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**AFDELINGEN FOR MATERIALEFORSKNING**

**METAL COMPOUNDS FOR HYDROGEN STORAGE**

**ALLAN SCHRØDER PEDERSEN**

**AND**

**TEJS VEGGE**

## Abstract

Most developed countries - including Denmark - depend heavily on fossil or nuclear energy sources, but also strive to replace these sources with renewables. However, the fluctuating nature of energy production from renewable sources dictates a need for energy storage to level out mismatches between the production and consumption of energy. Unfortunately, it is not easy to store energy in a dense and efficient way and strong, world-wide research efforts are therefore undertaken to identify suitable storage technologies.

One promising candidate for artificial storage of energy is the storage of hydrogen in metal compounds. Many alloys and metal-based compounds react reversibly with hydrogen to form hydrogen-rich chemical substances, which may liberate hydrogen again depending on imposed pressure and temperature. Although the energy density of such compounds does not match the properties of fossil fuels, they are still among the best known for man-made storage technologies. The presentation gives an introduction to research at Risoe National Laboratory on materials for hydrogen storage.

## Introduction

Industrialized countries generally depend strongly on fossil or nuclear fuels and this is true also for the rapidly developing economies in East Asia and South America. In the case of Denmark, approx. 84 % of the total energy consumption come from coal, oil and natural gas, see Figure 1. Although the fraction of energy supply from sustainable sources is certainly

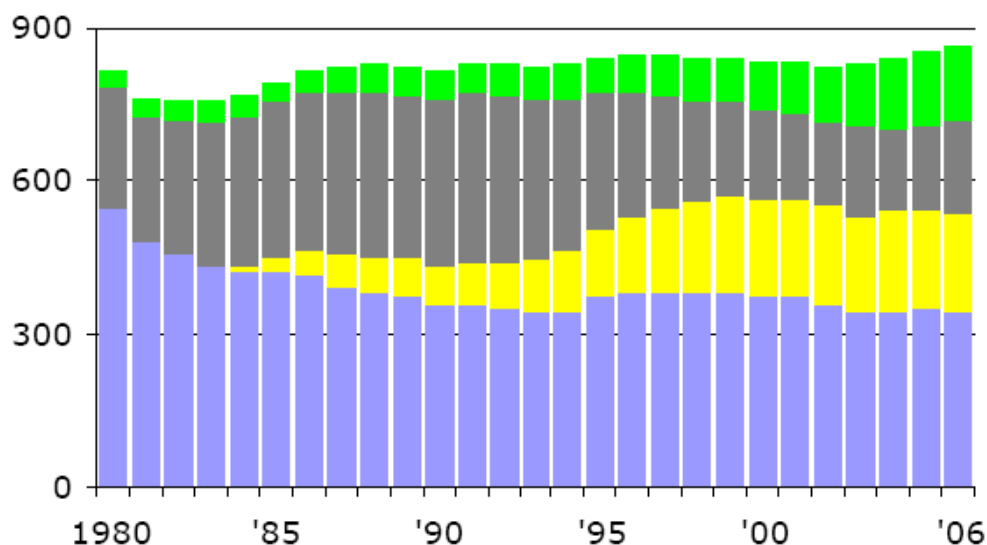


Figure 1. Development of gross energy consumption (PJ) in Denmark distributed on fuels. Blue: Oil, Grey: Coal, Yellow: Natural Gas, Green: Sustainable Energy Sources. [1]

Increasing, it must be foreseen, that fossil sources will be the dominating ones for probably at least decades. Nevertheless, there is almost a political consensus, that Denmark should be independent of fossils as soon as possible and latest when our own oil sources are depleted, expectedly in less than two decades. This is an ambitious goal and as there is a decision in the

Danish parliament, that Denmark should not have nuclear power, the most viable way to reach this goal is by installation of wind power.

Wind power production has a fluctuating nature. Production varies independently, and does not match the society's consumption pattern. This means that in some periods wind mills will produce more power than needed and in others the wind mills will be unable to fulfil the demand for energy. This is reflected in electricity prices, high prices meaning too low production and low prices too high production. As an example of this kind of price variation Figure 2 shows the variation in electricity price in West Denmark during November 2006. It is seen from the figure, that the price in short periods reaches very low levels – in some cases even zero - and in other periods the price almost reaches 3 times the average over the entire month.

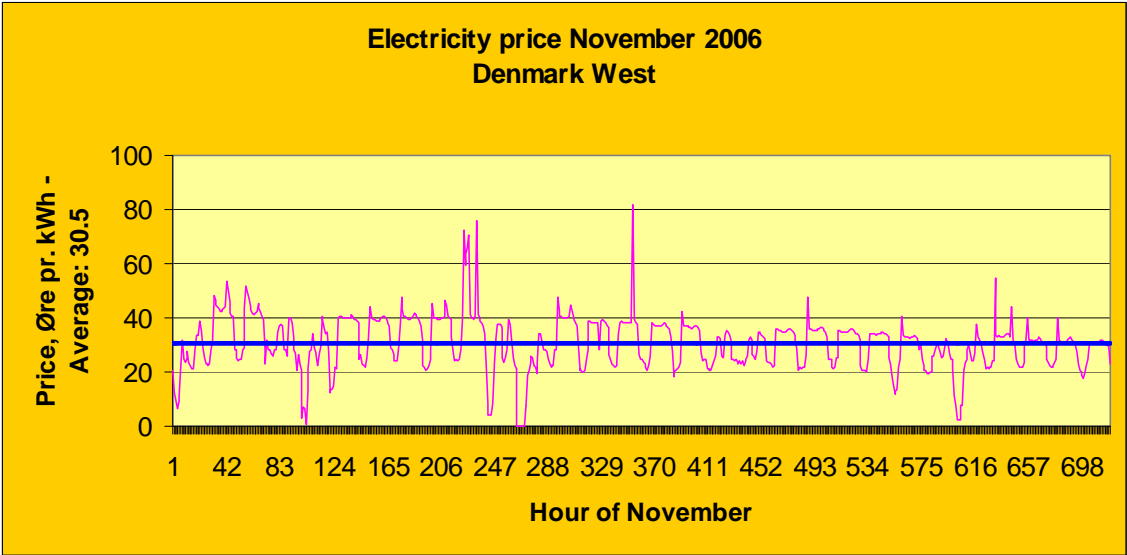


Figure 2 Variation of electricity price in West Denmark during November 2006 (source:[2]).

At the moment – because of the relatively small fraction of wind energy in the total Danish energy supply – this problem is not massive, but if wind capacity is expanded as planned, the problem will grow with serious economic consequences.

Yet another problem about exchanging fossil fuels with wind power is associated with transportation. Transport currently consumes 25-30 % of the total energy demand in Denmark and in addition the energy use in transportation is almost exclusively based on fossil fuels - more precisely oil and oil products. If we imagine an energy system without fossil fuels we would need to use electricity as the primary energy source for powering vehicles, meaning that we need technologies for storing electricity directly or indirectly. Access to such storage

technologies would allow storage of energy when it is cheap, and at the same time provide fuel for transportation.

Naturally electrical batteries are obvious candidates to solve the problem about storing electricity, but a close look at the energy density (cf. Table 1) of batteries shows, that it will be difficult to carry sufficient energy on-board a vehicle to allow a driving range, similar to what we know from gasoline powered cars. The volume and weight of batteries holding the amount of energy corresponding to 50 litres of gasoline are both prohibitively high.

<b><i>Energy carrier</i></b>	<b><i>kJ/ml</i></b>	<b><i>kJ/g</i></b>
<b><i>Gasoline (Octane)</i></b>	<b>33.4</b>	<b>47.6</b>
<b><i>LiBH<sub>4</sub></i></b>	<b>14.3</b>	<b>21.7</b>
<b><i>Magnesium Hydride</i></b>	<b>14.4</b>	<b>10.9</b>
<b><i>Mg(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub></i></b>	<b>14.3</b>	<b>11.4</b>
<b><i>Liquid Hydrogen</i></b>	<b>10.0</b>	<b>141.0</b>
<b><i>Hydrogen at 200 bar</i></b>	<b>2.4</b>	<b>141.0</b>
<b><i>Lead-Acid Battery</i></b>	<b>0.3</b>	<b>0.2</b>
<b><i>Advanced Battery</i></b>	<b>1.2</b>	<b>0.7</b>
<b><i>Fly Wheel</i></b>		<b>0.5</b>
<b><i>Methanol</i></b>	<b>18.0</b>	<b>22.7</b>
<b><i>Liquid Ammonia</i></b>	<b>17.9</b>	<b>25.2</b>

*Table 1. Energy densities of selected energy storage technologies. Weight and volume of containment and system components are not included in the numbers, which are based on the upper heating value for hydrogen*

The numbers in Table 1 also show that hydrogen is an attractive possibility as an on-board energy carrier, since it can be stored in a number of ways with high energy density, on both a gravimetric and volumetric basis. One of these ways is hydrogen stored in metal hydrides and it is interesting to note, that metal hydrides contain more hydrogen pr. unit volume, than does pure liquid hydrogen.

### **Metal Hydrides**

Numerous metals and alloys react directly with hydrogen to form binary or higher compounds according to the following equation (1):



For most systems of practical interest  $Q$ , the enthalpy involved in the process, is positive, meaning that the reaction is exothermic. However, a prominent example of endothermic hydride formation is  $\text{AlH}_3$ , which accordingly may only be formed by direct reaction under extreme pressure conditions [3].

The reversibility of (1) is central for the use of such systems because it allows that hydrogen can be stored during release of heat and released again upon heat addition. For many applications it is desirable, that  $Q$  in (1) is as low as possible.

For a traditional, simple hydrogen-metal system a typical uptake curve is shown in Figure 3. As hydrogen pressure is increased at a certain temperature  $T_1$  hydrogen atoms dissolve interstitially in the metal crystal lattice and form the  $\alpha$ -phase. At a certain point (certain hydrogen pressure) this phase is saturated and the precipitation of a new phase, the  $\beta$ -phase starts. From this point two solid phases are in equilibrium and therefore (Gibbs' phase rule) the hydrogen pressure remains constant (the plateau pressure) until all  $\alpha$ -phase has been converted to  $\beta$ -phase. Further increase of hydrogen pressure will lead to solution of hydrogen in the  $\beta$ -phase with a very steep slope. At a certain temperature,  $T_c$  in the figure, the so-called critical temperature it is no longer possible to identify phase transformations during hydrogen uptake and consequently the plateau pressure is substituted by an inflexion.

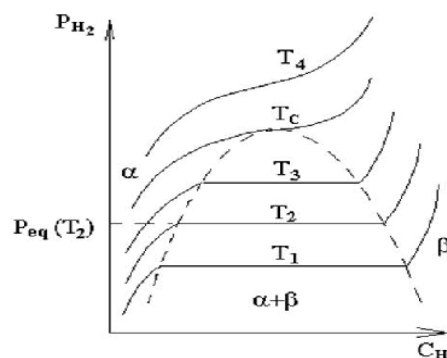


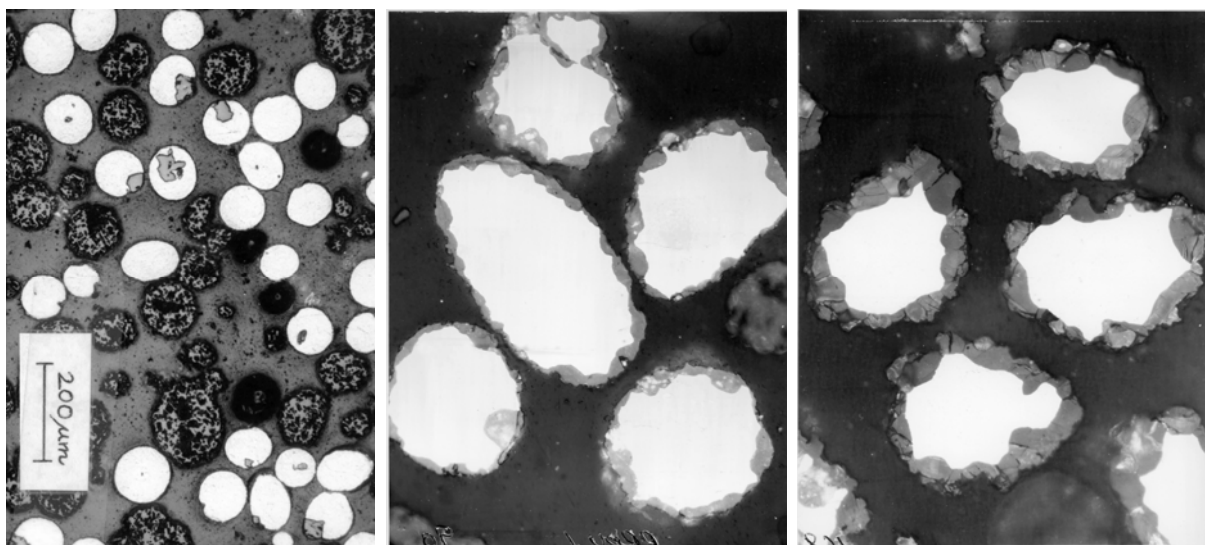
Figure 3.  $p$ - $c$ - $T$  relationship for a classical metal hydride (From [4]).

Depending on particularly the bonding nature metal hydrides may be considered as ionic, covalent, metallic or complex.  $\text{LiH}$  is an example of an ionic hydride, which is very stable and can be melted (melting point 689 C [5]) without decomposing. Ionic hydrides have no electronic conductivity similarly to other ionic compounds. An example of a metallic hydride with good electronic conductivity is  $\text{PdH}_x$ , where  $x$  may reach about 0.6. Visually there is no difference between Pd and its hydride, which both display the well-known metallic appearance and luster. The Pd-H system has often been used as a model to illustrate the behaviour of metal hydrogen systems because it almost ideally shows the features given in Figure 3 and in addition Pd has been used for hydrogen purification because of its hydrogen diffusion properties. The third type of hydride is the covalent type, exemplified by  $\text{AlH}_3$ ,

where a covalent bond type is found. Finally the complex hydrides, consisting complex hydrogen-rich cations, of have recently attracted interest (cf. section on Complex Hydrides).

### **Magnesium Hydride**

Magnesium hydride has high energy density based on the heat of combustion for the stored energy (cf. Table 1), but unfortunately for kinetic and thermodynamic reasons the Mg-H system is only operational at temperatures above 300 C. The hydride is readily formed by direct reaction above 300 C and 10 bar with heat of formation about 70 kJ/mole [6]. By hydride formation in magnesium nucleation starts on the magnesium surface and the hydride grows into the metal phase. Figure 4 shows a picture of magnesium powder hydrided to various degrees. It is seen how nucleation starts on the metal surface in many sites and that the hydride finally forms a coherent layer on top of the metal particles.



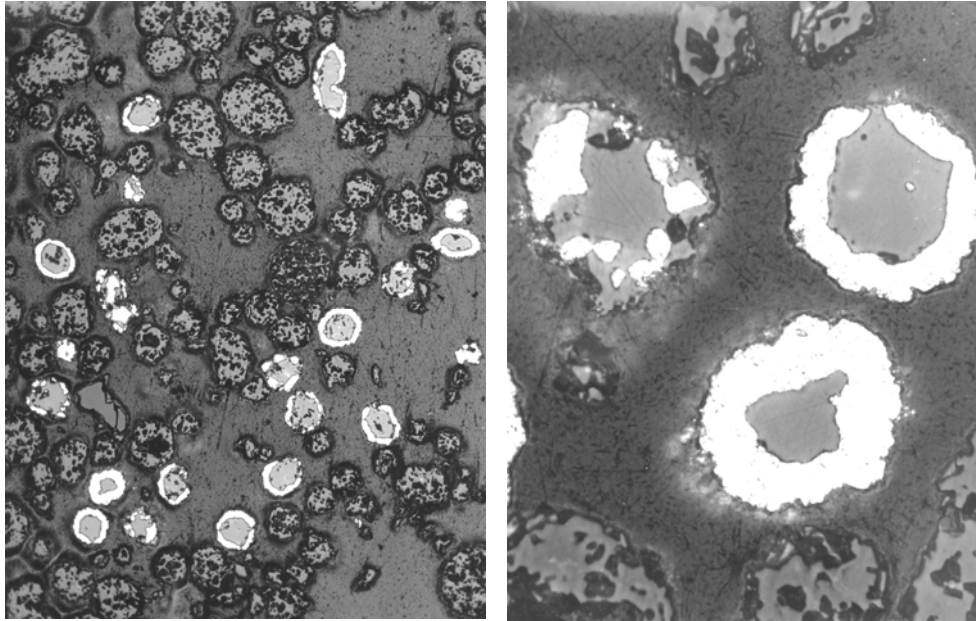
*Figure 4. Magnesium powder hydrided to different average reaction degrees. Left: 10%, Middle: 26%, Right: 55%. White is the metallic phase whereas the dark zones (optically transparent) are the hydride phase.*

Transportation of hydrogen in magnesium hydride is very slow and therefore further hydride formation virtually stops when a continuous hydride layer is formed on top of the magnesium material [7]. This means that for practical purposes magnesium can only be hydrided to a certain depth, which is about 40  $\mu\text{m}$  [7,8] and the consequence is that if a magnesium powder should be hydrided close to 100% the average particle diameter must not exceed approx. 80  $\mu\text{m}$ .

The reaction rate of hydride formation in magnesium depends strongly on the dimensions of the metal material. Fine powders or thin foils react relatively fast, but for particle size below 80  $\mu\text{m}$  it typically takes hours to reach 100% reaction, whereas 85 % is reached within approx. 20 minutes at 25 bar and about 400 C. By using ball-milled material and in particular by also adding 5wt% of vanadium, Schultz et al. [9] reached a dramatic increase in reaction

rate, both during formation and decomposition of magnesium hydride. Their results showed complete reaction within a few minutes, although the authors also found a decrease in hydrogen storage capacity as a result of the treatment.

During release of hydrogen from magnesium hydride, hydrogen starts to desorb from the hydride surface and a pure metal layer is formed as illustrated in Figure 5. The diffusion of hydrogen through the metal is fast and all hydride phase is readily transformed to metal.



*Figure 5. Desorption of hydrogen from magnesium hydride (same sample at different magnifications). Prior to microscopy the material had been hydrided 100% and is shown at a desorption degree of 57% hydride. A metallic (white in the photo) surface layer is formed during desorption and leaves a shrinking core of hydride (grey) in the central part of the particles. Particle size approx. 60  $\mu\text{m}$ .*

Magnesium is in general a reactive metal and is sensitive to other gases like oxygen, nitrogen and carbon monoxide [10]. Exposure of magnesium to oxygen causes a passivating surface oxide layer to be formed and oxidised magnesium is difficult to transform into hydride by direct interaction with hydrogen. The system must be temperature-cycled several times between room temperature and 400 C in hydrogen at 10 bar or higher, until a complete reaction is obtained.

### **Complex metal hydrides**

A significant breakthrough in solid state hydrogen storage occurred in 1997, when reversible storage of 4–5 wt.% of hydrogen in alkali metal aluminium hydrides ( $\text{NaAlH}_4$ ) was reported by Bogdanovic and Schwickardi [11]. This well known reductive complex hydride is stable and non-reversible under normal conditions, but the addition of a few mol-% of selected transition metals enables reversible ab-/desorption of hydrogen at moderate temperature and pressure. Subsequently, similar reversible properties have been demonstrated in a number of



other complex hydrides doped with transition metals, in particular in the form of halides such as  $\text{TiCl}_3$ , but the catalytic effect(s) of these dopants has remained elusive [12].

With respect to storage capacity, materials like aluminium and boron based complex hydrides, where the hydrogen is bound covalently in a  $(\text{AlH}_4)^-$ ,  $(\text{AlH}_6)^{3-}$  and  $(\text{BH}_4)^-$  type complexes, which are ionically bound to cations like  $\text{Li}^+$  and  $\text{Na}^+$ , are very attractive with theoretical capacities of up to 21.7 kJ/g (see Table 1). Significant improvements in kinetics and reversibility are, however, needed for most practical applications. Thus far, primarily two ways to improve the kinetics have been pursued: reducing the size of the particles/crystallites [13] (see Figure 6) and adding transition metal based catalyst, e.g.  $\text{TiCl}_3$  [14]. Recently, also so-called destabilized complex hydrides, where mixtures of e.g.  $\text{MgH}_2$  and  $\text{LiBH}_4$  have received attention, due to lowered desorption temperatures [15].

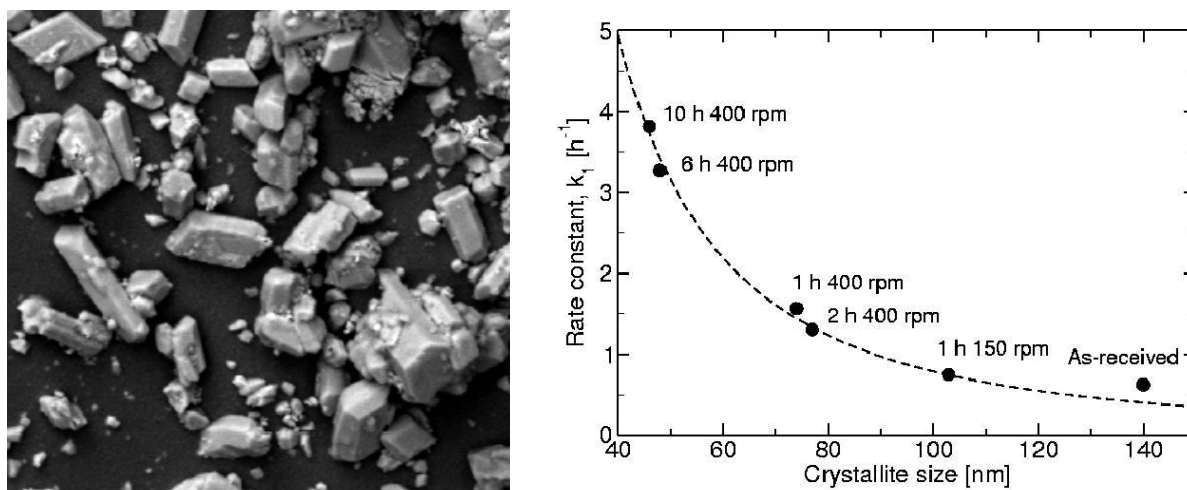


Figure 6. Left: Scanning Electron Micrograph of  $\text{LiAlH}_4$ . Right: The hydrogen desorption rate from  $\text{LiAlH}_4$  as a function of crystallite size determined from XRPD line broadening (from [13]).

Extensive efforts are now being placed on explaining the role(s) of the transition metal catalyst, as well as synthesizing novel compounds with high(er) storage capacity and more favourable kinetic and thermodynamic properties, e.g.  $\text{Mg}(\text{BH}_4)_2$ .

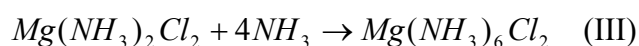
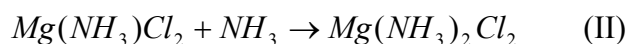
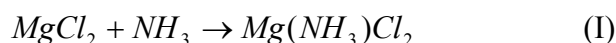
### Metal amines

The remaining challenges for reversible hydrogen storage in metal hydrides illustrated in the previous sections, has directed research activities toward indirect ways of storing hydrogen, e.g. in the form of ammonia stored in metal salts like  $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$  [15] and  $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$ , which can effectively store more than 9 wt.% hydrogen.

In these materials, gaseous ammonia, produced from hydrogen and nitrogen, reacts with the dry salt to form the metal ammine. The formation of a metal ammine is an exothermic process and the reaction heat varies with the material and degree of saturation. After saturation, the

ammonia can be released by heating the metal ammine; the energy required for desorption is the same as released during absorption. The desorbed ammonia can then be used in a fuel cell capable of using ammonia directly, e.g. SOFC, or be decomposed over a catalyst to hydrogen and nitrogen.

The absorption of ammonia into  $MgCl_2$  proceeds in three steps as shown in the reactions below:



The carrier salt can be chosen to have favourable thermodynamic properties and high reversibility and fast ab-/desorption of ammonia can be obtained due to the formation of a skeletal structure with an intrinsic nano-porosity [16].

## Summary

A brief introduction to the future need for energy storage in a sustainable energy system has been given and it has been demonstrated, that metal hydrides may be attractive candidates for such storage systems.

Magnesium hydride has been shown as an example of a metal hydrogen system with attractive energy density but rather poor reaction kinetics.

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