

2.3.4 Research Area “Hydrides for Hydrogen and Energy Storage” (M. Felderhoff, F. Schüth)

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Objective: Hydrogen storage materials based on complex hydrides for mobile applications have been in the focus of the group for more than ten years. However, it seems by now clear that the boundary conditions for on-board hydrogen storage in cars cannot be met by such materials.^[50] Nevertheless, the work in this direction is continued for two reasons: first, complex hydrides are rather simple, but little explored solids, and thus the exploration of the synthesis, structures, and properties is of interest, irrespective of whether they are immediately useful. Their synthesis, for instance, poses interesting challenges with respect to pressure and temperature range which needs to be realized. Secondly, while complex hydrides and metal hydrides do not appear to have application potential for hydrogen storage, they could be highly suitable as advanced latent heat storage systems, a field that had already been initially explored by B. Bogdanovic in the institute in the 1980s.

Results: After more than a decade of intense research on NaAlH_4 doped with transition metals as hydrogen storage material, the actual mechanism of the decomposition and rehydrogenation reaction is still unclear. Early on, monomeric AlH_3 was named as a possible transport shuttle for aluminum, but this compound has never been observed experimentally. It was now for the first time possible to trap the volatile AlH_3 produced during the decomposition of undoped NaAlH_4 by an adduct of sodium alanate and crown ether.^[50] The resulting Al_2H_7^- anion was identified by solid-state ^{27}Al NMR

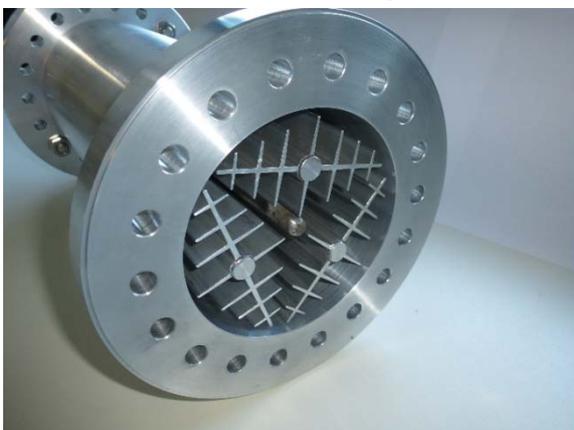


Fig. 1: Prototype of hydride storage tank without the hydride. Fins for cooling are visible.

spectroscopy. Based on this indirect evidence for the formation of the volatile alane, a simple description of the processes occurring during the reversible dehydrogenation of NaAlH_4 was possible.

Even if applications of complex hydrides as storage material for automotive applications appear to be remote, there are other application fields – albeit of smaller scale – where such materials

could be useful. In order to explore the technical implementation of the material in a storage system, a light-weight hydrogen storage tank, charged with Ti-doped sodium aluminum hexahydride Na_3AlH_6 , was developed.^[13,53] This intermediate hydride has a theoretical hydrogen storage capacity of 3 wt.% and can be operated at lower pressure compared to sodium alanate, NaAlH_4 . Therefore the tank can be constructed from Al-alloys, with mechanical properties suitable for safe operation of the system. A prototype of the tank is shown in Fig. 1. This prototype was tested under a wide range of pressure and temperature conditions and proved to be suitable for application in combination with high temperature polymer electrolyte fuel cell systems.

Investigations were also extended to other hydrides. Rare earth alanates, such as $\text{Eu}(\text{AlH}_4)_2$ or the related alkaline earth alanate $\text{Sr}(\text{AlH}_4)_2$ were studied with respect to structure, thermodynamics and kinetics of the hydrogen release and rehydrogenation.^[19] It was found that the decomposition proceeds through an intermediate phase (EuAlH_5 and SrAlH_5), which, however, is structurally rather different from the hexahydride phase observed in the NaAlH_4 system, as could be shown in a combination of powder XRD and solid state NMR spectroscopy. Detailed analysis of both systems revealed – as for most other hydrides – that the thermodynamic properties, but especially the gravimetric storage densities, are insufficient for use in mobile applications. Rehydrogenation of the fully dehydrogenated europium compound could only be achieved to a minor extent, even at pressures of 100 MPa of hydrogen or up to 30 MPa under milling in a pressure ball mill.

MgH_2 is a hydride which has a sufficiently high gravimetric storage capacity of approximately 7.5 wt.%. However, the temperatures for decomposition are too high, the hydrogen is only released above 300 °C. Doping this metal hydride with titanium or other compounds was investigated in order to address both the thermal stability by thermodynamic tailoring due to formation of additional compounds and to improve the kinetic behavior of the system. Direct synthesis via ball milling of magnesium and titanium powder under 30 MPa of hydrogen in a pressure mill allowed the synthesis of a nanostructured MgH_2 doped with TiH_2 .^[6,16] This composite released hydrogen at temperatures lower by 100°C than bulk- MgH_2 , and also rehydrogenation was substantially facilitated. Detailed analysis revealed that the thermodynamic properties of the system are essentially unchanged. For the kinetics the nanostructure is less important than the catalyst, since after several cycles grain growth had occurred, while the positive effect on the kinetics was still observed. This highlights a general problem of nanostructuring hydrogen storage compounds: due to the massive mass transfer during hydrogenation/dehydrogenation cycles the nanostructures are lost in practical

operation, so that special precautions are required to maintain the positive effects of nanostructuring.

Mg-based hydrides are not only interesting for hydrogen storage, but possibly even more useful as heat storage media.^[54] Intermediate heat storage for high temperature industrial applications based on thermochemical gas solid reactions possess the highest gravimetric and volumetric energy storage densities of all possible thermal energy storage methods. MgH₂ itself, but also other mixed metal hydrides, such as Mg₂FeH₆ are highly promising for such applications. In particular, Mg₂FeH₆ is suitable for temperatures exceeding 550°C; it is stable over hundreds of cycles and has a volumetric heat storage density of 1500 kWh m⁻³. Because all experimental results published are based on small lab-scale procedures, we have started a heat storage demonstration project with the development of the tank system, the in- and out-coupling of heat with salt melts and the production of several kg Mg₂FeH₆ as heat storage material. In addition to these technical developments the understanding



of the molecular processes during charging and discharging are in the focus of the project. Since such systems have to sustain hundreds or even thousands of cycles in practical applications, full reversibility has to be guaranteed, since otherwise storage capacity will fade. This requires a full understanding of all relevant processes, from the atomic scale up to the level of the grain.