

# Light metal hydrides and complex hydrides for hydrogen storage

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The availability of feasible methods for hydrogen storage is one of the key—maybe the key—requirements for the large scale application of PEM fuel cells in cars. There are in principle four different approaches, *i.e.* cryostorage in liquid form, high pressure storage, storage in the form of a chemical compound which is converted to hydrogen by on-board reforming, or reversible chemical storage in different kinds of storage materials. New developments in the field of chemical storage make such systems attractive compared to the other options. This review will discuss the different possibilities for chemical storage of hydrogen and the focus on the presently most advanced system with respect to storage capacity and kinetics, *i.e.* catalyzed alanates, especially  $\text{NaAlH}_4$ .

## 1 Introduction

With the advent of new legislation, *i.e.* reduced fleet carbon dioxide emissions or the requirement of zero emission vehicles, and, on a longer timescale, the decreasing oil reserves, alternatives to internal

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combustion engines need to be developed. One such technology is the fuel cell driven car, with the PEM (proton exchange membrane) fuel cell being the most developed one. The fuel for this type of fuel cell is hydrogen, which consequently needs to be stored in the car or generated on board. One should keep in mind though, that the advantage of PEM fuel cells is not used to its full potential, as long as the hydrogen is still being produced from fossil resources. Several advantages could still be exploited to some extent, such as an improved energy efficiency compared to internal combustion engines and lower  $\text{CO}_2$  emissions, if  $\text{CH}_4$  is reformed to generate hydrogen instead of higher hydrocarbons, which have a carbon : hydrogen ratio close to 0.5. However, if well-to-wheel efficiencies are considered, highly efficient Diesel cars are not much inferior to fuel cell cars powered with hydrogen generated by methane reforming. Therefore, simultaneously with the development of fuel cell systems, alternative pathways for hydrogen production from renewable resources are necessary.

One of the crucial problems for the large scale application of fuel cell driven cars is the lack of feasible methods to store hydrogen on board the vehicle. Presently, four methods are being discussed or used in prototype vehicles, reviewed by Schlapbach and Züttel.<sup>1</sup>

(1) High pressure storage:<sup>2</sup> In order to achieve sufficiently high volumetric storage densities, pressures have to exceed 50 MPa and with the goals set to 70 MPa or even higher. In experimental cars, this has already been realized, such as in the HydroGen 3 by Opel/General Motors. This poses demanding requirements on the pressure tanks, which are made of high performance composite materials with correspondingly high prices. In addition, in order to withstand the high pressures, tanks have to be cylindrical, which is a severe limitation with respect to efficient packaging of the tank in the car, thus taking away passenger or luggage space. Also the energy needed to compress the hydrogen should not be underestimated. Even for a relatively moderate pressure of 20 MPa it consumes about 18% of the specific energy content.<sup>3</sup> Since this energy is basically lost, it reduces the overall energy efficiency of the system.

(2) Cryostorage:<sup>3</sup> In cryostorage systems, the hydrogen is stored in liquefied form. The most severe disadvantage of such systems are evaporation losses, estimated at roughly 1% per day after three days. Within about the first three days, however, the losses are negligible, since the insulation of advanced cryotanks has reached a standard that within this time the pressure build-up is so small that no hydrogen needs to be vented, and advanced technologies even allow to prolong this time.<sup>3</sup> However, the volumetric storage density of liquefied hydrogen is relatively low ( $\rho = 70.8 \text{ kg m}^{-3}$ ), and the liquefaction is energy consuming.

(3) On-board reforming of liquid hydrogen containing fuels: On-board reforming of hydrogen containing feedstocks seems an interesting alternative to direct hydrogen storage. Possible feedstocks, which have been investigated more closely and, in some cases, developed to the prototype stage, are methanol and gasoline. All three have problems with respect to practical applications. Steam reforming of methanol is technically easiest, and viable catalytic solutions have been developed by BASF AG which were tested, for instance, in the NECAR 5 by Daimler–Chrysler. One of

the most challenging problems is the reduction of the CO content of the product gas, since CO poisons the catalyst of the PEM fuel cell at the temperatures of use in present generation fuel cells. However, with preferential oxidation catalysts also this problem can in principle be solved.<sup>4</sup> The real problem seems to be more a socio-economic one: methanol as the transport form of hydrogen would need its own infrastructure, which in most countries does not seem to be acceptable, if a hydrogen based economy is the ultimate target. This would be totally different for gasoline as the hydrogen source. All of the conventional infrastructure could remain in place. However, the technical problems for higher hydrocarbon steam reforming or autothermal reforming seem so severe that they appear almost insurmountable. Reasonable rates are only achieved at temperatures well above 500 °C, and even then the activities of the catalysts are so low that the reformer would need to be unacceptably large.<sup>4</sup> Research on direct hydrocarbon reforming thus seems to have been discontinued in most car companies. In addition, one should keep in mind that with respect to CO<sub>2</sub> emissions, on-board reforming is comparable to internal combustion engines, unless the methanol or the hydrocarbon is produced from renewable feedstocks.

(4) Chemical storage in different solid storage materials: Many different materials are used for chemical storage of hydrogen which will be discussed in more detail in the following sections. Storage can be reversible or irreversible. In the latter case, severe problems arise, because the storage material has to be completely exchanged for refuelling. This contribution will thus focus on reversible materials. A recent comprehensive review on the thermal decomposition of various different hydrides (reversible and irreversible) covers many important aspects on the fundamentals and thermodynamics of binary and multinary hydrides.<sup>5</sup>

In addition to the four methods for hydrogen storage discussed above, there are also studies concentrating on storage in high surface area materials, such as carbon nanotubes or metal organic framework materials. For carbon nanotubes, after first exciting reports on very high storage capacities,<sup>6</sup> there now seems to be convergence to storage capacities in the range of slightly above 1 wt.%,<sup>7,8</sup> too low for applications in cars. Relatively low storage capacities were also reported for metal organic frameworks, where the storage capacities at room temperature and 1 MPa do, so far, not exceed 2 wt.%.<sup>9</sup>

## 2 Materials requirements and general considerations for solid storage materials

The specific requirements for mobile applications exclude many of the materials. Table 1 summarizes these requirements, another compilation of development targets can be found, for instance, in the hydrogen posture plan of the US Department of Energy.<sup>10</sup> When reading this table, one should keep in mind that most of the values are not sharply defined, but should be more considered as guidelines. Compromises may be possible, depending on the values of other parameters. For instance, if the storage capacity is sufficiently high, one may accept slower hydrogenation kinetics, since then it is not necessary to load the material to the full capacity. The loading curve typically resembles a logarithmic curve, *i.e.* the last few percent of the storage capacity take comparably long. If the overall storage capacity is high, these last percent of capacity do not have to be exploited.

A few explanations are necessary with respect to the requirements. The most stringent requirements with respect to gravimetric and volumetric storage capacities are posed by applications in cars. The background for the values given is the acceptable weight and volume of a storage tank which is around 100 kg and 100 L, respectively. In order to achieve a similar mileage per filling, target storage capacities in the range given are required. Rehydrogenation is more time crucial than dehydrogenation. Dehydrogenation should be sufficiently quick to empty the tank within a typical time

**Table 1** Requirements for complex metal hydrides as reversible hydrogen storage materials for mobile applications. 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 storage density  | > 6.5%   |
| Volumetric storage density   | > 6.5%   |
| De/rehydrogenation kinetics  | Dehydrogenation < 3 h<br>Rehydrogenation < 5 min   |
| Rehydrogenation pressure   | < 5 MPa  |
| Equilibrium pressure   | Around 0.1 MPa near room temperature   |
| Enthalpic effects  | As low as possible (but basically fixed due to requirement of reversibility near room temperature) |
| Safety   | As high as possible, <i>i.e.</i> no ignition on exposure to air or water                           |
| Cycle stability  | > 500  |
| Memory effect ( <i>i.e.</i> loss of storage capacity upon incomplete de- or rehydrogenation) | Ideally absent   |
| Price  | As low as possible (rough guideline: 100 € kg <sup>-1</sup> H <sub>2</sub> )                       |

period between refuelling plus some safety margin to have sufficiently high hydrogen flow at almost empty tank and full energy demand, which gives the estimate of roughly 3 h. Rehydrogenation time is the time which needs to be spent at the filling station, and obviously, customers would not accept much more than 5 min. The PEM fuel cell operates at a temperature of about 90 °C, and this is the temperature at which the storage system can be operated. The hydride should supply a hydrogen pressure of at least around 0.5 MPa under these conditions which means that at room temperature an equilibrium pressure around 0.1 MPa is reasonable. Since the entropy of the dehydrogenation reaction is dominated by the entropy of the gaseous hydrogen (about 40 kJ mol<sup>-1</sup>) and all other contributions can be neglected to a first approximation, the enthalpy of the decomposition of a hydride needs to be 40 kJ mol<sup>-1</sup> H<sub>2</sub> in order to result in a free enthalpy of about zero, *i.e.* an equilibrium pressure of 0.1 MPa. For a reversible storage material, there is thus not much flexibility with respect to the enthalpy changes. Cycle stability limitations are more severe for stationary applications. If on a long term perspective hydrogen is generated by solar energy, for instance, one can expect loading of such a storage module during the day, when solar hydrogen is produced, and discharging during the night, when more energy is consumed. This means in the extreme one cycle per day, and under the assumption that an energy system for a house has a lifetime of more than ten years, a cycle stability of many thousand cycles is expected. However, considering the typical lifetime of a car, a cycle stability of 500 cycles seems to be acceptable. Finally, the price estimate: if one uses the price of an internal combustion engine driven car as the benchmark, one may conclude that the tank of a fuel cell driven car should not cost much more than 1000 €. Since 5 to 10 kg of hydrogen are needed for a driving distance corresponding to the one achieved by current cars, a price estimate to create the storage material of around 100 € kg<sup>-1</sup> H<sub>2</sub> stored seems reasonable.

Most of the above considerations hold only for reversible storage systems. However, there are also concepts to generate the hydrogen by the hydrolysis of alkali metals, light metal hydrides, and complex hydrides. These concepts should briefly be addressed in the next section.

## 3 Hydrolytic generation of hydrogen

Table 2 gives a survey over some of the possible hydrolytic hydrogen storage systems. As can be seen, hydrides have in general

**Table 2** Storage capacities of some light metal hydrides, if hydrogen is released *via* hydrolysis. Reaction equations should be considered as formal only, in reality, no such well defined state would be reached. Capacities would change slightly if one would reformulate with NaBO<sub>2</sub> or NaAlO<sub>2</sub>, for instance, as products

| Hydride            | Reaction  | Storage capacity (wt.%) |
|--------------------|---|-------------------------|
| LiH                | LiH + H <sub>2</sub> O → LiOH + H <sub>2</sub>  | 7.7                     |
| LiBH <sub>4</sub>  | LiBH <sub>4</sub> + 4H <sub>2</sub> O → LiOH + H <sub>3</sub> BO <sub>3</sub> + 4H <sub>2</sub> | 8.6                     |
| LiAlH <sub>4</sub> | LiAlH <sub>4</sub> + 4H <sub>2</sub> O → LiOH + Al(OH) <sub>3</sub> + 4H <sub>2</sub>           | 7.3                     |
| NaH                | NaH + H <sub>2</sub> O → NaOH + H <sub>2</sub>  | 4.9                     |
| NaBH <sub>4</sub>  | NaBH <sub>4</sub> + 4H <sub>2</sub> O → NaOH + H <sub>3</sub> BO <sub>3</sub> + 4H <sub>2</sub> | 7.3                     |
| NaAlH <sub>4</sub> | NaAlH <sub>4</sub> + 4H <sub>2</sub> O → NaOH + Al(OH) <sub>3</sub> + 4H <sub>2</sub>           | 6.4                     |
| MgH <sub>2</sub>   | MgH <sub>2</sub> + 2H <sub>2</sub> O → Mg(OH) <sub>2</sub> + 2H <sub>2</sub>                    | 6.3                     |

high storage capacities, since the hydrogen from the hydride as well as the hydrogen from the water is liberated. One has to keep in mind, though, that no on-board regeneration of such systems is possible, so that modules have to be exchanged and workup of the spent storage material has to be done in centralized plants. Considering the costs most of the materials have, hydrolytic storage systems seem to be only suitable for niche applications.

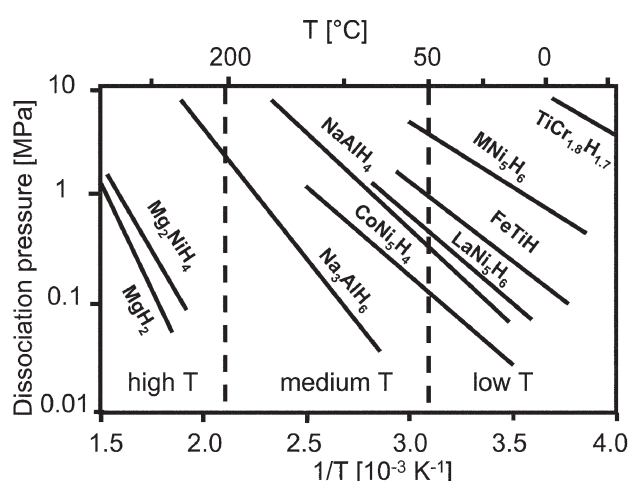
Nevertheless, there are some systems which are being considered for commercial application. The system which is promoted by the company Powerball<sup>11</sup> uses the hydrolysis of either Na or NaH. Since these compounds are not easy to handle under consumer conditions, they are coated with polyethylene in form of small balls, which are broken up under water and thus the content is hydrolyzed.

A solution which seems to be more practical is offered by Millenium.<sup>12</sup> This concept uses the fact that sodium borohydride (NaBH<sub>4</sub>) is reasonably stable in alkaline aqueous solution, but can be catalytically decomposed, a fact which has been known for over 50 years.<sup>13,14</sup> The transport and storage form is thus a 25% solution of NaBH<sub>4</sub> in 2% NaOH aqueous solution. For the release of the hydrogen, this solution is contacted with a Ru-catalyst, which induces the hydrolysis of the complex hydride,<sup>15</sup> resulting in the formation of hydrogen and an aqueous NaBO<sub>2</sub> solution. This needs to be regenerated. For the stoichiometric reaction, a hydrogen storage capacity of 7.3 wt.% can be calculated. However, since the hydride is only used in 25 wt.% solution, the capacity is reduced to 5.3% (the water is available as the solvent anyway). The advantage of this system is that the fuel is liquid and easy to handle, however, other than for the gasoline in internal combustion engines, the major product is also liquid and has to be stored on board the vehicle.

Systems like this or related systems may find niche applications or applications in high price segments. Larger scale applications, however, at present seem to be out of reach due to the high cost and complex system requirements of such solutions.

## 4 Reversible hydrides

Reversible hydrides have been technically used for quite a long time already. However, the application field is not hydrogen storage, but hydride based batteries. These hydrides, such as LaNi<sub>5</sub>H<sub>6</sub> or FeTiH, are typical low temperature hydrides, *i.e.* they have a dissociation pressure higher than 0.1 MPa already at room temperature, as can be seen in the van't Hoff diagram (Fig. 1). On the other, the high temperature side, are most of the light metal binary hydrides. MgH<sub>2</sub> is the least stable one of the ones shown, with an equilibrium pressure of 0.1 MPa slightly below 300 °C. The light alkali metal hydrides LiH and NaH are even more stable, with decomposition temperatures exceeding 500 °C. Due to their high stability, these materials are not suitable for hydrogen storage in fuel cell applications. MgH<sub>2</sub>, however, is an excellent material for reversible heat storage and can be used in solarthermal systems.<sup>16,17</sup>

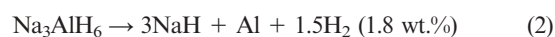


**Fig. 1** Van't Hoff plot for different metal hydrides. As can be seen in the plot, there are only few hydrides available with equilibrium pressures around 0.1 MPa in the temperature range slightly above room temperature, which is highly desirable for applications in fuel cell driven cars.

In between is at present only one material which seems to be promising on a short timescale, *i.e.* NaAlH<sub>4</sub>, which decomposes in two steps to give NaH, Al, and about 5.5 wt.% of hydrogen.

### 4.1 Sodium alanate (NaAlH<sub>4</sub>)

One of the most promising systems at present is sodium alanate, NaAlH<sub>4</sub>. Its theoretical reversible storage capacity is about 5.5 wt.%, although in practice only about 5 wt.% capacity has been reported so far. The hydrogen is released in two steps, where first the hexahydridoaluminate and then NaH and Al are formed (eqns. (1) and (2)).

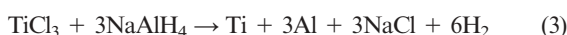


As can also be extracted from Fig. 1, the first decomposition step has an equilibrium pressure of 0.1 MPa at about 30 °C, the second step at about 100 °C. The sodium alanate is the only known complex hydride with favourable thermodynamics and an acceptable gravimetric storage capacity for use in conjunction with a PEM fuel cell system, which operates at a temperature level of about 90 °C. However, until the middle of the 1990s, it was considered impossible to rehydrogenate this material under practical conditions. There had been reports, that the NaAlH<sub>4</sub> system was reversible.<sup>18,19</sup> However, the kinetics were so slow and the conditions reported were so severe, *i.e.* temperatures of 200–400 °C (above the melting point at 183 °C) and pressures of 10–40 MPa, that practical applications seemed out of reach. This situation drastically changed when Bogdanović and Schwickardi reported that the system could be rehydrogenated under much milder conditions, if the NaAlH<sub>4</sub> was doped with small amounts of metal catalysts, the best and most thoroughly investigated being titanium.<sup>20</sup> The Ti-catalyzed decomposition of alanates, for instance of ether solutions of LiAlH<sub>4</sub>, had been known for much longer.<sup>21</sup> This triggered an intensive investigation of this system and the search for more efficient dopants or methods to dope the NaAlH<sub>4</sub>. Nowadays, most rehydrogenation experiments are carried out at temperatures slightly above 100 °C and pressures around 10 MPa. The optimum temperature is not easy to predict. Rates are higher at higher temperature, but since the hydrogen equilibrium pressure also increases with increasing temperature, this offsets to some extent the kinetic effect. Therefore, a compromise between fast rate and proximity to equilibrium has to be found. In any case, in a recent study it was described that rehydrogenation is possible also at substantially lower temperatures

and pressures, albeit on the expense of slower rates and lower capacities.<sup>22</sup>

**4.1.1 Dopants and doping methods.** Many different elements have been investigated as possible catalysts to accelerate adsorption and desorption of hydrogen.<sup>23,24,25</sup> These include predominantly titanium, zirconium and iron, but especially in the work of Bogdanović *et al.*<sup>23</sup> and Anton<sup>25</sup> almost all transition metals and also some of the rare earth elements were investigated, some of them also using different precursors. However, in spite of intensive search, titanium based materials still seem to have both the most favourable kinetics and also the highest reversible storage capacities. One should bear in mind, though, that both the actual catalyst precursor and the method of doping strongly influence the performance of the resulting materials. While the original experiments of Bogdanović and Schwickardi were carried out with titanium alkoxides, especially with titanium butoxide, which was introduced either by mixing the precursor with NaAlH<sub>4</sub> solution in THF or with slurries of NaAlH<sub>4</sub> in organic solvents, research nowadays turns more towards TiCl<sub>3</sub><sup>23,26,27,28</sup> or Ti-colloids.<sup>29,30</sup> If one compares the kinetics of the systems after doping with three different dopants, all *via* ball milling (Fig. 2), one realizes that there are pronounced differences of more than a factor of ten in hydrogenation kinetics between the three dopants. The reason for these pronounced differences is at present not clear, just like the mode of action of the catalyst is not clarified, yet. It may be related to the more homogeneous dispersion of the titanium in the materials, as suggested by a recent XRD/XAS-study.<sup>31</sup>

In addition to the differences in the kinetics, also the reversible storage capacity differs for the different dopants. As stated above, the theoretical storage capacity is around 5.5 wt.%. However, in reality, the capacity is invariably lower, due to different effects. First of all, many of the commercial NaAlH<sub>4</sub> samples are not pure, which reduces the sorption capacity appreciably. This problem can be solved by recrystallization of the raw material. Any dopant also reduces the reversible storage capacity, mostly for two different reasons. (i) The dopant adds weight to the sample, which is not used for the storage. Doping levels are mostly between 2 and 4 mol%. If heavy dopants are used, such as TiCl<sub>3</sub>, already this means a substantial reduction of storage capacity. However, even more severe is the fact that non-zero valent dopants are reduced, for instance according to eqn. (3) in the case of TiCl<sub>3</sub>.



This further reduces the storage capacity. Clearly, in this respect, zerovalent dopants are superior to dopants containing titanium in positive oxidation states. However, metallic titanium or aluminium–titanium alloys have so far proven to be unfavourable with respect to the kinetics. The titanium colloids are in principle

suitable. However, the synthesis process for these colloids is rather complex,<sup>32</sup> and for practical applications such colloidal titanium species are most probably far too expensive. The highest reversible storage capacity so far (around 5 wt.%) has been reported for TiN-nanoparticles,<sup>33,29</sup> which do not seem to be reduced under cycling conditions. However, although the storage capacities are close to the theoretical value in this case, the kinetics are too slow so that TiN cannot be considered a viable candidate for further optimization.

Important as the nature of the dopant can be, as important is the method of doping. The first studies typically used solution or slurry based synthesis.<sup>20,23</sup> Ball milling for the synthesis of doped NaAlH<sub>4</sub> was introduced in 1999<sup>34,35</sup> and is nowadays used more often than solution based methods. For doping of NaAlH<sub>4</sub> with 2% TiCl<sub>3</sub> the optimum milling time was found to be  $\approx 15$  min.<sup>25</sup> However, one should keep in mind that ball milling is a complex process and dependant on many parameters, such as the nature of the milling vessel, the material and the weight of the balls, the amounts milled and many other factors. Thus, for each system optimum conditions have to be determined. The completion of the doping process can easily be indicated by the full amount of hydrogen released according to eqn. (3). It was observed, that under the conditions of ball milling, even over-stoichiometric amounts of hydrogen are liberated, which indicates that under the milling conditions partially catalytic decomposition of the sodium alanate takes place.<sup>36</sup> It has also been observed that ball milling with diamond powder, which is not expected to react with the alanate, has a positive effect on the kinetics and reversibility of the system.<sup>37</sup>

**4.1.2 State of the catalyst and hydrogenation/dehydrogenation reaction.** The exact nature of the titanium catalyst action is still unknown. However, several facts have been elucidated, which give some insight into the reaction system. As formulated in eqn. (3), dopants are reduced to the zerovalent state during the doping reaction. This can be seen when the hydrogen evolution is recorded during ball milling of sodium alanate with various dopants. In many cases, hydrogen is recorded in an amount corresponding to eqn. (3), in case of very efficient catalysts and/or efficient milling, even more hydrogen is evolved during the doping due to the onset of the catalytic decomposition (Fig. 3).<sup>36</sup>

Additional support for the zerovalent state of the catalyst comes from detailed XRD and EXAFS studies. Such studies had been carried out for the reaction between stoichiometric mixtures of titanium halides and light metal hydrides before, and consistently, the formation of Al–Ti alloys had been observed from TiCl<sub>3</sub> and LiAlH<sub>4</sub> (Al<sub>3</sub>Ti or AlTi, depending on the molar ratios of the reagents),<sup>38</sup> from TiCl<sub>4</sub> and LiAlH<sub>4</sub> (Al<sub>3</sub>Ti after ball milling),<sup>39</sup> and from TiCl<sub>3</sub> and NaAlH<sub>4</sub> (Al<sub>3</sub>Ti after ball milling).<sup>40</sup> However, at the doping level normally used for hydrogen storage applications, *i.e.* <5%, no clear indications of alloy formation have been

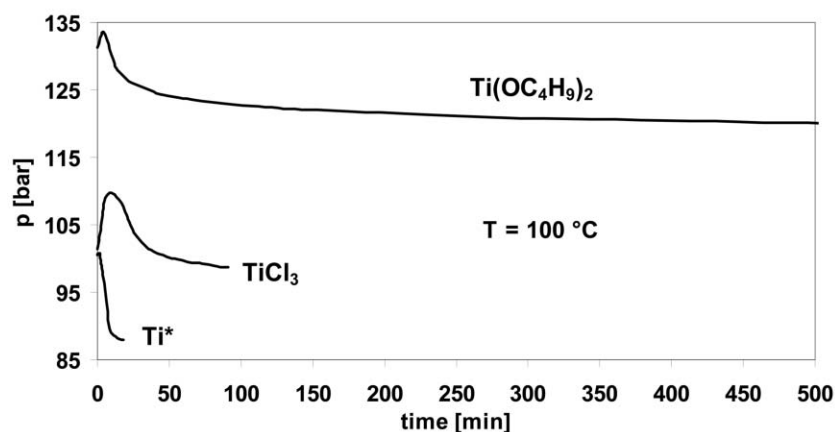
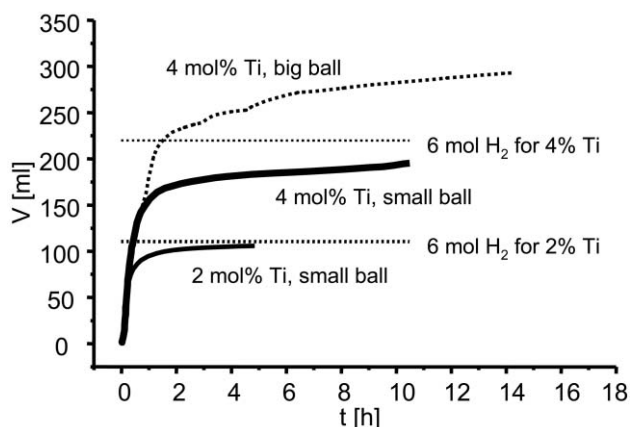


Fig. 2 Rehydrogenation curves for NaAlH<sub>4</sub> doped with different doping agents *via* ball milling.



**Fig. 3** Evolved hydrogen over milling time during the ball milling of  $\text{NaAlH}_4$  with  $\text{TiCl}_3$  under different conditions. The horizontal lines indicate the amount of hydrogen expected for full reduction of the  $\text{TiCl}_3$  to zerovalent titanium according to eqn. (3).

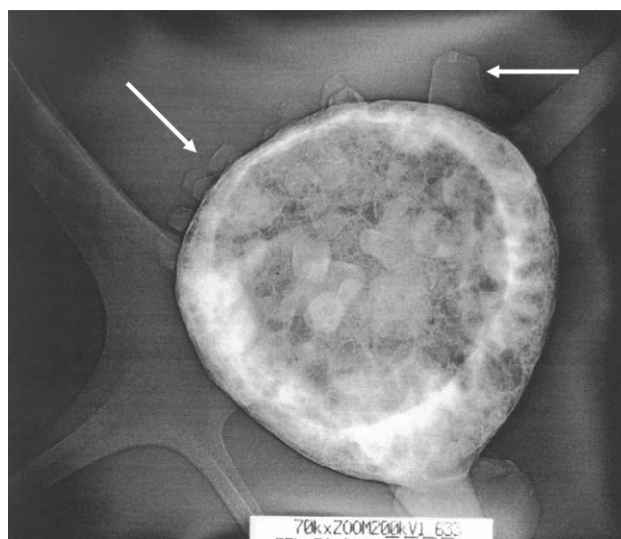
observed so far. A shoulder in XRD reflections of the aluminium in a dehydrogenated sample have tentatively been attributed to the formation of an  $\text{AlTi}$  alloy, but no clear assignment was possible.<sup>41</sup> A recent, similar study reproduced these findings, however, due to the use of synchrotron radiation, signal to noise ratios were improved.<sup>42</sup> Also Gross *et al.*<sup>28</sup> have suggested the formation of  $\text{Ti-Al}$  phases as an important step, but no experimental evidence could be given in these earlier publications.

More clarity on the state of the aluminium could be obtained, after milling of 4 mol%  $\text{TiCl}_3$  with  $\text{NaAlH}_4$  and subsequent dissolution of the residual, unreacted  $\text{NaAlH}_4$  in THF. XRD analysis of the remaining solid only gave reflections corresponding to metallic aluminium and  $\text{NaCl}$  formed as a product of the doping reaction. No evidence for either metallic titanium or an  $\text{Al-Ti}$  alloy was observed. This changed upon heating to elevated temperatures, though gradually, the formation of an  $\text{Al}_3\text{Ti}$  alloy was observed in the XRD which proves that titanium was present in the sample in X-ray amorphous form.<sup>43</sup> This result was corroborated by XAS analysis of titanium doped  $\text{NaAlH}_4$  samples in various stages of the dehydrogenation/hydrogenation reaction.<sup>31</sup> Already after doping, the signature of zerovalent titanium could clearly be identified in the XANES region of the spectra. More detailed analysis of both the XANES and EXAFS region of the spectra give strong indications, that the titanium is present in a form resembling an  $\text{Al}_3\text{Ti}$ -like local environment both in the hydrogenated and the dehydrogenated state.

This view, however, is not undisputed. There are publications in the literature, where changes of the  $\text{NaAlH}_4$  lattice parameters have been reported, which were attributed to incorporation of Ti with a charge between +2 and +4 on sodium sites.<sup>44</sup> However, we have never observed such changes in our own measurements. Moreover, substitution of titanium on aluminium sites would be more plausible from a crystal chemical point of view, and quantum chemical calculations rather favour aluminium substitution than sodium substitution.<sup>45</sup> However, in these calculations only different substitution models have been compared, not the full reduction of the titanium and formation of titanium species highly dispersed in aluminium. The quantum chemical study could thus only discriminate between possible modes of substitution, if substitution is assumed to occur, but not distinguish between substitution of titanium in the  $\text{NaAlH}_4$  framework and reduction of titanium to the zerovalent state. Based on all our own evidence and results from the literature we propose that titanium is in the zerovalent state highly dispersed in an aluminium matrix in the working hydrogen storage material. The better the dispersion, both on an atomic level and on the meso- to macroscopic scale, the better is the kinetics of the hydrogenation/dehydrogenation reaction. It is clear,

that the use of different precursors and preparation methods can influence this dispersion, either on only one level or on both, and thus have a strong influence on the kinetics of the reaction.

Although the state of the titanium in the alanate seems to be clear, the mode of action is still poorly understood.  $\text{H}_2/\text{D}_2$  scrambling experiments<sup>46</sup> have shown that the titanium facilitates hydrogen dissociation at the surface of the storage material which may contribute to the enhanced de- and rehydrogenation rates. However, this cannot be the only factor controlling the overall rate of the reaction, since the timescale of  $\text{H}_2/\text{D}_2$  scrambling at room temperature is much shorter than re- and dehydrogenation times under these conditions. Several studies have shown that these reactions are associated with massive mass transfer.<sup>23,41,47,31</sup> While sodium and aluminium are mixed on an atomic scale in the sodium alanate, they are phase separated on the scale of several hundred nanometers in the dehydrogenated material which consists of  $\text{NaH}$  and  $\text{Al}$  (probably alloyed with  $\text{Ti}$ ). This can clearly be seen in the TEM pictures of such a sample (Fig. 4). Micrometer sized aluminium particles are present which are decorated with  $\text{NaH}$  crystallites. EDX elemental analysis corroborates the results of the XRD and EXAFS study: the titanium is exclusively associated with the aluminium phase in the dehydrogenated material. Since the dehydrogenation and rehydrogenation reactions take place on timescales of less than ten minutes for optimized samples, mass transfer of sodium and/or aluminium must occur over micrometer distances also on this timescale. Incorporation of titanium in the material may help to facilitate this mass transfer and thus increase the rate of de- and rehydrogenation. One may be tempted to invoke local melting as a major factor in allowing such fast mass transfer (the melting point of  $\text{NaAlH}_4$  is only 183 °C) due to the exothermic hydrogenation reaction. However, this would only explain the hydrogenation, but not the migration of atoms over  $\mu\text{m}$  length scale in the dehydrogenation, which is correspondingly endothermic. Aluminium transport *via* the mobile  $\text{AlH}_3$  has also been suggested as a means to provide sufficient mass transfer rates.<sup>48</sup> However, so far no experimental evidence could be found for the intermediate formation of  $\text{AlH}_3$  or related species. The rehydrogenation reaction thus seems to be a process occurring initially at the interface between aluminium and  $\text{NaH}$  particles, where first  $\text{Na}_3\text{AlH}_6$  is formed. In later stages, several gas solid reactions have to proceed, *i.e.* the conversion of  $\text{Na}_3\text{AlH}_6$ ,  $\text{Al}$  and  $\text{H}_2$  to give the tetrahydride as well as further transformation of  $\text{NaH}$ ,  $\text{Al}$  and  $\text{H}_2$  to convert the remaining  $\text{NaH}$  to  $\text{Na}_3\text{AlH}_6$ . There are indications, that under some conditions, the aluminium particles may be



**Fig. 4** TEM image of a dehydrogenated titanium doped  $\text{NaAlH}_4$  sample. The light shaded areas on the periphery of the particle are  $\text{NaH}$  crystals (indicated by arrows), the bulk of the particle consists of aluminium, together with titanium, according to EDX analysis.

covered rather effectively by a layer of  $\text{Na}_3\text{AlH}_6$ , and that the remaining aluminium in the core of the particles is excluded from further reaction.<sup>41</sup> This could be one of the reasons why rehydrogenation is often incomplete. It was found that addition of excess aluminium could drive the reaction to completion, since this added aluminium was not protected by the hexahydride shell.<sup>41</sup>

Even if mass transfer is the rate limiting step, the dehydrogenation kinetics can still be described by a simple Arrhenius type rate law. In a very careful study of the dehydrogenation of pure  $\text{NaAlH}_4$  and samples doped with different amounts of titanium down to room temperature, Sandrock *et al.* found, that both stages of the decomposition follow an Arrhenius rate law.<sup>26</sup> Addition of titanium leads to an increase of the rate constant for both decomposition steps over several orders of magnitude (Fig. 5). Interestingly, if one determines the activation energy in dependence of the titanium content, one realizes, that the activation energy only decreases on titanium addition at low loading levels (0.9% was the smallest loading investigated) from about  $120 \text{ kJ mol}^{-1}$  to about  $80 \text{ kJ mol}^{-1}$ . Further increase of the rate at higher titanium levels must therefore be attributed to changes in the preexponential. This suggests that the mode of action of the catalyst is not a single one, but that at least two different factors contribute to the rate increase. One may speculate that the decrease of the activation energy is due to the hydrogen dissociation, for which small amounts of titanium may be sufficient, and that additional titanium provides more and more pathways for facile diffusion of the constituent atoms. However, this is purely speculative at this point, and certainly more work is necessary to clarify the mechanism of the titanium catalyzed reaction.

In this study, the dehydrogenation of the hexahydride was observed to have a higher activation energy (slightly below  $100 \text{ kJ mol}^{-1}$ ). Recently it was observed that the activation energy of the dehydration of a freshly doped hexahydridoaluminate was in fact identical to the one of the  $\text{NaAlH}_4$ ,<sup>49</sup> both for titanium ( $100 \text{ kJ mol}^{-1}$ ) and zirconium ( $135 \text{ kJ mol}^{-1}$ ) doping. The absolute values differ compared to ref. 26, the reason for which is not clear at present.

#### 4.1.3 Considerations with respect to practical applications.

Favorable thermodynamics, kinetics and storage capacity alone are not sufficient for practical applicability. For use of hydride based materials in practical systems, additional engineering problems

have to be solved. In a study concerning the scale up of the alanate system, Sandrock *et al.*<sup>50</sup> studied the behaviour of a 100 g bed in hydrogenation and dehydrogenation. When larger amounts of storage material are handled, especially the heat released upon reloading is a severe problem and needs to be efficiently removed. In the study mentioned, the temperature increased during the loading within one minute from  $155 \text{ }^\circ\text{C}$  to  $234 \text{ }^\circ\text{C}$ , substantially above the melting point of the alanate. However, this does not seem to have had a detrimental effect on the performance, as the authors state. Sintering of the bed to a "porous, reasonably strong mass" occurred over four cycles, the density being  $0.85 \text{ g cm}^{-3}$ . Although such a sintered mass may have advantages over loose powder (reduced particle migration, better gas distribution, safety), melting or partial melting of the bed during recharging will certainly be undesired, since this generated an ill-defined stage of the material. The development of an efficient heat exchange system will therefore be an engineering challenge which needs to be solved.

Another problem which has to be solved from an engineering point of view are the volume changes associated with charging and discharging. X-ray densities give the intrinsic limiting values for the changes to be expected. From these data<sup>50</sup> one can conclude that the first step of the dehydrogenation corresponds to a volume contraction of 30.3%, the second step to an expansion of 13.8%. The overall net effect is thus a contraction by 16.5% from the fully hydrogenated to the fully dehydrogenated state. This agrees well with the contraction of 14.7% observed for the 100 g bed.<sup>50</sup> The results obtained for the 100 g bed essentially corresponded to those obtained with a 72 g bed.<sup>51</sup> This study also demonstrated good cycle stability. Stable capacities and hydrogenation/dehydrogenation rates were observed over the course of a 116 cycle test for a  $\text{TiCl}_3$  doped material. A similar observation was made in our laboratory, where also a test involving more than 100 cycles showed stable capacities and rates (Fig. 6).

Safety of a hydride based storage system is an issue with respect to practical implementation as well. Although also the tank in a gasoline driven car certainly creates a safety problem, a novel technology should nevertheless address this issue.  $\text{NaAlH}_4$ , especially when loaded with titanium, is a very reactive solid, which can ignite with air or moisture. Strategies have to be developed which reduce this problem. One such strategy could be the encapsulation of the material in an inert high porosity solid which keeps the alanate in a distributed form so that local

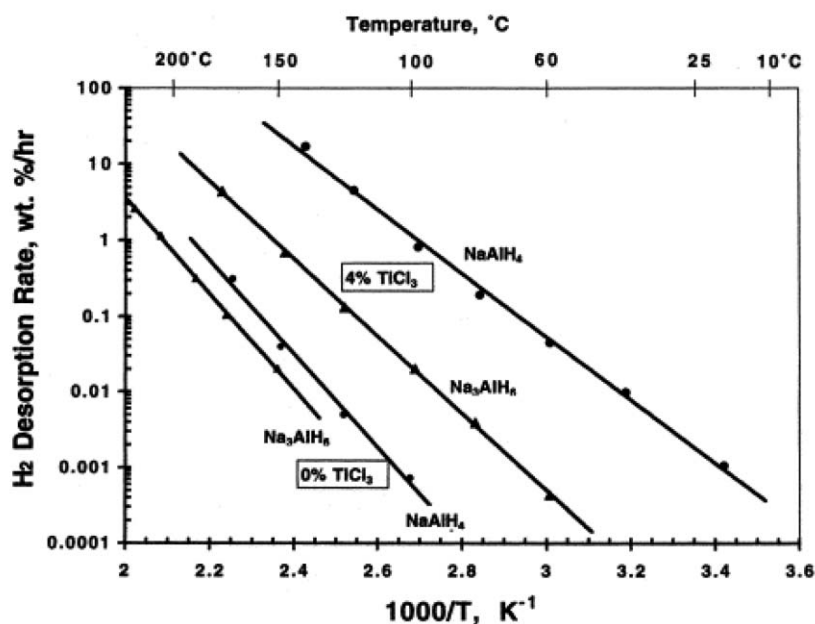
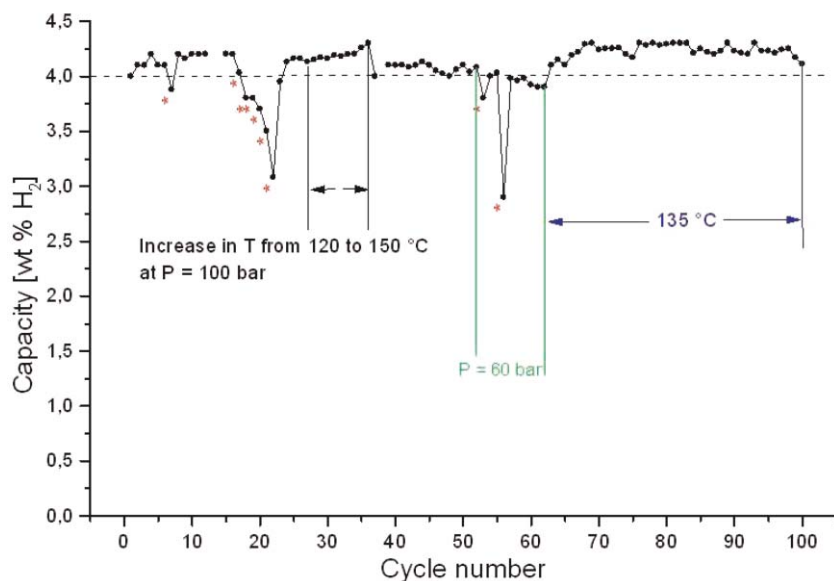


Fig. 5 Arrhenius plots of the dehydrogenation kinetics for the two steps of sodium alanate decomposition with and without titanium doping (from ref. 48, with kind permission).



**Fig. 6** Cycle stability of NaAlH<sub>4</sub> doped with TiCl<sub>3</sub> *via* ball milling. Typical conditions were 120 °C, 10 MPa initial pressure for rehydrogenation. In some cases temperatures or pressures were changed, as indicated in the figure. Asterisks indicate cycles which were carried out for times too short for complete rehydrogenations in order to check for possible memory effects.

temperature excursions do not immediately lead to a runaway of the reaction. However, work in this direction is only at its beginning, since some of the more immediate problems addressed in the previous sections have to be solved first.

#### 4.1.4 Options for improvements in the NaAlH<sub>4</sub> system.

Improvements of the system are possible in three directions: (i) the kinetics is still not fully satisfactory, (ii) the storage capacity should be increased, and (iii) the thermodynamics is not optimal for use in conjunction with PEM fuel cells. While the first goal can be reached with improved catalysts or methods for doping, the last two possibilities require changes of the chemical composition of the systems, *i.e.* partial substitution of elements.

With respect to the improvement of the kinetics, there does not seem to be a principle limit reached, yet. Although many catalysts have already been screened, it is by no means obvious, that titanium really is the best material, especially, since the method of doping and the compound used were found to have a very strong influence as well. Over the last years, we have seen a gradual increase of the rehydrogenation rates, both brought about by new methods of doping and new precursor compounds. Also the combination of different dopants is only little explored. We have observed, that the combination of titanium and iron can lead to a synergistic effect, the group of Jensen has reported, that addition of zirconium (in form of the propoxide) selectively accelerates the decomposition of the second step.<sup>35</sup> Still different doping methods can be explored, and also this route seems promising. The direct synthesis, starting from NaH, Al and H<sub>2</sub> in the presence of a catalyst,<sup>52,53,54,55</sup> is very advantageous from an economic point of view due to the cheap raw materials, but has also been reported to yield materials with improved system kinetics.<sup>54</sup> Moreover, this method could be modified in that not a separate titanium compound is used to introduce the catalyst, but that a Ti/Al alloy serves as raw material. Little data is available for this pathway,<sup>56,57</sup> and our own experiments in this direction did so far not result in the production of materials with improved performance. However, since many different parameters have to be investigated, this does by no means say that no more improvements can be achieved following such routes.

In order to improve the storage capacity, improved catalyst systems, for which less catalyst is needed, already helps to some extent. If bigger changes are desired, substitution of Na and/or Al are the only options, which shifts the focus of attention to other

complex hydrides, such as LiAlH<sub>4</sub> or NaBH<sub>4</sub>. However, one does not necessarily substitute one of the elements completely, since also mixed hydrides are known. First steps in this direction have been undertaken theoretically, where it has been shown that substitution of Na by Li should reduce the hydrogen affinity, while substitution of K should increase it.<sup>58</sup> This is in principle an interesting finding because it shows that in general the energies will change. However, experimentally it was found for the compound LiNa<sub>2</sub>AlH<sub>6</sub> the dissociation pressure was lowered<sup>59</sup> so that the calculations should be re-examined. Also substitution of Al by B or Ga have been studied theoretically,<sup>58</sup> and in this case both substitutions are predicted to decrease the stability of the hexahydridoaluminate, which would mean that the dissociation temperature of the second step would approach the one for the first step, which is technically very desirable. Whether the predictions can experimentally be confirmed remains to be seen.

## 4.2 Other hydrides

In the last section replacement of some of the constituent elements of NaAlH<sub>4</sub> has already been addressed which brings the discussion to alternative hydrides. Most other light metal hydrides are studied to a much lesser extent than the NaAlH<sub>4</sub> system, for many there are only reports on the synthesis in the literature, but no properties relevant for hydrogen storage are known. Selected examples of such hydrides will be discussed in the following. The focus will be on such systems with a sufficiently high storage capacity to make them interesting for practical applications. Systems such as KAlH<sub>4</sub>, for instance, which has been reported to be reversible at higher temperatures<sup>60</sup> but has an even lower capacity than NaAlH<sub>4</sub>, will therefore not be included

**4.2.1 Other alanates.** Of the well studied alanates, only NaAlH<sub>4</sub> has favourable thermodynamic properties for hydrogen storage. LiAlH<sub>4</sub> is kinetically stabilized, but thermodynamically too unstable, it decomposes already below room temperature. However, with LiAlH<sub>4</sub> an important aspect can be highlighted. The catalysis of the dehydrogenation reaction is not restricted to NaAlH<sub>4</sub>, but seems to be more general also for other alanates. If LiAlH<sub>4</sub> is ball milled with titanium compounds, part of the hydrogen is released already under the conditions of the ball milling,<sup>39,61,62</sup> which does not occur without the titanium compound. This would suggest that the titanium acts primarily

on the  $[\text{AlH}_4]^-$  unit which is present in most alانات. Even reversible storage up to 1.8 wt.% has been reported for titanium catalyzed  $\text{LiAlH}_4$ , although no full dehydrogenation/rehydrogenation cycles have been carried out, but only DSC and TG analysis.<sup>63</sup>

Of the alkaline earth metal alانات, only  $\text{Mg}(\text{AlH}_4)_2$  has an attractive gravimetric storage density with slightly above 7 wt.%, if one does not consider beryllium alانات, which is impractical due to the toxicity of beryllium and its compounds. Pure  $\text{Mg}(\text{AlH}_4)_2$  has recently been prepared by Fichtner and Fuhr,<sup>64</sup> and in a combination of powder XRD and theoretical studies on the DFT-level, the structure of  $\text{Mg}(\text{AlH}_4)_2$  could be determined as a sheet like structure of the  $\text{CdI}_2$  type.<sup>65</sup> As interesting as  $\text{Mg}(\text{AlH}_4)_2$  may in general be, the thermodynamic properties of this material appear to be unfavourable for reversible hydrogen storage under practical conditions, as the enthalpy seems to be close to  $0 \text{ kJ mol}^{-1}$ .<sup>66</sup>

The alانات of the heavier alkaline earth metals probably have too low gravimetric storage density for practical applications, but they should be mentioned here nevertheless. In addition to  $\text{Mg}(\text{AlH}_4)_2$ ,<sup>67</sup> also  $\text{Ca}(\text{AlH}_4)_2$ <sup>68</sup> was recently obtained by a relatively simple ball milling process from the alkaline earth hydrides and  $\text{AlCl}_3$ . However, the product is mixed with the alkaline earth chloride, which is formed as a byproduct and which is rather difficult to separate from the hydride.  $\text{Sr}(\text{AlH}_4)_2$ <sup>69,70</sup> on the other hand, can be synthesized directly by ball-milling from the two binary hydrides and is obtained in pure form.

Compared to the alkali alانات, the alkaline earth alانات on first sight seem to follow a different decomposition pathway. Instead of the hexahydrides  $\text{M}_3\text{AlH}_6$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) the pentahydrides  $\text{MAlH}_5$  are normally formed as intermediate phases, having sometimes rather interesting structures, as in the case of  $\text{BaAlH}_5$ .<sup>71</sup> However, if one inspects the structures more closely, they are rather similar. The pentahydrides can be considered as H-bridged hexahydrides, and the decomposition pathways may be related. In addition, also higher hydrides, such as  $\text{Sr}_2\text{AlH}_7$  are known.<sup>72</sup>

**4.2.2 Boron hydrides.** With respect to gravimetric storage density, the complex boron hydrides would be ideal candidates.  $\text{LiBH}_4$  has the highest gravimetric storage capacity of the complex hydrides with 18.4 wt.% (if one disregards  $\text{Be}(\text{BH}_4)_2$  which would be impractical due to the beryllium content). However, complex boron hydrides suffer from two problems. Firstly, the thermodynamic properties are unfavourable for use in mobile hydrogen storage applications (except hydrolytic storage, see above), since the boron hydrides are much more stable than the corresponding alانات. Second, volatile boranes can be formed in small amounts during the decomposition of boron hydrides, which (i) could damage subsequent aggregates in a fuel cell system and (ii) over time would lead to loss of storage capacity, and (iii) are quite toxic.

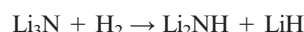
$\text{LiBH}_4$  starts to decompose thermally above  $320^\circ\text{C}$ , with the major decomposition proceeding between  $400$  and  $600^\circ\text{C}$ . The total amount released as typically only around 50% of the theoretical capacity. There is work of the group of Züttel *et al.* where it is reported that addition of  $\text{SiO}_2$  powder can reduce the onset temperature of the decomposition and that 9 wt.% of hydrogen are already released below  $400^\circ\text{C}$ .<sup>73,74</sup> The mechanism of this acceleration of the hydrogen release is not clear, yet. In principle, decomposition of the stable hydrides could be made easier, if compounds would be added which form either stable compounds with the boron generated by the boron hydride decomposition or with the  $\text{LiH}$  generated, thus providing an additional thermodynamic driving force. However, on the other hand that would lead to a reduction of the storage density.

The same considerations as for  $\text{LiBH}_4$  are valid for  $\text{NaBH}_4$ . This system, however, is even less well investigated than the  $\text{LiBH}_4$  for reversible hydrogen storage. In the unmodified form, the thermodynamic properties are certainly not favourable for

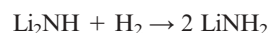
reversible storage, with  $\Delta G_f(298) = -123.9 \text{ kJ mol}^{-1}$ . Even less well known are the alkaline earth boron hydrides.

**4.2.3 Miscellaneous systems.** There are some other systems which do have interesting properties. With respect to storage capacity, lithium beryllium hydrides are amongst the best materials. Ball milling of  $\text{LiH}$  with  $\text{Be}$  and subsequent hydrogenation at temperatures above  $250^\circ\text{C}$  leads to different lithium beryllium hydrides of the general formula  $\text{Li}_n\text{Be}_m\text{H}_{n+2m}$ .<sup>75</sup> The material with  $n:m = 3:2$  has an equilibrium pressure of 1 atmosphere at around  $250^\circ\text{C}$  and can reversibly store around 8 wt.% hydrogen. As interesting as these properties may be, the toxicity of beryllium will certainly prevent larger scale applications.

An interesting lithium based system is  $\text{Li}_3\text{N}/\text{Li}_2\text{NH}$ .<sup>76</sup> Lithium nitride can be hydrogenated to lithium imide and lithium hydride (5.4 wt.%  $\text{H}_2$ ) according to



The imide formed can be hydrogenated in a second step to the amide (6.5 wt.%)



The second reaction can be used for reversible storage around  $250^\circ\text{C}$ . It is reported, that ammonia formation can be avoided completely, especially, if 1%  $\text{TiCl}_3$  is added to the system, which has the positive additional effect to improve the kinetics.<sup>77</sup> Very fast kinetics have been reported for a partially oxidized lithium nitride.<sup>78</sup> However, one has to keep in mind that  $\text{NH}_3$  would poison the polyelectrolyte membrane of the conventional PEM fuel cells, which is nowadays used, even at trace levels, so that even the smallest ammonia slip cannot be tolerated presently.

Related to the storage in carbon nanotubes is hydrogen storage in inorganic nanotube materials, which was recently reviewed by Chen and Wu.<sup>79</sup> Gravimetric storage capacities range around 1%, occasionally slightly higher. With respect to gravimetric storage capacity, the materials formed from the light elements seem to be most attractive, especially BN-nanotubes. For so-called "collapsed nanotubes" an uptake of 4.2 wt.% at 10 MPa hydrogen pressure was reported.<sup>80</sup> However, the majority of the hydrogen is only released at temperatures between  $300$  and  $450^\circ\text{C}$ , suggesting that it is bound to dangling bonds, which were formed during the collapse of the nanotubes. Cycling experiments were not performed, so that it is at present not clear, what the perspectives for such materials are.

In addition to the systems discussed so far, there is a multitude of transition metal complex hydrides which have been synthesized and studied structurally by the groups of Bronger,<sup>81</sup> Yvon,<sup>82</sup> Noreus<sup>83</sup> and many others. However, for practical large volume applications these systems are either too expensive or have an insufficient gravimetric storage density. Remarkable among them is  $\text{Mg}_2\text{FeH}_6$ <sup>84,85</sup> which shows high storage capacity (5.5 wt %  $\text{H}_2$ ), an exceptionally high volumetric hydrogen density ( $150 \text{ kg m}^{-3}$ ) and excellent stability in cycle tests.<sup>86</sup> The thermodynamic properties do not allow the use of  $\text{Mg}_2\text{FeH}_6$  for hydrogen storage in mobile applications. However, it is a promising candidate for thermochemical high temperature ( $400$ – $500^\circ\text{C}$ ) thermal energy storage, as for instance required for solar thermal power plants.

## 5 Conclusions

The discussion above has shown, that tremendous success has been achieved over the last few years in reversible hydrogen storage in complex metal hydrides, and the properties of some of the systems, most notably doped sodium alانات, are approaching the performance needed for technical applications. However, the storage capacities reached so far do not exceed 5wt.%, and for



sufficiently quick rehydrogenation (<10 min) the required conditions are still too severe.

If one considers the rate at which progress has occurred over recent years, it can be expected that the limits will be pushed further in the years to come. It is clear, though, that the most promising system today, NaAlH<sub>4</sub>, will not meet the criteria formulated by various organizations and industrial companies. For system capacities over 5wt.%, other materials will have to be developed, possibly based on boron hydrides or lithium imide as discussed above. The future will show whether systems based on chemical storage will be able to compete with high pressure storage systems or ones based on cryo-tanks.

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