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Catalytically Enhanced Sodium Aluminum Hydride

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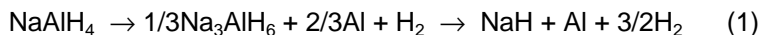
[Editor's note: This Project is a chronological continuation of Project 10.]

Introduction

Pioneering studies by Bogdanovic and Schwickardi demonstrated that, upon doping with selected titanium compounds, the dehydriding of anionic aluminum hydrides could be kinetically enhanced and rendered reversible under moderate conditions in the solid state [1,2]. Following on this breakthrough discovery, we have achieved further improvement in the dehydriding kinetics and stabilization of the cyclic hydrogen capacity by variation in the method of the introduction of titanium into NaAlH₄ [3,4]. The findings of rapid dehydriding at 100°C and a stable, hydrogen cycling capacity of over 4.0 wt %, in conjunction with the low cost and bulk availability of NaAlH₄, suggested that this material might be suitable for application as hydrogen carriers for onboard fuel cells. In order to explore this possibility, we have examined the engineering properties of the catalytically enhanced hydride in this project [5-9]. During the course of these studies, we have also achieved a better understanding of the dehydriding/rehydriding mechanisms of these materials [6-8].

Equilibrium Pressure Measurements

The net reaction of the equation 1 represents a theoretical reversible hydrogen capacity of 5.6 wt.%.



In order to evaluate the feasibility of harnessing this hydrogen capacity under moderate conditions, equilibrium pressure measurements were carried out in the solid-state studies at temperatures ranging as low as 20°C [5,9]. These low-temperature desorption measurements and an accurate van't Hoff analysis are shown in Figure 1. Our low temperature data is in good agreement with the extrapolation of our previous high temperature data [6]. Thus, it has now been accurately shown that the temperature required for an equilibrium-desorption pressure of 1 atm from NaAlH₄ is 33°C. This is a very convenient temperature for fuel cell and other applications. The 1 atm van't Hoff temperature for Na₃AlH₆ is estimated to be about 110°C. This temperature is somewhat higher than desired for a PEM fuel cell and future work will aim at lowering this temperature.

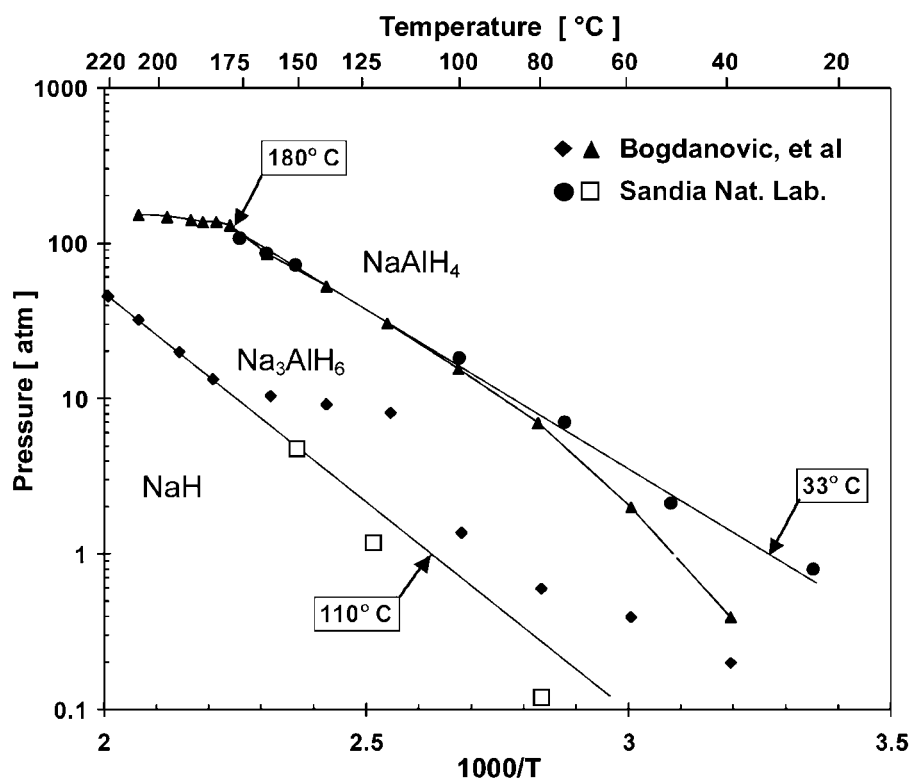


Figure 1 - Van't Hoff Diagram showing equilibrium pressures as a function of temperature for the NaAlH₄ and Na₃AlH₆ decomposition reactions. Samples doped with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPrⁿ)₄. Plateau pressure data are also plotted from measurements made by Bogdanovic' et al [2].

Morphology of the Desorption Reactions

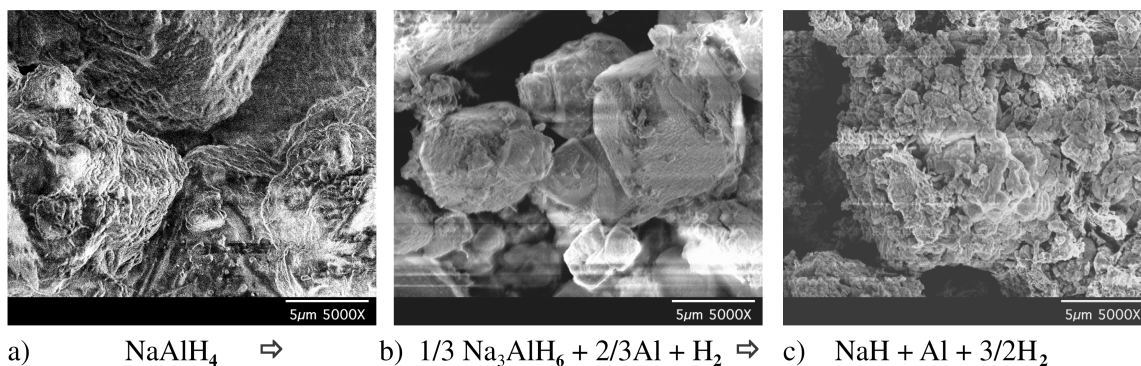


Figure 2 - SEM images showing changes in morphology that occur during the decomposition of NaAlH₄ doped with 2 mol.% each of the liquid catalysts Ti(OBuⁿ)₄ and Zr(OPrⁿ)₄.

The SEM images of Figure 2 show the pronounced changes in morphology that occur during the two-stage desorption of Ti/Zr doped NaAlH₄ (Eq.1). This is an indication of the segregation of the constituent phases. Surface EDS analysis was also used to examine impurity effects on the samples. Measurements taken after the homogenization process also clearly showed the presence of large amounts of residual oxygen introduced by the decomposition of Ti(OBuⁿ)₄ and Zr(OPrⁱ)₄ catalyst precursors [7]. Dynamic in-situ x-ray diffraction measurements were made during the decomposition of both catalyzed and pure NaAlH₄ (Figure 3) [8]. The growth of relatively narrow aluminum diffraction peaks was observed. Thus, aluminum must segregate according to equation 1 to form crystallites with dimensions on the order of 1000 Å or larger. This implies the long-range transport of metal species. Surface EDS verified this notion by showing an increasing overall aluminum concentration on the surface of the powder particles during decomposition. In addition, Auger spectra analysis shows that most of the catalyst remains on the material's surface [8]. The observations of the formation of sub-micron aluminum crystallites by dynamic in-situ x-ray diffraction experiments [8], as well as by a microscopic elemental analysis (2,7), demonstrated the existence of long-range transport of metal atoms. This raises the question of how aluminum hydride anions paired with sodium cations in an ionic solid could be influenced by catalytic sites that are immobilized on the particle surface. One speculation is that the transported species is a more mobile hydride, such as AlH₃ [8]. The low melting point of NaAlH₄ demonstrates the weak nature of the ionic bond. It is possible that local disproportionation of 3 NaAlH₄ into Na₃AlH₆ and 2 AlH₃ takes place. The AlH₃ then transports to the catalytic site where it dissociates into Al and H₂. However, none of these mechanistic concepts have been verified experimentally.

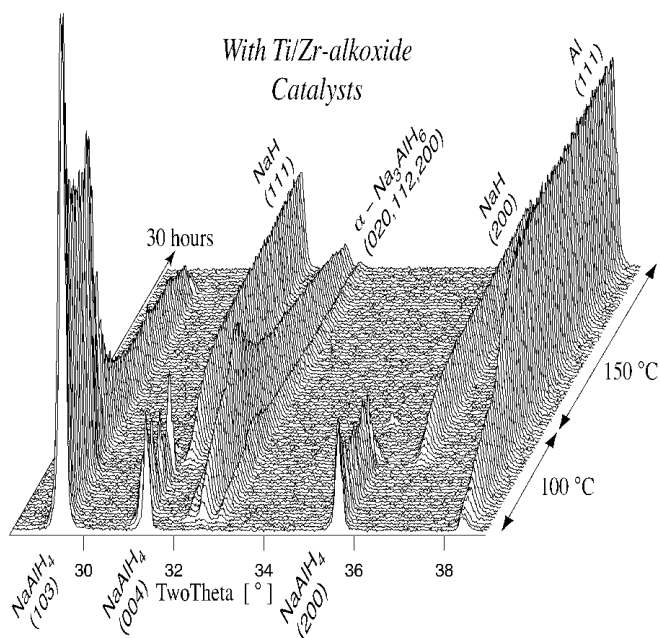


Figure 3 - Dynamic *in-situ* x-ray diffraction measurements taken during decomposition of NaAlH₄ mechanically mixed with 2 mol.% each of the liquid catalysts of Ti(OBuⁿ)₄ and Zr(OPrⁱ)₄.

Practical Studies, Applications-Oriented Materials Properties

A scaleup bed containing 100g of NaAlH_4 doped with Ti/Zr-alkoxides (2 mol.% each) was cycled through five absorption/desorption cycles [9]. The test bed was designed to simulate the heat transfer and gas impedance conditions that might be found in real hydrogen storage applications. Absorption H_2 pressures generally ranged from 100-200 bar and nominal absorption temperatures ranged from 125-165°C. Desorption was generally performed at 150-165°C against atmospheric backpressure. In addition to capacity and rate measurements, exothermic (charging) and endothermic (discharging) thermal effects were recorded. The desorbed hydrogen was monitored for gaseous impurities and a small sample was removed after the fourth desorption cycle for XRD and SEM/EDS analysis. The volume change of the alanate was measured over the last desorption half-cycle. The following are some highlights of that study.

Discharge and Recharge Rates. Desorption of hydrogen occurred rapidly at 150-165°C, with about two thirds of the hydrogen (30 SL) discharging in 3 hours. For the absorption of hydrogen a range of applied pressures and starting temperatures were tried (125-165°C, 122-210 bar). In all cases charging was more rapid than we had expected. Most of the hydrogen was absorbed in the first hour or two, even for the lowest pressure and starting temperature (125°C, 122 bar).

Thermal Effects. The higher than expected initial charging kinetics, combined with limited heat transfer, resulted in exothermic temperature excursions (Figure 4), as is common with many hydrides. A hydrogen pressure of 174 bar was applied to the fully dehydrided bed which had been equilibrated to 155°C. Within one minute, the exothermic hydriding reaction resulted in an internal temperature of 234°C (the van't Hoff temperature for NaAlH_4 at this pressure). This is above the melting point of NaAlH_4 (182°C). Therefore, any NaAlH_4 produced during this high-temperature excursion forms directly into the liquid phase. After this initial excursion a thermal arrest occurs at 182°C due to solidification (Figure 4). This demonstrates that liquid NaAlH_4 was formed during the initial charge. Our observations indicated no negative effects of partially melting the bed at least three times. In fact, partial melting may be beneficial. We opened the reactor between cycles 4 and 5 and found the bed to be sintered into a porous, solid mass. Such a structure may have distinct advantages for actual applications. In particular, such a sintered structure should reduce particulate migration, increase packing densities, allow expansion, provide constant internal gas impedance and enhance safety.

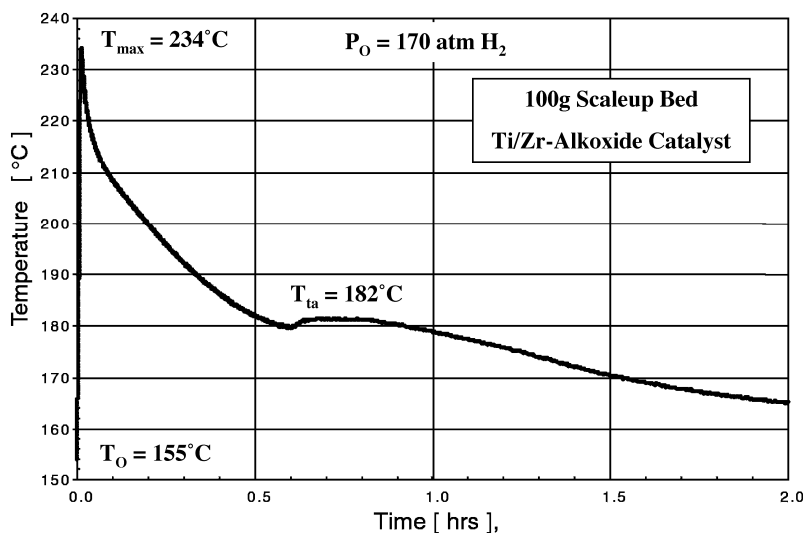


Figure 4 - Temperature excursion in 100 g scaleup test bed during the fourth hydrogen absorption cycle (initial: $T=155^\circ\text{C}$, $P=170 \text{ bar}$).

Hydriding Volume Change. In the classic metal hydrides, large volume changes associated with lattice expansion during hydride formation poses significant engineering problems. Therefore, the volume change of the active material in the scaleup bed was measured from the beginning to the end of fifth desorption cycle. The volume contracted by -14.7%, which is reasonably close to the theoretical value calculated from X-ray densities for the complete dehydriding reaction (-16.5 %) [9]. Unlike the traditional hydrides, the alanates have the distinct advantage of starting with the material in its fully hydrided state. Fully packed beds can be constructed, which simplifies bed design and allows a higher volumetric density to be achieved.

Impurity Gases. The composition of the desorption gases were examined regularly by RGA (Residual Gas Analysis [Mass Spectroscopy]) and occasionally using GC (Gas Chromatography). Typical RGA patterns of the desorption gasses showed, not only hydrogen, but also significant impurities along with the ubiquitous background RGA peaks for H₂O, CO and CO₂. GC analysis taken after the second cycle showed that butane and propane were present in the hydrogen. Thus, it appears that the liquid Ti(OBuⁿ)₄ and Zr(OPrⁱ)₄ catalysts decompose and release significant amounts of hydrocarbon impurities. PEM fuel cells are not very tolerant of impurity gases, especially hydrocarbons that lead to the formation of CO. Additionally, the alkoxide-based catalysts have high molecular weights and, thus, result in a 22 wt.% burden on the total material. These considerations lead us to an effort to develop catalysts that contain no organic groups. We are now investigating the catalytic properties of the titanium-halides. Recent experiments on NaAlH₄ doped with 2 mol.% α-TiCl₃ have shown reversible hydrogen capacities more closely approaching the theoretical limit with no degradation in kinetic properties and no gas impurities [9]. These materials desorb 3 wt % hydrogen in 90 minutes at 125°C and absorb 4.4 wt % hydrogen in an hour at the same temperature with an applied hydrogen pressure of 91 bar. Using x-ray diffraction, it was discovered that the α-TiCl₃ catalyst precursor decomposes during the mechanical milling process to form NaCl and a dispersed titanium-based catalyst. In a parallel investigation, liquid TiCl₄ was added by mechanical milling. TPD measurements gave results very similar to that found for the Ti-alkoxide catalyst [10]. The nature of the titanium-based catalysts is the focus of current investigations.

Conclusions and Outlook

We have prepared catalytically enhanced sodium aluminum hydride that can achieve reversible hydrogen capacities in excess of 4.2 wt.%. The current state of the art allows the desorption of 3 wt.% hydrogen in a little over one hour at 125°C. Precise plateau pressure measurements demonstrate that these materials are thermodynamically ideal for practical applications. The dehydriding of NaAlH₄ to Na₃AlH₆ and Al delivers 1 bar of hydrogen at 33°C. These are important achievements; however, further advances will be required in order for these materials to achieve practical viability. In particular:

1. The slow dehydriding and rehydriding kinetics remain a significant barrier to applications, such as fuel cell vehicles.
2. Subsequent dehydriding of Na₃AlH₆ to NaH and Al is necessary to obtain the full 5.6 wt.% theoretical capacity. Unfortunately, Na₃AlH₆ is a little too stable for many applications; releasing 1 bar hydrogen at about 110°C. Bulk substitution must be explored as a means of de-stabilizing this reaction.
3. Long-term cycling studies will be needed to ensure the viability of these materials for reversible hydrogen storage.
4. Safety is an important issue that must be addressed, as these compounds are highly reactive with water. Engineering solutions or material modifications will be required to reduce the hazards associated with a full exposure to air or water.

Acknowledgements

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