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Unstable Complex Hydrides as New Hydrogen Storage Materials

Michael Felderhoff, Claudia Weidenthaler, André Pommerin, Ferdi Schüth
Max-Planck-Institut für Kohlenforschung, Germany

1 Introduction

After several years of research in the field of solid state hydrogen storage no optimized material was developed which can be used for hydrogen storage in mobile applications [1]. One of the most discovered material over the last decade is the complex sodium aluminum hydride, $NaAlH_4$, which can store 5.6 wt.% H_2 and releases hydrogen over two decomposition steps. An important disadvantage, which limits the practical use of complex metal hydrides, is the high amounts of energy which must be dissipate during the refilling process in a short time of less than 5 min. Therefore high efficient heat exchangers are necessary, which decreases the overall storage capacity of the whole tank system.

One possible solution to overcome low storage capacities of tank systems is the combination of different types of hydrogen storage processes. The combination of conventional metal hydrides (storage capacity roughly 2 wt.% H_2) and a high pressure tank (350 bar) was developed in the last years [2]. Such systems show increased storage capacities for hydrogen in mobile applications. But the limiting factor of the storage capacity is the low hydrogen amount of the metal hydride. With new types of unstable metal hydrides the storable hydrogen amount in a metal hydride/high pressure tank can be significantly increased.

2 Transition Metal Complex Aluminium Hydrides

Figure 1 shows the theoretical hydrogen content of several transition metal complex aluminium hydrides, reaching more than 9 wt.% H_2 for $Ti(AlH_4)_4$. Most of these materials are unknown and were not prepared or characterized. Only several of these compounds were synthesized in the past in ether solutions according to the following metathesis reaction at low temperature of -110 °C (Equation 1) [3]. These materials are unstable under conditions of 1 bar pressure and at a temperature of 298 °C.

$$TiCl_4 + 4\ LiAlH_4 \xrightarrow[Et_2O]{-110°C} Ti(AlH_4)_4 + 4\ LiCl$$

Eq. 1

They decompose during heating up to room temperature releasing hydrogen and different metallic decomposition products. The decomposition products and the decomposition mechanism are not fully discovered yet.

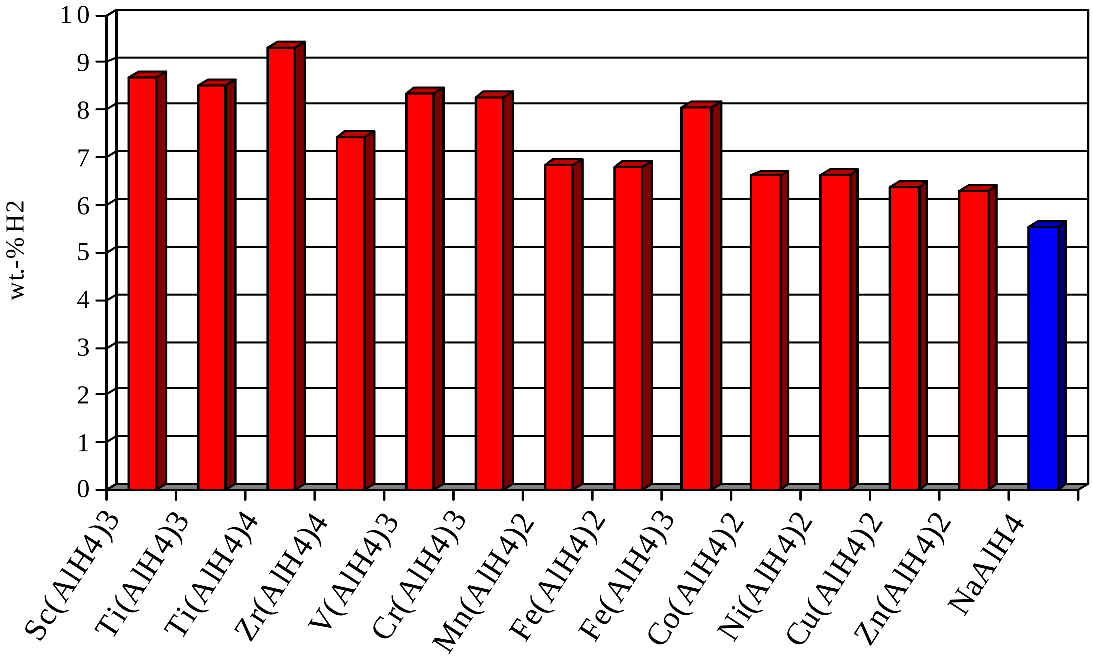

Figure 1: Theoretical hydrogen content of several transition metal complex aluminium hydrides.

With the combination of an unstable metal hydride and a high pressure tank the storage capacity of a tank system can significantly increased. Such a combination releases hydrogen in three steps (Figure 2):

1. pressure reducing step from 350 bar to 200 bar reaching the (assumed) equilibrium pressure of the unstable complex aluminium metal hydride
2. hydrogen release from the decomposition of the unstable complex aluminium hydride (equilibrium pressure)
3. pressure reducing step from 200 bar to 0 bar

The combination of an unstable metal hydride (complex hydride) system / high pressure tank shows several advantages over conventional storage systems:

- high gravimetric and volumetric storage capacity
- reduced heat release during the refilling step
- no cold start problem

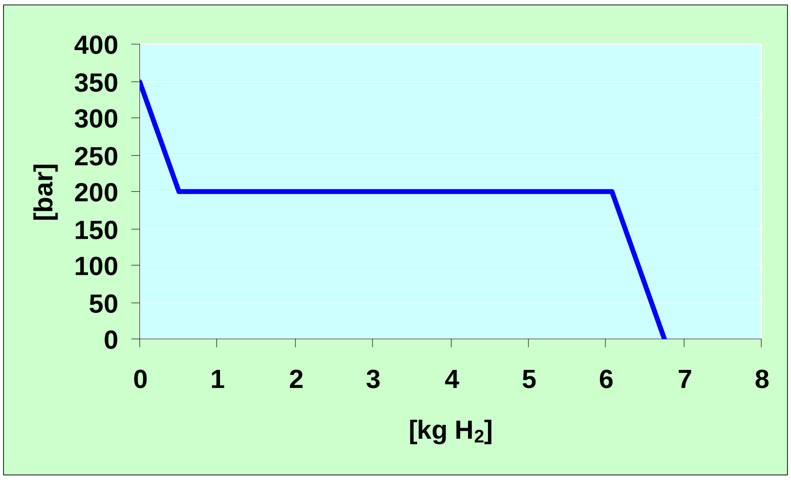

Figure 2: Hydrogen releasing process of a hydrogen storage tank consisting of the combination of an unstable complex hydride and a high pressure tank.

3 Synthesis and Characterization of New Rare Earth Complex Hydrides

Recently it was shown that complex hydrides can be prepared in pure form and without any decomposition products starting from a simple alkaline metal hydride and aluminium hydride through cryo milling according to Equation 2 [4].

$$MeH + AlH_3 \ _{(Me = Li, Na, K)} \xrightarrow[\text{b.m.}]{-196°C} MeAlH_4 \qquad \text{Eq. 2}$$

Starting from these experiments unstable metal hydrides should be synthesized from transition metal hydrides and aluminium hydride at -196°C with the ball millling method. These experimenst are currently under evaluation.

According to the metathesis reaction shown in Eq. 1 new types of rare-earth complex aluminium hydrides (Figure 3) were prepared and characterized [5]. These materials can serve as model substances to learn more about the stability, preparation methods and handling of unstable transition metal hydrides with high hydrogen storage capacity.

Rare-earth chlorides ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$) react with 3 moles of $NaAlH_4$ in a ball milling experiment at room temperature prodcucing unstable rare-earth aluminium hydrides $RE(AlH_4)_3$ in a first reaction step. These materials decompose during the synthesis and produce stable $REAlH_6$ compounds. The decomposition reactions of $REAlH_6$ are endothermic with about 30 kJ mol^{-1} H_2, as revealed by DSC analysis. This suggests that these compounds are reversible at lower temperatures and/or higher pressure, and thus, these compounds may constitute a new class of intermediate temperature hydrides.

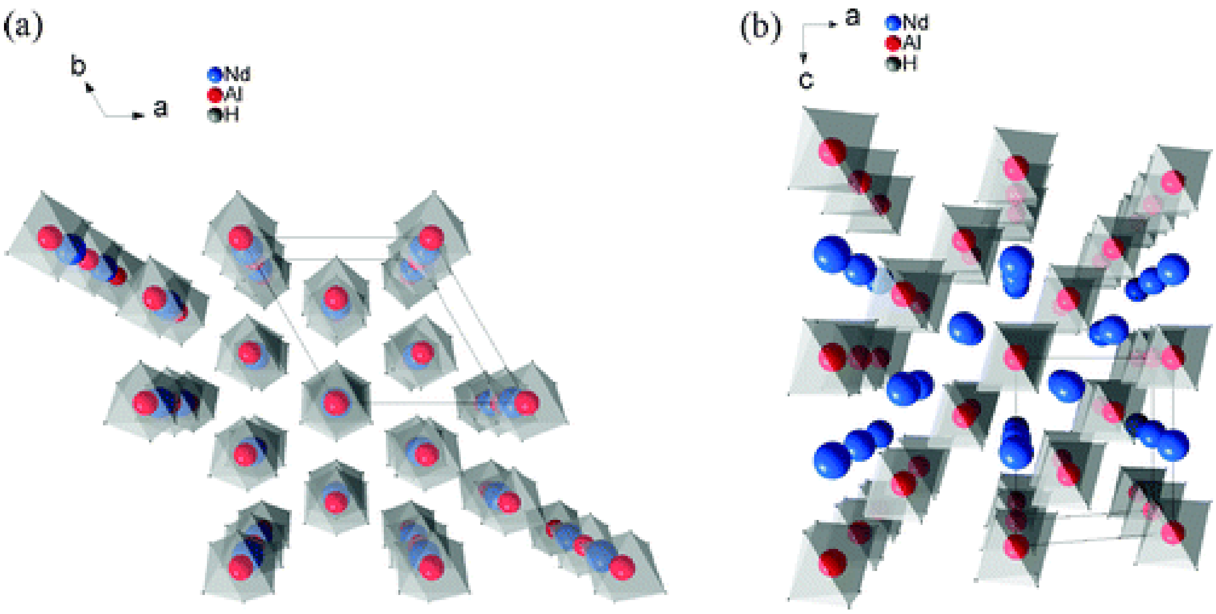

Figure 3: Crystal structure of $NdAlH_6$, from Ref. [4].

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