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Evaluation solid-state hydrogen storage systems

Current status

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Abstract

Upon going from a fossil fuel oriented to a hydrogen based economy, a new infrastructure and appropriate technologies have to be developed. An important target is the realization of suitable hydrogen storage systems. There are several methods to store hydrogen, all with their own advantages and limitations. The key issues for successful hydrogen storage are: the reversibility of hydrogen storage, high storage capacity under real-life conditions, appropriate kinetic and thermodynamic properties, safety and system costs. There are several techniques to store hydrogen, for example as a gas, a liquid, a chemical carrier, physisorbed on large surface structures or as chemically bound in e.g., metal hydrides. In this report to IEA annex XX task B, the current status of hydrogen storage in solid-state materials is evaluated.

In this rapport the main focus is on metals and metallic alloys based hydrogen storage materials. Up till now, Mg (doped, catalyzed, and alloyed) has been examined intensively as storage material. However, due to slow kinetics and high desorption temperature, the potential of Mg for on-board applications is limited. Recently, the attention has shifted towards light metals like Li, Be, Na, Mg, B and Al and their complexes and alloys. Although for some compounds the hydrogen storage capacity is promising, additional research has to be performed to improve the kinetics and thermodynamic properties.

A brief inventory of the current activities in the field of materials research and system development in the Netherlands and abroad is given.

The intrinsic properties of the most important compounds are shortly described in increasing order of being promising for on-board storage. In order of appearance we treat chemical hydrides, conventional intermetallic hydrides, Mg-based hydrides and complex light weight metal hydrides. Also some techniques to improve the hydrogenation behaviour are discussed. Special attention is paid to compounds that can store relatively large gravimetric amounts of hydrogen such as alanates and borides. Furthermore, the Li-N based ceramic systems for hydrogen storage are considered.

The main conclusion is that none of the hydrogen storage materials known today simultaneously fulfils all of the targets set by FreeDOM/CAR and the IEA. Some of these are of technical origin others deal with public acceptance but despite this there are already many niche markets with a different set of targets that can already be met. Hands-on experience in these markets would greatly enhance the practical knowledge on running hydrogen fuelled PEMFC powered vehicles.

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Summary

In this report to IEA annex XX task B, an overview is given of the current status of hydrogen storage materials in connection with on-board hydrogen storage applications. The storage methods and materials discussed here are:

- High pressure H_2 gas
- Cryogenic H_2 liquid
- Metal glasses
- Intermetallic compounds
- Mg based hydrides
- Complex hydrides,
- Lithium nitrides
- Borohydrides

For each type of compound the specific hydrogen storage properties and limitations are discussed. The physisorption of hydrogen on large surface area structures (for example carbon-based) is not evaluated here due to the required cryogenic conditions. Furthermore, techniques to improve hydrogenation kinetics, thermodynamics and storage capacity are presented (ball-milling, addition of catalysts, destabilizing the hydride phase etc).

For on-board hydrogen storage international organisations posed some criteria for efficient on-board hydrogen storage. The most important criteria posed by the FreedomCAR/DOE for mobile applications to be met in 2010 are; Useable energy density 1.5 kWh/L, storage weight percent 6 wt.% of H_2, operating temperature -30/50°C, cycle life (> 1000 cycles), delivery pressure 2.5 bar, refuelling time < 3 min (5 kg H_2).

From a storage point of view, classical intermetallic compounds have a too low gravimetric hydrogen storage capacity for on-board applications. Mg is more promising as storage material, however slow kinetics and unpractical thermodynamics limits its practical use for on-board storage. During the last years the attention has shifted towards light weight metals like Li, Be, Na, Mg, B and Al and their compounds. Although the amounts of stored hydrogen are promising for certain compounds, additional research has to be done to improve kinetics, thermodynamics (ad/desorption temperature) and reversibility of the hydrogenation of these compounds. Other promising systems are the Li-N based ceramic systems and combinations of different types of hydrides to modify the overall hydrogenation enthalpies. Considering all these metals and their alloys, it is concluded that none of the today known compounds will satisfy all the targets simultaneously.

Investigation of the current status of storage materials reveal that there are some very important properties which are more or less disregarded in research. Although it is generally accepted that catalysis plays a vital role in the feasibility of hydrogen storage in metallic compounds, their working mechanism is often unknown.

Furthermore, most of the experiments on hydrogen storage compounds are performed under ideal laboratory conditions. This implies small scale experiments under idealized conditions (high purity hydrogen gas, clean conditions). Therefore it is necessary to investigate the mechanical stability, chemical stability, thermal conductivity and cycle life, because a possible application will operate under non-ideal conditions. Also the tolerance to impurities and contaminations, the adsorption/desorption kinetics under realistic conditions and heat and mass transfers in the material are properties that need to be considered. In this context it is important to realize that in many reports only the maximal storage capacity is reported and not the effective <u>reversible</u> hydrogen storage capacity, which is in general much lower.

Also an inventory is given of the current activities and projects on material research and hydrogen storage in the Netherlands and abroad as well.

1. Introduction

The inventory of state-of-the-art technologies and new developments in on board hydrogen storage is performed by ECN and made available to IEA Annex XX task B, see Appendix A.

1.1 Hydrogen storage

For the transition from a fossil fuel to a hydrogen based economy, hydrogen storage is a key issue. One needs to pack the hydrogen as close as possible since the volumetric density at standard conditions is very low. To achieve this goal additional materials and energy are required, since hydrogen is merely an energy carrier. Hydrogen can be stored as a gas, a cryogenic liquid, physisorbed on large specific surface area structures, in metal hydrides, in complex hydrides, and chemical hydrides (by means of chemical reactions). The need to pressurize the gas (high pressures, safety issue, and energy losses) and cooling to liquefy (energy losses) makes the storage in metal-hydrides a very interesting option. Many metals (and alloys) are abundant, cheap, metal hydrides are relatively safe and can contain a high volume density of hydrogen, see Figure 1.1. The given values are based on a driving range of 500 km which requires around 4 kg of hydrogen. In this rapport an overview is given of the state-of-the art hydrogen storage materials. Furthermore, some techniques to improve hydrogen storage and system developments are described.

The research on new hydrogen storage materials during the last years has shifted towards light metals like Li, Be, Na, Mg, B and Al. These metals are particularly interesting due to the fact that they can contain a high weight percentage of hydrogen. The US Department of Energy (DOE) presented several requirements for an on-board hydrogen storage system. Furthermore, to obtain an easy and safe operating system, a low re-hydrogenation pressure is desired. The requirements for effective on-board hydrogen storage are (FreedomCAR/DOE, Japan and IEA targets are comparable):

1) Appropriate thermodynamics (favourable enthalpies of hydrogen absorption and desorption),
2) Fast kinetics (quick uptake and release),
3) High storage capacity (specific capacity to be determined by usage),
4) Effective heat transfer,
5) High gravimetric and volumetric densities
6) Long cycle lifetime for hydrogen absorption/desorption,
7) High mechanical strength and durability,
8) Safety under normal use and acceptable risk under abnormal conditions,
9) Cheap components and materials

The specific targets for mobile applications specified by the Department of Energy's Office of Energy Efficiency and Renewable Energy are given in Table A.1 and Table A.2.

From literature it is clear that to meet the requirements for hydrogen storage, the current status of the technology is insufficient. The posed goals cannot be met simultaneously and realization of these targets requires new breakthroughs in several research fields. For example to give an idea about the system requirements, to drive with an average car 100 km one needs 3 litre of gasoline (2.21 kg) (energy density gasoline 12.7 kWh/kg) for an average car. This is equivalent with 0.84 kg of hydrogen (energy density 33.3 kWh/kg). To drive 500 km, 4.2 kg of hydrogen is required. To store this amount of hydrogen in for example $LaNi_5$ (weight percentage of 1.4 wt.%), one needs 300 kg of metal-hydride material. Besides the weight problem also the heat development during hydrogenation is important. For an enthalpy of formation of $\Delta H = -35$

kJ/mol H_2, the heat release during a 3 minute refilling time is 405 kW, see Figure 1.1 (Schlapbach, Züttel, 2001).

$$Mg_2NiH_4 \qquad LaNi_5H_6 \qquad H_2 \text{ (liquid)} \qquad H_2 \text{ (200 bar)}$$
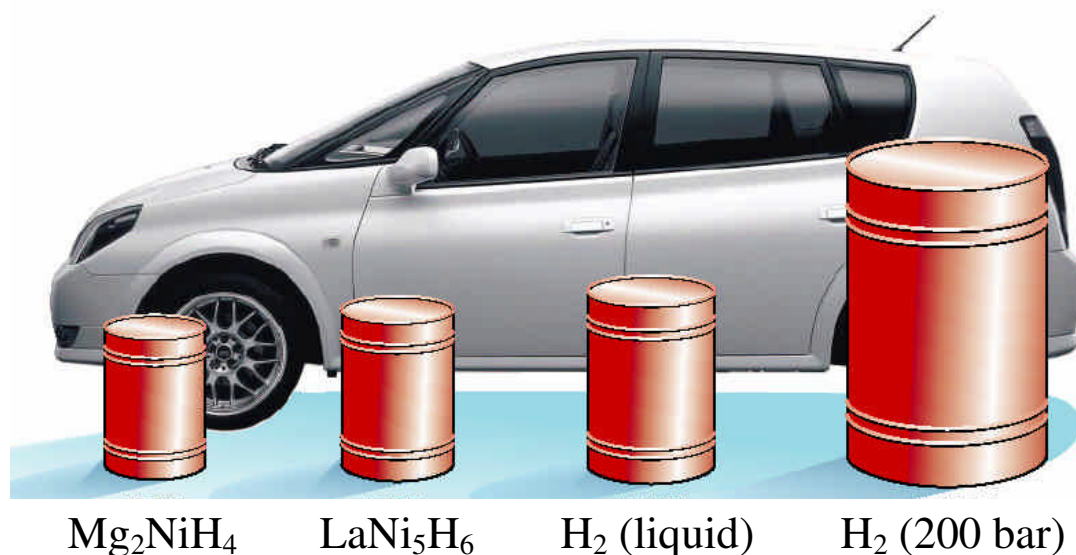
Figure 1.1   *Comparison the different hydrogen storage techniques. For on-board hydrogen storage a metal hydride is preferred due to the large volumetric density. However **at this moment** the weight penalty limits its practical application (Schlapbach, Züttel, 2001).*

In addition to the posed targets one can think of (metal) hydrogen storage systems which are suited for specific purposes. For example if the storage capacity is high enough, one may accept lower hydrogenation kinetics and not use the full storage capacity of the metal hydride. For on-board applications one can think of only using hydrogen based cars in certain regions, smaller (lighter) cars and metal hydrides for applications in which weight is not really a limitation.

Besides the intrinsic hydrogen storage properties of the metal-hydride system like thermodynamics, kinetics, etc, the mechanical and chemical properties of the storage system are equally important for an application. These include expansion and shrinking upon hydrogenation, embrittlement and sensitivity to temperature changes. Upon hydrogen absorption the metallic host obtains a reduced ductility and tensile strength and repeated hydrogen absorption and desorption can pulverize the material. A phase transition during hydrogenation can also be an undesired effect. This can be a metal-hydride phase transition in the same material (for example $Mg\text{-}MgH_2$) or a phase transition in a multi component system. Mass transfer and multiple reactions during the phase transition usually limit the kinetics and reversibility of the system and sensitivity to water, oxygen, CO etc. is also an issue.

Although metal hydrides are considered as ideal hydrogen storage system (mainly due to the high volumetric density), an obvious candidate for on-board (automotive) applications is not yet reported. To illustrate this, an extended database of metal hydrides is provided by http://hydpark.ca.sandia.gov. This database lists more than 2000 hydride forming elements, compounds and alloys, but does not report one single compound which meets all the posed tar-

gets simultaneously. Furthermore, it is reported by Grochala *et al.* (Grochala, Edwards, 2004) that a major dilemma exits for all today known hydrides: or the desorption temperature is low but the storage is irreversible or the hydrogen can be stored reversibly but the desorption temperature is too high for practical use. Furthermore, it is well worth to mention that these authors do not believe the storage problem will be solved with a binary or ternary metal-hydride compound.

In addition it is also important to consider that one has to make the distinction between the theoretical hydrogen storage capacity, hydrogen storage capacity under laboratory conditions, and hydrogen storage under "real-life" conditions. Often only the theoretical storage capacity is reported which can differ largely from the storage capacity under moderate and practical conditions. For intermetallic compounds only 50-90% of the maximum hydrogen storage capacity can be used and often this does not even include the complete storage system. Furthermore, the influence of activation, sensitivity to gas impurities, heat transfer, cyclic stability, protection of the metal hydride, and volumetric change on the hydrogen storage capacity is often neglected.

According to the U.S Department of Energy some important questions that need to be considered for practical applications are:

1) Does hydrogen physisorb or chemisorb?
2) Does it bind molecularly or dissociatively?
3) Where does the hydrogen reside?
4) What is the nature of its hydrogen diffusion mechanism?
5) What are the activation barriers for hydrogen desorption?
6) What adverse effect does hydrogen have on the structural and mechanical stability of the host material?
7) What is the nature of bonding of hydrogen with host atoms — ionic, covalent, or metallic?
8) What roles do surface morphology and defects play in hydrogen absorption and desorption?
9) In what ways is it beneficial to store hydrogen in novel materials, such as nanostructures and porous materials?
10) How do catalysts help in reducing the operating temperature and pressure for hydrogen uptake and release?

The posed targets for hydrogen storage are mainly based on the current status of the automotive industry. With this in mind, we are mainly interested in materials and techniques for on-board hydrogen storage since the storage properties for stationary applications greatly differ. To be complete we consider here the three most mature forms of hydrogen storage today: gas, liquid, and solid (sorption) materials, with the main focus on storage techniques and materials.

1.2   High pressure hydrogen storage

For gaseous hydrogen storage under high pressure there are some techniques like steel tanks, composite tanks, glass spheres etc. The most mature and promising technique are the carbon-fibre-wrapped hydrogen composite storage tanks. These tanks are available, safety-tested, simple of construction and can contain pressures up to 700 bar (6.7 wt.%). There are already several pilot applications in the world today using this technique, but high pressure storage has some disadvantages. The large physical volume required (does not meet the volumetric target), high costs and safety issues are still under investigation and discussion. Furthermore, as the storage capacity of a composite tank is limited by the molecular interaction of the hydrogen, an increase in pressure is not proportional to an increase in storage capacity at higher pressure, see Figure 1.2. Another restriction is the considerable energy loss during pressurization of the hydrogen

gas which is typically in the order of 12 – 16 % for compression to 800 bar (depending on the type of compression). Further research is required to obtain commercial applications.
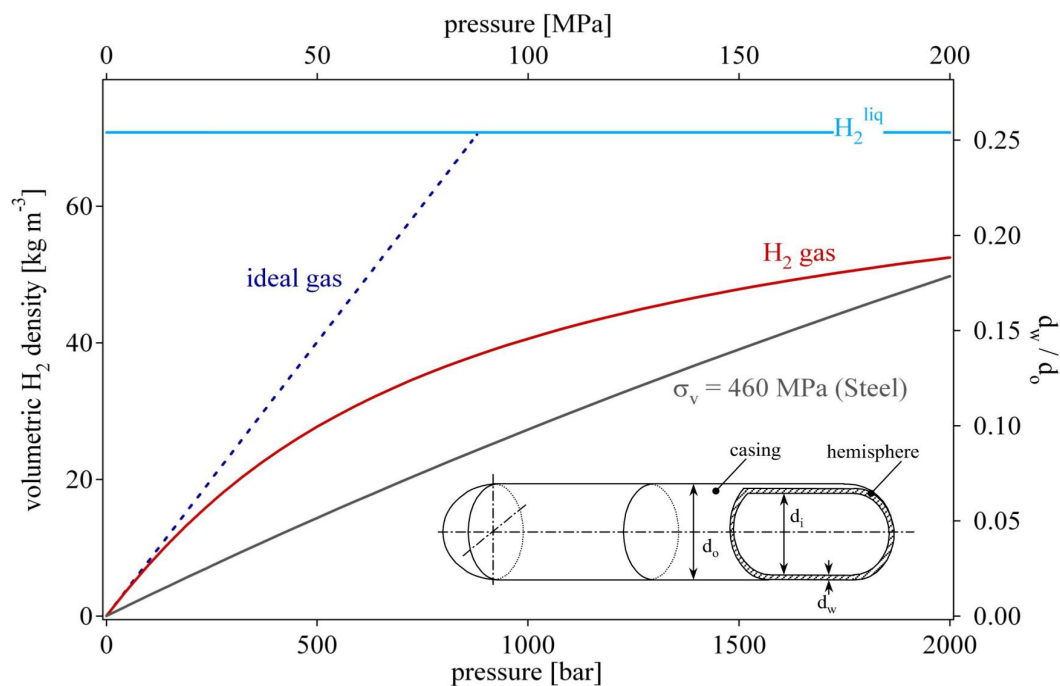
Figure 1.2 *Volumetric density of compressed hydrogen gas as a function of gas pressure including the ideal gas and liquid hydrogen storage. The ratio of the wall thickness to the outer diameter of the pressure cylinder is shown on the right hand side for steel with a tensile strength of 460 MPa. A schematic drawing of the pressure cylinder is shown in the inset. The deviations from the ideal gas line are indirect a consequence of the change in chemical potential as function of pressure and temperature (Züttel, 2003a).*

1.2.1 Summary high pressure hydrogen storage:

➢ Most mature method for the moment
➢ Requires further R&D on materials and techniques
➢ Many applications already realized (6.7 wt% 700 bar)
➢ Does not meet the vol.% target
➢ Energy loss (12-16% at 800 bar)
➢ Requires safety consideration and public acceptation

1.3 Cryogenic liquid hydrogen storage

Hydrogen can also be stored in the form of a cryogenic liquid (-253°C) or stored as a constituent in other liquids such as $NaBH_4$ solutions, rechargeable organic liquids, or anhydrous ammonia NH_3. Liquid hydrogen is already used in some commercial vehicles. Liquid hydrogen has a density of 70.8 kg/m^3 and a gravimetric density of 100% like gaseous hydrogen. However, in practical applications only 20 wt.% of hydrogen can be achieved today. The main advantage of liquid hydrogen is its high storage density at relative low pressures. Liquid hydrogen has a much better energy density then pressurized hydrogen but a large amount of energy is required for the liquefying process. The energy required for the liquefying process is W_{prac} = 10 kWh/kg while the higher heating value (HHV) of hydrogen 39.4 kWh/kg. This means that at least 25% of the energy is lost (30-40% is more realistic). To retain cryogenic conditions, super insulated tanks

should be used however the boil-off loss during dormancy is also a severe limitation. In order to limit these losses, the storage system becomes relatively complicated, see Figure 1.3.
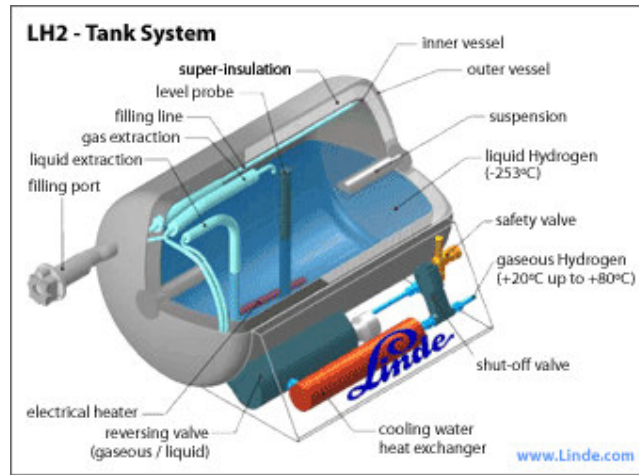
Figure 1.3 *Example of a cryogenic hydrogen storage system. (Source: www.Linde.com).*

1.3.1 Summary cryogenic hydrogen storage:

➢ High vol.% capacity (70.8 kg/m^3)
➢ High wt.% capacity (practical ~ 20 wt.)
➢ From ortho-hydrogen to para-hydrogen upon liquefaction, heat is released (phase transition)
➢ A minimum of 25% energy loss due to liquefaction
➢ Loss of efficiency due to evaporation (boil-off)
➢ Complicated system requirements

1.4   Other solid-state hydrogen storage mediums and techniques

Besides high pressure hydrogen storage, cryogenic liquid hydrogen storage and storage in metal based compounds, there are other hydrogen storage techniques. The ones based on the physisorption of hydrogen at relatively low temperatures on large surface structures or the encapsulation and physical trapping of hydrogen are: Carbon based structures, hydrogenated amorphous carbon, self-assembled nano composites/aerogels (foams), Zeolites (crystalline nano porous materials, Metal Organic Frameworks (MOF of which an example is shown in Figure 1.4), encapsulated in glass microspheres, boron nitride nanotubes, and hydrogen in hydrates and clathrates. When physisorption is involved, cryogenic processes are necessary with similar drawbacks as for liquid hydrogen storage.
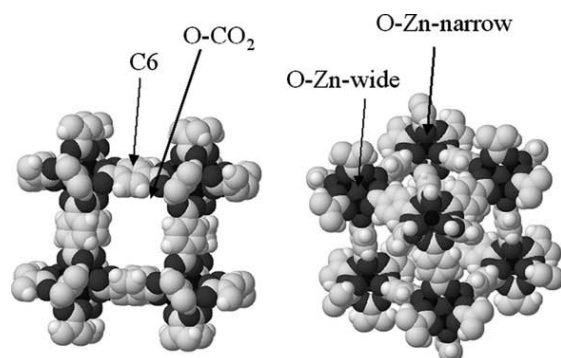
Figure 1.4 *The minimised unit cell of MOF5 viewed from two different direction directions. Left the open pore structure is visible. White spheres: hydrogen, light gray: carbon, dark grey: oxygen, black: zinc. The hydrogen adsorption sites are indicated by arrows (Mulder, 2005).*

Some based on chemical storage are: bulk crystalline/amorphous materials (multi-component alloys), chemical storage media or hydrogen carriers (methanol, ammonia, etc) and reversible hydrogenation of organic liquids (C_xH_y) where the efficiency of the last two depend on the conversion and selectivity of the reactions involved. Here three methods are discussed more extensively, namely the metallic glasses, gas hydrates/clathrate hydrates and the organic liquids.

1.4.1 Metallic glasses

Most metals and alloys of different types of metals adopt some crystalline structure. Metals without any form of crystalline structure are amorphous and referred to as metallic glasses or glassy metals. The hydrogen storage capacity of these materials depends strongly on the microstructure of the compound as the hydrogen is trapped at interstitial sites. Kumar *et al.* (Kumar, Wang, 2004) reported that Zr and Cu based metallic glasses can absorb an appreciable amount of hydrogen but the storage is irreversible. The hydrogen induced a crystallization process upon heating. Metal glasses based on Fe and Y are inert to hydrogen. The hydrogen absorption by the metal glass $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ is investigated by Soubeyroux *et al.* (Soubeyroux, 2003). They found that the formed hydride depends strongly on the specific structure of the metal glass. ZrH_2 is formed when hydrogen is applied to the amorphous phase and Zr_2NiH_4 is formed in case of the intermetallic phase. A Pd coated metal glass shows improved desorption kinetics and full desorption is obtained even below 300°C for hydrogen concentrations up to H/M = 0.4. However, higher hydrogen concentrations lead to irreversible changes in composition (Zander, 2003).

From the limited amount of publications on these compounds it is obvious that the hydrogenation process and the subsequent heating to release the hydrogen have a large impact on microstructure and crystalline structure of the metal glass. It is therefore questionable if these systems are stable under repeated cycling. Furthermore, the compounds considered so far contain Zr, Cu, and Ni, which are relative heavy elements which result in a low gravimetric hydrogen storage capacity. The research on these types of materials is still in an early stage and the focus is on light metal glasses.

1.4.2 Gas hydrates/clathrate hydrate

Clathrate hydrates can also be used to store hydrogen. A clathrate consist of a hydrogen-bonded water host lattice that can contain one or more types of so-called guest molecules. Current research is performed to identify mechanisms that decrease the stability of the clathrate hydrides and determine the thermodynamically most favoured cage occupancy (Sluiter, 2004).

It is known that hydrogen clusters can be stabilized in a clathrate hydrate at very high pressures of 220 MPa at 249K. (Mao, 2002) (Mao, Mao, 2004). Florusse *et al.* showed that hydrogen clus-

ters can be stabilized and stored at low pressures within the sII clathrate hydrate lattice by stabilizing the large water cages with the compound tetra-hydrofuran (THF). Tetra-hydrofuran is able to stabilize the clathrate at a pressure of 5 MPa at 279.6 K versus 300 MPa at 280K for a pure H_2 hydrate. It is shown that promoter guest molecules can be used to store hydrogen in a binary clathrate hydrate at low pressures. By the optimization of this promoter, the storage of hydrogen might be increased. However the use of these clathrates as hydrogen storage is a quite new research field. In case of sII binary hydrogen hydrate, with double occupancy of the small cavities by H_2 and the large cavities partially occupied by THF, the mass of hydrogen could be up to 4%. This is however far from the desired storage capacities required for on-board applications. Further research on this system has to be done to determine its full potential and limitations. It is obvious that temperature excursions of this type of storage system should be prevented.

1.4.3 Organic liquids

Hydrogen can also be stored in the form of hydrogen carriers, for example organic liquids. The reversible catalytic dehydrogenation of methylcyclohexane (C_7H_{14}) to toluene (C_7H_8) occurs according to the following reaction, see Figure 1.5:

$$C_7H_{14}(l) \rightarrow C_7H_8(l) + 3H_2 \ (g) \ (T_{des} = 300\text{-}400°C)$$
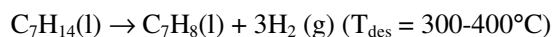
which involves 6.1 wt.% of hydrogen. The main disadvantages of organic liquids when used for hydrogen storage are the rest product after dehydrogenation which needs to be sent back to a recycle plant for rehydrogenation. Both rehydrogenation and hydrogenation are catalyzed processes with selectivity and conversion well below 100%. This means that by-products have to be removed which makes the process energy intensive, expensive, and dirty. The very limited cycle life is a restriction of this system. Furthermore, the methylcyclohexane is a liquid which can react strongly with oxidants resulting in explosion and fire. Therefore the use of these types of storage systems for on-board storage is questionable.
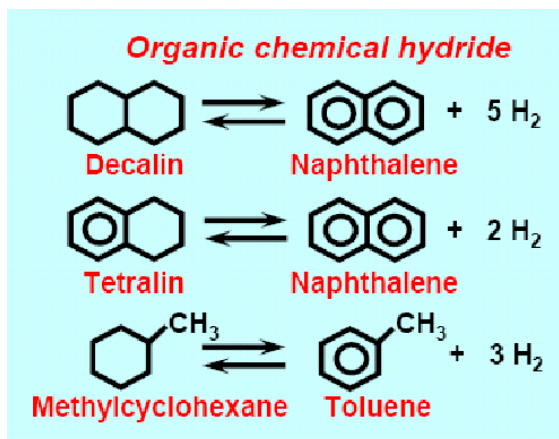
Figure 1.5 *Hydrogen storage in the form of organic liquids. Upon going from Decalin (Tetralin) to Naphthalene and from Methylcyclohexane to Toluene results in the release of hydrogen. This process can be used as hydrogen storage or hydrogen carrier material (Source: Y. Saito Organic Hydrides for Carrying Hydrogen, International H_2 storage Technologies Conference, Italy 2005).*

2. Hydrolytic, pyrolysis, intermetallic hydrogen storage compounds and intrinsic properties

2.1 Enthalpy of formation, targets for hydride formation

For a system in thermodynamic equilibrium, the equilibrium pressure p_0 of the monovariant heterogeneous equilibrium reaction (Bevers, 2006; Bevers, 2007),

$A(s) + xB(g) \leftrightarrow C(s)$
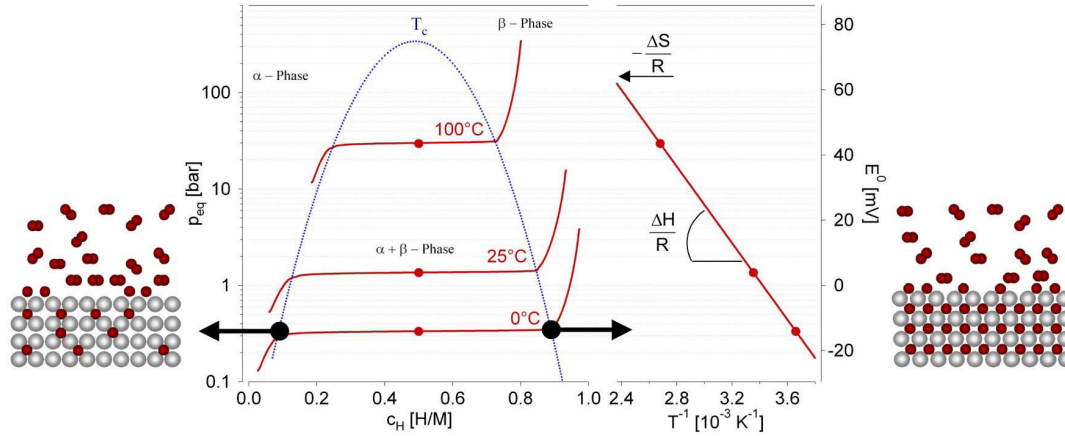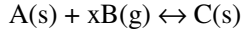
Figure 2.1 *For a typical intermetallic compound the pressure composition isotherms are shown on the left of the figure. From left to right are shown the α - phase, the coexistence of the α and β phase and the β - phase region. The coexistence of the two phases is characterized by the nearly flat plateau's which for increasing temperature ends up in the critical temperature. The slope of the Van 't Hoff plot is equal to the enthalpy of formation divided by the gas constant and its intercept is the entropy of formation divided by the gas constant (Züttel, 2003a)*

is given by

$$\Delta_r G(T) = \Delta_r G^0(T) + xRT \ln \frac{p(T)}{p_0} = 0$$

The molar Gibbs energy change of the reaction is given by ΔG, p_0 is a reference pressure, ΔG_0 is the Gibbs energy change at p_0, and R the gas constant. In combination with

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

where the enthalpy (kJ mol^{-1} H$_2$) and entropy (JK^{-1} mol^{-1} H$_2$ at 10^5 Pa) are given by H and S respectively, for the equilibrium pressure p(T) we find that

$$\ln \frac{p(T)}{p_0} = -\left(\frac{\Delta_r H^0}{xR}\right)\left(\frac{1}{T}\right) + \frac{\Delta_r S^0(T)}{xR}$$

The loss of entropy when the hydrogen gas is absorbed by the solid determines the entropy change $\Delta_r S^0 \cong -S_{H2} = -130.684$ J K^{-1} mol^{-1} H$_2$ at a pressure of 10^5 Pa and room temperature (300

K). By plotting the logarithm of pressure versus the reciprocal temperature, see Figure 2.1, the slope of the line is equal to minus the enthalpy of formation per mole H_2 divided by the gas constant, see Figure 2.2.
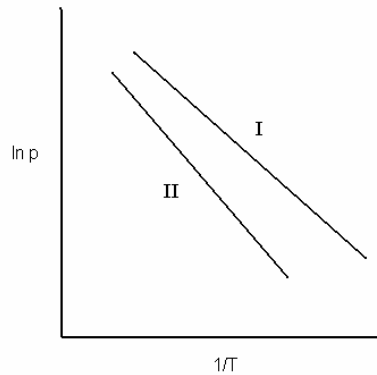
Figure 2.2 *Illustrative Van 't Hoff plot representing the pressure-temperature relation for a hydrogen storage material. The difference between hydride formation (I) and hydride decomposition (II) often has its origin in the mechanical restrictions and properties of the material.*

For a Gibbs free energy of around zero, a practical hydrogen storage material at a pressure of 10^5 Pa and room temperature (300 K), an enthalpy of formation of ~ 39 kJ mol^{-1} H_2 is required. To obtain storage materials which are interesting for on-board hydrogen storage, one needs to find materials with lower operating temperatures (meaning to the right in Figure 2.3) and lower enthalpy of formation (meaning a smaller slope in Figure 2.3).
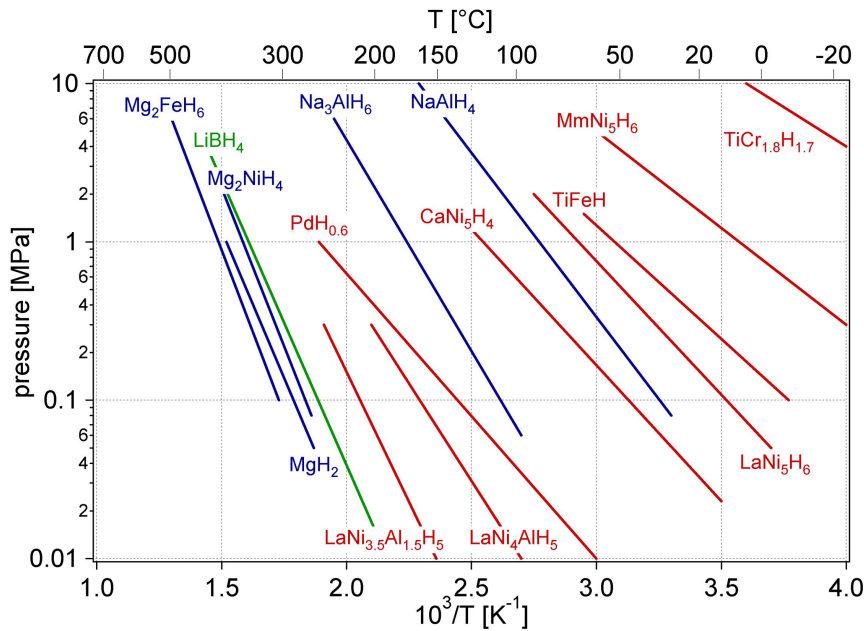
Figure 2.3 For several selected metal hydrides the Van't Hoff plots are shown. The influence of stabilization of $LaNi_5$ by the partial substitution of Ni by Al is also shown. The Van't Hoff as well as the substitution of La with mischmetal (e.g. 51% La, 33% Ce, 12% Nd, 4% Pr) (Züttel, 2003a).

2.2   Cycle stability

Besides the high storage capacity and reversibility of the hydrogen storage, the storage medium has to be stable under repeated hydrogenation/dehydrogenation cycles. This stability is largely determined by the microstructure and chemical changes during the hydrogen absorption and desorption process. The combination of temperature, pressure, hydrogen absorption/desorption (expansion and contraction) can result in a change in microstructure and chemical composition of the storage material which in combination with the sensitivity to oxidation and contamination makes the cycle stability one of the more difficult targets to achieve. For metal – hydride based batteries, metals (or combinations of) like Ce, La, Nd, Pr and metal oxides like Cr_2O_3, Al_2O_3 and CeO_2 are often used to improve the cycle stability (Song, Bobet& Darriet, 2002). For this reason these types of materials are also considered for improving the stability of the hydrogen storage materials (Song, Bobet& Darriet, 2002). A good cycling stability is reported for over-stoichimetric $La(Ni,M)_{5+x}$ (with M = Mn, Cu) (Latroche, Notten& Pervheron-Gue'gan, 1997; Notten, Latroche& Pervheron-Gue'gan, 1999). In addition one also has to keep in mind that the depth of hydrogen charge and discharge are of considerable influence on the cycle stability of the storage material.

In the rest of this report a categorization of new and novel materials and processes is given for the development of hydrogen storage metals. Furthermore, different compounds, alloys and elements are evaluated as being potential candidates for hydrogen storage.

2.3   "Classical" hydrogen storage metal hydrides: Hydrolytic

Li, Na and Mg can form a metal-hydride phase upon hydrogen absorption. When these hydrides are brought in contact with water they release hydrogen according to the reactions,

$$MH_x + XH_2O \rightarrow M(OH)_x + xH_2$$
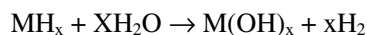
in which M is a metal and x its valence, or

$$MXH_4 + 4H_2O \rightarrow 4H_2 + MOH + H_3XO_3$$

here M is a group I metal and X is a trivalent element from group III. In reality the reactions are not as well defined as presented here. These hydrolysis reactions are generally characterized by high storage capacities since hydrogen from the hydride and from the water are released during the reaction. From the on-board storage perspective this is however not a suited technique due to the irreversibility of the process. The reaction products have to be sent back to the recycle plant to be regenerated. For storage percentages see Table A.3.

2.4 "Classical" hydrogen storage metal hydrides: Pyrolysis

For a certain category of metals and alloys a hydride phase can be formed at high hydrogen pressures. The hydrogen release is obtained by heating up the compound (pyrolysis) according to the reaction,

$$2M + xH_2 \leftrightarrow 2MH_x + heat$$
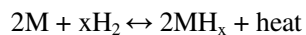
with M a metal or an alloy. Although these reactions are reversible, the high hydrogen pressures required for regeneration of the hydride limit the practical use for on-board hydrogen storage. Some examples of hydrogen release by heating together with hydrolysis and their properties are given in Table A.3.

2.5 "Classical" hydrogen storage metal hydrides: Intermetallic compounds

For many years it is known that intermetallic compounds can be used for reversible hydrogen storage. One of the first application oriented metal-hydrogen storage systems were $LaNi_5$ (1.4 wt.%) (Vucht, Kuijpers& Bruning, 1970), see Figure 2.4, and FeTi alloys (Reilly, Wiswall, 1974). However these intermetallic compounds have a rather low gravimetric hydrogen storage capacity. Due to this weight penalty these alloys are not suited for on-board storage applications (Reilly, Sandrock, 1980). The basic design principle for these storage systems is that they are formed by combining an element that forms a stable hydride phase and an element that forms a non stable hydride phase and the hydrogen is located in interstitial sites. Extended review articles on these intermetallic hydrogen storage compounds are given for example by Sandrock *et al.* (Sandrock, 1999), Schlapbach *et al.* (Schlapbach, 1988) and Yvon *et al.* (Yvon, 1998). The properties of the different types of intermetallic hydrogen storage compounds are given in Table A.4. The intermetallic hydrides are ordered according to their crystal structures such as AB_2, A_2B, AB and AB_5. The most commonly used hydrides are the AB_5 hydrides with A usually a lanthanide element (atomic number 57-71), Ca or mischmetals (rare earth metal mixtures, which are cheaper) and for B elements like Ni, Co, Al, Mn, Fe, Sn, Cu, Ti, etc.

The advantage of these systems is that the absorption and desorption can be tuned by alloying the correct concentrations and types of elements. The hydrogenation of intermetallic hydrides is reversible with good kinetics. Although these classical hydrides have good volumetric hydrogen densities (~130 kg H_2/m^3 for $LaNi_5H_6$), due to their weight penalty (1-2 wt.% H_2) they are mainly interesting for stationary applications.
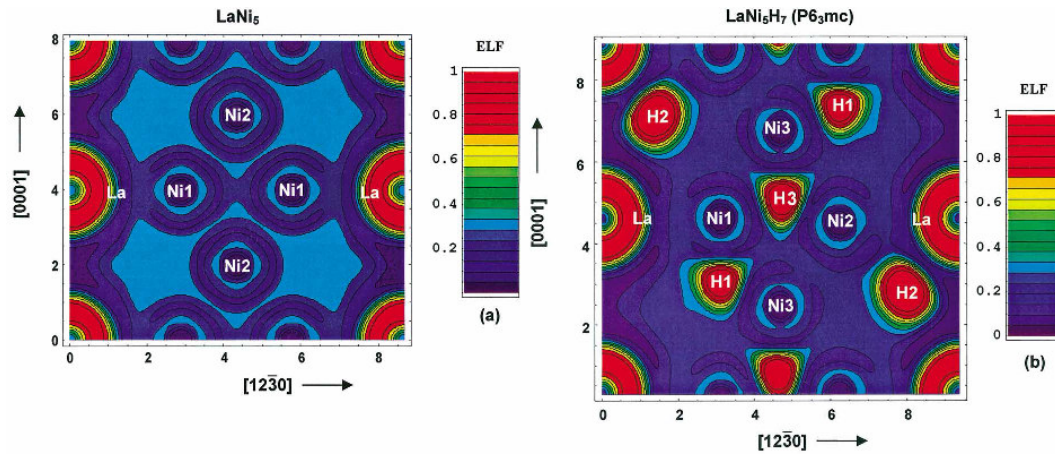
Figure 2.4 *Electron Localization Function ELF in the (2-1-10) plane of (a) LaNi₅ and (b) LaNi₅H₇ (P6₃me) (Hector, Herbst& Capehart, 2003).*

2.5.1 Summary intermetallic storage compounds:

- ➤ Low hydrogen absorption/desorption temperature/pressure
- ➤ Multiple cycles are possible
- ➤ High volume storage capacity
- ➤ Good hydrogenation kinetics
- ➤ Low gravimetric storage capacity
- ➤ Not suited for mobile applications

3. Mg based hydrides

Over the years Mg is seen as one of the most promising candidates for hydrogen storage due to the high hydrogen storage capacity of 7.6 wt.%, high energy density (9 MJ/kg Mg), reversible hydrogen absorption/desorption, Mg is abundant, safe (if protected from oxidation), heat-resistant, non-toxic and vibration absorbing (Zaluska, Zaluski& Ström-Olsen, 2001b) ((Zaluska, Zaluski& Ström-Olsen, 1997) (Zhu, 2006) (Wiswall, 1978).

However there are some properties of the Mg – H_2 system which limits its practical use as hydrogen storage system. The large negative enthalpy of formation results in a stable Mg hydride phase (desorption pressure of 1 bar is around 300°C) (Grochala, Edwards, 2004) (Imamura, 2005). In addition the hydrogen dissociation on the metallic Mg surface is an activated process with a high activation barrier of 8.0 10^{-20} J (Norskov, 1981) resulting in a slow chemisorption process. When the Mg hydride layer increases in thickness during hydrogenation it becomes more and more impenetrable for hydrogen. This process leaves the underneath lying Mg unreacted resulting in decreased kinetics and incomplete hydrogenation (Holtz, 1996) (Friedlmeier, Groll, 1997). During the past, intensive research has been done to improve the hydrogenation kinetics and thermodynamics of magnesium, see Table A.5.

To overcome the thermodynamic and kinetic limitations, the addition of a catalyst can play an important role. The main objectives are to overcome the dissociation barrier of the hydrogen and to destabilize the hydride phase (Reule, 2000) (Liang, 1998) (Aoyagi, Aoki& Masumoto, 1995) (Hong, 2000). A catalyst that improves the hydrogenation process considerably due to its catalytic properties is Pd (Zaluska, Zaluski& Ström-Olsen, 1999a; Zaluski, Zaluska& Ström-Olsen, 1995). However, the high cost and gravimetric weight of Pd limits its practical use for large scale and on-board applications. The addition of Ni and other transition metals (Ti, V, Mn and Fe) also improve the hydrogenation behavior (kinetics) of Mg and decrease the activation energy for hydrogen desorption (Baer, Zeiri& Kosloff, 1997; Bloch, Mintz, 1997) (Gennari, 2002; Holtz, Imam, 1999; Iwakura, 1999; Liang, 1999a) (Dehouche, 2000; Kyoi, 2004; Liang, 1999b), see Table A.5. Besides pure metals, the addition of certain metal oxides can improve the hydrogenation behavior considerably (Dehouche, 2002; Jung, Lee& Lee, 2005; Oelerich, Klassen& Bormann, 2001; Song, Bobet& Darriet, 2002) and some of these catalyst additions are shown in table Table A.5. A slightly different approach is to reduce the stability of the Mg hydride phase by addition of elements like Zn, Al, Ag, In and Cd for example (Liang, 2004). Although many types and compositions have been used, very often the exact working mechanism of the catalyst is unknown.

Also the microstructure, grain size and crystallinity of the Mg can have a large influence on the hydrogen absorption and desorption. For example ball-milling of Mg creates an increased surface area with many defects (also inside the material), phase boundaries, decreased grain size and porous surface structure with many active sites for hydrogen absorption/desorption but leaves the storage capacity almost unaltered. This results in improved kinetics and surface activity for hydrogenation, reduction in activation energy, decreasing desorption temperature, enhanced kinetics and higher hydrogen diffusion through the material. Also ball-milling in the presence of an hydrogen atmosphere or with the addition of a catalyst improves the hydrogenation kinetics (and thermodynamics) (Chen, Williams, 1995; Huot, 1999b; Huot, Akiba& Takada, 1995; Song, 2006; Zaluska, Zaluski& Ström-Olsen, 1997; Zaluska, Zaluski& Ström-Olsen, 1999a) (Wang, 2000b; Wang, 2000a) (Fabing, 2006).

In this context it is interesting to mention the work of Wagemans *et al.* (Wagemans, 2005) who calculated both the Mg and MgH_2 cluster energies as function of the number of Mg atoms in the cluster. They find that when going down in number of atoms, the energy of the clusters become less negative. Thus, reducing the grain size results in a less stable hydride phase. Although ball-milling is an effective and simple technique to improve the hydrogenation properties, it is an energy consuming process as the hydrogenation kinetics improves with milling time.

Based on Table A.5, the hydrogen storage capacity for Mg based hydrides is shown in Figure 3.1. The figure nicely indicates the large spread in storage capacity as function of the different additives and desorption temperatures. The number of reported Mg compounds having a desorption temperature below 250°C is very limited.
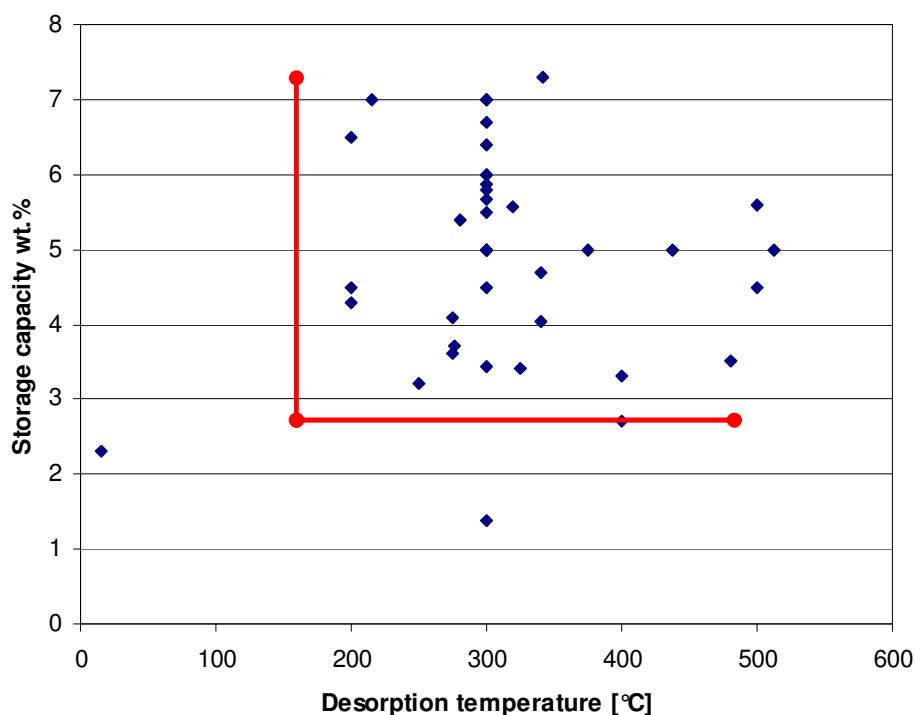
Figure 3.1   *Hydrogen storage capacity of Mg based hydride versus desorption temperature. If the desorption temperature is not available the absorption temperature is used. In case a range of values is given, the average value is taken. The corresponding desorption pressure can be obtained from* Table A.5.

Although extended research has been done to improve the hydrogenation properties of Mg, it is concluded that no Mg based hydride has been found that has a significantly lowered enthalpy of formation, improved kinetics and with a high gravimetric storage capacity (the desorption temperature is still around 300°C, see Figure 3.1) which allows practical on-board hydrogen storage. The spread in data is roughly indicated by the (red) bars. Another possibility to develop new Mg-based hydride systems with lowered reaction enthalpies and retaining high hydrogen capacities is the combination of MgH_2 with other types of light-metal hydrides. Dornheim *et al.* state that when the components of the composites react exothermic during desorption this system can be denoted as reactive hydride composites (Dornheim, 2007). This is based on an additional exothermic reaction of components of different hydrides during desorption to form a stable compound or an additional endothermic reaction during absorption. The heat generation and desorption temperature are determined by the enthalpy of formation (Barkhordarian, 2004; Barkhordarian, Klassen& Bormann, 2006; Vajo, Skeith& Mertens, 2005). In this way the effective enthalpy of hydride formation becomes smaller. This research is still fundamental (research stage) and typical reactive hydride composites are $MgH_2 + Ca(BH_4)_2$, $MgH_2 + 2NaBH_4$, $MgH_2 + 2LiBH_4$ based on the reactions (Dornheim, 2006),
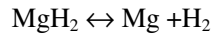
$MgH_2 \leftrightarrow Mg + H_2$ $T_{des, 1bar} = 300°C$
                                                          $\Delta H = -78$ kJ/mol H_2, 7.6 wt.%
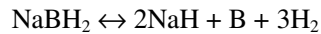
$NaBH_2 \leftrightarrow 2NaH + B + 3H_2$ $T_{des, 1bar} = 405°C$
                                                          $\Delta H = -88$ kJ/mol H_2, 7.9 wt.%
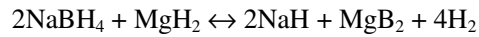
$2NaBH_4 + MgH_2 \leftrightarrow 2NaH + MgB_2 + 4H_2$ $T_{des, 1bar} = 350°C$
                                                          $\Delta H = -64$ kJ/mol H_2, 7.8 wt.%

And for the reactive hydride composites,
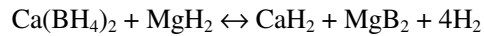
$Ca(BH_4)_2 + MgH_2 \leftrightarrow CaH_2 + MgB_2 + 4H_2$ $T_{des, 1bar} = 350°C$
                                                          $\Delta H = -20\text{-}30$ kJ/mol H_2, 8.3 wt.%
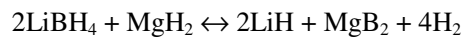
$2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2$ $T_{des, 1bar} = 350°C$
                                                          $\Delta H = -64$ kJ/mol H_2, 11.5 wt.%

It remains to be seen if all these different compounds will form or continue to form at these low temperatures.

3.1.1 Summary Mg-based storage compounds:

- ➢ High gravimetric storage capacity, up to 7.6 wt.% of H_2
- ➢ More hydrogenation cycles possible
- ➢ Slow absorption and desorption kinetics
- ➢ Unfavourable thermodynamics for mobile applications (high desorption temperature)
- ➢ A lot of research performed but no reversible Mg-based hydride with low ΔH and high wt.% has been found

4. New light-weight hydrogen storage compounds

4.1 Complex hydrides

4.1.1 Introduction

A novel category of hydrogen storage materials are the low weight complex metal hydrides. Alanates $[AlH_4]^-$, amides $[NH_2]^-$, imides and borohydrides $[BH_4]^-$ are interesting as potential hydrogen storage system due to their high storage capacities. They suffer from the drawback that their applicability is limited by both kinetic and thermodynamic properties. Furthermore, the hydrogen absorption and desorption reactions of alanates and borohydrides is a two step process which complicates the cyclic process.

4.1.2 Mg_2XH_y

Mg based compounds with a (XH_y) complex that are also considered as interesting for hydrogen storage applications are Mg_2Ni, Mg_2Co and Mg_2Fe. In contrast to MgH_2 the hydrogen in the Mg_2XH_y hydrides is located around the transition metal atom. Mg_2NiH_4 (3.6 wt.%), Mg_2CoH_5 (4.5 wt.%) and Mg_2FeH_6 (5.5 wt.%) show a relatively high hydrogen storage capacity, are inexpensive, light weight and low-toxicity. Mg_2Ni reacts with hydrogen and transforms into the Mg_2NiH_4 complex hydride phase. The dehydrogenation temperature at 2.5 bar is around 250°C-300°C which is better than for the pure Mg, however the low storage capacity is a limitation for on-board storage, see
Table A.6. It turns out that the microstructure plays a dominant role on the hydrogenation properties of this type of metal hydride. (Abdellaoui, 2006; Abdellaoui, Cracco& PercheronGuegan, 1998; Aymard, 1997; Han, Goo& Lee, 2003; Haussermann, Blomqvist& Noreus, 2002; Orimo, Fujii, 2001; Orimo, Fujii, 1998; Zaluska, 1995; Zaluska, Zaluski& Ström-Olsen, 1999a; Zaluska, Zaluski& Ström-Olsen, 1999b; Zaluska, Zaluski& Ström-Olsen, 2001a; Zhu, 2006). The Mg_2FeH_6-MgH_2 system is considered by Reiser *et al.* and Bogdanovic *et al.* (Bogdanovic, 2002; Reiser, Bogdanovic& Schlichte, 2000).

Mg doped with Ni and Mg_2CoH_5 is stable up to 800 cycles (Reiser, Bogdanovic& Schlichte, 2000). Mg_2CoH_5 (and Mg_2FeH_6) is an interesting system since Mg and Co (or Fe) do not form a single alloy phase and thus material transport plays an important role. MgH_2-5 wt.% V is stable up to 2000 cycles and MgH_2 + 0.2 mol% Cr_2O_3 is examined up to 1000 cycles (Dehouche, 2000; Dehouche, 2002). It is reported that after 4300 hydrogenation cycles the kinetics of Mg-2 at.% Ni decrease without a change in hydrogen capacity (Friedlmeier, 1995).

4.2 Alanates

4.2.1 $NaAlH_4$

$NaAlH_4$ (7.4 wt.%) by itself is an irreversible storage material with slow kinetics. Upon the addition of an appropriate catalyst (transition or rare-earth metal) hydrogenation becomes a reversible process resulting in a hydrogen storage capacity of up to 5.6 wt.% (Bogdanovic, Scwickardi, 1997) (Bogdanovic, 2000b). To improve the reversibility and hydrogenation kinetics most often titanium based compounds $(TiCl_3)$ are used which show the best kinetics in combination with the highest hydrogen storage capacity (Anton, 2003; Bogdanovic, 2000a; Gross, Majzoub& Spangler, 2003; Sandrock, 2002; Sandrock, Gross& Thomas, 2002). The temperature, pressure, kinetics, cycle stability and maximum weight percentage of some Na based storage materials are shown in
Table A.7.

Gross *et al.* (Gross, 2007) showed stable capacities and hydrogenation/dehydrogenation rates for 116 cycles with a $TiCl_3$ doping. Also the amount of released hydrogen for a Ti-doped $NaAlH_4$ is much larger (50 times) as compared to un-doped $NaAlH_4$ (Sun, 2003). Today's research is more focussed on $TiCl_3$ or Ti-colloids. Ti-based compounds improve the hydrogenation behavior and cycle stability of sodium alanates and it has been suggested that it plays a role in the material transport during hydrogenation (Schüth, Bogdanovic& Felderhoff, 2004). The International Energy Agency (IEA) (Hydrogen Implementing Agreement – Hydrogen production and storage) reports that the hydrogenation kinetics and reversibility are improved by the addition of a Ti catalyst and the working mechanism of this catalyst is "nearly" understood. By reducing the grain size and increasing the defect structure by for example ball milling the kinetics can be further improved (Huot, 1999a; Kircher, Fichtner, 2005; Sandrock, Gross& Thomas, 2002; Thomas, 2002; Wang, Jensen, 2004). The hydrogenation process takes place according to the two reactions,

$$3NaAlH_4 \ (7.4 \ wt.\%) \leftrightarrow Na_3AlH_6 + 2Al + 3H_2 \qquad\qquad 3.7 \ wt.\% \ H_2 \ release$$

$$Na_3AlH_6 \ (5.9 \ wt.\%) \leftrightarrow 3NaH + Al + 3/2H_2 \qquad\qquad 2.96 \ wt.\% \ H_2 \ release$$
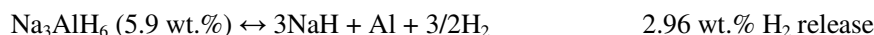
The heat release during hydrogenation is a severe limitation causing a change in microstructure of the compound (Sandrock, 2002). Furthermore, not all the hydrogen is released, some hydrogen remains in the form of NaH and can only be released at temperatures higher than 425°C, which is clearly too high for practical applications. This means that $NaAlH_4$ cannot meet the storage targets with only a reversible hydrogen storage capacity of 4-5 wt.%. $MgAlH_4$ suffers from irreversibility and the applicability of $MgAlH_4$ as storage material is unlikely. Many research problems need to be solved before these alanates are suited for storage applications, if at all.

4.2.2 $LiAlH_4$ and $KAlH_4$

Although lithium alanates would be a very interesting compound for hydrogen storage (10.5 wt.% and 11.2 wt.% for $LiAlH_4$ and Li_3AlH_6, respectively) their high equilibrium pressure makes them instable hydrides, which decompose very rapidly and cannot be hydrogenated easily (Zaluski, Zaluska& Ström-Olsen, 1999). The desorption reaction (at temperatures between 160°C and 200°C) of $LiAlH_4$ is comparable with that of $NaAlH_4$ and also occurs in a two step process:

$$3LiAlH_4 \leftrightarrow Li_3AlH_6 + 2Al + 3H_2 \qquad\qquad 5.3 \ wt.\% \ H_2 \ release$$

$$Li_3AlH_6 \leftrightarrow 3LiH + Al + 3/2H_2 \qquad\qquad 5.6 \ wt.\% \ H_2 \ release$$

To release the hydrogen from LiH, 680°C is required (Zaluski, Zaluska& Ström-Olsen, 1999). The reversible hydrogen decomposition of $KAlH_4$ has been investigated by Morioka *et al.* (Morioka, 2003). The hydrogen storage capacity found was above 3.5 wt.% at a hydrogen pressure of 10 bar and a temperature of 250°C-330°C, see
Table A.8. The reversible reaction proceeds without addition of a catalyst, which is different from the reactions of $NaAlH_4$ and $LiAlH_4$.

4.2.3   Summary alanates storage compounds:

➢ Effective hydrogen storage capacity 5.6 wt.% (hydrogen release)
➢ Relative low desorption temperature (< 150°C)
➢ Desorption is a 2 step process which complicates the regeneration process
➢ Kinetically hindered process for Na and Mg– a catalyst is required (TiO_2)

4.3 Lithium nitrides

The use of lithium and beryllium in alloys and compounds is very attractive due to their low atomic weight. However, beryllium and many of its compounds are very toxic which implies that scale controlled hydrogen storage is a possibility but small scale on-board and accident sensitive applications are not recommended (Grochala, Edwards, 2004; Zaluska, Zaluski& Ström-Olsen, 2000). In contrast, hydrogen storage in the system Li_3N - Li_2NH - $LiNH_2$ is an attractive option with a hydrogen storage capacity of 10.4 wt.% according to the two step reaction (Chen, 2002),

$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH$ 10.4 wt.% H_2 storage

The first step has an enthalpy of formation of -148 kJmol[-1] and the second step has an enthalpy of formation of -44.5 kJmol[-1]. Therefore only the second step from lithium imide to lithium amide is the most interesting for hydrogen storage, see
Table A.9.

It is reported that the addition of the catalyst $TiCl_3$ has two important effects namely suppressing the formation of NH_3 and improving the hydrogenation kinetics (Ichikawa, 2004). Also LiH limits the formation of NH_3 during dehydrogenation (Hu, Ruckenstein, 2003). The major limitation of this system is the irreversibility. Ichikawa *et al.* showed that a mixture of LiH and $LiNH_2$ doped with $TiCl_3$ can release 6 wt.% of hydrogen by reaction 2 in the temperature range from 150°C - 250°C, however the H-desorption equilibrium pressure is 0.1 MPa at 250°C. A comparable system with a potential for on-board storage applications is Li-Mg-N-H ($8LiH + 3Mg(NH_2)_2 \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$) which can desorb 7 wt.% H_2 at 120-200°C with an equilibrium pressure of > 5 MPa at 200°C (Ichikawa, 2006).

4.3.1 Summary lithium amide – lithium imide storage compounds:
  ➢ High gravimetric storage capacity of 10.4 wt.%
  ➢ Multiple hydrogenation reactions
  ➢ High desorption temperature
  ➢ Multiple cycles possible?
  ➢ R&D phase

4.4 Borohydrides

Complex boron hydrides can store large amounts of hydrogen for example $LiBH_4$ (0.68 g/cm^{3}) has a hydrogen storage capacity of 18.4 wt.% and a volumetric hydrogen density of 121 kg H_2/m^{3} (Fakioglu, Yürüm& Veziroglu, 2004). The $LiBH_4$ hydride, see Figure 4.1, is difficult to synthesize even at elevated temperatures and high pressures (up to 350 bar and 600°C) (Züttel, 2003c; Züttel, 2003d), see Table A.10. The formation of $LiBH_4$ is kinetically hindered despite the large thermodynamic driving force. In contrast to most other complex hydrides the lithium boron hydride is an expensive storage compound which should be kept in mind for large scale applications.
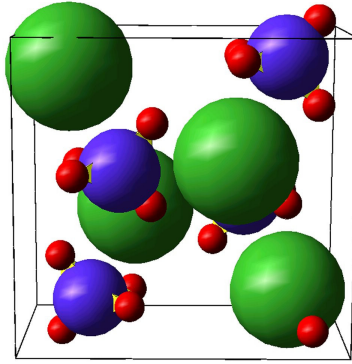
Figure 4.1 *Example of a complex boron based hydride in this case LiBH₄ (Li big green, BH₄ bue-red tetrahedra).*

The main limitation of boron hydrides is that they are very stable, e.g. LiBH₄ starts to decompose thermally above 320°C with the major desorption between 400°C and 600°C and not al the hydrogen is released during desorption (Stasinevich, Egorenko, 1968) (Fedneva, Alpatova, 1964) (Züttel, 2003b) (Orimo, 2006). Züttel *et al.* indicated that the desorption temperature can be lowered to 100°C with the main hydrogen desorption (13.5 wt.%) around 200°C by adding SiO_2-powder. Another undesired effect is the formation of boranes (B_xH_y) during the dehydrogation process which can severely damage downstream systems like fuel cells.

Metal borohydrides dehydrogenate by different reaction steps and temperature regimes and are in general too stable. At low temperatures, only 0.3 wt.% of hydrogen is released. 13.5 wt.% of hydrogen is released at higher temperatures and 4.5 wt.% remains in the form of LiH in case of lithium borohydride. LiBH₄ can be reversibly store 8-10 wt.% hydrogen at temperatures of 315°C - 400°C by addition of MgH_2 including 2-3 mol% $TiCl_3$. Furthermore, MgB_2 stabilizes the dehydrogenated state and destabilizes the LiBH₄ compound as indicated previously (Vajo, Skeith& Mertens, 2005) (COSY workshop may 10 2007 Geesthacht – M. Dornheim Department of Nanotechnology, institute for materials Research GKSS Research Center Geesthacht).
The mechanism is based on the formation of metal borides (MgB_2, AlB_2), possibly in combination with lithium compounds (Li_7Sn_2, $Li_{0.3}Mg_{0.7}$) to decrease the desorption enthalpy. The reaction enthalpies can be lowered by 10-25 kJ/mol H_2 (corresponding to a decrease of desorption temperature by 150°C-200°C). An additional substitution of suited catalysts can lower the decomposition temperature even more. Research on properties like structure, stability and hydrogen diffusion are investigated by Züttel *et al.* (Züttel, Borgschulte& Orimo, 2007). The heat of formation of complex hydrides is not necessarily high, for example for $Al(BH_4)_3$. This compound already decomposes below room temperature (at which it is liquid), it can contain 17 wt.% and 150 kg/m³ of hydrogen and has a melting point of -65°C. Although this seems an attractive compound for hydrogen storage, not much research has been done on this compound so far (Züttel, Borgschulte& Orimo, 2007).

In addition to the previous mentioned reactive metal hydrides, Nakamori *et al.* investigated the dehydrogenation reactions of the mixtures metal hydrides $LiBH_4 + 2LiNH_2$ and $LiAlH_4 + 2LiNH_2$:

$$LiBH_4 + 2LiNH_2 \leftrightarrow Li_3BN_2 + 4H_2$$

$$LiAlH_4 + 2LiNH_2 \leftrightarrow Li_3AlN_2 + 4H_2$$
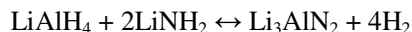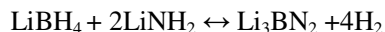
The theoretical gravimetric hydrogen desorptions are 11.9 wt.% and 9.6 wt.% respectively. Experimentally for the hydrogen desorption 7.9-9.5 wt.% and 4.1 wt.% are found. By mixing $LiBH_4$ with $LiNH_2$, the desorption temperature is reduced by 150 K. Dehydrogenation of $LiAlH_4$ is exothermic, however when mixed with $LiNH_2$ the dehydrogenation changes to endothermic, the stability of the dehydrogenation complex hydrides can be controlled by mixing. This mixing of hydrides can play a very important role in future development of hydrogen storage applications like for on-board use (Nakamori, 2006b). An interesting observation is done by Nakamori *et al.* who indicate that the Pauling electronegativity of M (in $M(BH_4)_n$ M = Mg, Sc, Zr, Ti and Zn; n = 2-4) is an important parameter that determines the desorption temperature for complex hydrides with high storage capacities (Nakamori, 2006a).

Summary intermetallic storage compounds:
- ➢ High gravimetric storage capacity up to 18.5 wt.%
- ➢ Desorption is a 2 step process – more cycles possible?
- ➢ High hydrogen desorption temperature (> 250°C)
- ➢ For hydrogen absorption – desorption cycles a TiO_2 catalyst is required
- ➢ Valuable metal hydrides (preparation and energy consumption)

4.5   Boranes

As last materials discussed here for hydrogen storage are the boranes NH_nBH_n with n from 1 to 4 (source: MRS Bulletin volume 33, The Hydrogen Fuel Alternative, G.W. Crabtree and M.S. Dresselhaus). In boranes the metal cation is replaced by an ammonium ion. This has the result of 4 more hydrogen atoms in the unit formula which results in a 24 wt.% storage capacity. However, the total amount of hydrogen is not instantaneously available but at different temperature regimes. It is indicated that confining boranes in a nanoporous scaffold reduces its decomposition temperature, improves kinetics and suppresses undesirable decomposition products. This system has a severe drawback; the reversible recharging is not yet possible.

5. Conclusions metal-hydride storage systems

From literature and recent review publications it is obvious that of all known hydride forming compounds and hydrogen carriers today, none of them satisfy the posed targets for on-board hydrogen storage simultaneously, see table Table 5.1 (as posed by the US Department of Energy (FreedomCAR/DOE), Japan and International Energy Agency (IEA)). One has to keep in mind that the posed targets are based on the current status of the automotive industry.

Table 5.1 *Selected H_2 – storage system and media targets for fuel cell vehicles*[+]

Property	Units	2010 USA	2007 Japan	2006 IEA*
System density (by weight)	wt.% H_2	6	3	-
System density (by volume)	kg H_2/m^3	45	-	-
System cost	US$/kg H_2	133	-	-
Refuelling time	minutes	3	-	-
Medium density (by weight)	wt.% H_2	-	5.5	5.0
H_2 liberation temperature	°C	-	150	80

[+] 500 km range = ca. 5-13 kg stored H_2
* IEA HIA Task 17

(Source: International Energy Agency, Hydrogen Implementation Agreement: Hydrogen Production and Storage, R&D Priorities and Gaps)

In this report the stated targets for on-board hydrogen storage are discussed and an overview of the current status of the most promising solid-state storage materials is given. Below the conclusions are given with respect to the different hydrogen storage materials. The conclusions are subdivided into the conclusions drawn by authors of several review articles (conclusions from the concerned articles) and from the authors of this report.

5.1 Conclusions from review papers

Conclusions (Grochala, Edwards, 2004)
It is concluded that the metal hydrides know today have or a low decomposition temperature and the hydrogenation process is irreversible or the metal hydride has a high decomposition temperature but the hydrogen absorption and desorption process is reversible. These authors are sceptical about the hydrogen storage material if it is to be a binary or ternary hydride only. It is indicated that the catalysis of the hydrogen absorption and desorption process and preparation of the metal hydride will play a very important role in the success of a metal hydride storage system.

Conclusions IEA Hydrogen Implementing Agreement – Hydrogen Production and Storage R&D Priorities and Gaps
The R&D issues for hydrogen storage for the gaseous, liquid and solid hydrogen storage are the following.
Gaseous H_2 Storage:
Status: Commercially available, but costly.
Best option: C-fibre composite vessels (6-10 wt.% H_2 at 350-700 bar).
R&D issues: Fracture mechanics, safety, compression energy, and reduction of volume.

Liquid H_2 Storage:
Status: Commercially available, but costly.
Best option: Cryogenic insulated dewars (ca. 20 wt.% H_2 at 1 bar and -253 °C).
R&D issues: High liquefaction energy, dormant boil off, and safety.

Solid H_2 Storage:

Status: Very early development (many R&D questions).

Best option: Too early to determine. Many potential options: Rechargeable hydrides, chemical hydrides (H_2O & thermally reactive), carbon, and other high surface area materials. Most-developed option: Metal hydrides (potential for > 8 wt.% H_2 and > 90 kg/m3 H_2-storage capacities at 10-60 bar).

R&D issues: Weight, lower desorption temperatures, higher desorption kinetics, recharge time and pressure, heat management, cost, pyrophoricity, cycle life, container compatibility and optimisation.

Conclusions (Schüth, Bogdanovic& Felderhoff, 2004)

It is indicated that during the last years a large success have been achieved in the reversible storage of hydrogen in complex metal hydrides. Some of them like the doped sodium alanates are approaching the targets that are posed for technical applications. However, the realistic storage capacities reached nowadays do not exceed 5 wt.%. Furthermore for sufficient quick rehydrogenation the targets are too severe. Even the most promising system today ($NaAlH_4$) will not meet the targets as formulated by the various organizations and industrial companies. R&D has to be continued to find new materials with improved hydrogenation properties. A possible direction will be the further development of the boron hydrides or lithium imide systems.

Conclusions (Van den Berg, Arean, 2008).

For the review of the state of the art hydrogen storage materials it is concluded that no materials tested so far meet the ideal requirements for on-board hydrogen storage. For applications that do not need to satisfy all of the targets like stationary applications, some of the hydrogen storage systems may be suited. However, it should be mentioned that there is still room for further improvements based on gained basic knowledge and practical experience. There seems room for performance improvement by working on the thermodynamics and kinetics of metal hydride storage systems. An early screening of destabilizing reactions is of significant importance and in the search for less stable metal hydrides. Furthermore, there is need to improve the knowledge about the basic mechanisms of different catalysts.

Conclusion (Sakintuna, Lamari-Darkrim& Hirscher, 2007).

Although several studies report promising results like improved hydrogenation kinetics and lower decomposition temperatures it is concluded that for all known materials today that they are still far from meeting the stated targets for on-board hydrogen storage. Further research is required for developing new materials that can satisfy the requirements for on-board applications. Technical improvements in vehicle design, system integration and cost efficiency will determine the on-board applicability of the hydrogen storage material.

- Intermetallic compounds:

These compounds do not meet the required targets for mobile applications due to their low storage capacities of roughly 2 wt.% and relatively high costs,.

- Mg-based metal hydrides:

Although Mg has a high storage capacity and is a reversible metal hydride, the high de hydrogenation temperature and slow kinetics limit the practical use for on-board hydrogen storage applications. Although much effort has been done to decrease the decomposition temperature, enhance the kinetics and cycle life by using appropriate catalysts and production methods the results indicate that additional research need to be done for optimization of the hydrogenation parameter.

- Complex metal hydrides:

Although the theoretical storage capacity of complex metal hydrides is generally high, there is a large difference between the theoretical storage capacity and the practical attainable storage capacity. Furthermore, the stepped reaction, reversibility, and slow kinetics are severe limitations on the hydrogen storage performance and need to be investigated further.

5.2 General conclusions of the authors

One of the key issues in the realization of a hydrogen based society is the appropriate storage of hydrogen especially for on-board applications. The most mature techniques today are the storage of hydrogen under high pressure and as cryogenic liquid. The implementation of these techniques also requires considering safety issues, system storage capacity, large energy penalty upon production and further technical developments (R&D). Since there is a large energy loss involved in the compression and liquefaction of hydrogen, solids, and especially metal hydrides are very interesting as hydrogen storage material. This is supported by the fact that other storage techniques as mentioned in the introduction are still in a very early R&D stage. The different types of storage metals and alloys discussed in this report are compared in Figure 5.1. For a suitable hydrogen storage material or technique one wants to be in the upper right corner of the figure which is indicated in red. From this figure one can get the idea that there are indeed materials that are interesting for on-board storage and satisfy (some of) the posed targets. However when one plots for example the gravimetric storage capacity versus desorption temperature (at approximately one bar desorption pressure) there are not many candidates qualifying, see Figure 5.2. NaAlH4 seems to be satisfying the targets; however this is the theoretical storage capacity and not the practical storage capacity.
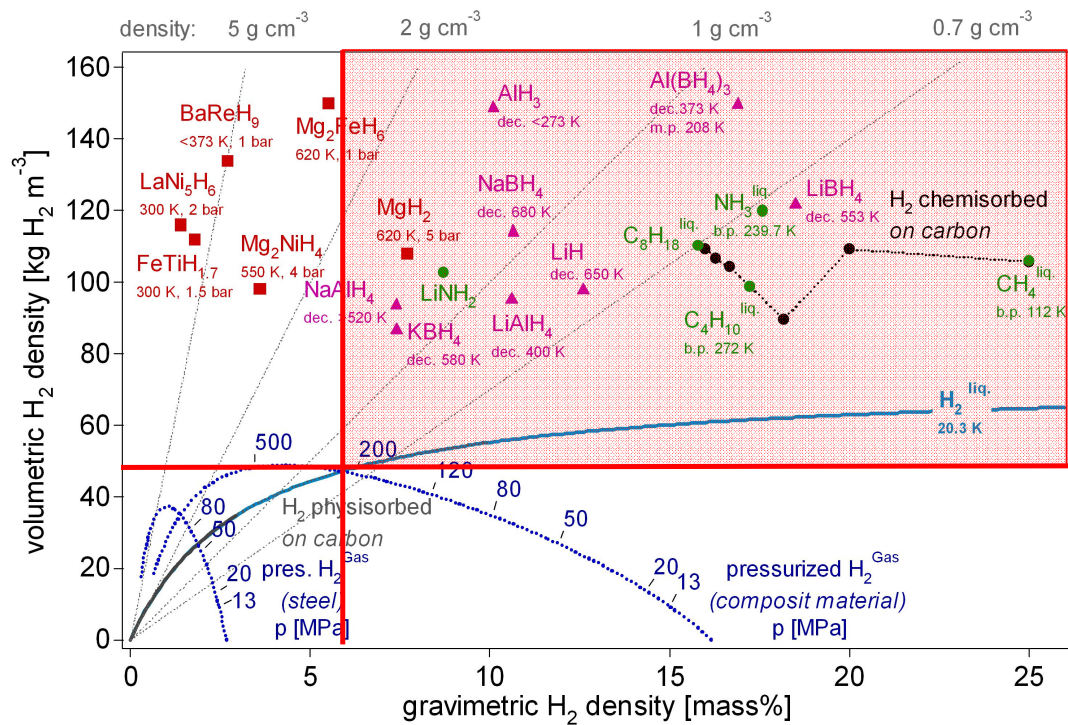
Figure 5.1 *Volumetric and gravimetric hydrogen density of some selected hydrides. Mg_2FeH_6 shows the highest known volumetric hydrogen density of 150 kg·m⁻³, which is more than double that of liquid hydrogen. $BaReH_9$ has the largest H/M ratio of 4.5, i.e. 4.5 hydrogen atoms per metal atom. $LiBH_4$ exhibits the highest gravimetric hydrogen density of 18 mass%. Pressurized gas storage is shown for steel (tensile strength σ_v = 460 MPa, density 6500Kg·m⁻³) and a hypothetical composite material (σ_v = 1500 MPa, density 3000 kg σ_v = 460 MPam⁻³) (Züttel, 2003a).*
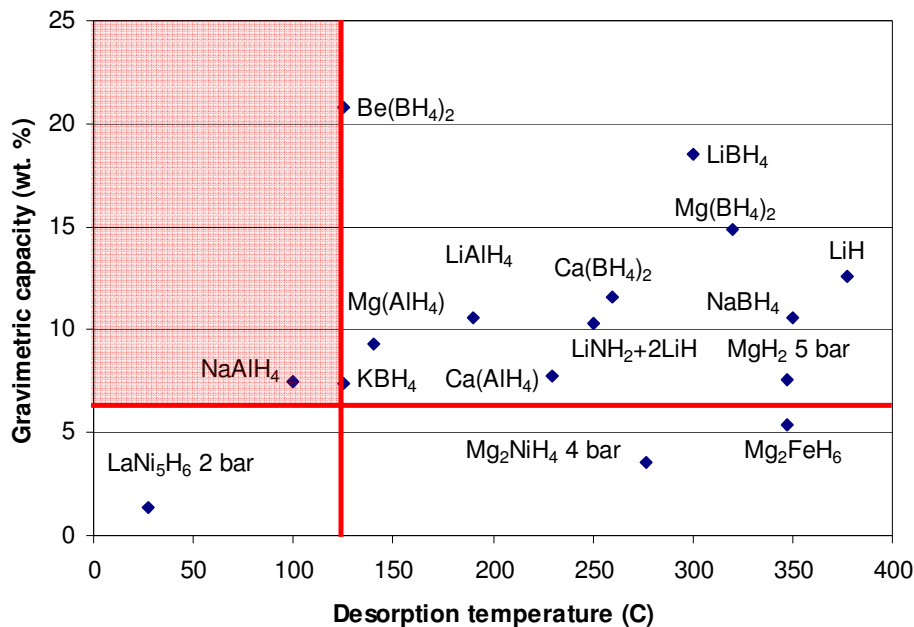
Figure 5.2 *Gravimetric storage capacity versus the desorption temperature (around 1 bar). From this figure it is obvious that many metal hydrides have too high hydrogen desorption temperature for practical applications.*

A short overview of the different types of metal hydride storage systems is given here with some general conclusions. For the classical intermetallic hydrides such as for example $LaNi_5$ it is obvious that although they have a high vol.% capacity, good hydrogenation kinetics, thermodynamics and cyclability, they suffer from the fact that the gravimetric hydrogen storage capacity of 1 – 4 wt.% is too low for on-board hydrogen storage.

Although Mg-based hydrides are very promising candidates for on-board hydrogen storage due to their high reversible hydrogen storage capacity of 7.6 wt%, they have some severe limitations. These types of metal hydrides suffer from slow kinetics and high hydrogen desorption temperatures. This makes them unfavourable for on-board hydrogen storage. The extensive research on the addition of other elements to Mg and preparation techniques to enhance the kinetics and decrease the decomposition temperature did not result so far in an applicable storage material. Further research is required to obtain Mg compounds with desired properties for on-board applications.

Alanates form an interesting hydrogen storage system with a maximal storage capacity of 5.6 wt.%. If they are doped with a proper catalyst they are approaching the targets for on-board hydrogen storage. For example, the hydrogen desorption temperature can be reduced to values below 150°C. However the kinetics are still sluggish and the two-step decomposition reaction can have a detrimental influence on the regeneration of this metal hydride compound.

During the last years the attention on Li based nitride ceramics as a hydrogen storage system has increased due to the high storage capacity. Especially the step from lithium amide ($LiNH_2$) to lithium imide (Li_2NH) is the most interesting one due to the enthalpies of formation involved. Also in this case, further research should indicate how the multiple reaction process influences

the hydrogen absorption and desorption cycles. An additional point of interest is the rather high desorption temperature, which needs to be decreased for on-board applications.

Borohydrides $M(BH_4)_n$ are very interesting as on-board hydrogen storage material due to their very high gravimetric hydrogen storage capacity. Borohydrides composed of calcium, lithium and magnesium are considered to be the most promising, although R&D is still in an early stage. For future applications, the high desorption temperature, the cycleability (SiO_2 catalyst is required and not understood as yet), slow kinetics, the development of diborane during dehydrogenation and the high costs (material and production process) of these hydrides are possible show stoppers.

Considering the results that have been achieved during the past years, it is expected that new hydrogen storage materials will be developed which are better suitable for on-board hydrogen storage. However, at this moment there is no hydrogen storage system that meets all the targets simultaneously, or is efficiently used in pilot automotive applications. Considering the current gap between the targets and the present status of the different storage materials it is very questionable if the posed targets for 2010 will be met on time. Despite a huge research effort, Mg compounds are still no suitable H_2 storage material and the development potential is considered to be low. One can think of the optimization of the boron based hydrides and the Li based hydrides.

From current literature it is obvious that certain research areas, which are of major importance for future applications, are hardly explored and investigated. For example it is well recognized that catalysts plays a vital role in the feasibility of hydrogen storage in metallic compounds. However, their exact working mechanism is often unknown, often it is not exactly know which type and quantity of catalyst can be used to obtain the best performance and the research is often based on trial and error. Therefore it is of utmost importance to address the working principle of the catalyst used in the different compounds. Some other fields that require attention for the actual application of metal hydrides for on-board hydrogen storage are indicated in the following.

During the last years some publications appeared on the heat development and management of metal hydride reaction beds and hydride reactors. It is stressed that the exothermic reaction during hydrogen absorption and the endothermic reaction during desorption have a large influence on the overall performance of the storage material and reactor. Although this is an aspect which is more related to engineering, it is of great importance to develop and design a practical hydrogen storage tank for mobile applications, in which heat exchangers play a pivotal role.

An other aspect is the purity of the used hydrogen gas. Hydrogen can be produced by several techniques: electrolysis of water (nuclear, renewable, conventional electricity), reforming processes (natural gas, coal, oil, diesel, and biomass) and some new/future techniques (photoelectrical, photobiological, thermal dissociation). The hydrogen produced by these techniques requires purification, which impacts the economical feasibility. Therefore in practical applications the hydrogen is not expected to be of very high purity (>5N) and thus the storage materials need to be insensitive to these impurities. The effect of gas impurities (H_2O, C_xH_y, H_2S, etc.) on the hydrogen storage capacity and the catalyst is often not considered as most research is performed under laboratory-conditions. This implies small scale experiments under idealized conditions, no contaminations, and identical hydrogenation experiments, small amounts of materials, etc. Therefore it is interesting to investigate the mechanical stability, chemical stability, thermal conductivity and cycle life, because real life applications will operate under non-idealized conditions. Also the tolerance to impurities and contaminations, the adsorption/desorption kinetics under these conditions are properties that need to be considered. In this context it is important to realize that in most research only the maximum storage capacity is reported and not the <u>reversible</u> hydrogen storage capacity, which is in general much lower.

To prevent pollution of the storage material one can think of "smart" nanofilms to protect the metal hydrides against air and moisture and at the same time permitting hydrogen transport through these permeable films. These layers can be comprised of polyelectrolyte layers and can be deposited on planar surfaces and colloidal particles as described by T. Dobbins *et al.* (Dobbins, Kamineni& Lvov, 2007). However the permeability's of these layers for H_2, O_2 and H_2O are still under investigation. In thin film research often a Pd caplayer is used to improve hydrogen absorption and protect the film from oxidation and contamination. Also alloys of Pd and Ag or Cu have been investigated with promising properties upon contamination. Another possibility to protect the storage material is to coat the outer surface with a stable oxide which is penetrable for hydrogen but protects the storage material. Here the addition of a catalyst is required because the hydrogen dissociation on oxides is in general an activated process which requires elevated temperatures. Other protection mechanisms and coatings should be developed for real-life applications.

6. Recommendations

Although at the moment hydrogen storage is a field of research which is characterized by physical and chemical limitations and energy penalties, efficient storage of hydrogen is one of the key issues for the success of a hydrogen based economy. This is especially the case for the automotive industry. Although the storage materials mentioned in the previous sections do not meet the hydrogen storage targets, quite some progress has been made in recent years. However, to obtain a suited hydrogen storage system, some major breakthroughs in material research and technical development have to be achieved. A possible route can be via the combination of different types of hydrides to destabilize the formed hydride phases. In this case the multiple reactions can limit the reversibility of the system under repeated hydrogen absorption and desorption. In addition, it is concluded that R&D should focus on the development of a suitable catalyst, the destabilization of the hydride and the preparation process of the metal hydride.

6.1 Combinatorial research and high throughput screening

Although a number of metal hydrides are highlighted in this report, other and more advanced compounds have to be developed to meet the requirements for on-board storage. Since the individual scanning of compounds is a time (and effort) consuming process, a high throughput combinatorial research approach is desired. The basic idea behind combinatorial research is the scanning of a large number of different compounds simultaneously, which are prepared under the same conditions. In material research this is a well known technique to obtain functional materials in an efficient manner (Fearn, 2006; Hanak, 1970; Koinuma, Takeuchi, 2004; Zhao, 2006). Although combinatorial high throughput screening is used in material research, it is rarely encountered in the search for appropriate hydrogen storage compounds. Some examples are the Rapid Throughput Facility set-up as reported by B. David (source: http://www.eurekamagazine.co.uk/article/11699/Hydrogen-storage-goal-in-sight.aspx).

Within the DOE Hydrogen Program a few Combinatoial High Throughput Screening techniques are mentioned (FY2007):
- Combinatorial Synthesis and High Throughput Screening of Effective Catalysts for Chemical Hydrides, by J. Melman, project ID # STP13. This research is focused on the determination of suited catalysts for the NH_3BH_3 dehydrogenation process.
- Discovery and Development of Metal Hydrides for Reversible On-board Storage, by E. Rönnebro, project ID # ST15. In this project the discovery of new complex hydride materials is the main goal. First principles calculations are combined with several experimental techniques.
- Lightweight Intermetallics for Hydrogen Storage, by M. Andrus, project ID # ST16. The objective of this project is to discover and develop storgage materials with a storage capacity of over 6 wt.% and capable of meting the FreedomCAR/DOE targets of 2010, mainly based on $Mg(BH_4)_2$.
- High Throughput Combinatorial Chemistry Development of Complex Hydrides, by D. Kundaliya, project ID # STP 25. In this project the goal is by using high-throughput combinatorial technique identifying and synthesizing novel metal hydride systems. Here the combinatorial ion beam sputtering technique is used for the synthesis of metal hydride catalysts. The high throughput screening is performed by applying optical techniques on thin films.
- Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods, by G.J. Lewis, project ID # ST12. This project is aimed at the discovery of complex metal hydrides that will meet the DOE 2010 goals. This will be done by Molecular Modeling and combinatorial methods.

New hydrogen storage materials require appropriate hydrogenation thermodynamics and kinetics and the investigation of each individual material is time consuming. One promising tech-

nique to perform a high throughput combinatorial screening of materials is discussed here and it is developed at the Vrije Universiteit Amsterdam called hydrogenography. The method is based on the fact that metals change their optical appearance upon hydrogen absorption. On large surface substrates a thin film of a compositional gradient of different metals is deposited. Since the local transmission is related to the local hydrogen concentration of the film, one is able to monitor in a simple optical set up, the rate of local hydrogen uptake. From this one is able to construct pressure composition isotherms for the different compositions at the same time for the different compositions. Thus for many compositions the key thermodynamic properties (enthalpy and entropy) and kinetics of hydride formation can be determined simultaneously (Dam, 2007; Gremaud, 2006; Gremaud, 2007b; Gremaud, 2007a).

Besides the development of new storage materials, further technical improvements in the automotive industry are required. This implies smart vehicle design and system integration which leads to smaller, lighter and more efficient cars. However, this also requires a change in people's attitude towards mobility and transport. Therefore a matching of the specific storage material and application is of extreme importance in this stage of R&D. Another equally important issue is the choice of storage material related to the mobile application in conjunction with getting hands-on experience in the storage-traction chain. Early markets that do not need the severe targets as formulated for instance by DoE: heavy duty vehicles in foresting industries, fork lifts in warehouses, airports etc must have a low lying centre of gravity which means the gravimetric hydrogen storage density does not play an important role. These niches are playing fields for combined hydrogen storage-PEMFC introduction. One can also argue that as opposed to the USA, Europe has a very dense refuelling network which does not ask for extreme driving ranges. In this respect light so-called city cars are also a very attractive early market. Furthermore, hydrides which are not directly suited for on-board hydrogen storage may be suited for stationary applications. This can be integrated with other (industrial) processes where waste heat can be used for the endothermic desorption process and vice versa. From this point of view it will be very important to estimate the suitability of a certain metal hydride for a specific application and not only focus on pushing the metal hydride system towards the maximum storage capacity.

6.2   Goals for on-board hydrogen storage

Currently there are two types of (demonstration) hydrogen powered vehicles, namely fuel cell and internal combustion based. These cars, vans and busses as currently running in different demonstration programmes use two types of hydrogen storage, high pressure hydrogen gas and cryogenic liquid hydrogen. Although the production process of high pressure gas and cryogenic liquid are energy consuming, these techniques are practical and most mature nowadays, where more and more car manufacturers focus on high pressure storage tanks. Since the posed storage targets for storage capacity (driving range), hydrogen absorption rate (tanking time), hydrogen desorption rate (maximal power) and heat development cannot be met simultaneously by solid state storage techniques, we will give here some considerations to develop acceptable solid state storage systems.

From the data presented in this report it is obvious that there is a considerable gap between the posed on-board hydrogen storage targets and the actual performance of today's used hydrogen storage systems. However these are based on the current status of the automobile industry and existing infrastructure. To avoid discarding suitable storage materials by comparing their properties with the targets, one can consider the following scenario. Since the success of a storage material is also determined by the availability of refuelling stations, it is recommended to start a pilot introduction in densely populated areas (larger cities) where the drive distances are short. This "local use" will result in a considerable decrease in the required amount of on-board stored hydrogen. Furthermore, the hydrogen absorption rate (driving range) and hydrogen desorption rate (max power/speed) can also be reduced in this case. This favourable effect can be increased

by also making the cars smaller, lighter and more efficient, which is in contrast to the currently used large and heavy (SUV) vehicles in cities.

The high heat evolution upon refuelling using adsorption processes can at present only be accommodated to comply with the public acceptance when hydrogen storage modules can be exchanged as a whole at the refuelling station.

Since this report is focussed only on the intrinsic hydrogen storage properties of solid state storage systems, a market study on driving range, efficient utilization and infrastructure is not incorporated and a specific market study should be done before starting a (local) pilot application. Nevertheless there already clear niche markets for which different targets can be met. These would greatly enhance hands-on experience in hydrogen driven PEMFC powered vehicles.

REFERENCES

Abdellaoui, M.; Cracco, D. & PercheronGuegan, A. (1998) *Structural characterization and reversible hydrogen absorption properties of Mg2Ni rich nanocomposite materials synthesized by mechanical alloying,* J Alloys Compds 268, pp. 233-240.

Abdellaoui, M.; Mokbli, S.; Cuevas, F.; Latroche, M.; Guegan, A. P. & Zarrouk, H. (2006) *Structural, solid–gas and electrochemical characterization of Mg2Ni-rich and MgxNi100-x amorphous-rich nanomaterials obtained by mechanical alloying,* Int J Hydrogen Energy 31/2, pp. 247-250.

Anton, D. L. (2003) *Hydrogen desorption kinetics in transition metal modified NaAlH4,* J Alloys Compds 356-357, pp. 400-404.

Aoyagi, H.; Aoki, K. & Masumoto, T. (1995) *Effect of ball milling on hydrogen absorption properties of FeTi, Mg2Ni and LaNi5,* J Alloys Compds 231, pp. 804-809.

Aymard, L.; Ichitsubo, M.; Uchida, K.; Sekreta, E. & Ikazaki, F. (1997) *Preparation of Mg2Ni base alloy by the combination of mechanical alloying and heat treatment at low temperature,* J Alloys Compds 259, L5-L8.

Baer, R.; Zeiri, Y. & Kosloff, R. (1997) *Hydrogen transport in nickel (1 1 1),* Phys Rev B 55/16, pp. 952-974.

Barkhordarian, G. (2004), Anon., patent number GKSS patent application.

Barkhordarian, G.; Klassen, T. & Bormann, R. (2006) *Kinetic investigation of the effect of milling time on the hydrogen sorption reaction of magnesium catalyzed with different Nb2O5 contents,* J Alloys Compds 407/1-2, pp. 249-255.

Bevers, E. R. T.; Ekeren, P. J.; Haije, W. G. & Oonk, H. A. J. (2006) *Thermodynamic properties of lithium chloride ammonia complexes for application in a high-lift high temperature chemical heat pump,* Journal of Thermal Analysis and Calorimetry 86/3, pp. 825-832.

Bevers, E. R. T.; Oonk, H. A. J.; Haije, W. G. & Ekeren, P. J. (2007) *Investigation of thermodynamic properties of magnesium chloride amines by HPDSC and TG,* Journal of Thermal Analysis and Calorimetry 90/3, pp. 923-929.

Bloch, J.; Mintz, M. H. (1997) *Kinetics and mechanisms of metal hydride formation—a review,* J Alloys Compds 253–254, pp. 529-541.

Bogdanovic, B.; Brand, R. A.; Marjanovic, A.; Schwickardi, M. & Tölle, J. (2000a) *Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials,* J Alloys Compds 302/1-2, pp. 36-58.

Bogdanovic, B.; Brand, R. A.; Marjanovic, A.; Schwickardi, M. & Tölle, J. (2000b) *Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials,* J Alloys Compds 302, pp. 36-58.

Bogdanovic, B.; Reiser, A.; Schlichte, K.; Spliethoff, B. & Tesche, B. (2002) *Thermodynamics and dynamics of the Mg–Fe–H system and its potential for thermochemical thermal energy storage,* J Alloys Compds 345, pp. 77-89.

Bogdanovic, B.; Scwickardi, M. (1997) *Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials,* J Alloys Compds 253–254, pp. 1-9.

Chen, P.; Xiong, Z.; Luo, J.; Lin, J. & Tan, K.-L. (2002) *Interaction of hydrogen with metal nitrides and imides,* Nature 420, 302.

Chen, Y.; Williams, J. S. (1995) *Formation of metal hydrides by mechanical alloying,* J Alloys Compds 217, pp. 181-184.

Dam, B.; Gremaud, R.; Broedersz, C. P. & Griessen.R. (2007) *Combinatorial thin film methods for the search of new lightweight metal hydrides,* Scripta Materialia 56, pp. 853-858.

Dehouche, Z.; Djaozandry, R.; Huot, J.; Boily, S.; Goyette, J. & Bose, T. K. (2000) *Influence of cycling on the thermodynamic and structure properties of nanocrystalline magnesium based hydride,* J Alloys Compds 305, pp. 264-271.

Dehouche, Z.; Klassen, T.; Oelerich, W.; Goyette, J.; Bose, T. K. & Schulz, R. (2002) *Cycling and thermal stability of nanostructured MgH2–Cr2O3 composite for h drogen storage,* J Alloys Compds 347, pp. 319-323.

Dobbins, T.; Kamineni, V. & Lvov, Y. (2007) *Nanoarchitecture of Protective Coatings for Air Sensitive Metal Hydrides,* Material MattersTM Chemistry Driving Performance, Aldrich, Hydrogen storage Materials.

Dornheim, M.; Doppiu, S.; Barkhordarian, G.; Boesenberg, U.; Klassen, T.; Gutfleisch, O. & Bormann, R. (2007) *Hydrogen storage in Mg-based hydrides and hydride composites,* Scripta Materialia 56, pp. 841-846.

Dornheim, M.; Eigen, N.; Barkhordarian, G.; Klassen, T. & Bormann, R. (2006) *Tailoring hydrogen storage matetrials towards application,* Advanced Engineering Materials 8, 377.

Fabing, L.; Lijun, J.; Jun, D.; Shumao, W.; Xiaopeng, L. & Feng, Z. (2006) *Synthesis and hydrogenation properties of Mg–La–Ni–H system by reactive mechanical alloying,* Int J Hydrogen Energy.

Fakioglu, E.; Yürüm, Y. & Veziroglu, T. N. (2004) *A review of hydrogen storage systems based on boron and its compounds,* Int J Hydrogen Energy 29, pp. 1371-1376.

Fearn, S.; Rossiny, J. C. H.; Kilner, J. A.; Zhang, Y. & Chen, L. (2006) *High throughput screening of novel oxide conductors using SIMS,* Appl. Surf. Sci.

Fedneva, E. M.; Alpatova, V. I. (1964) Zh. Neorg. Khim. 9, 1519.

Friedlmeier, G.; Groll, M. (1997) *Experimental analysis and modeling of the hydriding kinetics of Ni-doped and pure Mg,* J Alloys Compds 253–254, pp. 550-555.

Friedlmeier, G.; Manthey, A.; Wanner, M. & Grollm, M. (1995) *Cyclic stability of various application-relevant metal hydrides,* J Alloys Compds 231/1-2, pp. 880-887.

Gennari, F. C.; Castra, F. J.; Urretavizcaya, G. & Meyer, G. (2002) *Catalytic effect of Ge on hydrogen desorption from MgH2,* J Alloys Compds 334, pp. 277-284.

Gremaud, R.; Borgschulte, A.; Chacon, C.; Van Mechelen, J. L. M.; Schreuders, H.; Züttel, A.; Hjörvarsson, B.; Dam, B. & Griessen.R. (2006) *Structural and optical properties of*

MgxAl1-xHy gradient thin films: a combinatorial approach, Appl. Phys. A. 84, pp. 77-85.

Gremaud, R.; Broedersz, C. P.; Borsa, D. M.; Borgschulte, A.; Mauron, P.; Schreuders, H.; Rector, J. H.; Dam, B. & Griessen.R. (2007a) *Hydrogenography: An optical combinatorial method to find new light-weight hydrogen-storage materials,* Adv. Mater. 19, pp. 2813-2817.

Gremaud, R.; Slaman, M.; Schreuders, H.; Dam, B. & Griessen.R. (2007b) *An optical method to determine the thermodynamics of hydrogen absorption and desorption in metals,* Appl. Phys. Lett. 91, 231916.

Grochala, W.; Edwards, P. P. (2004) *Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen,* Chem Rev 104, pp. 1283-1315.

Gross, K. J.; Majzoub, E. & Spangler, S. W. (2003) J Alloys Compds 356, 423.

Gross, K. J.; Majzoub, E.; Thomas, G. J. & Sandrock, G. (2007) *Proceedings of the 2002 U.S. DOE Hydrogen Progrm Review*.

Han, S. S.; Goo, N. H. & Lee, K. S. (2003) *Effects of sintering on composite metalhydride alloy of Mg2Ni and TiNi synthesized by mechanical alloying,* J Alloys Compds 360/1-2, pp. 243-249.

Hanak, J. J. (1970) J. Mater. Sci. 5, 964.

Haussermann, U.; Blomqvist, H. & Noreus, D. (2002) *Bonding and stability of the hydrogen storage material Mg2NiH4,* Inorg Chem 41, pp. 3684-3692.

Hector, L. G.; Herbst, J. F. & Capehart, T. W. (2003) *Electronic structure calculations for LaNi5 and LaNi5H7: energetics and elastic properties,* J Alloys Compds 353, pp. 74-85.

Holtz, R. L. (1996) *Basic user's guide for NRL 6323 hydrogen storage system.*

Holtz, R. L.; Imam, M. A. (1999) *Hydrogen storage characteristics of ball milled magnesium–nickel and magnesium–iron alloys,* J Mater Sci 34, pp. 2655-2663.

Hong, T.-W. (2000) *Dehydrogenation properties of nano-amorphous Mg2NiHx by hydrogen induced mechanical alloying,* J Alloys Compds 312, pp. 60-67.

Hu, Y. H.; Ruckenstein, E. (2003) *Ultrafast reaction between LiH and NH$_3$ during H$_2$ storage in Li$_3$N,* J Phys Chem A 107/46, pp. 9737-9739.

Huot, J.; Akiba, E. & Takada, T. (1995) *Mechanical alloying of Mg–Ni compounds under hydrogen and inert atmosphere,* J Alloys Compds 231, pp. 815-819.

Huot, J.; Boily, S.; Güther, V. & Schulz, R. (1999a) *Synthesis of Na3AlH6 and Na2LiAlH6 by mechanical alloying,* J Alloys Compds 383, pp. 304-306.

Huot, J.; Liang, G.; Boily, S.; Neste, A. V. & Schulz, R. (1999b) *Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride,* J Alloys Compds 293-295, pp. 495-500.

Ichikawa, T.; Isobe, S.; Hanada, N. & Fujii, H. (2004) *Lithium nitride for reversible hydrogen storage,* J. Alloys Comp 365/1-2, pp. 271-276.

Ichikawa, T.; Leng, H. Y.; Isobe, S.; Hanada, N. & Fujii, H. (2006) *Recent development on hydrogen storage properties in metal–N–H systems,* Journal of Power Sources 159/1, pp. 126-131.

Imamura, H.; Masanari, K.; Kusuhara, M.; Katsumoto, H.; Sumi, T. & Sakata, Y. (2005) *High hydrogen storage capacity of nanosized magnesium synthesized by high energy ball-milling,* J Alloys Compds 386, pp. 211-216.

Iwakura, C.; Nohara, S.; Zhang, S. G. & Inoue, H. (1999) *Hydriding and dehydriding characteristics of an amorphous Mg2Ni–Ni composite,* J Alloys Compds 285, pp. 246-249.

Jung, K. S.; Lee, E. Y. & Lee, K. S. (2005) *Catalytic effects of metal oxide on hydrogen absorption of magnesium metal hydride,* J Alloys Compds 421/1-2, pp. 179-184.

Kircher, O.; Fichtner, M. (2005) *Kinetic studies of the decomposition of NaAlH4 doped with a Ti-based catalyst,* J Alloys Compds 404–406, pp. 339-342.

Koinuma, H.; Takeuchi, I. (2004) Nat. Mater. 3, 429.

Kumar, K. S.; Wang, P. (2004) *Hydrogen in Bulk Metallic Glasses: Storage Potential and Effects on Structure,* Defence Technical Information Center ADA425020.

Kyoi, D.; Sato, T.; Rönnebro, E.; Kitamura, N.; Ueda, A. & Ito, M. (2004) *A new ternary magnesium–titanium hydride Mg7TiHx with hydrogen desorption properties better than both binary magnesium and titanium hydrides,* J Alloys Compds 372, pp. 213-217.

Latroche, M.; Notten, P. H. L. & Pervheron-Gue'gan, A. (1997) *In situ neutron diffraction study of solid gas desorption of non-stoichimetric AB5 type hydrides,* J. Alloys Comp 253-254, pp. 295-297.

Liang, G. (2004) *Synthesis and hydrogen storage properties of Mg-based alloys,* J Alloys Compds 370, pp. 123-128.

Liang, G.; Boily, S.; Huot, J.; Neste, A. V. & Schulz, R. (1998) *Hydrogen absorption properties of a mechanically milled Mg–50 wt.% LaNi5 composite,* J Alloys Compds 268/1-2, pp. 302-307.

Liang, G.; Huot, J.; Boily, S.; Neste, A. V. & Schulz, R. (1999a) *Hydrogen storage properties of the mechanically milled MgH2–V nanocomposite,* J Alloys Compds 291, pp. 295-299.

Liang, G.; Huot, J.; Boily, S.; Nestea, A. V. & Schulz, R. (1999b) *Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH2–TM (TM5Ti, V, Mn, Fe and Ni) systems,* J Alloys Compds 292/1-2, pp. 247-252.

Mao, W. L. (2002) *Hydrogen clusters in clathrate hydrate,* Science 297/5590, pp. 2247-2249.

Mao, W. L.; Mao, H. K. (2004) *Hydrogen storage in molecular compounds,* Proc. Natl. Acad. Sci. U. S. A. 101, 708.

Morioka, H.; Kakizaki, K.; Chung, S.-C. & Yamada, A. (2003) *Reversble hydrogen decomposition of KAlH4,* J Alloys Compds 353, pp. 310-314.

Mulder, F. M.; T.J.Dingemans; Wagemaker, M. & Kearley, G. J. (2005) *Modelling of hydrogen adsorption in the metal organic framework MOF5,* Chemical Physics 317, pp. 113-118.

Nakamori, Y.; Li, H. W.; Miwa, K.; Towata, S. & Orimo, S. (2006a) *Syntheses and hydrogen desorption properties of metal-borohydrides M(BH₄)$_{(n)}$ (M = Mg, Sc, Zr, Ti, and Zn; n = 2-4) as advanced hydrogen storage materials,* Materials Transactions 47/8, pp. 1898-1901.

Nakamori, Y.; Ninomiya, A.; Kitahara, G.; Aoki, M.; Noritake, T.; Miwa, K.; Kojima, Y. & Orimo, S. (2006b) *Dehydriding reactions of mixed complex hydrides,* J Power Sources 155/2, pp. 447-455.

Norskov, J. K.; Houmøller, A.; Johansson, P. K. & Lundquist, B. I. (1981) *Adsorption and Dissociation of H$_2$ on Mg Surfaces,* Phys. Rev. Lett. 46, pp. 257-260.

Notten, P. H. L.; Latroche, M. & Pervheron-Gue'gan, A. (1999) *The influence of Mn on the crystallography and electrochemistry of non-stoichiometric AB5-type hydride forming compounds,* J. Electrochem. Soc 146, pp. 3181-3189.

Oelerich, W.; Klassen, T. & Bormann, R. (2001) *Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials,* J Alloys Compds 315, pp. 237-242.

Orimo, S.; Fujii, H. (2001) *Materials science of Mg–Ni-based new hydrides,* Appl. Phys. A. 72, pp. 167-186.

Orimo, S.-I.; Fujii, H. (1998) *Effects of nanometer-scale structure on hydriding properties of Mg–Ni alloys: a review,* Intermetallics 6, pp. 185-192.

Orimo, S.-I.; Nakamori, Y.; Ohba, N.; Miwa, K.; Aoki, M.; Towata, S. & Züttel, A. (2006) *Experimental studies on intermediate compound of LiBH4,* Appl. Phys. Lett. 89/2, - 21920.

Reilly, J. J.; Sandrock, G. D. (1980) *Hydrogen storage in metal hydrides,* Sci Am 242(2), pp. 118-9.

Reilly, J. J.; Wiswall, R. H. (1974) *Formation and properties of iron titanium hydride,* Inorg Chem 13(1), pp. 218-22.

Reiser, A.; Bogdanovic, B. & Schlichte, K. (2000) *The application of Mg-based metal-hydrides as heat energy storage systems,* Int J Hydrogen Energy 25, pp. 425-430.

Reule, H.; Hirscher, M.; WeissHardt, A. & Krönmuller, H. (2000) *Hydrogen desorption properties of mechanically alloyed MgH2 composite materials,* J. Alloys Compds 305, pp. 246-252.

Sakintuna, B.; Lamari-Darkrim, F. & Hirscher, M. (2007) *Metal hydride materials for solid hydrogen storage: A review,* Int J Hydrogen Energy 32, pp. 1121-1140.

Sandrock, G.; Gross, K. J. & Thomas, G. (2002) *Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates,* J Alloys Compds 339, pp. 299-308.

Sandrock, G.; Gross, K. J.; Thomas, G.; Jensen, C.; Meeker, D. & Takara, S. (2002) *Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage,* J Alloys Compds 303-332, pp. 696-701.

Sandrock, G. D. (1999) *A panoramic overview of hydrogen storage alloys from a gas reaction point of view,* J. Alloys Compd. 293-295, pp. 877-888.

Schlapbach, L. (1988) *Hydrogen in intermetallic compounds I: Electronic, thermodynamic, and Crystallographic Properties, Preparation,* Topics in Appl. Phys. 63.

Schlapbach, L.; Züttel, A. (2001) Nature 414, pp. 353-358.

Schüth, F.; Bogdanovic, B. & Felderhoff, M. (2004) *Light metal hydrides and complex hydrides for hydrogen storage,* Feature Article on the web Chem. Commun., pp. 2249-2258.

Sluiter, M. H. F.; Adachi, H.; Belosludov, R. V.; Belosludov, V. R. & Kawazoe, Y. (2004) *An initio study of hydrogen storage in hydrogen hydrate clathrates,* Materials Transactions 45/5, pp. 1452-1454.

Song, M. Y.; Bobet, J.-L. & Darriet, B. (2002) *Improvement in hydrogen sorption properties of Mg by reactive mechanical grinding with Cr2O3, Al2O3 and CeO2,* J Alloys Compds 340, pp. 256-262.

Song, M. Y.; Kwon, I. H.; Kwon, S. N.; Park, C. G.; Park, H. R. & Bae, J.-S. (2006) *Preparation of hydrogen-storage alloy Mg–10 wt% Fe2O3 under various milling conditions,* Int J Hydrogen Energy 31, pp. 43-47.

Soubeyroux, J. L. (2003) *Crystallization and hydrogenation of a bulk metallic glass, Zr50Ti5Al10Cu22Ni13,* J Alloys Compds 356, pp. 635-638.

Stasinevich, D. S.; Egorenko, G. A. (1968) Zh. Neorg. Khim. 13, 654.

Sun, D.; Srinivasan, S. S.; Kiyobayashi, T.; Kuriyama, N. & Jensen, C. M. (2003) *Rehydrogenation of dehydrogenated NaAlH4 at low temperature and pressure,* J Phys Chem B 107, pp. 10176-10179.

Thomas, G. J.; Gross, K. J.; Yang, N. & Jensen, C. (2002) *Microstructural characterization of catalyzed NaAlH4,* J Alloys Compds 330-332, pp. 702-707.

Vajo, J. J.; Skeith, S. L. & Mertens, F. (2005) *Reversible storage of hydrogen in destabilized LiBH4,* J Phys Chem B 109/9, pp. 3719-3722.

Van den Berg, A. W. C.; Arean, C. O. (2008) *Materials for hydrogen storage: current research trends and perspectives,* Chem. Commun., pp. 668-681.

Vucht, J. V.; Kuijpers, F. A. & Bruning, H. (1970) Philips Res. Rep. 25, 133.

Wagemans, R. W. P.; Lenth, J. H. V.; de Jongh, P. E.; Dillen, A. J. V. & de Jong, K. P. (2005) *Hydrogen storage in magnesium clusters: quantum chemical study,* J Am Chem Soc 127, pp. 16675-16680.

Wang, P.; Jensen, C. M. (2004) *Method for preparing Ti-doped NaAlH4 using Ti powder: observation of an unusual reversible dehydrogenation behavior,* J Alloys Compds 379, pp. 99-102.

Wang, P.; Wang, A.; Zhang, H.; Ding, B. & Hu, Z. (2000a) *Hydriding properties of a mechanically milled Mg–50 wt% ZrFe1.4Cr0.6 composite,* J Alloys Compds 297, pp. 240-245.

Wang, P.; Zhang, H. F.; Ding, B. Z. & Hu, Z. Q. (2000b) *Direct hydrogenation of Mg and decomposition behavior of the hydride formed,* J Alloys Compds 313, pp. 209-219.

Wiswall, R. (1978) *Topics in applied physics,* Hydrogen Met II 29, 209.

Yvon, K. (1998) *Complex Transition Metal Hydrides,* Chimia 52 (10), 613.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (1997) *Nanocrystalline metal hydrides,* J Alloys Compds 253–254, pp. 70-79.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (1999a) *Nanocrystalline magnesium for hydrogen storage,* J Alloys Compds 288, pp. 217-225.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (1999b) *Synergy of hydrogen sorptionin ball-milled hydrides of Mg and Mg2Ni,* J Alloys Compds 289, pp. 197-206.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (2000) *Lithium–beryllium hydrides: the lightest reversible metal hydrides,* J Alloys Compds 307, pp. 157-166.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (2001a) *Structure, catalysis and atomic reactions on the nano-scale: a systematic approach to metal hydrides for hydrogen storage,* Appl Phys A 72, pp. 157-165.

Zaluska, A.; Zaluski, L. & Ström-Olsen, J. O. (2001b) *Structure, catalysis and atomic reactions on the nano-scale: a systematic approach to metal hydrides for hydrogen storage,* Appl Phys A 72, pp. 157-165.

Zaluska, A.; Zaluski, L.; Tessier, P.; Ström-Olsen, J. O. & Schulz, R. (1995) *Catalytic effect of Pd on hydrogen absorption in mechanically alloyed Mg2Ni, LaNi5 and FeTi,* J Alloys Compds 217, pp. 295-300.

Zaluski, L.; Zaluska, A. & Ström-Olsen, J. O. (1995) *Hydrogen absorption in nanocrystalline Mg2Ni formed by mechanical alloying,* J Alloys Compds 217, pp. 245-249.

Zaluski, L.; Zaluska, A. & Ström-Olsen, J. O. (1999) *Hydrogenation properties of complex alkali metal hydrides fabricated by mechano-chemical synthesis,* J Alloys Compds 290, pp. 71-78.

Zander, D.; Tal-Gutelmacher, E.; Jastrow, L.; Koster, U. & Eliezer, D. (2003) *Hydrogenation of Pd-coated Zr-Cu-Ni-Al metallic glasses and quasicrystals,* J Alloys Compds 356, pp. 654-657.

Zhao, J. C. (2006) *Combinatorial approaches as effective tools in the study of phase diagrams and composition-structure-property relationships,* Prog. Mater. Sci. 51, 557.

Zhu, M.; Wang, H.; Ouyang, L. Z. & Zeng, M. Q. (2006) *Composite structure and hydrogen storage properties in Mg-based alloys,* Int J Hydrogen Energy 31(2), pp. 251-257.

Züttel, A. (2003a) *Materials for hydrogen storage,* Materials today 6, pp. 24-33.

Züttel, A.; Borgschulte, A. & Orimo, S.-I. (2007) *Tetrahydroborates as new hydrogen storage materials,* Scripta Materialia 56, pp. 823-828.

Züttel, A.; Rentsch, S.; Fischer, P.; Wenger, P.; Sudan, P.; Mauron, P. & Emmenegger, C. (2003b) *Hydrogen storage properties of LiBH$_4$,* J Alloys Compds 356-357, pp. 515-520.

Züttel, A.; Rentsch, S.; Fischer, P.; Wenger, P.; Sudan, P. & Mauron, P. L. (2003c) *Hydrogen storage properties of LiBH4,* J Alloys Compds 356–357, pp. 515-520.

Züttel, A.; Wenger, P.; Rentsch, S.; Sudan, P.; Mauron, P. & Emmenegger, C. (2003d) *LiBH4 a new hydrogen storage material,* J Power Sources 118, pp. 1-7.

Appendix A

Annex XX of the IEA Implementing Agreement on Advanced Fuel Cells is being organized to help the assessment and the commercialization of fuel cell technology by fostering information exchanges between experts from different countries and organizations engaged in developing fuel cell systems for transportation. As a result, balanced and objective information shall be provided that improves private and public decisions towards developing and implementing new vehicle technologies.

The scope of the work plan the next five years is defined in 4 main tasks, from these tasks a priority will be defined for execution until December 2008. These main tasks are:
- Task A: Advanced Fuel Cell Systems for transportation
- Task B: On board H_2 storage systems
- Task C: Hydrogen infrastructure
- Task D: Technology validation and economics

Within Task B, the following subtasks will be executed:
- B1. Status update for on-board hydrogen systems
- B2. Operating window and related targets for on/board storage options
- B3. Assessment of market readiness of storage materials

Appendix B   Metal hydrides and their properties

Note: The data presented in the tables below is a collection of several review articles. The corresponding references of which the data is obtained can be found in the respective review papers. For clarity the individual references of each contribution is not given here.

Table A.1 *Requirements for complex metal hydrides as reversible hydrogen storage materials for mobile application. Values are not strict thresholds and should be considered as approximate. Variations depend on target application, end user philosophy, system requirements and state of the art already reached.*

Property	Target
Gravimetric and Volumetric storage density	>6.5%
De/rehydrogenation kinetics	Dehydrogenation <3 h
	Rehydrogenation < 5 min
Rehydrogenation pressure	< 5 MPa
Equilibrium pressure	Around 0.1 MPa near room temperature
Cycle stability	>500
Memory effect (i.e. loss of storage capacity upon incomplete de- or rehydrogenation)	No memory effect
Price	~100 euro kg^{-1} H$_2$)

(Source: (Schüth, Bogdanovic& Felderhoff, 2004))

Table A.2 *FreedomCAR/DOE Hydrogen Storage System Targets*

DOE Technical Targets: On-Board Hydrogen Storage Systems [a, b, c]

Storage Parameter	Units	2007*	2010	2015
Usable, specific-energy from H$_2$ (net useful energy/max system mass) [d] ("Gravimetric Capacity")	kWh/kg (wt.% hydrogen)	1.5 (4.5%)	2 (6%)	3 (9%)
Usable energy density from H$_2$ (net useful energy/max system volume) ("Volumetric Capacity")	kWh/L (kg H$_2$/L)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost [e]	$/kWh net ($/kg H$_2$)	6 (200)	4 (133)	2 (67)
Fuel cost [f]	$ per gallon gasoline equivalent at pump	3	1.5*	1.5*
Operating ambient temperature [g]	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Cycle life (1/4 tank to full) [h]	Cycles	500	1000	1500

Cycle life variation[i]	% of mean (min) @ % confidence	N/A	90/90	99/90
Minimum and Maximum delivery temperature of H_2 from tank	°C	-20/85	-30/85	-40/85
Minimum full-flow rate	(g/s)/kW	0.02	0.02	0.02
Minimum delivery pressure of H_2 from tank; FC=fuel cell, I=ICE	Atm (abs)	8 FC 10 ICE	4 FC 35 ICE	3 FC 35 ICE
Maximum delivery pressure of H_2 from tank[j]	Atm (abs)	100	100	100
Transient response 10%-90% and 0%-0%[k]	s	1.75	0.75	0.5
Start time to full-flow at 20°C[l]	s	4	4	0.5
Start time to full-flow at minimum ambient[l]	s	8	8	2
System Fill Time for 5-kg hydrogen	min	10	3	2.5
Loss of useable hydrogen[m]	(g/h)/kg H_2 stored	1	0.1	0.05
Permeation and leakage[n]	Scc/h	Federal enclosed-area safety-standard		
Toxicity		Meets or exceeds applicable standards		
Safety		Meets or exceeds applicable standards		
Purity[o] (H_2 from storage system)		98% (dry basis)		

(http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf)

Footnotes to Table 1

* Note that some 2007 targets have been met with compressed hydrogen and liquid hydrogen tanks. These interim 2007 targets are primarily for materials-based technologies such as solid-state systems (e.g. complex metal hydrides) or liquids (such as liquid chemical hydrides).

[a] Based on the lower heating value of hydrogen and greater than 300-mile vehicle range; targets are for complete system, including tank, material, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and/or other balance-of-plant components.

[b] Unless otherwise indicated, all targets are for both internal combustion engine and for fuel cell use, based on the low likelihood of power-plant specific fuel being commercially viable.

[c] Systems must be energy efficient. For reversible systems, greater than 90% energy efficiency for the energy delivered to the power plant from the on-board storage system is required. For systems regenerated off-board, the energy content of the hydrogen delivered to the automotive power plant should be greater than 60% of the total energy input to the process, including the input energy of hydrogen and any other fuel streams for generating process heat and electrical energy. This is based on the DOE on-board target of 90% efficiency and the DOE off-board en-

ergy efficiency targets of 79% for hydrogen produced from natural gas and 85% for well-to-tank efficiency.

d Generally the 'full' mass (including hydrogen) is used, for systems that gain weight, the highest mass during discharge is used.

e 2003 US$; total cost includes any component replacement if needed over 15 years or 150,000 mile life.

f 2001 US$; includes off-board costs such as liquefaction, compression, regeneration, etc; 2015 target based on H_2 production cost of $1.50/gasoline gallon equivalent untaxed (subject to change based on DOE hydrogen production cost target).

g Stated ambient temperature plus full solar load No allowable performance degradation from –20C to 40C. Allowable degradation outside these limits is TBD.

h Equivalent to 100,000; 200,000; and 300,000 miles respectively (current gasoline tank spec).

i All targets must be achieved at end of life.

j In the near term, the forecourt should be capable of delivering 10,000 psi compressed hydrogen, liquid hydrogen, or chilled hydrogen (77 K) at 5000 psi. In the long term, it is anticipated that delivery pressures will be reduced to between 50 and 150 atm for solid state storage systems, based on today's knowledge of sodium alanates.

k At operating temperature.

l Flow must initiate within 25% of target time.

m Total hydrogen lost from the storage system, including leaked or vented hydrogen; relates to loss of range.

n Total hydrogen lost into the environment as H_2; relates to hydrogen accumulation in enclosed spaces. Storage system must comply with CSA/NGV2 standards for vehicular tanks. This includes any coating or enclosure that incorporates the envelope of the storage system.

o For fuel cell systems, steady state levels less than 10 ppb sulfur, 1 ppm carbon monoxide, 100 ppm carbon dioxide, 1 ppm ammonia, 100 ppm non-methane hydrocarbons on a C-1 basis; oxygen, nitrogen and argon can't exceed 2%. Particulate levels must meet ISO standard 14687. Some storage technologies may produce contaminants for which effects are unknown; these will be addressed as more information becomes available.

Table A.3 *Hydrogen Reactions of Selected Chemical Hydrides*

Hydride/Reaction Type	Reaction	Conditions	Storage capacity (wt.%)
Lithium Hydride			
Hydrolysis	LiH	$LiH+H_2O \leftrightarrow LiOH+H_2$	7.7
Pyrolysis	$2LiH \leftrightarrow H_2 + 2Li$	$\Delta H=132kJ/mol\ H_2$ @ 825°C, @950°C	Reaction yield H_2 13 wt.%
Regeneration	$2Li + H_2O \leftrightarrow 2LiH + \frac{1}{2} H_2 + \frac{1}{2} O_2$	Min. 0.67 V @ 350°C, @825°C, 0.317 bars H_2	
Magnesium Hydride			
Hydrolysis	$MgH_2 + 2H_2O \leftrightarrow Mg(OH)_2 + 2H_2$	4h for complete hydrolysis	Reaction yield H_2 wt.% ~6.3
Regeneration	N/A	20h ball milling	
Lithium Borohydride			
Hydrolysis	$LiBH_4 + 4H_2O \leftrightarrow LiOH + H_3BO_3 + 4H_2$	2.5 wt.% H_2 combined with organics	8.6
Regeneration (1)	$3LiH + 4BF_3 \leftrightarrow BH_3 + 3LiBF_4$	N/A	
Regeneration (2)	$LiH + BH_3 \leftrightarrow LiBH_4$		

Lithium Borohydride

Pyrolysis (1)	$LiBH_4 \leftrightarrow LiBH_{4-x} + 1/2$ $(x)H_2$	@108°C
Pyrolysis (2)	$LiBH_{4-x} \leftrightarrow$ "$LiBH_2$" $+$ $\frac{1}{2}(1-x)H_2$	@200°C
Pyrolysis (3)	"$LiBH_2$" $\leftrightarrow LiH + B +$ $1/2H_2$	@453°C

Lithium Aluminum Hydride

Hydrolysis	$LiAlH_4$	$LiAlH_4 + 4H_2O \leftrightarrow$ $LiOH + Al(OH)_3 + 4H_2$	7.3
Pyrolysis (1)	$LiAlH_4 \leftrightarrow Li_3AlH_6 + 2Al$ $+ 3H_2$	@160°C	10.6
Pyrolysis (2)	$Li_3AlH_6 \leftrightarrow 3LiH + Al +$ $3/2H_2$	@200°C	11.2
Regeneration 1st Method	$Li_3AlH_6 + 2Al + 3H_2 \leftrightarrow$ $3LiAlH4$	>50bar H_2	
Regeneration 2nd Method	$4LiH + AlCl_3 \leftrightarrow LiAlH_4$ $+ 3LiCl$	@ RT, in ether	

Sodium Hydride

Hydrolysis	NaH	$NaH + H_2O \leftrightarrow NaOH + H_2$	4.9

Sodium Borohydride

Hydrolysis	$NaBH_4 + 2H_2O \leftrightarrow$ $NaBO_2 + 4H_2$	@ RT with Ru	Reaction yield H_2 10.8 wt.%
$NaBH_4$	$NaBH_4 + 4H_2O \leftrightarrow$ $NaOH + H_3BO_3 + 4H_2$		7.3
Regeneration (1)	$3NaBH(OMe)_3 + 4BF_3 \leftrightarrow$ $BH_3 + 3NaBF_4 +$ $3B(OMe)_3$	N/A	
Regeneration (2)	$NaBH(OMe)_3 + BH_3 \leftrightarrow$ $NaBH_4 + B(OMe)_3$		

Sodium Aluminum Hydride

Hydrolysis	$NaAlH_4$	$NaAlH_4 + 4H_2O \leftrightarrow$ $NaOH + Al(OH)_3 + 4H_2$	6.4
Pyrolysis (1)	$3NaAlH_4 \leftrightarrow Na_3AlH_6 +$ $3H_2 + 2Al$	@120°C, Ti doped	Reaction yield H_2 5.55 wt.%
Pyrolysis (2)	$Na_3AlH_6 \leftrightarrow 3NaH + Al +$ $3/2H_2$	@250°C	
Regeneration	$NaH + Al + 3/2H_2 \leftrightarrow$ $NaAlH_4$	@104°C, 87 atm H_2, 17h	

(Source: (Fakioglu, Yürüm& Veziroglu, 2004), (Schüth, Bogdanovic& Felderhoff, 2004))

Table A.4 *Storage properties of intermetallic compounds*

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stabillity	Max wt.% of H_2
MgS	BM	T_{abs}:-196	P_{abs}: 50	No data	No data	0.50
$La_{0.90}Ce_{0.05}Nd_{0.04}$ $Pr_{0.01}Ni_{4.63}Sn_{0.32}$	Melting	T_{abs}: 100, 25	P_{abs}: 5-10	t_{abs}: 6.6	No data	0.95
		T_{des}: 100, 25	P_{des}: 0.24	t_{des}: 6.6		
$Mm_{0:85}Ca_{0:15}Ni_5$	RF melting	T_{abs}: 25	P_{des}: 10	t_{des}: 60	100cyc.: stable	1.10
$LaNi_{4.8}Sn_{0.2}$	Arc melting	T_{abs}: 80	P_{des}: 3-4	No data	1000cyc.: stable	1.16

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stability	Max wt.% of H$_2$
		T$_{des}$: 80				
Ti$_{0.9}$Zr$_{0.15}$Mn$_{1.6}$ Cr$_{0.2}$V$_{0.2}$	Rf melting	T$_{des}$: 25	P$_{des}$: 10	t$_{des}$:60	100 cyc.: stable	1.30
La$_{0.7}$Mg$_{0.3}$Ni$_{2.65}$ Mn$_{0.1}$Co$_{0.90}$	Melting	T$_{des}$: 30	P$_{abs}$: 5	No data	No data	1.56
		T$_{des}$: 30	P$_{abs}$: 0.33			
Ti$_{1.1}$CrMn	Arc melting	T$_{abs}$: 23	P$_{abs}$: 33	t$_{abs}$: 1	1000 cyc.: stable	1.80
		T$_{des}$: 23	P$_{des}$: 1	t$_{des}$: 5		
FeTi	BM	T$_{abs}$: 25	P$_{abs}$: 100	No data	No data	1.92
V$_{0.375}$Ti$_{0.25}$Cr$_{0.30}$Mn$_{0.075}$	Arc melting	T$_{abs}$: 30	P$_{abs}$: 50	No data	No data	2.20
		T$_{des}$: 30	P$_{abs}$: 0.2			
Ti$_{45}$Zr$_{38}$Ni$_{17}$ Quasicrystal powders	BM	T$_{abs}$: 300	P$_{abs}$: 80	t$_{abs}$: 1200	No data	2.23
		T$_{des}$: 427				
TiCr$_{1.1}$V$_{0.9}$	Melting +BM	T$_{abs}$: 30	P$_{abs}$: 17	No data	No data	3.50
		T$_{des}$: 30	P$_{abs}$: 0.5			
Ti$_{43.5}$V$_{49}$Fe$_{7.5}$	Arc melting	T$_{abs}$: -20	P$_{abs}$: 100	t$_{abs}$: 20	50 cyc.: stable	3.90
		T$_{des}$: 300	P$_{des}$:10			
Ti-V-Cr-Mn	Magnetic levitation melting	T$_{des}$: 247-472	P$_{abs}$: 30	No data	No data	3.98
			P$_{des}$: 0.03			
La$_{0.5}$Ni$_{1.5}$Mg$_{17}$	Hydriding combustion sythesis	T$_{abs}$: 280-400	P$_{abs}$: 2.21-11.34	t$_{abs}$: 15	Not stable	4.03
La$_{1.8}$Ca$_{0.2}$Mg$_{114}$N$_{13}$	BM	T$_{abs}$: 27-327	P$_{abs}$: 40	t$_{abs}$: 15	6 cyc.: not stable	5.00
		T$_{des}$: 27-327	P$_{des}$: 1	t$_{abs}$: 10		
La$_{0.9}$Ce$_{0.1}$Ni$_5$	CO surface treatment	T$_{abs}$: 0-100	P$_{abs}$: 50	t$_{des}$: 1.8	20 cyc.: stable after fifth cycle	1.40
		T$_{des}$: 25				
LaNi$_5$	CO surface treatment	T$_{abs}$: 0-100	P$_{abs}$: 50	t$_{des}$: 13.6	20 cyc.: stable after fifth cycle	1.44
		T$_{des}$: 25				

(Source: (Sakintuna, Lamari-Darkrim& Hirscher, 2007))

Table A.5 *Storage properties of Mg-based hydrides*

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stability	Max wt.% of H$_2$
MgH$_2$-5mol%Fe$_2$O$_3$	BM	T$_{abs}$: 300	P$_{abs}$: 2-15	t$_{abs}$: 20	No data	1.37
30wt.% Mg-MmNi$_{5-x}$(CoAlMn)$_x$	BM	T$_{abs}$: 15	P$_{abs}$: 6	t$_{abs}$: 83	No data	2.30
MgH$_2$-5mol%V$_2$O$_5$	BM	T$_{abs}$: 250	P$_{abs}$: 15	t$_{abs}$: 1.6	No data	3.20
Mg-10wt.%CeO$_2$	BM	T$_{abs}$: 300	P$_{abs}$:11	t$_{abs}$: 60	5 cyc.: not stable	3.43

Material	Method	T (°C)	P (bar)	t (min/h)	Cycling	wt%
La$_2$Mg$_{17}$-40wt.%LaNi$_5$	BM	T$_{des}$: 300 T$_{abs}$: 250-303	P$_{des}$: 0.5 P$_{abs}$: 4-7	t$_{des}$: 60 t$_{abs}$: 0.45	20 cyc.: not stable	3.70
MgH$_2$-5mol%Al$_2$O$_3$	BM	T$_{des}$: 250-303 T$_{abs}$: 300	P$_{des}$: 4-7: P$_{abs}$:15	t$_{des}$: 4 t$_{abs}$: 67	No data	4.49
1.1MgH$_2$-2LiNH$_2$	BM	T$_{abs}$: 200	P$_{abs}$:30	t$_{abs}$: 30	9 cyc.: stable	4.50
Mg-20wt.%TiO$_2$	BM	T$_{abs}$: 350	P$_{abs}$:20	t$_{abs}$: 2	No data	4.70
MgH$_2$-5wt.%V	BM	T$_{des}$: 330-350 T$_{abs}$: 300	P$_{des}$: 1 P$_{abs}$: 1-3	t$_{des}$: 10 t$_{abs}$: 2	2000cyc.: stable	5.00
MgH$_2$-Mg$_2$FeH$_6$	Mixing	T$_{des}$: 300 T$_{abs}$: 350-525 T$_{des}$: 350-525	P$_{des}$: 1-3 P$_{abs}$:36-93.7 P$_{des}$: 3.6-93.7	t$_{des}$: 10 t$_{abs}$: 90-1440	600cyc.: stable	5.00
MgH$_2$-5at%Ti	BM	T$_{abs}$: 200 T$_{des}$: 300	P$_{abs}$:10 P$_{des}$:0.15	t$_{des}$: 3.33 t$_{abs}$: 0.83	No data	5.00
Mg-30wt.%LaNi$_{2.28}$	BM	T$_{abs}$: 280	P$_{abs}$: 30	t$_{abs}$: 1.6	3 cyc.: stable	5.40
Mg-10wt.%Fe$_2$O$_3$	BM	T$_{abs}$: 320	P$_{abs}$: 12	t$_{abs}$: 60	3 cyc.: stable	5.56
MgH$_2$-5wt.%V	BM	T$_{abs}$: 200 T$_{des}$: 300	P$_{abs}$: 10 P$_{des}$: 0.15	t$_{abs}$: 10 t$_{abs}$: 4.2 t$_{des}$: 33	No data	5.80
Mg/MgH$_2$-5wt.%Ni	Wet-chemical method	T$_{abs}$: 230-370	P$_{abs}$: 4.0-1.4 P$_{des}$: 4.0-1.4	t$_{abs}$: 90	800 cyc.: stable	6.00
MgH$_2$-5at%Mn	BM	T$_{abs}$: 200 T$_{des}$: 300	P$_{abs}$: 10 P$_{des}$: 0.15	t$_{des}$: 8.33 t$_{abs}$: 13.33	No data	6.00
MgH$_2$-0.2mol%Cr$_2$O$_3$	BM	T$_{abs}$: 300 T$_{des}$: 300	P$_{abs}$: 1-2 P$_{des}$: 1-2	t$_{abs}$: 6 t$_{des}$: 10-35	1000cyc.: stable	6.40
MgH$_2$-2mol%Ni	BM	T$_{des}$: 150-250	P$_{des}$: 1	t$_{des}$: 150	2 cyc.: not stable	6.50
MgH$_2$	BM	T$_{abs}$: 300 (milled) T$_{des}$: 300 (milled)	P$_{abs}$: 3-10 P$_{des}$: 0.15	t$_{des}$: 12.5 (milled) t$_{des}$: 50 (un-milled)	No data	7.00
3Mg(NH$_2$)$_2$-8LiH	BM	T$_{des}$: 140-190	P$_{des}$:1	No data	No data	7.00
Mg-0.5wt.%Nb$_2$O$_5$	Mixing	T$_{abs}$: 300 T$_{des}$: 300	P$_{abs}$: 8.4 P$_{des}$: vacuum	t$_{abs}$: 1 t$_{des}$: 1.5	No data	7.00
MgH$_2$-1at%Al	BM (benzene and cyclo-hexane medium)	T$_{abs}$: 180 T$_{des}$: 335-347	P$_{abs}$:0.6	t$_{abs}$: 420	No data	7.30

(Source: (Sakintuna, Lamari-Darkrim& Hirscher, 2007))

Table A.6 *Storage properties of Mg-TM-based hydrides*

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stability	Max wt.% of H_2
Mg_2Ni-1 wt.% Pd	BM	T_{abs}: 200	P_{abs}: 15	t_{abs}: 27	4 cyc.: stable	2.50
Mg_2Ni	BM	T_{abs}: 300	P_{abs}: 11.6	t_{abs}: 10	4 cyc.: stable	3.50
Mg-Mg_2Ni	BM	T_{abs}: 300	P_{abs}: 12	t_{abs}: 83	2 cyc.: not stable	3.60
70 wt.% Mg_30wt.% $LaNi_5$	BM	T_{abs}: 350 T_{des}: 350	P_{abs}: 10 P_{des}: 1.5	t_{abs}: 30 t_{des}: 10	10 cyc.: stable	4.66
65 wt.% MgH_2-35wt.% Mg_2NiH_4	BM	T_{des}: 220-240	P_{des}: 0.5	t_{abs}: 10	20 cyc.: stable	5.00
Mg_2CoH_5	Mixing	T_{abs}: 450-550	P_{abs}: 17-25	No data	1000cyc: stable	4.48

(Source (Sakintuna, Lamari-Darkrim& Hirscher, 2007))

Table A.7 *Storage properties of sodium alanates*

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stability	Max wt.% of H_2
Na_3AlH_6	Mechano-chemical synthesis	T_{des}: 200	P_{des}:1	t_{des}: 150	No data	2.50
Na_2LiAlH_6	BM	T_{des}: 211	P_{abs}:45	t_{abs}:100	No data	2.50
$NaAlH_4$-4mol%Ti	BM	T_{abs}: 120	P_{abs}:120	t_{abs}: 60	8 cyc.: not stable	3.30
$NaAlH_4$-2mol%Ti	BM	T_{des}: 150 T_{des}: 25-160	P_{des}:1 P_{abs}:20-120	t_{des}: 600 t_{abs}: 300-720	No data	3.80
$NaAlH_4$-2mol%Ti(Obu^n)$_4$	Mixing	T_{abs}: 25-193 T_{abs}: 135-120	P_{des}:1 P_{abs}: 150-130	t_{des}: 40 t_{abs}: 330	33 cyc.: not stable	4.00
$NaAlH_4$-2mol%TiCl$_3$	BM	T_{des}: 180-160 T_{des}: 125-100	P_{des}: 150-130 P_{des}: 83-91	t_{des}: 90 t_{des}: 20	5 cyc.: not stable	4.00
$NaAlH_4$-2mol%Zr(OPr)$_4$	Mixing	T_{des}: 200	P_{des}: 1	No data	3 cyc.: stable 3 after second cyc.	4.00
$NaAlH_4$	Mechano-chemical synthesis	T_{abs}: 80-180	T_{abs}: 76-91	t_{abs}: 120-300	2 cyc.: not stable	5.0
$NaAlH_4$-2mol%TiN	BM	T_{des}: 80-180 T_{des}: 104-170	T_{des}: 76-91 T_{abs}: 115-140	t_{des}: 300 t_{des}: 30-1200	25 cyc.: stable after 17th cycle	5.0

(Source: (Sakintuna, Lamari-Darkrim& Hirscher, 2007))Obu = butoxide, OPr=propoxide.

Table A.8 *Alanates: Storage properties of the most-common types*

Type	Storage density*, wt.% H_2	Desorption temperature, °C
$LiAlH_4$	10.6	190
$NaAlH_4$	7.5	100
$Mg(AlH_4)$	9.3	140
$Ca(AlH_4)$	7.8	>230

*Theoretical maximum (Source: IEA Hydrogen Implementing Agreement – Hydrogen Production and Storage R&D Priorities and Gaps)

Table A.9 *Storage properties of Li-based hydrides*

Material	Method	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cycling stability	Max wt.% of H_2
$LaNi_3BH_3$	Arc melting	T_{abs}: 25	P_{abs}: 4	t_{abs}: 30	2 cyc.: not stable	0.84
$LiNH_2$-LiH-1mol%$TiCl_3$	BM	T_{des}: 150-250	P_{abs}: 30	t_{abs}: 30	3 cyc.: stable	5.00
Li_3N	Mixing	T_{abs}: 50 T_{des}: 240-270	P_{abs}: 0.5 P_{des}: 1	t_{abs}: 20	No data	6.00
Li_2NH	Mixing	T_{abs}: 255-285 T_{des}: 255-285	P_{abs}: 10 P_{des}: 1.5	No data	No data	6.50
$Li_3BN_2H_8$	BM	T_{des}: 250-364	P_{des}: 1	t_{des}: 228	No data	10.00

(Source: (Sakintuna, Lamari-Darkrim& Hirscher, 2007))

Table A.10 *Storage properties of metal borohydrides*

Hydrogenated form	Dehydrogenated form	Hydrogen capacity wt.%	Hydrogen capacity g H_2/L	-ΔH, kJ/molH_2	Decomp. Temp., °C Calc.	Decomp. Temp., °C Obs.
$LiBH_4$	LiH+B	13.9	93	75	402	470
$2LiBH_4+MgH_2$	$3LiH+MgB_2$	11.4		46	225	315
$2LiBH_4+Al$	$2LiH+AlB_2$	8.6			188	
$NaBH_4$	NaH+B	7.9	85.5	90	609	595
$2NaBH_4+MgH_2$	$3NaH+MgB_2$	7.8		62	351	
$Mg(BH_4)_2$	Mg+2B	14.9	113	40		323
$Ca(BH_4)_2$	2/3 CaH_2+1/3CaB_6	9.7	108	75.5		360
$Ca(BH_4)_2+MgH_2$	CaH_2+MgB_2	8.3			159	
$Zn(BH_4)_2$	Zn+2B*	8.5				85
$Al(BH_4)_3$	Al+3B*	16.9	121	6		150
$Ti(BH_4)_3$	TiB_2+B*	13.1				25

(Source: Metal Borohydrides as hydrogen storage materials, Sigma-Aldrich, Dr. G. L. Soloveichik General Electric Global Research)

Table A.11 *Borohydrides: Key properties of most common types*

Type	Storage density*, wt.% H_2	Desorption temperature, °C
$LiBH_4$	18.5	300
$NaBH_4$	10.6	350
KBH_4	7.4	125
$Be(BH_4)_2$	20.8	125
$Mg(BH_4)_2$	14.9	320
$Ca(BH_4)_2$	11.6	260

* Theorectical maximum (Source: IEA Hydrogen Implementing Agreement – Hydrogen Production and Storage R&D Priorities and Gaps)

Table A.12 *Comparison of the key properties of main (condensed-phase) hydrogen stores*

Material	Practical wt.% H	Kinetic reversibility	T_{dec} (°C)	Notes	Criteria met
$PdH_{0.6}$	0.6	excellent	ambient	$ 1000/oz	(ii,iii,v)
Mg_2NiH_4	3.6	very good	ambient	Fails to meet wt.% criterion	(ii,iii,iv,v)
$NaAlH_4:TiO_2$	5.5	good	125°C	Fails to meet wt.% criterium	(ii,iii,iv,v)
Li_2NH	6.5-7.0	good	285°C		(i,iii,iv,v)
MgH_2	7.6	Vvery poor	330°C	Cheap Mg metal	(i,iv,v)
$LiBH_4:SiO_2$	9.0[d]	irreversible[b]	200-400°C	At present $LiBH_4$ is expensive	(v)
$H_2O_{(l)}$	11.1	a	e	Environmentally friendly MHS	(i,iii,iv,v)
$SiH_{4(l)}$	12.5	irreversible	Broad range	c	(i,iv)
LiH	12.6	poor	720°C	Aggressive Li vapour formed upon decomposition	(i,iv,v)
$NaBH_4$	13.0	irreversible	400°C	cheap	(i,iv,v)
$NH_{3(l)}$	17.6	irreversible	e	Toxic liquid	(i,iv)
C^g	???[g]	g	g	Very expensive and ill-defined at present	(i,ii,iii,v)???
petroleum	17.3				
BeH_2	18.2	irreversible	250°C	Extremely toxic and volatile powder	(i)
NH_3BH_3	18.3	irreversible	Melts at +104°C	Multistage decomposition	(i,iv,v)
$LiBH_4$	19.6	irreversible	380°C	Expensive as compared to Na compound	(i)
NH_4BH_4	24.4	irreversible	-40 to +100°C	Multistage decomposition	(i,iv)
$CH_{4(l)}$	25.0	irreversible	e	Gas difficult to liquidify	(i,iv)

(Source: (Grochala, Edwards, 2004))
(a) Risk of explosive regeneration of HSM if H and non-metal are stored in the liquid or gaseous phase (b) Investigations in progress (c) toxic liquid low storage temperature, risk of explosion (d) SiO_2 is added in substantial amounts, thus lowering by 4 times the practical hydrogen

storage efficiency (e) Thermal activation very difficult (f) Nanotubes, including alkali metal-doped nanotubes (g) Highly irreproducible data, ranging from 0 to 20 wt.%.

Table A.13 *Hydrogen Storage Capacity of Amine Borohydrides NH_nBH_n*

Reaction of NH_nBH_n	Wt.%	T (°C)
$NH_4BH_4 \rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	6.5	<120
$NH_2BH_2 \rightarrow NHBH + H_2$	6.9	~155
$NHBH \rightarrow BN + H_2$	7.3	>500

(Source: MRS Bulletin volume 33, The Hydrogen Fuel Alternative, G.W. Crabtree and M.S. Dresselhaus).

Appendix C   Research on hydrogen storage in the Netherlands

In this chapter a short overview of projects in The Netherlands is given which are connected to sustainable hydrogen. Here only the projects related to hydrogen storage are described. These projects are performed under the ACTS – NOW Sustainable Hydrogen Programme and the aim of this program is to develop a knowledge and technical base for the transition towards a hydrogen based society. The programme consists of 7 research fields and some of them are hydrogen production, separation, storage, transport, and conversion. The descriptions of the different projects are obtained from the websites
http://www.nwo.nl/nwohome.nsf/pages/NWOA_6NSGYZ_Eng
http://www.nwo.nl/nwohome.nsf/pages/NWOA_6P69LY

C.1   ACTS-NWO Sustainable Hydrogen Programme (First Tender)

C.1.1 Atomistic modelling of lightweight metal-hydrides

Project Leaders
Dr. G. Brocks, UT; Dr. Ir. G. A. de Wijs, KUN; Prof. Dr. P. J. Kelly, UT; Prof. R. A. de Groot, RUG

In a future hydrogen economy safe and robust hydrogen storage is essential. Metals and metal alloys can act as a sponge and absorb hydrogen in large quantities, thus enabling a storage mode that is intrinsically safe. The hydrogen is dissolved in atomic form inside the crystal lattice of the bulk metal. Since using containers filled with bulk metals generally add a lot of extra weight, the search is for suitable lightweight metal alloys. In addition the process of hydrogen absorption and desorption from such alloys needs to be fast and not consume a lot of energy (since this energy would then be lost). The aim is to find a lightweight metal that has all these desirable properties. In this project we apply accurate, stare-of-the-art computer modeling to simulate the behavior of hydrogen atoms inside the crystal lattice of metals. We hope to learn where the hydrogen atoms want to go inside the material, how difficult it is for them to get in there and how difficult to get back out again (ultimately to be burned cleanly). Moreover, because these simulations "see" directly into the structure of the materials, we can look for causes of undesirable behavior, e.g. positions at which the hydrogen atoms get trapped, and possibly provide suggestions for remedies. We start from lightweight metals everybody is familiar with, such as magnesium. Improving its properties involves alloys (i.e. mixtures on an atomic scale) with other lightweight metals. The Holy Grail is to find an alloy with an unprecedented hydrogen storage capability and, of course, to understand how it works.

C.1.2 Metal-hydride thin films as a tool to find new/improved light weight storage materials

Project Leaders
Dr. B. Dam and Prof. Dr. R. Griessen Vrije Universiteit Amsterdam

Many western states have committed themselves to a reduction of their CO_2 output. Fuel cell powered cars running on hydrogen, would reduce the CO_2 output considerably. An essential ingredient for this development is a hydrogen storage system that is light and compact. A safe way to store hydrogen is to incorporate it in a solid. In spite of the enormous amount of work on metal-hydrides carried out for decades the best metalhydrides available commercially today are still too heavy (typically 430 kg for the 6 kg of hydrogen necessary for a medium-sized car with a 400 km range) although the volume (68 liter) is acceptable. Magnesium-based hydrides would be significantly lighter but, due to their stability, it is difficult to desorb the hydrogen from these materials. Recent discoveries, for example of catalysed alanates (compounds containing AlH_4 building blocks) and lithium nitrides with high hydrogen densities, have made clear that there are completely new classes of hydrogen storage materials waiting to be explored. The search for

new hydrogen storage materials and the appropriate catalysts is a work of titans if carried out on bulk samples. This is the reason why we propose here a completely new combinatorial technique based on matrix thin film samples. By using simultaneously several sources (for example of materials A, B and C) in a suitable configuration, one produces large area films (typically 7 cm in diameter) with large spatial variations in A-B-C composition. The loading of such a matrix-film with hydrogen can then be observed with a video system, since we know from our work on switchable metal-hydride mirrors, that hydrogen absorption leads to large changes in their optical properties. The absorption kinetics is determined for essentially each pixel of the video camera. With this technique it is possible to monitor typically 104 samples (all with a different A-B-C composition) simultaneously under exactly the same conditions. In this way we hope to enforce a breakthrough in the search for hydrogen storage materials that are suited to be used in transportation.

C.1.3 Optical fibre hydrogen sensors

Project Leaders
Prof. Dr. R. Griessen, Dr. B. Dam, Ing. K. Heeck Vrije Universiteit Amsterdam

Safety is essential for the implementation of a future hydrogen based economy. For the operation of hydrogen powered devices there is a great need for sensitive, selective, fast, reliable, stable and cheap hydrogen sensors. Most of the sensors available commercially are based on electrical measurements at the sensing point. This is undesirable in potentially explosive environments. Furthermore, they are often expensive and not stable over long periods of time. These disadvantages can be circumvented by using optical detectors in which the end of an optic fiber is coated with a hydrogen sensitive layer. The changes induced in the optical properties of this layer during absorption of hydrogen are detected optically at the other end of the fiber. This type of sensors is easily scaled up to large numbers of fibers converging to a unique detector. We propose to use the switchable "black mirror" materials discovered in our group at the Vrije Universiteit as hydrogen sensitive layer. A typical example of a "black mirror" material is a compound of magnesium and nickel. Without hydrogen it is a shiny mirror that reflects effectively the light in the optic fiber. However, absorption of small amounts of hydrogen changes it into a highly absorbing, i.e. black layer. The great advantage of our "black mirror" materials is that the optical changes occur at low concentrations of hydrogen (thus avoiding deleterious strains that limit the lifetime of sensors) and that diffusion of hydrogen in the sensor is sufficiently fast over a large temperature range (- 40 °C to +90 °C). In this proposal we investigate the implementation of these switchable mirrors in a practical device.

C.1.4 Novel nanostructured light metal hydrides for hydrogen storage-
fundamentals and application

Project Leaders
Prof. Dr. K. P. de Jong Division of Inorganic Chemistry and Catalysis Utrecht University, Prof. Dr. F. H. P. M. Habraken Physics Dept. Division Surfaces, Interfaces and devices, Utrecht University.

Sustainable energy is based on sun, wind and water. Large scale use of especially solar energy makes storage and transport of energy necessary. Hydrogen is often proposed as energy carrier of the future because its use only results in the formation of water. The main challenge is safe, efficient and cheap hydrogen storage. Chemical bonding of the hydrogen gas in a metal to a solid metalhydride is investigated in this research as a promising possibility. The emphasis of this research is focused on magnesium (Mg) which forms with H_2 the hydride MgH_2. Because the stability of MgH_2 is in general too high, which leads to high hydrogen desorption temperatures, this research is focused in the destabilization of MgH_2. This can be done by preparing thin films of Mg in a different way for example by making the films amorphous or bombarding them with high energetic particles. Another way is creating very small particles of Mg with the di-

mensions of 1-10 nm (1 nm = 1 10^{-9} m). These very small particles probably enable us to desorb hydrogen at lower temperatures.

C.1.5 Mechanisms of hydrogen storage in alanates a first principles approach

Project Leaders
Dr. G.-J. Kroes,Leiden Institute of Chemistry, Dept. Theoretical Chemistry, Leiden University: Prof. Dr. Gert-Jan Kramer, Dept. Chemical Engineering, Division Catalysis (ST/SKA) Division Catalysis (ST/SKA), Eindhoven University of Technology: Prof. Dr. Evert Jan Baerends, Dept. Theoretical Chemistry Dept., Vrije Universiteit, Amsterdam: Dr. Hans Geerlings, Shell Global Solutions International BV, Dept. Innovation and Exploratory Research, SRTCA, Amsterdam

We propose research on storage of hydrogen in alanates. Hydrogen is a clean fuel: in a car, burning hydrogen only results in water, and the greenhouse gas CO_2 is not produced. Alanates are compounds that contain aluminum, (stored) hydrogen, and a metal like sodium or lithium. The focus of our investigation will be on $NaAlH_4$. This material is very promising, because: (i) the reversible hydrogen content is 5.6 wt.%, above the target of 5 wt.% specified by the international energy agency, and (ii) in contrast to compounds containing magnesium, $NaAlH_4$ can release hydrogen at temperatures close to 353 K, the temperature at which a so called PEM fuel cell would extract energy from hydrogen in, for instance, a car. The problem now standing in the way of the large-scale use of $NaAlH_4$ is a problem of kinetics: the speed at which hydrogen release from or uptake in $NaAlH_4$ takes place is too low with the current state of the art. Catalysts like titanium and zirconium are known to enhance this speed, but not yet enough. Better catalysts are needed. These could be obtained if the mechanisms of the reactions through which hydrogen is released or taken up were known, and if the roles played by the known catalysts were understood. Our research is aimed at this understanding. Using three new methods, the technical details of which are described in the research proposal, we will simulate the motion of the atoms that give rise to the solid state reactions through which hydrogen is stored and released. In the simulations, the motion of the atoms will be based on accurately calculated interatomic forces. Our research may point the way to faster loading and unloading of hydrogen from $NaAlH_4$, which could make this material applicable in on-board storage of hydrogen in cars.

C.1.6 High energy density, fluorite-based, hydrogen storage materials

Project Leaders
Prof. dr. P.H.L. Notten,Inorganic Chemistry and Catalysis, Eindhoven University of Technology: Dr. M. Ouwerkerk, Philips Research Laboratories, Integrated Device Technologies, Eindhoven

The application of $LaNi_5$ -type hydrogen storage materials in rechargeable NiMH batteries has become a great commercial success in the last decade. Almost half of the small rechargeable battery market is currently devoted to this battery system, while the potentials in Hybrid Electrical Vehicles (HEV) are even greater. In addition, efficient hydride-forming materials are crucial in future Fuel Cells. A new class of materials has recently been discovered, revealing very high hydrogen storage capabilities. At the Philips Research it has been found that a specific fluorite-type of Mg-based compounds can store up to 4 times the amount of hydrogen compared to that of the conventional $LaNi_5$, making these new materials very attractive for extremely high energy storage devices and offering serious potentials to meet the target of 6.5 wt.% hydrogen storage set by the US Department of Energy. It has been argued that the crystallographic structure seems to play a crucial role in the favorable transportation properties s. Apart from this high hydrogen storage capacity (i), other requirements have to be fulfilled, such as (ii) optimum thermodynamics, i.e. more favorable hydrogen pressures, (iii) the rate at which hydrogen can be absorbed and desorbed and (iv) resistance against corrosion upon repeatedly absorption/desorption. The impact of the materials composition on all these aspects is of crucial importance and will be investigated on both thin film electrodes and powder materials. The developed materials can be used for hydrogen storage in both gas phase driven and electrochemically

driven energy storage devices. The developed materials can, in the bulk form, directly be implemented in both rechargeable NiMH batteries and Fuel Cells. It is to be expected that this new class of materials will strongly contribute to the development of lightweight energy storage devices and hence to the future hydrogen economy.

C.1.7 University of Twente, The Neterlands

Project Leaders
Dr.G. Brocks, Dr. G. de Wijs
Computational Materials Science, Faculty of Science and Technology, University of Twente, The Netherlands and Electronic Structure of Materials, Faculty of Science, Radboud University Nijmegen, The Netherlands.

The group's main expertise is in ab initio electronic structure methods which they have developed and applied to a wide variety of condensed matter situations (metalhydrides, semiconductors, permanent magnetic materials, organic materials; (surface) energetics, lattice dynamics, transport, optical excitations etc.) using both localized-orbital and plane-wave based methods in all-electron and pseudopotential forms. They started work on switchable mirror metal hydrides in 1997, addressing the energetics, the optical and the lattice dynamical properties and since 2003 they focus upon hydrogen storage materials. Solid-state DFT (density functional theory) codes are the appropriate tools for addressing bulk properties. The most flexible and powerful of such codes at present are based upon pseudo-potentials and plane wave basis sets, and use Car-Parrinello techniques for simultaneous electronic and structural optimization. Optical properties are obtained by combining such results with those obtained in first-principles GW calculations. The two groups have a long-standing collaboration and work together in a project on hydrogen storage materials, supported by the Dutch organization "Advanced Technology for Sustainability (ACTS)".

C.2   ACTS-NWO Sustainable Hydrogen Programme (Third Tender)

C.2.1 Destabilized, multi-component, Mg-based hydrogen storage materials

Hydrogen has been proposed as emission-free energy carrier in the future hydrogen economy, e.g. in fuel-cell powered cars. One of the major challenges to be overcome in realizing such hydrogen economy is finding an efficient and safe hydrogen storage medium. Mg can store 7.7 wt% hydrogen but suffers from slow absorption/desorption rates and low equilibrium hydrogen pressure. The kinetic shortcomings can be overcome by alloying with Mg with Sc/Ti, which induces a change in crystal structure from rutile to favorable fluorite. New ternary and quaternary Mg-Ti alloys will be proposed to raise the equilibrium pressure while preserving the crystallographic structure. By adopting a combinatorial electrochemical approach, new materials will be investigated to quickly scan suitable alloying elements.

Subsequently, promising new compositions will be 'translated' into bulk materials. The eventual goal of the work is to develop light-weight, bulk storage materials with near atmospheric equilibrium pressure in the working range of fuel cells.

Project leaders:

- Prof. dr. P.H.L. Notten, Eindhoven University of Technology

- Dr. B. Dam, Free University, Amsterdam

- Dr. E.M. Kelder, Delft University of Technology

C.2.2 Search for new light-weight hydrogen storage materials using Hydrogenography

Hydrogen storage is essential for the implementation of hydrogen as an energy carrier in a sustainable economy. Hydrogen storage in metal hydrides is especially attractive due to the high volumetric capacity (larger than that of liquid hydrogen) that can be attained. However, the conditions to store and retrieve hydrogen need to be in a practical range of temperatures (<100°C) 1-10 bar). Finding new materials is very much like the search~and pressures (for a needle in a haystack. For this we use hydrogenography, a powerful technique developed in our group, which probes the properties of thousands of samples simultaneously. This combinatorial approach also allows us to systematically analyze the trends in storage behavior. We also investigate a number of fundamental aspects such as the role of meta-stable structures and the effect of crystalline order and the existence of an intriguing enthalphy/entropy correlation.

Project leaders:

- Dr. B. Dam, Free University, Amsterdam

- Prof. dr. R.P. Griessen, Free University, Amsterdam

C.2.3 In situ NMR analysis of hydrogen storage materials

Efficient hydrogen storage is a key element for organizing the world's energy demand in a sustainable way. To make hydrogen storage efficient it is essential to store large amounts safely in a relatively low volume.
Furthermore, hydrogen loading and unloading should be energy efficient with minimum risk. Storage by chemically binding hydrogen in metal hydride compounds is a promising route to achieve this goal.
At present there is no material that meets all these requirements. A possible route to find suitable materials is 'combinatorial chemistry' which means that the composition of materials is varied systemically. Compositions that show favorable performance can then be further optimized. Using thin films of material this can be done with a very low consumption of base materials and essentially zero waste production.
In principle, one can monitor the hydrogen uptake and release for virtually thousands of compositions optically in a fast and flexible way. However, to fully understand the materials structure and hydrogen dynamics it is important to combine these optical measurements with advanced spatially resolved analytical techniques. Nuclear Magnetic Resonance (NMR) is the most powerful analytical technique but existing spectrometers do not have the sensitivity and flexibility to be applied for thin film samples.
It is the purpose of the present project to develop scanning NMR micro-imaging device to study thin hydrogen storage layers. In essence it is comparable to an MRI scanner in the hospital, which can provide pictures based on the location and amount of hydrogen (in the form of water) in the body. The proposed instrument will have a sensitivity that is at least a factor 1000 higher than a hospital scanner.
In addition, it can determine in what chemical form the hydrogen is present and how the process of hydrogen storage and desorption can be optimized for energy storage applications.

Project leaders:

- Dr. P.J.M. van Bentum, Radboud University

- Prof. dr. A.P.M. Kentgens, Radboud University

C.2.4 Hydrogen surface adsorption in porous crystalline materials

Hydrogen storage is a major bottleneck for the realization of a future energy economy based on hydrogen a s an energy carrier. Key to competitive hydrogen storage is the development of lightweight, cheap and safe materials that can be reversibly loaded under for applications, suitable temperature and pressure conditions.

Surface adsorption of hydrogen in porous, crystalline materials such as metal organic frameworks (MOFs) and covalent organic frameworks (COFs) provide materials with record specific surface areas per gram material and are therefore proposed as potential hydrogen storage materials.

Our research focuses on the design of new materials from first principles, chemical synthesis and the fundamental characterization of the hydrogen sorption. In situ neutron diffraction will be performed to determine, which are the most favorable positions of hydrogen in the crystals that have the highest adsorption interactions strength. With this knowledge new materials can be designed with improved characteristics and higher capacity.

Project leaders:

- Dr. F.M. Mulder, Delft University of Technology

- Dr. T. J. Dingemans, Delft University of Technology

- Prof. dr. ir. T.H.J.J. van der Hagen, Delft University of Technology

C.2.5 Nanostructured hydrogen storage materials: the benefits of particle size effects and support interaction

Hydrogen, if produced from renewable sources, would be an attractive fuel for cars, as it does not lead to emission of polluting or greenhouse gases. However, efficient, compact and safe storage of hydrogen on board is a challenge.

Hydrogen gas is voluminous and difficult to compress, while liquefaction takes much energy. To solidify hydrogen is no option, but it can nevertheless be stored as a solid: certain light metals can take up (and release upon heating) considerable amounts of hydrogen gas.

However, so far no material has been unidentified that meets all requirements, especially the combination of fast hydrogen release and uptake at reasonable temperatures is difficult to find. We investigate the possibility to use known combinations of light metals, but change their properties by making them in the form of a very fine powder (nanoparticles) and put this powder inside a carbon sponge. After making the materials, we will measure the rate and temperature of hydrogen release and absorption.

Also theoretical calculations will be performed to better understand the system, and to predict which experiments would be most useful. Furthermore model systems, very thin films, will be used to learn about the structure of nanophase-composites.

It is expected that due to very small grain size in the powder (and the influence of the carbon sponge), hydrogen can be released and absorbed easier and faster, and at more moderate temperatures and pressured than is normally the case for these light metals.

Project leaders:

- Dr. P.E. de Jongh, Utrecht University

- Dr. J.H. Bitter, Utrecht University

- Dr. B. Dam, Free University, Amsterdam

- Prof. dr. ir. K.P. de Jong, Utrecht University

- Prof. dr. G.J. Kroes, Leiden University

- Dr. R.A. Olsen, Leiden University

C.2.6 Atomistic modelling of advanced hydrogen storage materials

In a future hydrogen economy safe and robust hydrogen storage is essential. Many materials, in particular metals can absorb hydrogen in large quantities. The hydrogen is stored in atomic form or inside molecules in the crystal lattice of the material. Since containers filled with bulk materials can be heavy, the search is for lightweight materials that has all these desirable properties. In this project we apply computer modeling to simulate the behavior of hydrogen atoms inside a crystal lattice. We hope to learn where an how strong the hydrogen atoms are bonded and how difficult it is to get them out again.

A microscopic model for these (de)hydrogenation reactions will help to overcome present bottlenecks in finding suitable hydrogen storage materials.

Project leaders:

- Dr. G.H.L.A. Brocks, University of Twente

- Prof. dr. R.A. de Groot, Radboud University

- Prof. dr. P.H.J. Kelly, University of Twente

- Dr. ir. G.A. de Wijs, Radboud University

C.2.7 Realisation and application of in-situ TEM of hydrogen storage materials at 1-10 bar hydrogen pressure and 200 °C

There are serious disadvantages associated with the petroleum based transport system, such as petroleum shortage and global warming. Using hydrogen as an energy carrier instead of petroleum is the most promising solution, whereby the main bottleneck is hydrogen storage (in vehicles). Metal hydride materials are amongst the most effective storage materials with hydrogen contents. Dopant materials such as titanium have led to spectacular low temperatures for hydrogen (un)loading, but the underlying mechanisms are still not understood. Therefore the nanostructure of the different material phases will be studies using a transmission electron microscope under real industrial conditions, in contrast with the currently used high vacuum conditions. We will investigate the materials phases during the transformation, with a hydrogen environment at high pressures (1-10 bar) and at different temperatures. These demanding experiments are made possible by the design and construction of nanoreactors inside the microscope.

Project leaders:

- Prof. dr. H.W. Zandbergen, Delft University of Technology

- Dr. ir. J.F. Creemer, Delft University of Technology

- Prof. dr. J.J.C. Geerlings, Shell

- Dr. P.J. Kooyman, Delft University of Technology

C.2.8 Promoted hydrogen storage in nanoporous clathrate hydrate materials with enhanced storage capacity

Improved methods for hydrogen storage form an essential step towards a hydrogen economy in which hydrogen is used in traffic. Hydrogen results only in water as waste product at which the

emission of cabondioxide, one of the greenhouse gasses, is avoided. Potential and promising materials for hydrogen storage are the so called clathrates, at which hydrogen is trapped in cages of water ice. Hydrogen storage in clathrates at low pressures (1 bar and 20°C) is possible by addition of a promoter molecule, which stabilizes part of the cages. The positive effect has already been showed for one clathrate structure (the so called sII structure), however the obtained storage capacity (about 1 wt.%) is too low. The goal of the proposed research is to find a suitable promoter molecule for other clathrate structures (the so called sH structure), which possibly can contain 5 wt.%. If this goal is achieved then Shell Hydrogen will investigate if it is possible to further develop the found material for practical applications.

Project leaders:

- Dr. ir. C.J. Peters, Delft University of Technology

- Prof. dr. G.J. Kroes, Leiden University

C.2.9 Hydrogen sensors and safety detectors for the hydrogen economy

Hydrogen sensors are essential for the implementation of a hydrogen economy, since safety needs to be guaranteed. Our research aims to develop a hydrogen sensor for the automotive industry. The sensor exploits the very large changes in the optical properties of a metal hydride deposited at the tip of an optic fiber when it is in contact with hydrogen gas. The light from a laser diode shining through the fiber is reflected at its tip. The change in reflection after exposure to hydrogen, is measured by a photodiode at the other end of the fiber. The advantage of this approach is what the (readout) electronics is kept out of the potentially explosive sensor area. We will develop the hydrogen sensor in parallel to the optimization of our recently developed hydrogen detector which is based on the dame principles.

Project leaders:

- Dr. B. Dam, Free University, Amsterdam

- Prof. dr. R.P. Griessen, Free University, Amsterdam

Appendix D Hydrogen storage and future applications programs in Europe

In this appendix some European research programs and projects related to hydrogen storage are given. These projects give an impression of the current focus of the different research fields.

D.1   STORHY: Hydrogen Storage systems for Automotive Application

The integrated project STORHY aims to develop robust, safe and efficient on-board vehicle hydrogen storage systems, suitable for use in hydrogen fuelled fuel cell or internal combustion engined vehicles. Three systems are under development – compressed gaseous, cryogenic (liquid hydrogen), and metal hydrides. The aim is to develop systems that are capable of being produced at industrial scale and meet commercially viable goals for cost and energy density and durability. Achieving sufficient hydrogen storage capacity for adequate vehicle range is currently a major technology bottleneck (source ECN Waterstof & Schoon Fossiel, Petten 2 februari 2006, Startnotitie werkgroep Waterstof)

D.2   COSY: research network develops novel hydrogen storage materials

The Marie Curie Research Training Network COSY (Complex Solid State Reactions for Energy Efficient Hydrogen Storage) was launched on November, 1st, 2006. The network, which receives € 2.5 million in funding from the European Union, was established to develop new types of reactive light-metal hydride composites that can be used for more effective hydrogen storage. During the project's four-year duration, GKSS-Forschungszentrum Geesthacht will coordinate the collaboration between the 13 participating research institutes from seven European countries.
Hydrogen can easily be produced by using renewable sources of energy, which will have to replace fossil fuels once the latter are depleted at some point in the future. However, the use of hydrogen as an environmentally friendly source of energy for mobile devices such as automobiles, laptops and cameras is still hindered by a number of factors, including the excessive size and weight of existing hydrogen storage systems. If it becomes possible to store hydrogen more effectively than is currently the case, the gas would serve as an ideal energy carrier for mobile applications.
Over the next four years, the scientists involved in the COSY network will be working to achieve this goal by developing new nano-structured composites of various light-metal hydrides for use as storage materials. "Light-metal hydrides are solid materials that chemically bind hydrogen atoms and release them again when heated," explains Professor Rüdiger Bormann, Director of the Institute for Materials Research at GKSS-Forschungszentrum Geesthacht and coordinator of COSY. "The 'reactive hydride composites' discovered by the scientists at GKSS-Forschungszentrum Geesthacht will allow us to significantly increase the storage density. By storing hydrogen in solids, we can avoid a number of material- and safety-related technological difficulties, such as those encountered during high-pressure storage of gaseous hydrogen or the storage of liquid hydrogen at low temperatures."
The COSY network aims to prepare and optimize the new reactive hydride composites for use in hydrogen storage systems of mobile applications. To make this possible, the COSY scientists investigate how the light-metal hydrides and hydride composites can be produced economically, characterise the micro- and nano-structures generated during production, evaluate and optimize the thermodynamics and kinetics of the hydrogen absorption and release, and model these processes.

D.3   FuncHy - Functional Materials for Mobile Hydrogen Storage

Exploratory focus of the Helmholtz Initiative 'FuncHy: Functional Materials for mobile Hydrogen Storage' is the development of novel light-weight hydrogen storage materials with high gra-

vimetric capacity (> 5 mass%), low operating temperatures (< 150°C) and fast sorption kinetics. The project combines various scientific and technical approaches and methods, considering the total value-added chain from fundamentals of materials science to production on industrial scale. For this, FuncHy assembles five renowned European research institutions with complementary experience in the field of hydrogen storage materials. Together with associated partners from industry and academia, FuncHy provides a basis for a European centre of excellence for hydrogen technology for mobile applications. Solid storage offers the best opportunities for meeting the requirements of on-board storage. Within Europe, considerable effort has been put into the search for materials suitable for hydrogen storage through various fragmented and clustered EU and national projects, for both stationary and mobile applications. While the results for stationary and portable applications have in few cases reached some of their targets (e.g. EU project HYSTORY), the demands for transport applications for car industry, in terms of storage kinetics, weight ratio and operating conditions, have not yet been met. There is some disagreement in these demands. However, the large variability of some technical targets mainly depends on the various applications and is, somehow, locally influenced: a range of 600-700 km is foreseen for USA passenger cars (2000-2500 kg of gross vehicle weight, GVW), much heavier than the reference cars for Japan and Europe (1000 kg of GVW). The relevance of the various technical targets is evident, when comparing the fuel economy of an American passenger fuel cell vehicle of 7 kg of hydrogen for 560 km range with the consumption of a European passenger car aiming at 3.1 kg of hydrogen for a 500 km range (Mario Conte in 'Materials Science and Engineering Bulletin, 108 (2004) 2-8). FuncHy refers to the requirements on a storage system for vehicle applications, as proposed by the European Hydrogen project "StorHy: Hydrogen Storage Systems for Automotive Applications":

- reversible hydrogen storage capacity of more than 6 mass% = 2 Wh/kg (FuncHy: >5 mass%)

- desorption temperature of less than 150°C

- capacity loss per 10 cycles of less than 0.2%

- Storage of 5 kg hydrogen, tank volume less than 120 l

- fast sorption kinetics: tank filling within 3 min

State of the art and specific objectives

The research of the Helmholtz initiative FuncHy will concentrate on the development of hydrogen storage materials for mobile applications. The work will focus on non-conventional storage materials under considerations of most recent nanotechnology results on the preparation and characterization of the materials and the optimization of hydrogen sorption kinetics. For this, seven work packages were defined:

- Alanates (Dr. Matthias Fichtner, Research Centre Karlsruhe GmbH)

- Boro hydrides (Prof. Andreas Züttel, Empa, Dübendorf, Switzerland)

- Amides (Dr. Wiebke Lohstroh, Research Centre Karlsruhe GmbH)

- Reactive hydride composites (Dr. Martin Dornheim, GKSS Research Centre Geesthacht GmbH)

- Thermodynamic and kinetic characterisation (Dr. Oliver Gutfleisch, Leibniz Institute for Solid State and Materials Research Dresden)

- Combinatorial search for hydrogen storage materials (Prof. Ronald Griessen, <u>Vrije Universiteit</u>, Amsterdam, The Netherlands)

- System integration of selected hydrogen storage materials (Dr. Nico Eigen, <u>GKSS Research Centre Geesthacht GmbH</u>)

At a longer term this Helmholtz initiative shall become core of a European network of competence (work title: "Multi-functional Materials for Mobile Hydrogen Technology"). Therefore already now an intensive co-operation with the Helmholtz Virtual Institute "Asymmetric Structures for Polymer Electrolyte Fuel Cells", with the European Integrated Project " StorHy : Hydrogen Storage Systems for automotives Applications " as well as with the European Integrated Project " NESSHY : Novel Efficient Solid Storage for Hydrogen" is aimed at.

D.4 NESSHY

Integrated Project NESSHY, partly funded by the European Commission in the context of the 6th Framework Programme for Research (6FP), is coordinated by the Environmental Research Laboratory of the National Research Center "Demokritos" (EL) and aspires to comprise the major European initiative in the field of Hydrogen Storage in Solids. The project started officially on January 1, 2006, with a contractual duration of five years.

Objectives

NESSHY aims at developing novel materials, storage methods and fabrication processes that provide the energy density and the charge/discharge, storage/restitution rates necessary for mobile applications with spin-offs in stationary systems. The final aim of the project is to identify the most promising solid storage solutions for such applications. The envisaged objectives cover porous storage systems**,** regenerative hydrogen stores (such as the borohydrides) and solid hydrides having reversible hydrogen storage and improved gravimetric storage performance. Initially, two categories of reversible stores will be investigated – light/complex hydrides**,** such as alanates and imides**,** and intermetallic systems involving magnesium, although further categories may be included later. In all cases, the performance of different systems will be compared by a standards laboratory (working in collaboration with the US DoE standardisation activity). Further, efforts will be made to understand the mechanisms involved by innovative modelling activities. When promising new materials are identified, industrial and R&D collaborators will be brought in to upscale the material production, develop appropriate demonstration storage tanks and test out the prototype stores in practical conditions.

Approach and innovation

NESSHY addresses key issues related to hydrogen storage in solid materials such as new materials, novel analytical and characterization tools and measurement techniques, storage methods and fabrication processes, ab initio and phenomenological modelling. Special attention is paid to the enhancement of energy efficiency, storage kinetics, operating conditions and safety aspects of produced materials and to the tank design.
The overall S&T workplan involves mainly two different types of activities. The <u>vertical</u> type includes four "material development" workpackages, focusing on respective classes of candidate solid stores. For transport applications, both "reversible on-board storage" based on porous solids and metal hydrides, and "regenerative off-board storage", based mainly on chemical hydrides, are addressed. The <u>horizontal</u> activities include the development and application of ab initio numerical simulation techniques for the prediction of the actual behavior of real storage materials and the numerical optimization of storage systems, the use of novel analytical and characterization tools and combinatorial techniques to better understand the physico-chemical mechanisms of hydrogen storage in the novel materials investigated, the development of test protocols, evaluation facilities, safety and certification aspects in the framework of the Virtual

Laboratory, upscaling, tank development and testing, and Dissemination/Training. Participating parties: University of Hawaii: Mechanisms of Ti-doping enhanced kinetics. University of Geneva (IEA): New Complex Hydrides. Tohoku University (IEA): Li-Amides Characterization. University of Singapore: Li-Amides Synthesis and Performance. Brookhaven National Laboratory – Reversible Borohydrides.

D.5 Current running European projects

(source: www.cosy-net.eu/links.html)

- The European Hydrogen and Fuel Cell Technology Platform
  http://www.hfpeurope.org/
  http://ec.europa.eu/research/energy/nn/nn_rt/nn_rt_hlg/article_1261_en.htm

- European Hydrogen Association http://www.h2euro.org/

- EU IP StorHy http://www.storhy.net/

- EU IP NessHy http://www.nesshy.net/

- EU IP HyWays http://www.hyways.de/

- EU CA HyLights http://www.hylights.org/

- EU MC RTN Hydrogen http://www.mcrtn-hydrogen.eu

- EU MC RTN HyTrain http://www.hytrain.net

- HYFLEET:CUTE - Hydrogen bus project http://www.global-hydrogen-bus-platform.com/

- HYCHAIN - Hydrogen vehicles project http://www.hychain.org/

- EU IP ZeroRegio - Hydrogen cars project http://www.zeroregio.de/

- EU IP AutoBrane: Automotive high temperature fuel cell membranes http://www.autobrane.eu/

- Roads2Hycom - Hydrogen research roadmap http://www.roads2hy.com/

- HyApproval - Hydrogen vehicle approval project http://www.hyapproval.org/

- HyWays - European hydrogen energy roadmap http://www.hyways.de/

Appendix E   Research Institutes working on metal hydrides Europe-Japan

GKSS Research Center Geesthacht GmbH, Germany: is Germany's largest research institute on hydrogen related research areas. Hydrogen purification, conditioning and hydrogen storage in nanocrystalline light metal hydrides. Involved in several projects like StorHy, NessHy EU-FP5 networks FC-TEST-NET and EU-RTN H-Sorption in Mg.

Max Planck Institute fur Kohlenforschung, Germany. The main areas of research are organometallic chemistry and catalysis and their application in organic and inorganic synthesis and metal hydrides for reversible chemical energy storage.

Institut National, Polytechnique de Grenoble, Laboratoire de thermodynamique LTPCM, France. The main areas of research are developing new materials on basis of their kinetic and thermodynamic properties.

Institut de recherché sur l'hydrogène. The main areas of research are nanostructures (Mg) based hydrogen storage materials and catalysis.

Hy-Energy (Scientific Instruments), Newark England. This company can provide, consultancy, specialized services and scientific equipment on hydrogen storage.

Département de Mines et Métallurgie, Université Laval Québec Canada. The main area of research is Mg based hydrogen storage materials and catalysis.

IMR Tohoku University, Institute for Materials Research, Tohoku University. The main area of research is Mg-Ni based hydrides.

Centre for the Physics of Materials and Department of Physics, McGill University, Ernest Rutherford Building, 3600 University Street, Montréal, Québec H3A 2T8, Canada. Metal hydrides, storage, Mg.

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

University of Fribourg, Physics Institute, Perolles 1700, Switzerland

NIS Centre of Excellence "Nanostructured Interfaces and Surfaces", Dipartimento di Chimica I.F.M. Universita' di Torino, Italy. The Centre offers a multi-disciplinary laboratory equipped with the most advanced techniques in microscopy and spectroscopy. The research groups of NIS of the University of Torino have focused their activities on several topics. Hydrogen storage is currently studied on different materials, including metallic hydrides.

Leibniz Institute for Solid State and Materials Research, IFW Dresden, Germany The "Hydrogen storage materials" group at the IFW Dresden, within the Institute of Metallic Materials, consists of materials scientists, physicists and chemists and has special expertise in the development, synthesis and characterisation of novel nanoscale, light metal hydrides by non-equilibrium processing routes. Within the EU 5th framework project *FUCHSIA*, work has focussed on novel hydrogen storage compounds such as nano-crystalline Mg-based alloys (MgH_2, Mg_2NiH_4 and Mg_2FeH_6) modified with PGM (platinum group metals) or graphite to enhance kinetics. Work on complex hydrides such as $Mg(AlH_4)_2$ or $LiBH_4$ is in progress.
Computational Materials Science, Faculty of Science and Technology, University of Twente, The Netherlands and Electronic Structure of Materials, Faculty of Science, Radboud University

Nijmegen, The Netherlands. The group's main expertise is in ab initio electronic structure methods which they have developed and applied to a wide variety of condensed matter situations (metal hydrides, semiconductors, permanent magnetic materials, organic materials; (surface) energetics, lattice dynamics, transport, optical excitations etc.) using both localized-orbital and plane-wave based methods in all-electron and pseudopotential forms.

Instituto de Ciencia de Materiales de Sevilla, (Materials Science Institute of Sevilla). The research group "Nanostructured Materials and Microstructure", integrated in the Materials Science Institute of Sevilla, has a wide experience in research in the field of nanomaterials and especially in the correlation between preparation conditions, microstructure and properties. In particular they have previously investigated the oxidation behaviour of nanocrystalline Mg and MgH2 and the role of transition metal oxide additives during hydrogen storage in nanocrystalline magnesium.

Research Centre Karlsruhe GmbH, Germany. Several activities on hydrogen storage have been accomplished at the INT. The main topic of these works is the question how hydrogen behaves in nanoscale materials and their grain boundaries and whether nanomaterials with tunable electric properties are suitable for hydrogen storage. The institute has also developed synthesis methods for novel nanocrystalline aluminum hydrides.

Institut National Polytechnique de Grenoble, Laboratoire de Thermodynamique LTPCM, France. Using the principles of thermodynamics with kinetic calculations, we develop new materials from undercooled liquids and metastable solid mixtures of alloy and ceramic phases within appropriate temperature/internal energy constraints. Among experimental facilities, it can be founded a high-temperature mass spectrometry coupled with Knudsen effusion cells in order to study vapours and high temperature gases in view of determining thermodynamic properties of different materials: ceramics, electronic composite materials, alloys, molten salts.

Condensed Matter Physics Department, Faculty of Science, Vrije Universiteit Amsterdam, Netherlands. Very recently it became clear that the changes induced by hydrogen in a switchable mirror material could be used for hydrogenography, i.e. the 2-dimensional detection of hydrogen in metal hydrides and the determination of the enthalpy of formation thereof. This opens completely new ways to investigate the hydrogen ab/desorption in new materials. Exploring the benefits of this technique on well-known Mg2NiH4, it immediately showed the remarkable compositional dependence of the kinetics of hydrogen storage in this material. In addition, certain Mg-based switchable mirrors exhibit a strongly absorbing black-state at intermediate hydrogen compositions between the shiny metallic and transparent state. This black state offers interesting possibilities for technological applications in smart solar collectors and fiber optic hydrogen sensors.

Física de Materials II, Dept. Física, Universitat Autònoma de Barcelona, Spain. In addition to most characterisation equipment available in large university facilities, this group has worked with several generations of calorimetric devices and is equipped with state-of-the-art equipment for isothermal, scanning calorimetry and differential thermal analysis. Also available are TGA devices, Thermomagnetic balances and various equipment for magnetisation measurements.

Empa, Dübendorf, Switzerland. The section 138, "Hydrogen & Energy", at Empa addresses scientific questions and technological problems from hydrogen in solids to hydrogen as an energy carrier. The investigations range from the fundamental aspects of the hydrogen interaction with solids e.g. the physisorption and chemisorption of hydrogen on the surface, the hydrogen induced structural changes of solids like metal insulator transitions, the occupation of interstitial sites by deuterium and the thermodynamics of hydrogen in the lattice. Our experience ranges from hydrogen sorption in metals, hydrogen in metallic nanoclusters, hydrogen adsorption on carbonous nanostructures, and electrochemical hydrogen sorption in intermetallic compounds to

p-element complex hydrides. We develop instruments for the specific investigation of hydrides and we have demonstrated several solid hydrogen storage systems.

Laboratoire de Réactivité et de Chimie des Solides LRCS, Université de Picardie Jules Verne, Amiens, France. The research activities of our team are focused on the chemistry and physical-chemistry of solids. The general orientation consists in developing new synthesis strategies to optimise the properties of the materials that we prepare towards applications. Indeed, the new synthesis makes the most of the reactivity of pulverulent materials under special reaction conditions (" chimie douce " methods, mechanical grinding) and are then used for the wished application (battery, catalysis, hydrogen storage, electrochromism...). The LRCS has more than 10 years of experience in hydrogen storage in form of nanocrystalline light element metal hydrides for mobile applications. More recently interesting developments were achieved in thin films for applications in switchable mirrors. For instance, based on our expertise on bulk materials, we have demonstrated easier and faster hydrogenation for Mg-C thin films as compared to pure Mg ones.

Appendix F   Research Institutes working on metal hydrides USA

Below some laboratories and institutes are listed working on storage materials and application oriented goals in the USA (source: DOE Hydrogen Program, FY 2004 Progress Report, II.F.2 Metal Hydride Center of Excellence).

James Wang Sandia National Laboratories
P.O. Box 969, Livermore, CA 94551 Phone: (925) 294-2786; Fax: (925) 294-3410; E-mail: jcwang@sandia.gov
Team Members:
Sandia National Laboratory-Livermore,
Brookhaven National Laboratory,
California Institute of Technology,
GE Global Research,
HRL Laboratories, LLC,
Intematix Corporation,
Jet Propulsion Laboratory,
National Institute for Standards & Technology,
Oak Ridge National Laboratory,
Savannah River National Laboratory,
Stanford University,
University of Hawaii,
University of Illinois at Urbana-Champaign,
University of Nevada, Reno,
University of Pittsburgh in partnership with Carnegie Mellon University,
University Of Utah,

The Metal Hydride Center of Excellence involves seven universities, three industrial companies, and six federal laboratories. The Metal Hydride Center focuses on the development of advanced metal hydride materials, including lightweight, high-capacity complex hydrides; destabilized binary hydrides; intermetallic hydrides; modified lithium amides; and other on-board reversible hydrides. The Metal Hydride Center has two main objectives: (1) develop improved lightweight, high-capacity hydride-based materials for vehicular applications, and (2) pursue systems engineering science for the ultimate integration and demonstration of these advanced materials into a complete hydrogen storage and delivery system.

The Metal Hydride Center proposes to develop an advanced hydrogen storage system based on parallel research in four classes of hydride-based materials. These include 1) advanced complex hydrides of the light elements Li, Na, Mg, Ti, Ca, B, Al, Si; 2) destabilized binary hydrides (e.g., Li-Si destabilized H_2 release from LiH); 3) novel intermetallic hydrides (e.g., Mg-M-H alloys); and 4) other on-board reversible hydride materials, such as lithium amides, that demonstrate promising hydrogen storage properties. The following paragraphs are brief summaries of the work proposed to be completed by each Metal Hydride Center team member

Metal Hydride R&D for Hydrogen Storage
James Wang Sandia National Laboratory-Livermore Phone: (925) 294-2786; E-mail: jcwang@sandia.gov
Sandia National Laboratory-Livermore (SNL) will play a major role in the Metal Hydride Center to help coordinate research among the partners in addition to its role in materials discovery and engineering science. For materials discovery, SNL will lead coordination of a team that proposes to focus on complex hydrides and other hydride-based materials such as the lithium amides. SNL plans to explore the modification of sodium alanates to obtain higher capacity

without a loss in hydrogen sorption kinetics, look for new hydrides, develop low-temperature reversible lithium amides, and investigate novel materials synthesis methods and processes. SNL will also conduct a parallel effort in safety and engineering sciences for the design of a lightweight, high-capacity hydrogen storage system. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Synthesis of Novel Metal Hydrides for Automotive Applications
James Wegrzyn Energy Research Division Brookhaven National Laboratory Phone: (631) 344-7917; E-mail: jwegrzyn@bnl.gov
Brookhaven proposes to develop and test a new series of aluminum hydrides that have the potential to meet DOE's 2010 and 2015 system performance targets. The research plan includes investigation of sample synthesis and preparation, sample characterization, sample decomposition and regeneration of α-aluminum hydride and other aluminum hydride phases. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage
Channing Ahn California Institute of Technology Phone: (626) 395-2174; E-mail: cca@caltech.edu
The California Institute of Technology (CalTech) proposes to synthesize nanophase metals and hydride precursors to improve hydride kinetics and to investigate the thermodynamics of nanoscale systems. The hydrogen sorption properties of these nanophase materials will be measured and evaluated. CalTech will use a novel preparation technique to synthesize Li- and Mg-based hydrides that will enable a decoupling of size-related surface effects from grain boundary effects. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Lightweight Intermetallics for Hydrogen Storage
J.-C. Zhao GE Global Research Phone: (518) 387-4103; E-mail: zhaojc@research.ge.com
GE Global Research proposes to discover and develop a high-capacity (> 6 wt.%) lightweight hydride that is practical and inexpensive for reversible vehicular hydrogen storage and delivery systems and capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. GE will be using internally developed high-throughput, combinatorial techniques for materials discovery and characterization. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage
Gregory L. Olson HRL Laboratories, LLC, Malibu, CA Phone: (310) 317-5457; E-mail: olson@HRL.com
HRL Laboratories proposes to develop and to implement hydride destabilization methods for thermodynamic control of reactions in light metal hydrides with gravimetric storage capacities greater than 6 wt.% hydrogen. The research will identify, synthesize and characterize nanoscale hydride materials and catalysts having the requisite dimensions and structural properties to promote hydrogen dissociation, diffusion and exchange at rates that greatly exceed those in bulk materials. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

High-Throughput Combinatorial Chemistry Development of Complex Hydrides
Young K. Yoo Intematix Corporation, Moraga, CA Phone: (925) 631-9005 x112; E-mail: yyoo@intematix.com
Intematix proposes to implement high-throughput combinatorial techniques for new multi-element complex metal hydrides in order to deliver suitable on-board reversible hydrogen storage materials that meet or exceed DOE/FreedomCAR targets for 2010 and 2015. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Robert C. Bowman, Jr.Jet Propulsion LaboratoryPhone: (818) 354-7941; E-mail: robert.c.bowman-jr@jpl.nasa.gov

The Jet Propulsion Laboratory (JPL) proposes to develop and demonstrate a safe and cost-effective light-metal hydride materials system that meets or exceeds the DOE/FreedomCAR goals for on-board hydrogen storage. JPL plans to characterize and validate storage capacity and hydrogen sorption reversibility in the destabilized hydrides developed by partners under practical operating conditions. JPL will also develop lightweight and thermally efficient hydride storage vessels to reduce storage system mass and experimentally demonstrate their compatibility with appropriate complex and destabilized nano-phase hydrides. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Neutron Scattering Characterization and Thermodynamic Modeling of Advanced Metal Hydrides for Reversible Hydrogen Storage
Terrence J. Udovic National Institute for Standards & Technology Center for Neutron Research Phone: (301) 975-6241; E-mail: terrence.udovic@nist.gov

The National Institute of Standards & Technology (NIST) proposes to provide expertise and capabilities in neutron metrology and Calphad thermodynamic modeling as part of the DOE Metal Hydride Center of Excellence. The support includes fundamental, physicochemical property characterization of hydrogen-storage materials using neutron metrology techniques. NIST will also combine experiment and Calphad thermodynamic modelling to aid in critical assessments of hydrogen content, heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of materials. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage
Gilbert M. BrownOak Ridge National Laboratory (ORNL)Phone: (865) 576-2756; E-mail: browngml@ornl.gov

The hydrogen storage development work at ORNL has as its objective to achieve the DOE/FreedomCAR system storage targets for 2010. Central to this effort is the development of new methods of preparation of a suitable variety of high-content hydrogen compounds. The ORNL team has expertise in the synthesis of organo-metallic compounds by solution-based synthetic methods, and they will apply this knowledge to prepare Ti-catalyzed $NaAlH_4$ and other complex hydrides by solution methods. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Hydrogen Storage R&D at Savannah River
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SRNL will concentrate its efforts on looking at a new electrochemical process for charging aluminum to aluminum hydride, or alane. The SRNL process is currently being patented. Alanes have a 10 wt.% hydrogen storage capacity. Recent results by other researchers indicate that alanes can be decomposed at reasonable conditions with the addition of the proper catalyst or dopant. The biggest challenge, however, will be in recharging the material. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials
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Stanford proposes to develop an understanding of the dynamics of hydrogen diffusion and phase transformations during hydrogenation/dehydrogenation in nanoscale materials using real-time in-situ synchrotron x-ray diffraction. They also plan to develop model nanostructured materials systems using the flexibility of physical vapor deposition to engineer atomic-level structural and chemical features. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Fundamental Studies of Advanced High-Capacity Reversible Metal Hydrides

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The University of Hawaii proposes to determine the chemical nature of the titanium species responsible for the enhanced dehydrogenation and re-hydrogenation processes in Ti-doped $NaAlH_4$ and elucidate the mechanism of action of the dopants. They also plan to explore reversible hydrogen storage materials based on complex aluminum hydrides as well as "thermodynamically tuned" binary hydrides, each with at least 7 wt.% materials-based gravimetric capacity with potential to meet DOE 2010 system-level targets. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Metal Hydride-based Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

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The University of Illinois plans to determine the structural, chemical and bonding changes occurring during the hydriding/dehydriding cycles for candidate complex hydrides, other lightweight hydride materials, and destabilized binary hydrides through combining advanced characterization tools including controlled-environment transmission electron microscopy and multiple-scattering density-function-based methods. Determination of the role of impurities and contaminants on charging/discharging properties is planned as well. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides

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The University of Nevada proposes to determine the effect of contaminants during hydrogen cycling and aging and observe any degradation in the hydrogen storage properties of complex hydrides, including Li amides. They also plan to develop complex hydrides and to characterize the hydrides using elastic and inelastic neutron scattering, in-situ neutron work using a portable Sievert's apparatus, and in-situ X-ray diffraction. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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The University of Pittsburgh plans to use Density Functional Theory methods coupled with Monte Carlo techniques to predict the heats of formation and finite temperature phase stability information for a variety of metal hydrides of interest. They plan to calculate the structure, interfacial energies, work of separation, and electronic properties of a number of different alanate interfaces and study the role of Ti doping of the Na_3AlH_6 phase on the dehydrogenation and transport reactions. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

Chemical Vapor Synthesis of Nanocrystalline Binary and Complex Metal Hydrides for Reversible Hydrogen Storage

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The University of Utah proposes to develop a chemical vapor reaction process for synthesis of nanosized complex metal hydrides that meet reversibility and kinetics requirements with at least 7 wt.% materials-based gravimetric capacity and 50 g H_2/L materials-based volumetric capacity, with potential to meet DOE 2010 system-level targets. They also plan to demonstrate the feasibility and economical viability of the synthesis process. (Note: Subject to congressional appropriations, work on this project is anticipated to begin in FY 2005.)

F.1.1 Center of Excellence carbon nanotubes

In July 2003, the DOE issued a "Grand Challenge" to the global scientific community for research and development in hydrogen storage with open competition to universities, industry and national laboratories. This "Grand Challenge" called for the establishment of hydrogen storage Centers of Excellence on Metal Hydrides, Chemical Hydrogen Storage, and Carbon-Based Materials, with multiple university, industry, and federal laboratory partners. In addition, independent projects were solicited on new materials and concepts, off-board hydrogen storage systems, and analyses of life cycle cost, performance and environmental impact.
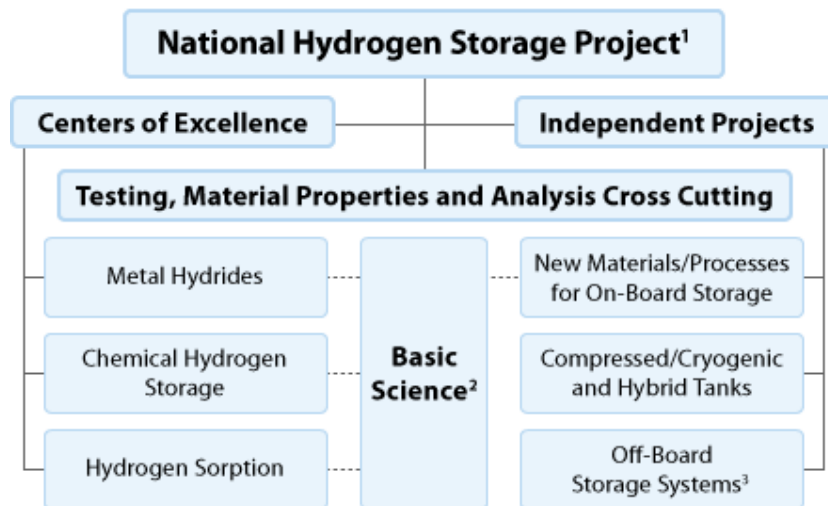
The new Centers of Excellence and independent projects, together with existing DOE hydrogen storage efforts, constitute the framework of the National Hydrogen Storage Project. The Secretary of Energy announced the selections for the Hydrogen Storage Grand Challenge on 27 April 2004. The DOE plans to provide funding at a level of $150 million over a five-year period (subject to congressional appropriations) for the National Hydrogen Storage Project. The result of this R&D effort will be the development of hydrogen storage systems capable of meeting the long-term DOE targets. Complementing the Grand Challenge, the DOE Office of Science issued a solicitation in 2004 for basic research to help overcome key hurdles in hydrogen production, storage, and conversion.

The Metal Hydride Center of Excellence targets the development of advanced metal hydride materials including light-weight complex hydrides, destabilized binary hydrides, intermetallic hydrides, modified lithium amides, and other on-board reversible hydrides. This Center involves seven universities, three industrial partners, and six federal laboratories.

The Chemical Hydrogen Storage Center of Excellence targets three "tiers" of R&D for chemical hydrogen storage: borohydride-water, novel boron chemistry, and innovation beyond boron. This Center involves seven universities, three industrial partners, and two federal laboratories.

The Carbon-Based Materials Center of Excellence targets breakthrough concepts for storing hydrogen in high surface area sorbents such as hybrid carbon nanotubes, aerogels, and nanofibers, as well as metal-organic frameworks and conducting polymers. This Center involves seven universities, one industrial partner, and four federal laboratories.

The National Hydrogen Storage Project also involves independent research projects that explore promising new hydrogen storage materials and concepts, off-board hydrogen storage needed for a hydrogen delivery infrastructure, standardized testing of hydrogen storage properties, and analyses of life-cycle cost, energy efficiency, and environmental impact for hydrogen storage systems. Some of the new materials/concepts being studied are nanostructured materials, amine borane complexes, metal perhydrides, clathrates, lithium nitride, and irradiation activation of materials. With the plan to initiate these projects in FY2005, early results will be reported within the next one to two years.

National Hydrogen Storage Project[1]

- **Centers of Excellence** — **Independent Projects**

Testing, Material Properties and Analysis Cross Cutting

Centers of Excellence	Basic Science[2]	Independent Projects
Metal Hydrides		New Materials/Processes for On-Board Storage
Chemical Hydrogen Storage		Compressed/Cryogenic and Hybrid Tanks
Hydrogen Sorption		Off-Board Storage Systems[3]

1. Coordinated by DOE Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells and Infrastructure Technologies
2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences

Source http://www1.eere.energy.gov/hydrogenandfuelcells/storage/national_proj.html

F.1.2 Hydrogen Storage, Engineering Center of Excellence

The U.S. Department of Energy's (DOE) Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program plans to solicit applications from multidisciplinary teams to advance on-board vehicular hydrogen storage systems. The HFCIT Program will release a funding opportunity announcement (FOA) in the December 2007–January 2008 timeframe. The team selected to receive the funding will become the DOE Hydrogen Storage Engineering Center of Excellence (CoE). It is envisioned that the CoE will be comprised of industry, university, and federal laboratory partners leveraging their diverse technical capabilities and facilities to operate as a virtual Center of Excellence.

Pending congressional appropriations, total estimated funding available is $25–$35 million over approximately 5 years, with the expectation of awarding one team to complement the existing National Hydrogen Storage Project activities.

The Hydrogen Storage Engineering Center of Excellence will focus on the research and development of on-board vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles. Specific objectives of the new CoE are to:

- Develop an understanding of storage system requirements for light-duty vehicles and design innovative components and systems with the potential to meet DOE performance and cost targets.
- Develop innovative on-board *system* concepts for materials-based storage technologies.
- Develop and test innovative concepts for storage sub-systems and component designs.
- Develop engineering, design, and system models that address both on-board subsystems and the fuel cycle, including refuelling, thermal management, and the storage-delivery interface.
- Design, fabricate, and test subscale prototype fixtures, components, and/or systems based on adsorbents, advanced metal hydrides, and/or chemical hydrogen storage, based upon a go/no-go decision to be made by DOE.