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Tailoring Thermodynamics of Hydrogen Storage Materials

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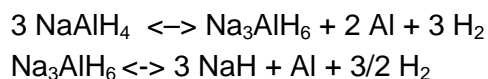
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Hydrogen has the potential to serve as clean and versatile energy carrier, but efficient, reliable and safe storage systems have to be developed for a future hydrogen economy. Besides pressurized gas or liquid hydrogen tanks, solid state storage systems are a viable alternative. However, the materials investigated so far for solid state storage still show too low capacity at sufficiently low working temperatures to meet the targets set by the automotive industry. This is not necessarily due to the amount of stored hydrogen but thermodynamic and kinetic reasons restraining the application. Two alternative pathways to adjust thermodynamic properties are currently discussed: (i) restriction of particle sizes of the active material or (ii) the use of a reaction system introducing a second partner to alter the final products and thus the reaction enthalpy [1, 2].

Among the materials with the largest amount of hydrogen stored are complex hydrides such as aluminohydrides (e.g. NaAlH_4) or borohydrides (e.g. $\text{Mg}(\text{BH}_4)_2$, LiBH_4) or amides ($\text{Mg}(\text{NH}_2)_2 + x \text{ LiH}$ composites). They have in common that hydrogen is released in a solid state reaction and the desorbed state is comprised of two or (more) segregated solid phases. Upon rehydrogenation the opposite reaction has to take place and the reaction kinetics is mainly determined by mass transfer. That is the reason why initial investigations on free standing small particles of NaAlH_4 suffered from insufficient reversibility. One possibility to circumvent this problem is the encapsulation of a complex hydride in a mesoporous host [3, 4, 5, 6].

1 NaAlH_4 and Mesoporous Host Materials

Among the most studied materials for solid state hydrogen storage is NaAlH_4 . Using a transition metal based additive e.g. TiCl_3 , or ScCl_3 reversible hydrogen uptake can be achieved at moderate temperature and pressure conditions (temperatures and pressures below 150°C and 100 bar H_2 , respectively). Hydrogen is released in a two step reaction [7]:



and in total 5.6 wt% H_2 are liberated. Under the condition outlined above, NaH can not be decomposed ($T_{\text{des}} > 400^\circ\text{C}$) nor does uncatalysed NaAlH_4 show any significant H_2 desorption.

In order to elucidate the hydrogen sorption properties of nanoscaled particles of NaAlH_4 composites of NaAlH_4 and different carbon host material have been studied.

NaAlH_4 (Albemarle, purity 96%) was used as received, while the carbon materials were heated in Ar/H_2 gas stream prior to any use to remove water and other volatile impurities. Various composites were prepared either by melt infiltration ($T_{\text{m}}(\text{NaAlH}_4) = 181^\circ\text{C}$) under H_2 pressure or by ball milling in Ar atmosphere. The pore widths distributions of the host materials (except graphite) show the majority of pores to be in the range of 1-4 nm. The samples were chosen as to compare different hosts (i.e. surface area, ash content and transition metal impurities of the carbon) and preparation methods (melt infiltration, ball milling), a summary is given in table 1.

Table 1

Carbon (surface area / free pore volume)		NaAlH_4 content [wt%] Preparation method	Remarks
ACF 25 (transition metal and ash free carbon fibre made from organic precursors)	1815 m^2/g 0.66 cm^3/g	ACF #1 (M): 48 wt% ACF #2 (M): 31.6 wt% Melt infiltrated (185°C , 160 bar H_2)	#1: (crystallographic) NaAlH_4 volume equals free pore volume
Activated carbon AC Alfa Aesar Transition metal impurities	1170 m^2/g 0.48 cm^3/g	AC (M): 50 wt% Melt infiltrated (185°C , 150 bar H_2), AC (BM): 50 wt% Ball milled 10 min (600rpm)	Excess NaAlH_4 compared to free pore volume
PFA 600 preparation according to Ref. [8] Transition metal and ash free carbon	774 m^2/g 0.33 cm^3/g	PFA (BM): 50 wt% Ball milled 10 min (600rpm, Si_3N_4 vial and balls)	Excess NaAlH_4 compared to free pore volume
Graphite	-	GR (BM): 50 wt% Ball milled 10 min	

Figure 1 shows the first and second desorption for the various samples measured in a Sieverts' type apparatus ($T = 150^\circ\text{C}$, reabsorption took place at 125°C and 100 bar H_2). The amount of released hydrogen has been normalized to the weight of the active material NaAlH_4 to facilitate comparison of the data. All composites show reversible H_2 uptake, independent from the preparation method with the exception of non-porous graphite. The ball milled samples AC (BM) and PFA (BM) release almost 5 wt.% H_2 in the initial desorption while the melt infiltrated samples show considerably lower values. Presumably, some hydrogen is already released during melt infiltration. This is in agreement with the XRD data which show some Al and Na_3AlH_6 alongside NaAlH_4 after preparation. In the second desorption (after rehydrogenation) less hydrogen is released. However, there is no clear trend for the reversible capacity in dependence on the carbon host.

It is well known that carbon based additives enhance kinetic performance of the hydrogen sorption of NaAlH_4 [9]. In order to investigate the influence on the thermodynamic properties, pressure-composition isotherms were measured for the various composites (except

graphite). In the former case, the smaller particle size increases the surface contribution to the free energy in both the hydrogen rich and poor phase and thus changes of the reaction enthalpy are expected [10]. However, the relevant particle sizes are quite small e.g. for Mg/MgH₂ significant changes are predicted to occur at particle sizes below 1.3 nm [11]. The results for NaAlH₄ – carbon composites are summarized in Figure 2. The measurements were done during absorption at 140 °C and the pressure was increased stepwise following by some rest time (typically 20 000s) to allow the sample to reach equilibrium.

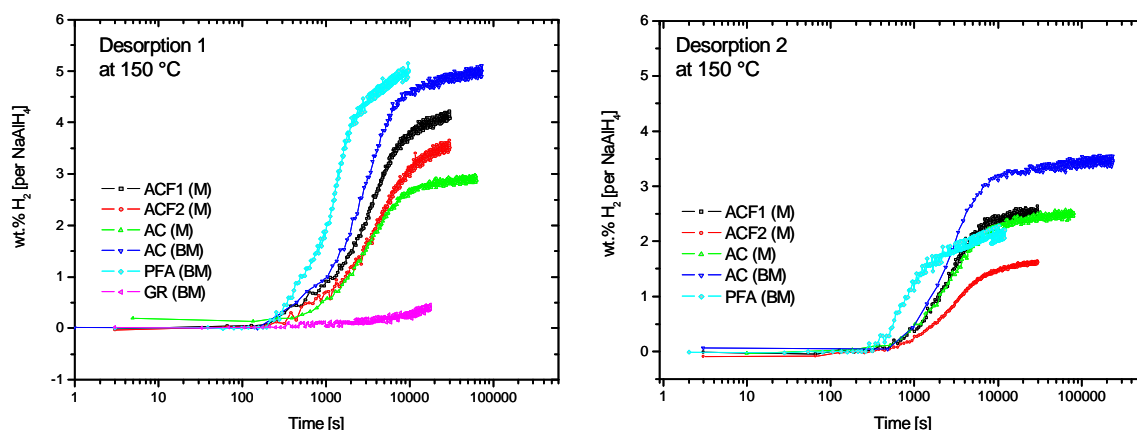


Figure 1: Desorption 1 and 2 of various NaAlH₄-carbon composites at 150 °C. Composites of NaAlH₄ and mesoporous carbon show reversible H₂ uptake while composites with graphite show hardly any hydrogen release.

The obtained PCI curves are significantly changed compared to the data obtained for NaAlH₄ (doped with 4 mol % CeCl₃, shown in the inset). Besides the lower H₂ capacity, most prominently, the two plateaus (originating from the two reaction steps) get smaller while simultaneously a sloping region develops extending to low pressures and low hydrogen concentrations. This feature is most prominent for sample ACF 1 (M) where the original plateaus have completely vanished. A similar PCI is observed for sample ACF 2 (M) (not shown)[12]. For these two samples, the NaAlH₄ content is chosen in such a way that the volume of the active material equals or is smaller than the available free pore volume. In all other samples a surplus of NaAlH₄ was contained in the samples. These results suggest that the small remains of the original plateau stem from NaAlH₄ outside the pores. This is catalysed although not very efficiently by the carbon, and as a result, “bulk” like plateaus are observed in the PCI measurements. In contrast, NaAlH₄ that is in close contact with the mesoporous host (i.e. inside the pores) exhibits altered thermodynamic properties.

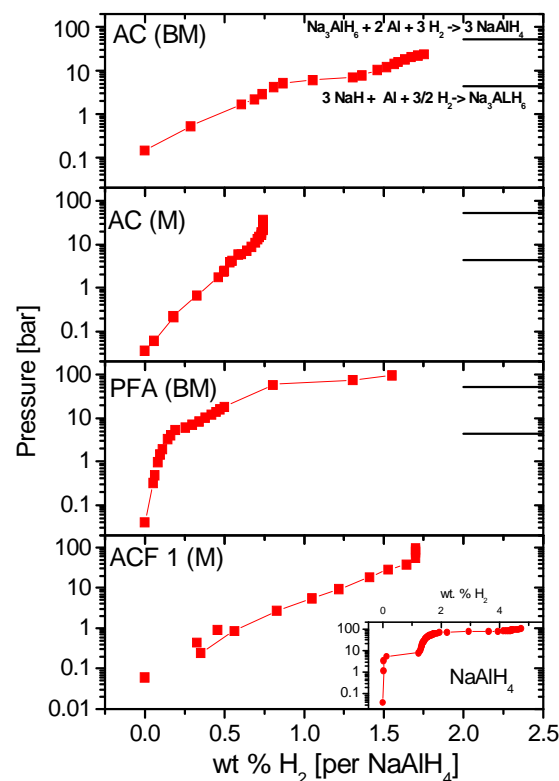
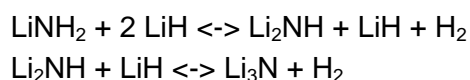


Figure 2: Pressure composition isotherms of various NaAlH_4 –carbon composites at 140 °C. The inset shows the PCI obtained for NaAlH_4 catalysed with 4 mol% CeCl_3 , moreover the expected plateau pressures for reaction step 1 and 2 are indicated (Data from Ref [7]).

2 Reaction Based Systems: $\text{Mg}(\text{NH}_2)_2 + x \text{LiH}$

Another potential route changing thermodynamics is by use of so called reactive hydride composite mixtures. For these compounds thermodynamic parameters of a single component are changed by the presence of a second one. In 2000, Chen et al. [13] presented a Lithium amide based reaction system that reversibly takes up hydrogen according to the following reactions:



and in total 10.4 wt% H_2 are liberated at temperatures up to 320°C. The single compounds emit either ammonia (LiNH_2) or need higher temperatures for decomposition ($T_{\text{LiH}} > 600^\circ\text{C}$). Substituting LiNH_2 with the analogue magnesium compound lowers the operating temperature to ~ 200°C and the overall reaction can be described as [14, 15]



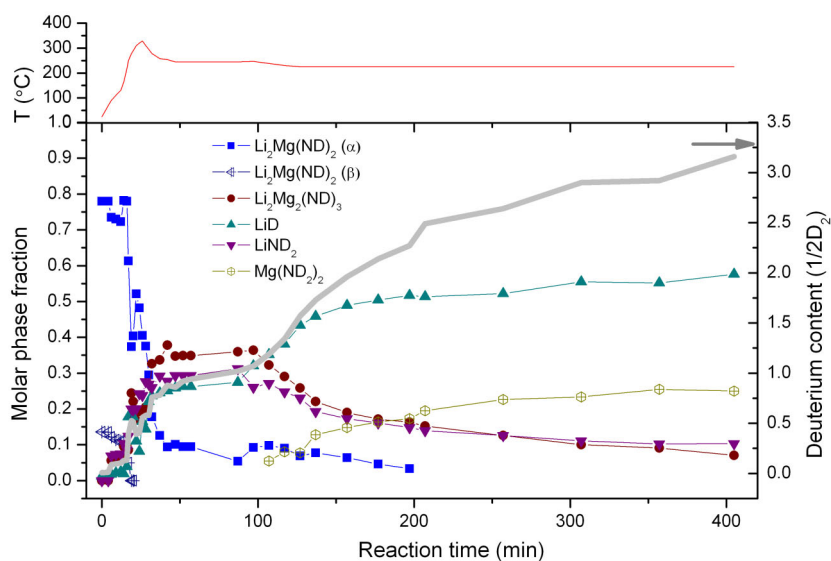
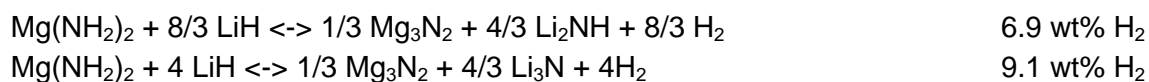


Figure 3: Phase evolution of $\text{Li}_2\text{Mg}(\text{NH})_2$ during hydrogen uptake. The initial H_2 pressure was 60 bar, and it was increased to 70 bar at $t_{\text{reaction}} = 100$ min.

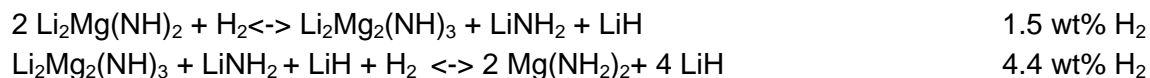
Moreover, $\text{Mg}(\text{NH}_2)_2 + x \text{LiH}$ compounds with $x = 3/8$, and 4 have been proposed for storage purposes with hydrogen capacities of 6.9 wt% and 9.1 wt% H_2 , respectively. The reactions were proposed [16,17] as follows:



To get deeper insight into the mechanism of hydrogen release the different $\text{Mg}(\text{NH}_2)_2 + x \text{LiH}$ were studied using in-situ neutron diffraction. Experiments were carried out at the SPODI instrument, FRM II (Munich) and the D20 beamline, ILL (Grenoble). Prior to the neutron scattering experiments the samples have been cycled in a Sieverts type apparatus using D_2 gas to exchange hydrogen with deuterium and the scattering experiments have been done during absorption.

Starting from $\text{Li}_2\text{Mg}(\text{NH})_2$ (1:2 system) a new intermediate phase was identified during the initial stages ($p = 60$ bar, $T = 245^\circ\text{C}$) of hydrogen uptake [18]. Moreover, LiNH_2 as well as LiH occur in the scattering patterns, while $\text{Mg}(\text{NH}_2)_2$ only is formed as the pressure is raised to 70 bar H_2 (and T lowered to 225°C). The composition of the intermediate phase is proposed to be $\text{Li}_2\text{Mg}_2(\text{NH})_3$ and its structure is related to $\text{Li}_2\text{Mg}(\text{NH})_2$ and LiNH_2 : the underlying crystal structure can be referred to as anti-fluoride type with cations/vacancies residing on tetrahedral sites and nitrogen occupying fcc lattice sites. The phase evolution during hydrogen uptake was evaluated using Rietveld analysis and the results are shown in Figure 3.

Thus, the hydrogen uptake reaction is proposed to be:



The hydrogen uptake in composites with higher LiH content ($x = 3/8$ and 4) has also been measured using in-situ neutron scattering technique (starting from the desorbed state). The results show that the same phases $\text{Li}_2\text{Mg}_2(\text{NH})_3$, LiNH_2 and LiH appear initially when the hydrogen pressure is increased stepwise while $\text{Mg}(\text{NH}_2)_2$ is formed only at pressures above 40 bar ($T = 200^\circ\text{C}$). A quantitative analysis using Rietveld refinement yields a ratio of $\text{Li}_2\text{Mg}_2(\text{NH})_3 : \text{LiNH}_2$ of 1:1 at the intermediate hydrogenation step. For $x = 8/3$ and 4, the LiH content is naturally higher, however there are no indications that under the given conditions ($T = 200^\circ\text{C}$) the additional LiH takes part in the reaction. Consequently, for all three $\text{Mg}(\text{NH}_2)_2 : x \text{LiH}$ compositions ($x = 2, 8/3$, and 4) the same hydrogen uptake reaction occurs (for $T < 250^\circ\text{C}$) albeit the gravimetric hydrogen density decreases with increasing LiH content. The additional hydrogen in these systems is only accessible at higher temperatures.

3 Conclusions

The above presented examples demonstrate the possibility of tailoring thermodynamic properties of hydrogen storage materials. NaAlH_4 in close contact with a mesoporous host shows drastically altered pressure-composition isotherms compared to “bulk” material whereby the porous nature of the material and its high surface area seems to be essential.

Amide based materials are one example how hydrogen release can be obtained in a reaction based system. The occurrence of the intermediate phase at intermediate H_2 pressures is representative for the potential and the difficulties of this approach: Suitable material combinations and their reaction pathway are hard to predict but new promising systems potentially remain to be discovered.

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