Adjustment of the decomposition path for Na$_2$LiAlH$_6$ by TiF$_3$ addition

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ABSTRACT

The decomposition of Na$_2$LiAlH$_6$ is studied by in-situ synchrotron diffraction. By addition of TiF$_3$ and dehydrogenation-rehydrogenation cycling of the samples new decomposition paths are found. Na$_3$AlH$_6$ is formed on decomposition in the presence of TiF$_3$. The additive brings the system closer to equilibrium, and decomposition through Na$_3$AlH$_6$ is demonstrated for the first time. The results are in agreement with previously published computational data. For a cycled sample with 10 mol% TiF$_3$ Na$_2$LiAlH$_6$ decomposes fully into Na$_3$AlH$_6$ before further decomposition to NaH and Al. This shows clear changes in the kinetics of the system, and may open possibilities of tailoring the decomposition path by the use of additives.

1. Introduction

The increasing climatic problems caused by the use of fossil fuels as well as the limited amount of these resources, raise the need of introducing new, clean energy sources and energy carriers. One of the most widely accepted alternatives for a versatile and reliable energy carrier of the future is hydrogen. Efficient and safe storage of hydrogen is however a main challenge remaining before hydrogen may be introduced as a wide-spread energy carrier. A promising solution to this challenge is to use light-weight complex metal hydrides as the hydrogen storage medium, in which hydrogen is stored chemically [1,2]. This option was introduced by the discovery by Bogdanović and Schwickardi of reversible hydrogenation of NaAlH$_4$, Na$_3$AlH$_6$ and Na$_2$LiAlH$_6$ promoted by the addition of catalytic amounts of transition metal based additives [3].

Among the aluminohydrides (alanates) the NaAlH$_4$-system has received greatest interest, having the combination of good reversible gravimetric hydrogen capacity and relatively rapid hydrogenation kinetics within reasonable temperature and pressure ranges [4–6]. However, the decomposition of NaAlH$_4$ is a two step process, which means technical challenges related to different pressures and temperatures during the process, as well as different kinetics in the two steps. The decomposition of Na$_3$AlH$_6$, being the second step of the NaAlH$_4$-system, releases 3.0 wt% H$_2$ in one reaction. The lithium-analogue, Li$_3$AlH$_6$, has a higher hydrogen content of 5.6 wt%, but the plateau pressure at ambient temperature is too high to make it reversible for mobile use [7]. The mixed
alinate Na₄LiAlH₆ has higher thermodynamic stability than Na₂AlH₄ and Li₃AlH₆, and can be made reversible at moderate conditions by addition of small amounts of transition metal or rare earth metal compounds [3]. Recent years several mixed alanates has been investigated as potential candidates for hydrogen storage media [5,8–11].

Na₂LiAlH₆ decomposes through a one step process at around 255 °C with a theoretical release of 3.5 wt% H₂ [12]:

\[
\text{Na}_2\text{LiAlH}_6 \rightarrow 2\text{NaH} \leftrightarrow \text{LiH} + \text{Al} + \frac{3}{2} \text{H}_2
\]  

(1)

The binary hydrides NaH and LiH must be heated to very high temperatures to release hydrogen, which will not be considered here. Even though Na₂LiAlH₆ has a lower theoretical hydrogen density than e.g. NaAlH₄, the advantage of releasing all the hydrogen in a single-step decomposition makes it a potential material for a one step hydrogen storage media fulfilling many of the international requirements of hydrogen storage materials for vehicular applications. Furthermore, calculations by Opalka et al. show that the dehydrogenation of NaAlH₄ combined with LiH through Na₂LiAlH₆ to the end products LiH and NaH gives favorable thermodynamics compared to dehydrogenation of NaAlH₄ through Na₂AlH₆ [13].

The mixed alanate Na₂LiAlH₆ was first synthesized by Claudy et al. in 1982 by reaction of LiAlH₄ with NaH either in toluene or by a solid state reaction at elevated temperatures and high H₂-pressures [14]. Huot et al. demonstrated the preparation of Na₂LiAlH₆ without solvents by mechanochemical synthesis [12]. This was done by ball milling a mixture of NaAlH₄, LiH and NaH for 40 h. Zaluski et al. reported to have prepared Na₁.₇Li₁.₃AlH₆ and Na₁.₅Li₁.₅AlH₆ from the same starting materials [15].

The deuteride Na₂LiAlD₆ was synthesized by Brink et al. by ball milling LiAlD₄ and 2 NaAlD₄ followed by annealing under D₂ [16]. Mechanochemical synthesis of Na₂LiAlH₆ by ball milling has later been done through several reaction paths; by mixing of 2 NaH + LiAlH₄ [17,18], NaH + LiHAlH₄ [19], 2NaAlH₄ + LiH [20] and by mixing of LiAlH₄ + LiH + NaH [21]. Na₂LiAlH₆ takes an ordered perovskite-type structure (space group Fm3 m) [16]. The kinetics and thermodynamic properties of Na₂LiAlH₆ was investigated by both Bogdanović et al. [3] and Zaluski et al. [15], and several further studies have been reported on the system the last years [20–27]. All experimental studies observing dehydrogenation of Na₂LiAlH₆ confirm the decomposition through reaction 1. But in a theoretical study of the thermodynamics of the Na–Li–Al–H system, performed by Opalka et al., alternative decomposition paths of the system are discussed [13].

The present study describes the decomposition of Na₂LiAlH₆ with the addition of TiF₃. Samples with varying amount of additive have been investigated, as well as a reference sample of pure Na₂LiAlH₆. In-situ synchrotron powder x-ray diffraction (SR-PXD) has been done to determine the decomposition of the samples prior to and after de- and rehydrogenation cycles.

2. Experimental method

Na₂LiAlH₆ was mechanochemically synthesized in a Fritsch Pulverisette 7 planetary mill. A 1:1 mixture of NaAlH₄ (Albermarle, > 99% purity), NaH (Sigma–Aldrich, 95% purity) and LiH (Sigma–Aldrich, 95% purity) was milled for 3 h at a speed of 700 rpm. After milling the material was annealed at 80 bar H₂ and 150 °C for about 14 h. All operations and material handling were performed under purified argon atmosphere (< 1 ppm O₂, < 1 ppm H₂O) in a Mbraun glove box and sealed milling vials.

The expected reaction path was the formation of Na₂LiAlH₆ according to the following reaction:

\[
\text{NaAlH}_4 + \text{NaH} + \text{LiH} \rightarrow \text{Na}_2\text{LiAlH}_6
\]  

(2)

The sample composition was checked by powder X-ray diffraction (PXD) using an ENEL XRG300 diffractometer with monochromized Cu Kα₁ radiation, flat-plate geometry, and a CPS-120 curved, position-sensitive detector that continuously covers the 2θ range from 2° to 120° (Δ2θ = 0.029°). The sample was covered by a thin plastic film to prevent reaction with air.

The synthesized powder was divided into four samples. One was kept unchanged, as a reference (sample 1). TiF₃ was added to the remaining powder by ball milling in a Fritsch Pulverisette 7 planetary mill for 20 min at 350 rpm in different amounts; 2 mol% TiF₃ (sample 2), and 10 mol% (samples 3 and 4), respectively. The difference between samples 3 and 4 was the treatment after milling: sample 3 was kept without further treatment (“as milled”), while sample 4 was dehydrogenated and rehydrogenated (cycled) once. Sample 2 was also cycled once. The cycling was performed by keeping the samples at a hydrogen pressure below 1 bar for 2–5 h during dehydrogenation, and reloading with hydrogen at an initial pressure of 80 bar for 16 h.

Time-resolved in-situ SR-PXD-data were collected at the Swiss-Norwegian Beam Line (station BM01A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The wavelength of 0.8000 Å was obtained from a channel-cut Si(111) monochromator. The samples were contained in boron-silica glass capillaries of 0.5 mm diameter mounted in a Swagelok fitting. The capillaries were connected to a vacuum pump and heated from 50 to 400 °C at a constant rate of 1 °C/min (sample 2) or 2 °C/min (samples 1, 3 and 4) using a hot air blower. Two-dimensional data were collected using a MAR345 image plate detector with an exposure time of 30 s. The capillary was rotated approximately 30° during the exposure. Data readout and erasing required 90 s, thus a full diffraction pattern was collected every second minute. The two-dimensional data were converted into one-dimensional powder diffraction patterns with the program Fit2d [28]. Diffraction data were collected in the range 2θ = 0.03°–36.4° and were rebinned in steps of Δ(2θ) = 0.02°.

The obtained SR-PXD data were analyzed using the Rietveld refinement program Fullprof (version 3.40) [29]. X-ray form factors were taken from the Fullprof library. Pseudo-Voigt profiles were used, and the backgrounds were modeled by linear interpolation between manually chosen points.

3. Results

The synthesized Na₂LiAlH₆ starting material was checked by laboratory x-ray. It was confirmed that the composition was...
nearly single phase, with only a small amount of Na₃AlH₆ — the latter was most probably formed by direct reaction between NaAlH₄ and NaH in the milling process. Small amounts of remaining LiH are therefore also expected in the mixture, but this is not easily detected by laboratory x-ray due to the weak scattering of LiH.

Quantitative phase analysis based on Rietveld refinements was performed on the in-situ SR-PXD data in order to determine the amount of each crystalline phase in the samples during the thermal decomposition. The analysis was done for selected data sets from each series of SR-PXD-data for the 4 samples. For all samples the diffraction data showed reaction with the capillary giving unknown phases and peaks at temperatures above 300 °C. Therefore the quantitative analysis is presented only for temperatures below 300 °C. Structural data for the different phases were taken from the ICSD database [30]. During the refinements the scale factors, unit cell dimensions, profile- and displacement parameters were allowed to vary to obtain a best possible fit to the observed diffraction data. The unit cell dimensions increased with increasing temperature according to thermal expansion of the unit cell. A typical refinement pattern is shown in Fig. 1.

To visualize the evolution of the reactions in the samples the diffraction patterns are shown as 3-dimensional graphs in Figs. 2 and 3 for sample 1 and 3 respectively. Sample 1 is shown for reference, displaying the behaviour according to reaction 1. For samples 3 it is clearly seen that the decomposition follow a different route. The phase compositions during heating found from quantitative phase analysis are shown in Fig. 4. Standard deviations taken from the Rietveld refinement are within the points in the graph. It is clear that both the addition of TiF₃ and cycling have dramatic effects on the dehydrogenation process. The decomposition routes for the different samples are presented in the following.

![Fig. 1 – SR-PXD of sample 4, Na₂LiAlH₆ + 10 mol% TiF₃. Observed intensities (dots) and calculated intensities (line). Positions for Bragg reflections are shown as vertical bars for the phases (from top): Na₂LiAlH₆, Al, NaH and Na₃AlH₆. The difference between observed and calculated values is shown in the bottom line.](image1)

![Fig. 2 – In-situ SR-PXD data for sample 1, as milled Na₂LiAlH₆, heated at 2 °C/min. The decomposition of the sample follows reaction 1.](image2)

### 3.1. Sample 1

The as milled Na₂LiAlH₆ sample behaves as expected, see Fig. 2; the amount of Na₂LiAlH₆ starts to decrease at 215 °C, in parallel with an increase of Al and NaH. This is consistent with reaction 1. According to this reaction LiH should also be present. However, the coherent scattering from LiH is weak, and in addition its peaks overlap with the stronger reflections from Al. LiH is therefore not visible by PXD in this case, but its presence is assumed. The reaction is finished at 250 °C. The next reaction starts at around 300 °C, where NaH starts to disappear. In addition, a rise in the background is observed. This indicates amorphous or liquid phases, possibly due to decomposition of NaH to Na(l) and H₂ gas above 300 °C. This
reaction is completed at around 325 °C. The only remaining phase detected in the diffraction data at this temperature is Al, but the presence of LiH is assumed also here. A similar reaction was seen for the other samples, though at slightly lower temperatures.

3.2. Sample 2

The decomposition of sample 2 (2 mol% TiF3 and cycled once) is quite similar to that of sample 1, with some notable differences. The first is that the relative amount of Na2LiAlH6 has decreased to around 80%, while a substantial amount of NaH (around 16%) is present after cycling, due to incomplete rehydrogenation. Contrary to sample 1, where no reaction is seen before 150–200 °C, a change is observed in sample 2 already from 50 °C. As the temperature is raised, the amount of NaH decreases, accompanied by an increase of Na3AlH6 to 30 mol%. As the temperature is increased to 200 °C, the relative amount of Na3AlH6 increases further, while the amount of Na2LiAlH6 has decreased to 50 mol%. Both Na2LiAlH6 and Na3AlH6 disappear above 200 °C, with corresponding increase of NaH and Al.

Since the decomposition of Na2LiAlH6 below 180 °C occurs simultaneously as an increase of Na3AlH6, it is reasonable to assume that the reaction up to around 180 °C is:

\[
\text{Na}_2\text{LiAlH}_6 \rightarrow \frac{2}{3}\text{Na}_3\text{AlH}_6 + \text{LiH} + \frac{1}{3}\text{Al} + \frac{1}{2}\text{H}_2(g)(\sim 50 - 180 \, ^\circ\text{C})
\]

However the increase in Al is lower than predicted from this reaction, and no other phases accounting for the lacking Al were found. Based on reaction 3 LiH should also be present, but as previously mentioned this is not easily detected by PXD.

3.3. Sample 3

When the amount of TiF3 is increased to 10 mol% (sample 3), the changes relative to sample 1 are more pronounced. During ball milling significant amounts of Na3AlH6 and Al have been formed. The decomposition of Na2LiAlH6 starts already at 50 °C, the content of Na2LiAlH6 decreases to 60 mol% without any formation of NaH, and is accompanied by an increase of Na3AlH6 to 30 mol%. As the temperature is increased to 200 °C, the relative amount of Na3AlH6 increases further, while the amount of Na2LiAlH6 has decreased to 50 mol%. Both Na2LiAlH6 and Na3AlH6 disappear above 200 °C, with corresponding increase of NaH and Al.

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\]

However the increase in Al is lower than predicted from this reaction, and no other phases accounting for the lacking Al were found. Based on reaction 3 LiH should also be present, but as previously mentioned this is not easily detected by PXD.
especially in the presence of Al. The main part of the decomposition of the sample at temperatures above 180 °C is a mixture of the direct decomposition of Na2LiAlH6 (reaction 1) and the decomposition of Na3AlH6 according to:

\[ \text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2(g) \ (\sim 180 - 225 \ ^\circ \text{C}). \]  

(4)

These reactions start at a significantly lower temperature than the decomposition in sample 1; the amount of NaH already starts to increase somewhat at 150 °C. However, the rapid part of the reaction(s) takes place from 200 °C — around the same temperature as for sample 2. For both samples Na2LiAlH6 is still present when all Na3AlH6 is decomposed. In sample 3 Na3AlH6 is completely decomposed at 210 °C, while Na2LiAlH6 remains until 225 °C. This means that, as the temperature increases, reaction 4 is more rapid than the combination of reactions 1 and 3 for these samples.

3.4. Sample 4

Sample 4 is similar to sample 3 (10 mol% TiF3 added), but has been through a dehydrogenation-rehydrogenation cycle before the in-situ SR-PXD measurement. This has led to some significant changes. At the start of the measurement the cycled sample contains 40 mol% Na2LiAlH6 and 30 mol% NaH, in addition to appreciable quantities of Al and Al1–xTi phase (see below). Between 70 and 150 °C, the amount of Na3AlH6 increases, while Na2LiAlH6 and NaH decrease. In the range from 70 to 150 °C weak peaks or shoulders are observed around the 111 and 200 diffraction peaks of Al. This could origin from NaOH at the low angle side and LiF at the high-angle side of the Al peaks. But the content could not be precisely determined due to strong overlap with Al peaks. An impurity phase, Li2O, has also emerged at 125 °C. As previously mentioned, the capillaries were strongly corroded after the in-situ PXD measurement. This has led to some significant changes. At the start of the measurement the cycled sample contains 40 mol% Na2LiAlH6 and 30 mol% NaH, in addition to appreciable quantities of Al and Al1–xTi phase (see below). Between 70 and 150 °C, the amount of Na3AlH6 increases, while Na2LiAlH6 and NaH decrease. In the range from 70 to 150 °C weak peaks or shoulders are observed around the 111 and 200 diffraction peaks of Al. This could origin from NaOH at the low angle side and LiF at the high-angle side of the Al peaks. But the content could not be precisely determined due to strong overlap with Al peaks. An impurity phase, Li2O, has also emerged at 125 °C. As previously mentioned, the capillaries were strongly corroded after the measurements. The presence of Li2O only in sample 4, may show that the corrosion occurs earlier in this sample due to the high content of TiF3 and the dehydrogenation-rehydrogenation cycle.

The fact that the amount of NaH present in the sample is decreasing instead of increasing up to about 180 °C (as expected from reaction 1) indicates that Na3AlH6 is formed in a reaction involving both NaH and Na2LiAlH6 in this temperature range. Thus, most of the decomposition of Na2LiAlH6 takes place due to the presence of NaH without the release of hydrogen through the following reaction:

\[ \text{Na}_2\text{LiAlH}_6 + \text{NaH} \rightarrow \text{Na}_3\text{AlH}_6 + \text{LiH} \ (\sim 70 - 180 \ ^\circ \text{C}). \]  

(5)

At 180 °C there is no more Na2LiAlH6 left. The main part of the dehydrogenation, starting around 180 °C, thus follows reaction 4.

For all the three samples containing TiF3 there are small peaks or shoulders on the high-angle side of the strongest Al reflections, 111 and 200. These peaks are identified as an Al1–xTi–phase, and are most clearly seen in sample 4. In samples 2 and 3 the phase is formed upon heating and is observed from 300 °C to 250 °C, respectively. In sample 4 this phase is present at the start of the measurement, showing that it has been formed during the initial dehydrogenation-rehydrogenation process. The formation of Al-Ti-phases in alanates mixed with Ti-additives has earlier been confirmed, and formation of both a solid solution Al1–xTi and a crystalline Al3Ti have been reported [24,31–33]. The Al1–xTi–phase (x = 0.15) with unit cell dimensions a = 4.038 Å has been found after cycling in several samples, but Al3Ti (a = 3.987 Å) is only seen after prolonged cycling for 7 weeks.

In the present study the the lattice constant of the found phase is a = 3.98 Å in all three samples, indicating formation of Al1–Ti even in the first dehydrogenation cycle. The 100 reflection of Al1–Ti was not seen, and the 110-peak is hidden under the stronger 111-reflection of NaH, therefore the solid solution Al1–xTi can not completely be ruled out, but based on the unit cell dimensions the phase is identified as Al3Ti. The content of Al3Ti remains constant during the in-situ PXD measurement of sample 4.

4. Discussion

All earlier publications on the synthesis and decomposition of Na2LiAlH6 report the decomposition through reaction 1. Small amounts of Na3AlH6 are often seen after synthesis of Na2LiAlH6 by ball milling [16,17,20,23,24], but no deviation from the expected decomposition path is reported. Mamatha et al. observe co-existence of Na2LiAlH6 and Na3AlH6 in a sample studied by in-situ PXD [23]. Na2LiAlH6 was found to decompose before Na3AlH6, but no additional formation or participation of Na3AlH6 in the decomposition is discussed. Thus the present study represents new findings, and the observed results must originate from the use of additive and cycling.

In all the samples with added TiF3, formation of Na3AlH6 was observed, both in the as milled sample and after cycling. Opalka et al. have calculated the phase diagram of the Na–Li–Al–H system from first principles, and concluded that below 87 °C reaction 3 is thermodynamically favorable compared to reaction 1 [13]. Thus thermodynamically Na2LiAlH6 should decompose to Na3AlH6 at low decomposition temperatures, while the direct decomposition of Na2LiAlH6 to binary hydrides, Al and H (reaction 1) should only occur at higher decomposition temperatures. This is in agreement with the present observation of decomposition from Na2LiAlH6 through Na3AlH6 at lowered decomposition temperature obtained by additives. Based on the calculations by Opalka et al. reaction 3 should be seen in all the samples, including the decomposition of pure Na2LiAlH6 (sample 1), if the system was in equilibrium. As this is not the case the reaction must be limited by kinetic barriers. Thus introduction of a suited catalyst would bring the system closer to equilibrium and facilitate the decomposition through reaction 3. A recent study reports a similar effect for the combined system Na3LiAlH6–Mg(NH2)2 [34]. Varying the ball milling conditions results in new decomposition paths, showing that the stability of the system is sensitive to the sample treatment.

The presence of Na3AlH6 in the as milled sample 3 shows that the decomposition of Na3LiAlH6 to Na3AlH6 occurs already during ball milling when TiF3 is added. This shows that the increased energy and temperature during milling is sufficient to start reaction 3. The decomposition of the sample does not proceed further during milling, since no NaH is seen.
NaH is seen at the start of the measurement in both the cycled samples 2 and 4. This shows that the cycling has not been complete; meaning that the reverse reaction 1 has not been completely finished. This is particularly pronounced in sample 4, where more than 30 mol% remains as NaH in the rehydrogenated sample.

The onset temperatures for the decomposition reactions of Na2LiAlH6 decrease when TiF3 is added. This is most readily explained as a catalytic effect. The lower heating rate for sample 2 compared to the other samples might play a role, but as the change in decomposition temperature is much more pronounced in sample 3 and 4, the contribution from a change in heating rate is regarded as a minor effect.

Comparisons of the decomposition of the four investigated samples clearly show that there are at least three reactions involved in the decomposition of Na2LiAlH6: reactions 1, 3 and 5, and that they are sensitive to the altered conditions by addition of TiF3 and cycling. Sample 1 decomposes solely by reaction 1. In samples 2 and 3 the decomposition starts by reaction 3 and switches to reaction 1 as the temperature is increased. This is consistent with the modeling results of Opalka et al. Up to around 200 °C, the amount of Na2AlH6 increases at the expense of Na2LiAlH6, but above 200 °C the desorption proceeds through direct decomposition of Na2LiAlH6. At the same time a direct decomposition of Na2AlH6 through reaction 4 is seen. Na2AlH6 decomposes faster than Na2LiAlH6, and the decomposition is completed at a lower temperature. In sample 4 all the Na2LiAlH6 has decomposed through reactions 3 and 5 before the decomposition path changes to reaction 4. The observed temperature of the switch between the two reactions 3 and 1 is higher than what was predicted by modeling, but this may be due to different kinetic barriers for the various possible reactions. Also, the uncertainty of the transition temperature predicted by modeling is quite large.

The fact that the contribution from reaction 3 increases first by addition of TiF3 in sample 2 and then a further increase by larger amount of additive in sample 3 strongly indicates a catalytic effect of the additive. Several reports show an enhanced decomposition rate of Na2LiAlH6 by addition of Ti species, even at low fractions of the additive [3,20–22,24]. From this kinetic enhancement by cycling the sample with additives the same results should be expected in both sample 2 and 4. But sample 4 seems to decompose by the suggested reaction 5 by combination of Na2LiAlH6 and NaH to form Na2AlH6. This indicates that when NaH is present, reaction 5 is favorable and happens faster than reaction 3.

One mechanism that may promote the production of Na2AlH6 from Na2LiAlH6 (reaction 3 and 5) is growth without nucleation. Since there is already Na2AlH6 present in all samples 2–4, growth of this phase may take place without the need for nucleation, which may be a rate-limiting step. This effect has been reported by Blanchard et al. for the LiAlD4–system [35]. It is shown that the decomposition rate increases significantly when some crystallites of the end product are present.

Finally, partial substitution of the added species could be a source of enhanced kinetics. Fluoride anion substitution has shown to give enhanced kinetics in doped NaAlH4-systems [36–38]. The diffraction data of the present study was therefore investigated for substitution, but no sign of substitution of neither F− or Ti3+ in Na2LiAlH6 was found. Thus it is concluded that the changed decomposition routes origin from a catalytic effect of the additive and cycling.

5. Conclusion

The addition of TiF3 and cycling changes the dehydrogenation reactions of Na2LiAlH6. The temperature of the decomposition of Na2LiAlH6 is lowered by the addition of TiF3, and new decomposition paths are found. The additive shows a catalytic effect on the system, and three competing decomposition reactions are observed. Decomposition of Na2LiAlH6 through Na2AlH6 is shown for the first time, in accordance with previously published theoretical studies predicting this to be thermodynamically favorable for the system. This decomposition is not observed in pure Na2LiAlH6-samples, thus the present study shows that the catalytic effect of the additive brings the system closer to equilibrium. Na2LiAlH6 partially decomposes to Na2AlH6 before the expected decomposition to NaH, LiH an Al. Prior to cycling Na2LiAlH6 decomposes directly to Na2AlH6. However in a cycled sample containing NaH the initial Na2LiAlH6 combines with NaH to form Na2AlH6 in parallel with the direct decomposition from Na2LiAlH6 to Na2AlH6. Better understanding of this effect could give the possibility of changing and tailoring the decomposition route of the major phases by selective use of additives.

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