at much higher temperatures with  $\Delta H = 140 \text{ kJ}/(\text{mol H}_2)$  (Orimo et al., 2007). While the second reaction step, the decomposition of  $\text{Li}_3\text{AlH}_6$  and rehydrogenation of  $\text{LiH} + \text{Al}$  shows rather suitable thermodynamic properties, sluggish kinetics prevent this system so far from being used for hydrogen storage.

To increase the storage capacity and tailor the reaction enthalpy of the  $\text{NaAlH}_4$  system it is a comprehensible approach to replace some of the  $\text{Na}$  by  $\text{Li}$ . Indeed Huot et al. (Huot et al., 1999) proved the existence of  $\text{Na}_2\text{LiAlH}_6$  and the possible formation by high energy ball-milling of  $\text{NaH} + \text{LiH} + \text{NaAlH}_4$ . Reversible hydrogen sorption is found to be possible in the  $\text{Na-Li-Al-H}$  system according to the following reaction:



As in case of the pure  $\text{Na-Al-H}$  system and the  $\text{Li-Al-H}$  system kinetics can be improved by the addition of transition metal compounds like metal oxides, chlorides and fluorides, see (Ares Fernandez et al., 2007), (Ma et al., 2005) and (Martinez-Franco et al., 2010). However, due to the lack of any stable compound in the dehydrogenated state and the formation of a rather stable hydride the value of reaction enthalpy isn't decreased but increased if compared to the original single  $\text{Na}$  and  $\text{Li}$  based aluminium hydrides. Fossdal et al. (Fossdal et al., 2005) has determined the pressure-composition isotherms of  $\text{TiF}_3$ -doped  $\text{Na}_2\text{LiAlH}_6$  in the temperature range of  $170 \text{ }^\circ\text{C} - 250 \text{ }^\circ\text{C}$ . They determined the dissociation enthalpy and the corresponding entropy from the Van't Hoff plot:  $|\Delta H| = 56 \text{ kJ}/(\text{mol H}_2)$  and  $S = 138 \text{ J}/(\text{K mol H}_2)$ . Therefore, instead of a lowering the heat of reaction the opposite is observed. The heat of reaction of the hexa-hydride phase is increased by about  $10 \text{ kJ}/(\text{mol H}_2)$  if compared to the pure  $\text{Na}_3\text{AlH}_6$  hydride phase.

In 2007 Yin et al. (Yin et al., 2007) presented DFT calculations about the doping effects of  $\text{TiF}_3$  on  $\text{Na}_3\text{AlH}_6$ . Their calculations suggested  $\text{F}$ -substitution for the  $\text{H}$ -anion leading to a reduction of the desorption enthalpy and therefore for a favourable thermodynamic modification of the  $\text{Na}_3\text{AlH}_6$  system which was experimentally confirmed by Brinks et al. (Brinks et al., 2008) and Eigen et al. (Eigen et al., 2009).

### Borohydrides

Only a very few hydrides show a higher gravimetric storage capacity than  $\text{MgH}_2$ . For this they must be composed from very light elements. Knowing that  $\text{Al}$ -containing compounds can form reversible complex metal hydrides it is a reasonable approach to look for Boron-containing compounds as reversible hydrogen storage materials with even higher storage capacity. Borohydrides are known since 1940 when Schlesinger and Brown report about the successful synthesis of  $\text{LiBH}_4$  by reaction of  $\text{LiEt}$  and diborane (Schlesinger & Brown, 1940). Despite the early patent from Goerrig in 1958 (Goerrig, 1960) direct synthesis from gaseous  $\text{H}_2$  was not possible for long times. Until in 2004 three different groups from the USA (Vajo et al., 2005), South Korea (Cho et al., 2006) and Germany (Barkhordarian et al., 2007) independently discovered that by using  $\text{MgB}_2$  instead of pure Boron as starting material formation of the respective borohydrides occurs at rather moderate conditions of  $5 \text{ MPa H}_2$  pressure. Orimo et al. (Orimo et al., 2005) reports on the rehydrogenation of previously dehydrogenated  $\text{LiBH}_4$  at  $35 \text{ MPa H}_2$  pressure at  $600 \text{ }^\circ\text{C}$ . Mauron et al. (Mauron et al., 2008) report that rehydrogenation is also possible at  $15 \text{ MPa}$ . As in case of the  $\text{Mg}$ -based alloys



and the aluminum hydrides the reaction enthalpy of many borohydrides is rather unsuitable for most applications.  $\text{LiBH}_4$  as one of the most investigated borohydrides with a very high gravimetric hydrogen density of 18.5 wt.% shows an endothermic desorption enthalpy of  $|\Delta H| = 74 \text{ kJ}/(\text{mol H}_2)$  (Mauron et al., 2008) which is almost the same as in  $\text{MgH}_2$ . Therefore the tailoring of the reaction enthalpy by substitution is a key issue for these materials as well. As in case of the aluminium hydrides there are two different possibilities for substitution in these complex hydrides: cation substitution and anion substitution. Nakamori et al. (Nakamori et al., 2006) reports about a linear relationship between the heat of formation  $\Delta H_{\text{boro}}$  of  $\text{M}(\text{BH}_4)_n$  determined by first principle methods and the Pauling electronegativity of the cation  $\chi_P$ :

$$\frac{\Delta H_{\text{boro}}}{\text{kJ}(\text{mol BH}_4)^{-1}} = 248.7 \chi_P - 390.8 \quad (23)$$

Aiming to confirm their theoretical results the same group performed hydrogen desorption experiments which show that the experimentally determined desorption temperature  $T_d$  shows correlates with the Pauling electronegativity  $\chi_P$  as well, see Fig. 11.

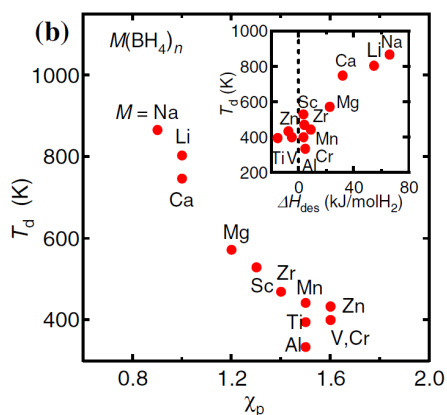


Fig. 11. The desorption temperature  $T_d$  as a function of the Pauling electronegativity  $\chi_P$  and estimated desorption enthalpies  $\Delta H_{\text{des}}$  (Nakamori et al., 2007).

Based on these encouraging results several research groups started to investigate the partial substitution of one cation by another studying several bialkali metal borohydrides. The decomposition temperature of the bialkali metal borohydrides like  $\text{LiK}(\text{BH}_4)_2$  is approximately the average of the decomposition temperature of the mono alkali borohydrides (Rude et al., 2011). Investigations of Li et al. (Li et al., 2007) and Seballos et al. (Seballos et al., 2009) confirmed that this correlation between desorption enthalpy / observed  $T_d$  holds true for many double cation  $\text{MM}'(\text{BH}_4)_n$  systems, see Fig. 12.

Several experiments are indicating that transition metal fluorides are among the best additives for borohydrides (Bonatto Minella et al., 2011). While for some cases the function of the transition metal part as additive is understood (Bösenberg et al., 2009; Bösenberg et al., 2010; Deprez et al., 2010; Deprez et al., 2011), the function of F so far remained unclear. DFT calculations performed by Yin et al. (Yin et al., 2008) suggest a favourable modification

of hydrogen reaction enthalpy in the  $\text{LiBH}_4$  system by substitution of the H-ion with the F-ion. However, no clear indicative experimental results for F- substitution in borohydrides are found yet. In contrast to the F the heavier and larger halides Cl, Br, I are found to readily substitute in some borohydrides for the  $\text{BH}_4$ -ion and form solid solutions or stoichiometric compounds and are so far reported to stabilize the hydride phase leading to an increase of the desorption enthalpy  $|\Delta H|$  (Rude et al., 2011).

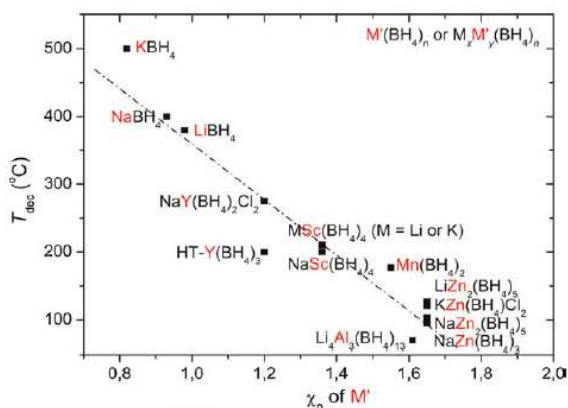
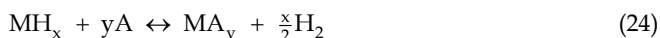


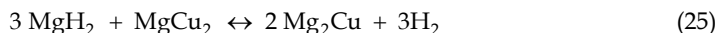
Fig. 12. Decomposition temperatures,  $T_{\text{dec}}$  for metal borohydrides plotted as a function of the electronegativity of the metal,  $M'$ . (Rude et al., 2011)

### 3.2 Thermodynamic tuning using multicomponent systems: reactive additives and reactive hydride composites

In 1967 Reilly and Wiswall (Reilly & Wiswall, 1967) found another promising approach to tailor reaction enthalpies of hydrides ( $\text{MH}_x$ ) by mixing them with suitable reactants (A):



They investigated the system  $\text{MgH}_2/\text{MgCu}_2$  which reversibly reacts with hydrogen according to:



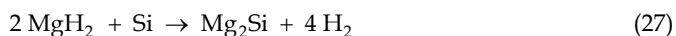
The formation of  $\text{MgCu}_2$  from  $\text{Mg}_2\text{Cu}$  and Cu is exothermic and thus counteracts the endothermic release of hydrogen. Thereby, the total amount of hydrogen reaction enthalpy is reduced to roughly  $|\Delta H| = 73 \text{ kJ}/(\text{mol H}_2)$  (Wiswall, 1978). The equilibrium temperature for 1 bar hydrogen pressure is reduced to about 240 °C. In spite of the lower driving force for rehydrogenation,  $\text{Mg}_2\text{Cu}$  is much more easily hydrogenated than pure Mg. A fact found in many other systems like the Reactive Hydride Composites as well.

Aluminum is another example of a reactive additive for  $\text{MgH}_2$ . The reaction occurs via two steps (Bouaricha et al., 2000):



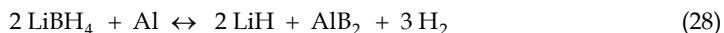
The system can reversibly store 4.4 wt.% H<sub>2</sub>. Since the formation enthalpy  $\Delta H_{\text{Form}}$  of Mg<sub>17</sub>Al<sub>12</sub> is -102 kJ/mol the total value of reaction enthalpy of reaction (26) is reduced by ~ 6 kJ/(mol H<sub>2</sub>) if compared to pure MgH<sub>2</sub>. An equilibrium pressure of 1 bar is reached at around 240 °C again.

To further decrease the reaction enthalpy of a Mg-based system a much more stable compound would have to be formed during dehydrogenation. A system investigated by many groups is the MgH<sub>2</sub>-Si system. Mg<sub>2</sub>Si has an enthalpy of formation of  $\Delta H_{\text{Form}} = -79$  kJ/mol. Due to the formation of Mg<sub>2</sub>Si the value of reaction enthalpy of MgH<sub>2</sub>/Si should therefore be reduced by 37 kJ/(mol H<sub>2</sub>) to about  $|\Delta H| = 41$  kJ/(mol H<sub>2</sub>) (Dornheim, 2010). Theoretically 5 wt.% H<sub>2</sub> can be stored via the reaction



The thermodynamic data indicate a very favourable equilibrium pressure of about 1 bar at 20 °C and 50 bar at 120 °C (Vajo, 2004). While so far rehydrogenation of Mg<sub>2</sub>Si was not shown to be possible the system LiH-Si turned out to be reversible. The enthalpy of dehydrogenation of LiH being 190 kJ/(mol H<sub>2</sub>) an equilibrium H<sub>2</sub> pressure of 1 bar is reached at 910 °C (Sangster, 2000; Dornheim, 2010). LiH reversibly reacts with Si via a two step reaction with the equilibrium pressure being more than 10<sup>4</sup> times higher and the dehydrogenation enthalpy being reduced by 70 kJ/(mol H<sub>2</sub>) (Vajo, 2004).

This approach has recently also been applied to borohydrides. According to Cho et al. (Cho et al., 2006) the decomposition temperature of pure LiBH<sub>4</sub> is determined by CALPHAD to 1 bar H<sub>2</sub> pressure at 403 °C while the corresponding equilibrium temperature for the reaction

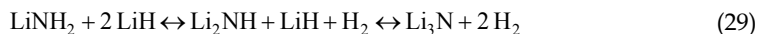


is reduced to 188 °C. Kang et al. (Kang et al., 2007) and Jin et al. (Jin et al., 2008) could show that this system indeed is reversible if suitable additives are used.

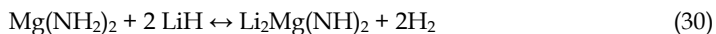
The only disadvantage of this approach is that the total reversible storage capacity per weight is reduced if something is added to the hydrogen storing material which contains no hydrogen.

The problem of reduced hydrogen capacity by using reactive additives has recently overcome by the approach of the Reactive Hydride Composites (Dornheim, 2006). Thereby, different high capacity hydrogen storage materials are combined which react exothermically with each other during decomposition, see Fig. 13.

One of the first examples of such a system is the LiNH<sub>2</sub>-LiH system which was discovered by Chen et al. (Chen et al., 2002):



However, the value of reaction enthalpy is  $|\Delta H| = 80$  kJ/(mol H<sub>2</sub>) and therefore for most applications still much too high. In contrast the system



shows a much more suitable desorption enthalpy of  $|\Delta H| \sim 40$  kJ/(mol H<sub>2</sub>) with an expected equilibrium pressure of 1 bar at approximately 90 °C (Xiong et al., 2005; Dornheim, 2010).

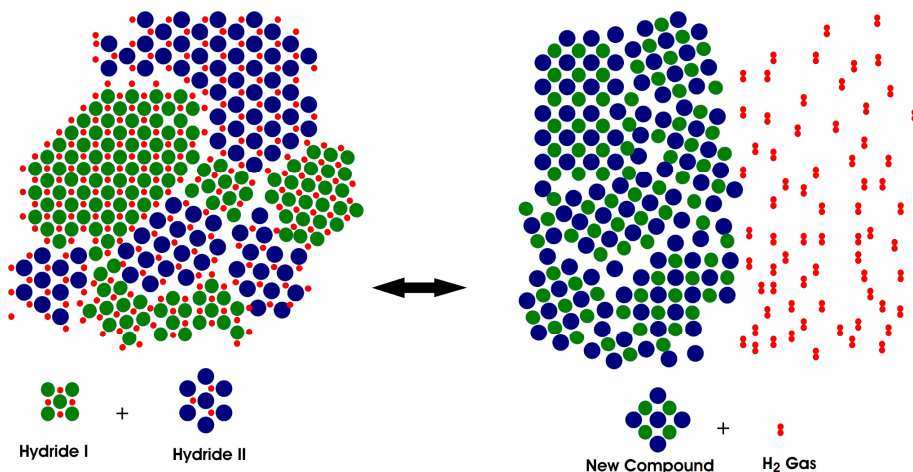
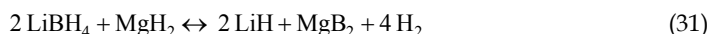


Fig. 13. Schematic of the reaction mechanism in Reactive Hydride Composite.

In 2004 Vajo et al. (Vajo et al., 2005), Cho et al. (Cho et al., 2006) and Barkhordarian et al. (Barkhordarian et al., 2007) independently discovered that the usage of borides especially  $MgB_2$  as a starting material facilitates the formation of different borohydrides. This finding initiated the development and investigation of several new reversible systems with high storage capacities of 8 – 12 wt.%  $H_2$  and improved thermodynamic and kinetic properties such as  $2 LiBH_4 + MgH_2$  (Bösenberg et al., 2009; 2010; 2010b),  $2 NaBH_4 + MgH_2$  (Garroni et al., 2010; Pistidda et al., 2010; 2011; Pottmaier et al., 2011),  $Ca(BH_4)_2 + MgH_2$  (Barkhordarian et al., 2008),  $6 LiBH_4 + CeH_2$ ,  $6 LiBH_4 + CaH_2$  (Jin et al., 2008b),  $LiBH_4 / Ca(BH_4)_2$  (Lee et al., 2009). One of the most intensely studied systems hereof is the  $2 LiBH_4 + MgH_2$  system. The intended reaction pathway is:



However, several other reaction pathways are possible leading to products such as  $LiB_2$ , amorphous B,  $Li_2B_{12}H_{12}$  or  $Li_2B_{10}H_{10}$ . Bösenberg et al. (Bösenberg et al., 2010b) could show that due to a higher thermodynamic driving force for the favoured reaction the competing reactions can be suppressed by applying a hydrogen back pressure and limiting the dehydrogenation temperature. Nevertheless, since long-range diffusion of metal atoms containing species is required, see Fig. 13, in bulk ball-milled samples dehydrogenation so far occurs only at temperatures higher than 350 °C, hydrogenation at temperatures higher than 250 °C.

The dehydrogenation temperatures of this Reactive Hydride Composite, however, can be significantly reduced by using nanoconfined  $2 LiBH_4 + MgH_2$  stabilised in inert nanoporous aerogel scaffold materials whereby long-range phase separation is hindered and thus the diffusion path length reduced (Gosalawit-Utke, 2011).

#### 4. Conclusion

Metal hydrides offer a safe and compact alternative for hydrogen storage. The thermodynamic properties of them determine both their reaction heat as well as hydrogen

equilibrium pressure at given temperature and, therefore, are important parameters to be taken into account. Optimised system integration for a given application is not possible without selecting a hydride with suitable thermodynamic properties. To achieve highest possible energy efficiencies the heat of reaction and temperature of operation of the metal hydride should be adapted to the waste heat and temperature of operation of the fuel cell / fuel combustion system. It has been found that the thermodynamic properties of metal hydrides can be tailored in a wide range. Unfortunately, so far all the known conventional metal hydrides with more or less ideal reaction enthalpies and hydrogen equilibrium pressures above 5 bar at room temperature suffer from a rather limited reversible hydrogen storage capacity of less than 2.5 wt.%. With such a material it is not possible to realise a solid storage hydrogen tank with a total hydrogen storage density of more than 1.8 wt.% H<sub>2</sub>. Such tank systems still have advantages for the storage of small quantities of hydrogen for larger quantities, however, modern high pressure composite tank shells have a clear advantage in respect of gravimetric storage density. To realise a solid storage tank for hydrogen with a comparable gravimetric storage density it is required that novel hydrogen storage materials based on light weight elements are developed. There are several promising systems with high gravimetric storage densities in the range of 8 - 12 wt.% H<sub>2</sub>. For the applications of these novel material systems it is important to further adapt thermodynamic properties as well as the temperatures of operation towards the practical requirements of the system.

The discovery of the approach of combining different hydrides which react with each other during hydrogen release by forming a stable compound, the so-called Reactive Hydride Composites, show a great promise for the development of novel suitable hydrogen storage material systems with elevated gravimetric storage densities. However, so far, the ideal storage material with low reaction temperatures, a reaction heat in the range of  $|\Delta H| = 20\text{-}30$  kJ/(mol H<sub>2</sub>) and a on-board reversible hydrogen storage density of more than 6 wt.% H<sub>2</sub> has not been found.

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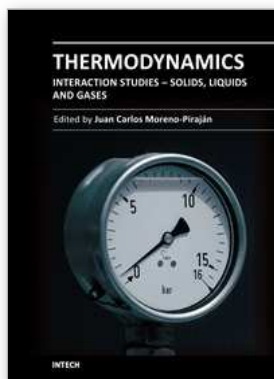


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