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Dynamic in situ X-ray diffraction of catalyzed alanates

K.J. Gross[a,*], G. Sandrock[a,b], G.J. Thomas[a]

[a]Sandia National Laboratories, P.O. Box 969, MS 9402, Livermore, CA 94551, USA
[b]SunaTech, Inc., 113 Kraft Pl., Ringwood, NJ 07456, USA

Abstract

The discovery that hydrogen can be reversibly absorbed and desorbed from $NaAlH_4$ by the addition of catalysts has created an entirely new prospect for lightweight hydrogen storage. $NaAlH_4$ releases hydrogen through the following set of decomposition reactions:

$$NaAlH_4 \rightarrow \tfrac{1}{3}(\alpha\text{-}Na_3AlH_6) + \tfrac{2}{3}Al + H_2 \rightarrow NaH + Al + \tfrac{3}{2}H_2$$

These decomposition reactions as well as the reverse recombination reactions were directly observed using time-resolved in situ X-ray powder diffraction. These measurements were performed under conditions similar to those found in PEM fuel cell operations (hydrogen absorption, 50–70°C, 10–15 bar H_2; hydrogen desorption, 80–110°C, 5–100 mbar H_2). Catalyst doping was found to dramatically improve kinetics under these conditions. In this study, the alanate was doped with a catalyst by dry ball-milling $NaAlH_4$ with 2 mol.% solid $TiCl_3$. X-ray diffraction clearly showed that $TiCl_3$ reacts with $NaAlH_4$ to form NaCl during the doping process. Partial desorption of $NaAlH_4$ was even observed to occur during the catalyst doping process. Published by Elsevier Science B.V.

Keywords: Metal hydride; Complex hydride; Hydrogen storage; Fuel cell; $NaAlH_4$; Na_3AlH_6

1. Introduction

The synthesis and decomposition of the compound $NaAlH_4$ have been known for many years [1–6]. However, it was not until the recent work of Bogdanovic and Schwickardi that the potential use of $NaAlH_4$ for reversible hydrogen storage was considered practical [7]. They demonstrated that doping (in solution) the alkali metal hydride with Ti-based catalysts enabled the ready release and absorption of hydrogen gas under moderate conditions. The advantage of this class of hydrides is their high hydrogen weight capacities. $NaAlH_4$ has a theoretical reversible capacity of 5.6 wt.% H_2.

Unlike classic interstitial metal hydrides, the alanates (alkali-metal aluminum hydrides) desorb and absorb hydrogen through chemical decomposition and recombination reactions. In particular, $NaAlH_4$ decomposes with the formation of at least one intermediate compound, Na_3AlH_6:

$$NaAlH_4 \rightarrow \tfrac{1}{3}(\alpha\text{-}Na_3AlH_6) + \tfrac{2}{3}Al + H_2 \rightarrow NaH + Al + \tfrac{3}{2}H_2 \tag{1}$$

Detailed investigations of decomposition at elevated temperatures (100–180°) [8], as well as the thermodynamic and kinetic properties of this material, were reported in previous works [9–12].

In this paper we will present a study of these decomposition reactions, as well as the recombination reactions. These were investigated by dynamic in situ X-ray diffraction (XRD). In situ XRD measurements provide a means to directly observe the hydride reactions that take place during hydrogen loading and unloading. They are useful in identifying the formation of metastable phases that may otherwise not be observed in ex situ measurements [8]. Dynamic in situ X-ray diffraction experiments consist of making a continuous sequence of XRD scans during the reaction process. Among other things, dynamic XRD enables the direct measurement of individual rates of reaction.

We will also present results of an XRD study of the interaction between $NaAlH_4$ and a catalyst added to kinetically enhance the reactions of Eq. (1). The choice of catalyst and doping process is critical to achieving practical hydrogen absorption and desorption rates. Catalyst

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*Corresponding author. Analytical Materials Science Department, Sandia National Laboratories, P.O. Box 969, MS 9403, Livermore, CA 94551-0969, USA. Tel.: +1-925-294-4639; fax: +1-925-294-3410.

E-mail address: kjgross@sandia.gov (K.J. Gross).

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development and material processing has been the focus of work by several groups [10–14]. Our recent investigations have led to a catalyst and doping method with greatly improved kinetics and substantially reduced hydrogen impurities [15]. This entails catalyst doping the samples by dry ball-milling solid $NaAlH_4$ in argon with 2 mol.% solid $TiCl_3$.

2. Sample preparation and experimental details

Samples were prepared from solid $NaAlH_4$ (90% purity, Aldrich) which were purified by solvating in THF, decanting and vacuum drying. Catalyst doping consisted of adding 2 mol.% solid $TiCl_3$ to about 2 g $NaAlH_4$, which was then sealed into a tungsten-carbide milling pot (in an argon glove box). This mixture was milled in a SPEX® mill for 3 h. Undoped samples were prepared in the same manner without the addition of a catalyst.

X-ray powder diffraction experiments were performed on a Scintag XDS 2000 diffractometer using Cu Kα radiation. Dynamic studies consisted of collecting a series of consecutive XRD scans. The low reaction rates allowed scan times of 42 min per scan. In situ hydrogen absorption and desorption XRD measurements were performed at elevated temperatures in a specially designed sample cell fitted with a beryllium window (described elsewhere [8]). Following the catalyst doping, samples were loaded into the in situ X-ray diffraction cell under argon. Both the sample temperature and hydrogen pressure in the cell were monitored during the dynamic absorption and desorption experiments. Changes in the hydrogen pressure during absorption were too small to precisely determine the quantity of hydrogen absorbed by the sample. Desorption experiments were performed by opening a valve on the cell and allowing the sample to desorb into an evacuated vessel of a known volume. The pressure change (5–50 mbar) was more than sufficient to precisely measure the amount of hydrogen desorbed from the sample.

Ex situ XRD studies of the reaction of $TiCl_3$ with $NaAlH_4$ were performed on samples prepared as described above. These were spread onto special background-free glass sample holders. They were then sealed under argon using a thin Mylar film (100 microns). The Mylar film is relatively transparent to X-rays and produces no diffraction peaks in the angle range of interest. This allowed ex situ XRD measurements to be made without exposing the samples to air.

3. Results and discussion

3.1. Dynamic in situ XRD measurements — absorption

In light of the potential use of these materials for on-board hydrogen storage in vehicular applications, the dynamic in situ XRD measurements were performed under conditions similar to those found in PEM fuel cell operations. These were: hydrogen absorption, 50–70°C, 10–15 bar H_2; and hydrogen desorption, 80–110°C, 5–100 mbar H_2. The first experiment consisted of re-hydriding $TiCl_3$ catalyzed $NaAlH_4$ from its desorbed state (i.e. $NaH+Al$). In this case, 319 mg of material was removed from a larger sample that had already undergone five absorption and desorption cycles. This dynamic in situ XRD absorption measurement was performed in two steps. In the first step, the sample was heated to 70°C and subjected to a hydrogen over-pressure of 10.2 bar. These conditions were sufficient to convert the sample from NaH and Al to Na_3AlH_6. In the second part of the experiment, the pressure was increased to 15.8 bar to promote the formation of $NaAlH_4$. A maximum applied pressure of 16 bar was imposed by limitations in the XRD cell design. However, this relatively low applied pressure is appropriate because it represents a typical pressure limit of a lightweight on-board hydride storage vessel that might be used in a fuel cell vehicle.

The series of in situ XRD scans measured during hydrogen absorption have been compiled into a dynamic representation of the hydriding reactions, which is presented in Fig. 1a and b. The transition from Na_3AlH_6+Al to $NaAlH_4$ was considerably slower than the $NaH+Al$ to Na_3AlH_6 reaction. For this reason only a few representative scans were made during the second half of the absorption experiment. Since direct measurements of the change in over-pressure were unreliable, the quantity of hydrogen absorbed by the sample was inferred from the relative intensities of the XRD peaks of each phase. By the start of the second part of the absorption measurement only Na_3AlH_6 and Al were visible in the diffraction patterns. [Note: some additional intensity remains at 31.7° overlapping both the NaH (111) and $NaAlH_4$ (004) peaks. This is a remnant of the catalyst doping procedure as will be discussed later.] Thus, the integrated peak intensities of Na_3AlH_6 are proportional to the sample's hydrogen content at this point. The hydrogen content of the active material in the sample was assumed to be equal to the theoretical value for the formation of Na_3AlH_6 from NaH and Al (1.9 wt.%). The effective hydrogen contents of the sample for each of the previous XRD scans were calculated based on the integrated peak intensities of Na_3AlH_6. For the second part of the measurement the integrated peak intensities of Na_3AlH_6 were again used to calculate the sample's hydrogen content. This was based on a theoretical value of 3.7 wt.% for the Na_3AlH_6 to $NaAlH_4$ transformation. In this case, the intensities of the $NaAlH_4$ peaks were not used to calculate the hydrogen content because the absorption was not complete, so the fully charged $NaAlH_4$ peak intensities were not known. Hydrogen content is plotted versus time in Fig. 1c and d. Rough estimates of the hydrogen absorption rates have been determined from these plots. These are: ($NaH+Al+$

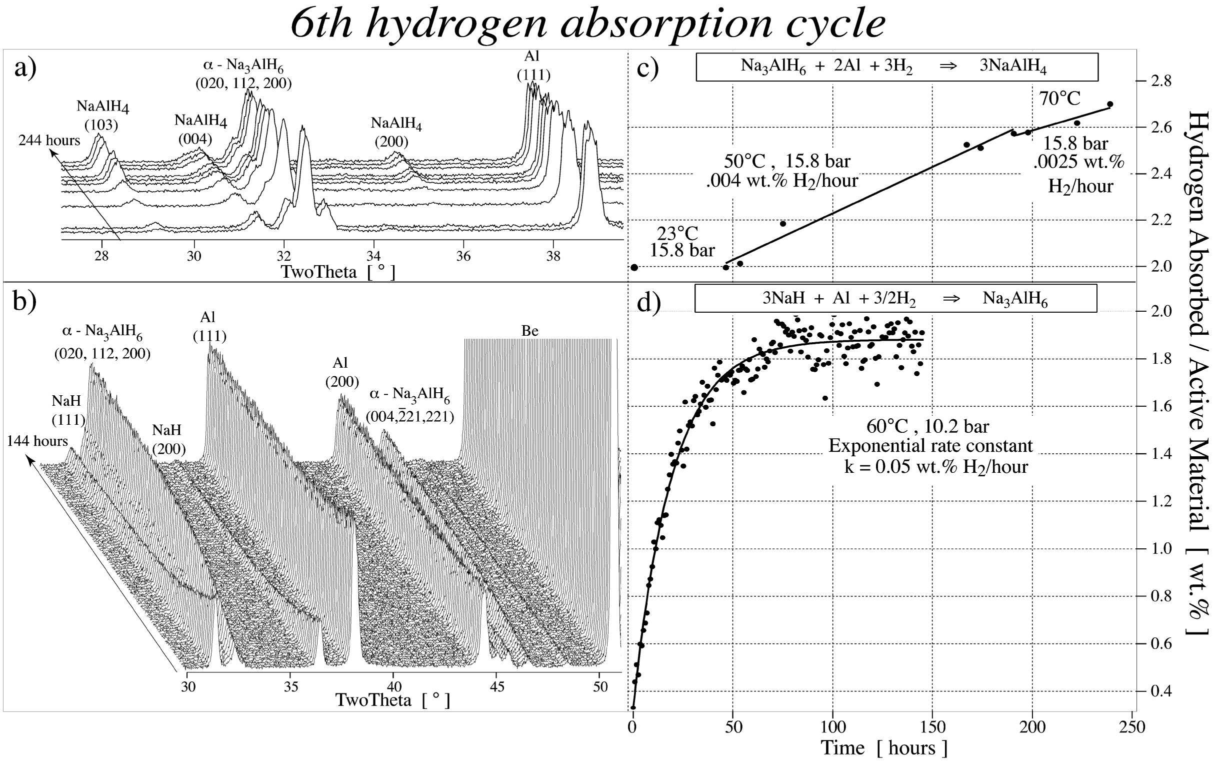

Fig. 1. (a,b) Compilation of a series of dynamic in situ X-ray diffraction patterns taken during the sixth hydrogen absorption cycle of a previously desorbed sample (2 mol.% $TiCl_3$ catalyzed $NaAlH_4$). (c,d) The quantity of hydrogen absorbed by the sample inferred from the relative XRD peak intensities of Na_3AlH_6. Reactions: (b,d) $NaH+Al+\frac{3}{2}H_2 \rightarrow \frac{1}{3}Na_3AlH_6$; (a,c): $\frac{1}{3}Na_3AlH_6+\frac{2}{3}Al+H_2 \rightarrow NaAlH_4$.

$\frac{3}{2}H_2 \rightarrow \frac{1}{3}Na_3AlH_6) = 0.05$ wt.% H_2/h and $(\frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \rightarrow NaAlH) = 0.004$ wt.% H_2/h. Thus, at these low temperatures and pressures the re-hydriding reaction do occur, albeit slowly. It is also important to note that the reaction $\frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al$ to $NaAlH_4$, which contributes most of the reversible hydrogen (3.7 wt.%), is an order of magnitude slower than the $3NaH+Al$ to Na_3AlH_6 reaction. From these results it can be estimated that the complete transformation from $NaH+Al$ to $NaAlH_4$ would require about 40 days. The dependence of the reaction rates on the degree of hydrogen over-pressure as well as temperature (see Fig. 1c) is the subject of current studies that will be presented elsewhere.

3.2. Dynamic in situ XRD measurements — desorption

The sixth desorption cycle of $TiCl_3$-catalyzed $NaAlH_4$ was characterized by in situ XRD using a sample that was charged ex situ at 125°C and 75 bar for 24 h. The two decomposition reactions were recorded in a single series of in situ XRD scans. Once again, these XRD scans have been compiled into a dynamic representation shown in Fig. 2a. From the starting diffraction pattern it can be seen that the ex situ rehydriding had gone to about 90% completion. Thus, the measurements begin with the sample in an already slightly desorbed state. The desorption measurement was carried out in two steps. In the first step, the $NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al$ decomposition reaction was performed at 80°C. When this reaction was complete the desorbed hydrogen pressure was too near the plateau pressure for the second reaction to proceed. Therefore, to drive the decomposition of Na_3AlH_6 the sample temperature was raised to 111°C. Unlike the absorption measurements, the sample's hydrogen content during desorption was directly determined by measuring the increase in pressure (Fig. 2b). The following reaction rates were determined from these curves: $(NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al) = 0.06$ wt.% H_2/h and $(Na_3AlH_6 \rightarrow 3NaH + Al) = 0.02$ wt.% H_2/h. Because of the temperature difference these rates are of about the same order of magnitude. These rates imply that $TiCl_3$-catalyzed $NaAlH_4$ would take about 6.5 days to desorb completely under these conditions.

3.3. Catalyst doping

The interaction between $NaAlH_4$ and $TiCl_3$ was also investigated by XRD. Two different samples were prepared by dry ball-milling solid $NaAlH_4$ in argon for 3 h. One sample was milled without any catalyst and the other was milled together with 9 mol.% solid $TiCl_3$. The XRD patterns of these two samples are compared in Fig. 3. Diffraction peaks from $TiCl_3$ are not observed in the sample to which $TiCl_3$ was added. On the other hand, NaCl is clearly present. These measurements demonstrate

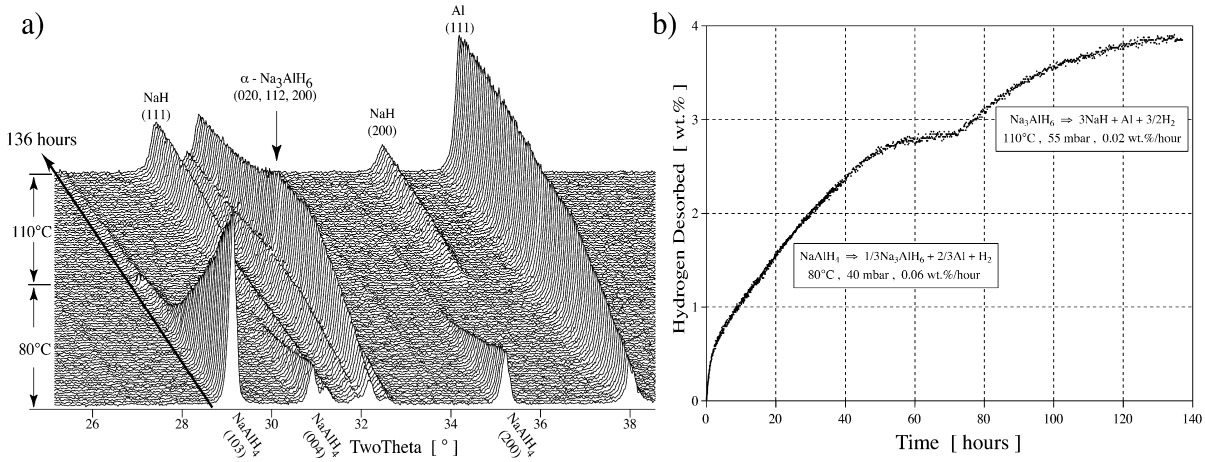

Fig. 2. (a) Compilation of a series of in situ X-ray diffraction patterns taken during the sixth hydrogen desorption cycle of 2 mol.% $TiCl_3$ catalyzed $NaAlH_4$. (b) The quantity of desorbed hydrogen determined volumetrically.

that $NaAlH_4$ and $TiCl_3$ react during the milling process to form NaCl. This finding is significant with respect to understanding the nature of the catalyst and its role in enhancing both the hydrogen absorption and desorption processes.

Another important observation is that $NaAlH_4$ decomposes to a considerable degree during mechanical milling, but only when $TiCl_3$ is added. This can be seen in the greatly reduced intensities of the $NaAlH_4$ peaks and the presence of reflections from Na_3AlH_6 and Al (XRD pattern of the catalyzed sample Fig. 3). This indicates that $TiCl_3$ adds a component which acts as a potent catalyst in the desorption of $NaAlH_4$, even at the only moderately elevated temperatures created during ball milling.

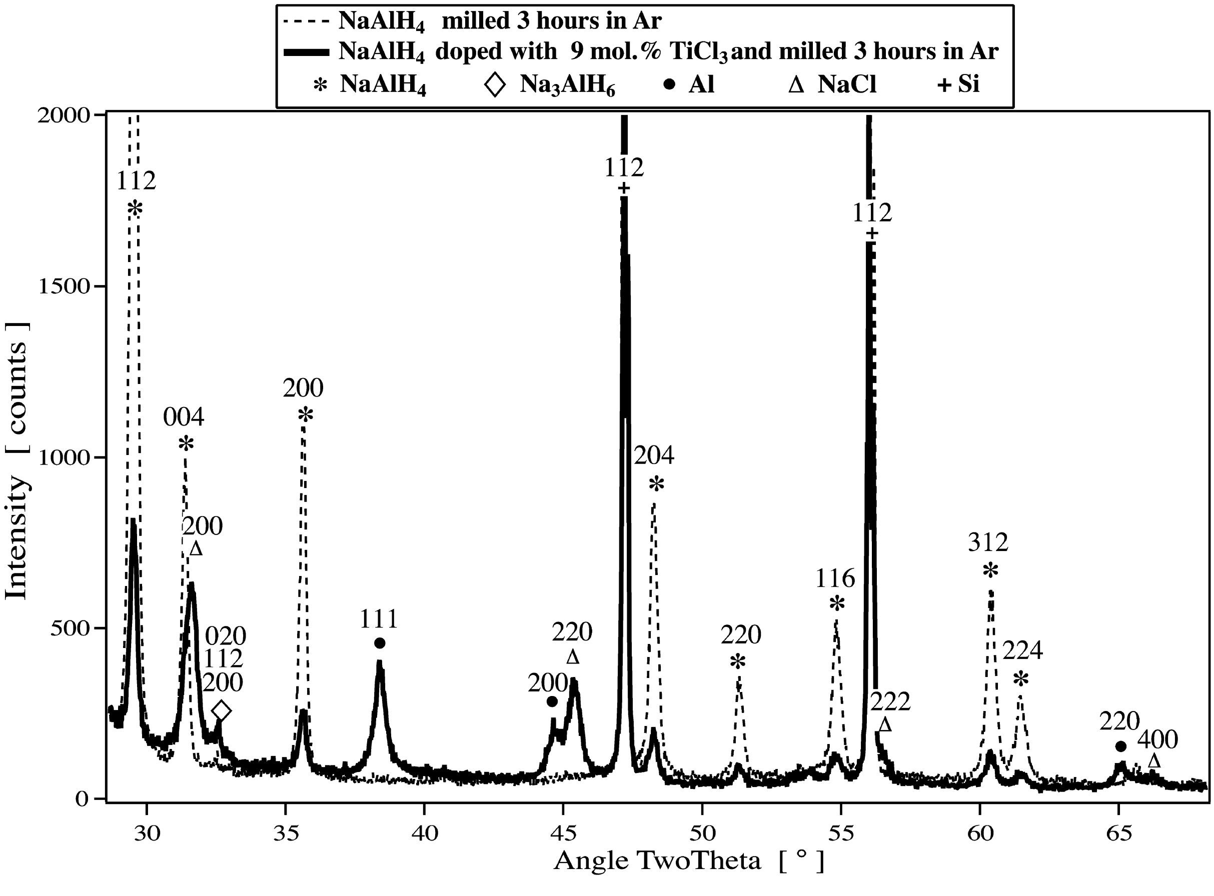

Fig. 3. X-ray diffraction patterns taken after 3 h of milling $NaAlH_4$ with and without 9 mol.% $TiCl_3$.

4. Conclusion and outlook

Hydrogen absorption and desorption from $NaAlH_4$ doped with 2 mol.% $TiCl_3$ was measured by dynamic in situ X-ray diffraction under conditions similar to those found in fuel cell operations. Thanks to the catalyst and doping procedures we have improved the kinetics at these low temperatures (50–110°C) to the point where the hydriding reaction are clearly observed. From these measurements we were able to determine rates of the hydrogen absorption and desorption. XRD measurements also demonstrated that $TiCl_3$ reacts with $NaAlH_4$ during the mechanical doping process to form NaCl. Moreover, it was found that the addition of $TiCl_3$ promotes the partial decomposition of $NaAlH_4$ into Na_3AlH_6 and Al during the doping process. While the rates for this level of catalyst loading are low, these results are significant in demonstrating the achievement of low pressure and temperature reversibility in catalyzed $NaAlH_4$. However, much progress remains to be made in improving kinetics before these materials will be practical for hydrogen storage in fuel cell vehicle applications.

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