

Characterization of Al–Ti phases in cycled TiF₃-enhanced Na₂LiAlH₆

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Abstract

TiF₃-enhanced Na₂LiAlH₆ was investigated after dehydrogenation–hydrogenation cycles by synchrotron X-ray diffraction. There was no sign of Ti after ball-milling with TiF₃, but two types of Al–Ti phases were observed in the cycled samples. In a sample after measuring five pressure–composition isotherms in the temperature range from 170 to 250 °C, a fcc phase with $a = 3.987 \text{ \AA}$ was observed. This phase is considered to be Al₃Ti with the L1₂ structure. Samples after one or four cycles at selected temperatures between 170 and 250 °C showed diffraction from another fcc phase with $a \approx 4.03 \text{ \AA}$. This indicates formation of an Al_{1–y}Ti_y solid-solution phase with $y \approx 0.15$ similar to previously reported for cycled NaAlH₄ with Ti additives.

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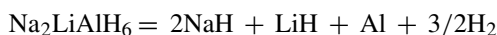
Keywords: Powder X-ray diffraction; Synchrotron radiation; Metal hydrides; Crystal structure; Alanates

1. Introduction

Complex Al-based hydrides, so-called ‘alanates’, have been investigated intensively as a candidate for hydrogen-storage materials with a high gravimetric capacity since reversible hydrogenation was reported for Ti-doped NaAlH₄, Na₃AlH₆ and Na₂LiAlH₆ [1]. After that, dehydrogenation and rehydrogenation of LiAlH₄, Li₃AlH₆ [2–7], Mg(AlH₄)₂ [8,9] and KAlH₄ [10] were investigated, but only KAlH₄ was proven rechargeable.

The mixed alanate Na₂LiAlH₆ has been successfully synthesized by ball-milling [11–13]. It takes an ordered perovskite-type structure with an ordering of LiH₆ and AlH₆ octahedra [13]. Alternatively, it may be described as a fcc of AlH₆ with Li in all the octahedral sites and Na in all the tetrahedral sites. This structure is similar to the high-temperature β-Na₃AlH₆ phase [14,15], where 1/3 of the Na is in the Li positions of Na₂LiAlH₆. Na₂LiAlH₆ with Ti additives showed only one plateau in the pressure–composition (*P–C*) isotherms with a reversible hydrogen capacity larger than 3 wt.% (theoretical value: 3.5 wt.%) [1,16]. It is dehydrogenated and rehydrogenated in a similar

way to Na₃AlH₆ as follows:



Na₂LiAlH₆ is more stable than Na₃AlH₆. The dissociation enthalpy was determined as 56.4 kJ/mol H₂ [16], which is larger than for Na₃AlH₆ (~47 kJ/mol H₂ [17]).

Reversibility and kinetics of the reaction of the alanates greatly depend on catalysts. A number of catalysts have been tested [1,17–21]. The results indicate that Ti-based additives are most effective. However, how the additives work is still not understood. In the NaAlH₄ system, a lot of efforts have been done for clarifying the mechanism of Ti [22–29]. No species containing Ti was detected in as-milled samples (before dehydrogenation) by diffraction [25,26]. After 7 cycles of NaH + Al with 2% Ti(OBu)₄ [25], 100 cycles of NaAlH₄ with 2% Ti(OBu)₄ and 3 cycles of NaAlH₄ with 10% TiCl₃ [29], diffraction from a fcc phase with a unit-cell dimension slightly smaller than Al was observed. This phase was assigned to an Al_{1–y}Ti_y solid-solution phase, with $y < 0.25$. The fraction of Ti in this phase was estimated to $y \approx 0.07$ based on the unit cell volume [25], and from the more accurate quantitative phase analysis, $y \approx 0.15$ was found [29].

In this study, formation of Al–Ti phases during dehydrogenation–hydrogenation cycles was investigated for TiF₃-enhanced Na₂LiAlH₆ by synchrotron radiation powder X-ray

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diffraction (SR-PXD). Four series of samples were examined: (1) samples after ball-milling with TiF_3 , (2) a sample after measuring five P – C isotherms at 170–250 °C, (3) samples after one cycle at selected temperatures between 170 and 250 °C, and (4) samples after four cycles and one cycle spending 4 days at 200 °C. Comparison of the results for the samples in (3) will give the temperature dependence of the phase formation, and the differences among (2), (3) and (4) will provide the dependence on preparing process and the cycling spending times.

2. Experimental

$\text{Na}_2\text{LiAlH}_6$ after P – C isotherm measurements at five temperatures (170, 200, 210, 230 and 250 °C), which totally took 7 weeks, was examined as sample 1. The synthesis and measurement conditions are described in Ref. [16].

The other samples were synthesized as follows: a mixture of NaAlH_4 (Albemarle, recrystallized before use), NaH (Sigma–Aldrich) and LiH (Sigma–Aldrich) with a molar ratio of 1:2:1 was ball-milled at a speed of 700 rpm for 3 h. The milled sample was then subjected to 80 bar of hydrogen at 150 °C overnight (for ~14 h). The synthesized sample was confirmed to be nearly single phase, with only a trace of Na_3AlH_6 . Before cycling, the sample was mixed with 2 mol% TiF_3 by ball-milling for 20 min at 350 rpm. Then, the sample was split into six portions. Four of them were dehydrogenated and re-hydrogenated (one cycle) at 170, 200, 230 and 250 °C, respectively (samples 2–5). The samples were held in a hydrogen pressure lower than 1 bar for 2–5 h during dehydrogenation, and subjected to hydrogen at the initial pressure of 80 bar for ~16 h during hydrogenation. The fifth sample was cycled once at 200 °C spending 4 days (sample 6), and the sixth sample was cycled four times at 200 °C (sample 7). A sample with 10 mol% TiF_3 was also synthesized in the same way as samples 2–7 before cycling (sample 8). All operations were performed under argon atmosphere with <1 ppm oxygen and water. The preparing conditions for the samples described above are listed in Table 1.

SR-PXD data at 22 °C was collected at the Swiss–Norwegian beam line (station BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were contained in rotating boron–silica–glass capillaries with 0.5-mm diameter. The data was collected in steps of $\Delta(2\theta) = 0.003^\circ$ to 0.012° . The wavelength was 0.51979 Å (for sample 1) and 0.49957 Å (for samples 2–8).

The obtained SR-PXD data were analyzed by the Rietveld refinement programs Fullprof version 2.50 [30] (for sample 1) and RIETAN-2000 [31] (for the other data).

Table 1

Preparing conditions for the examined samples

Sample no.	Amount of TiF_3 (mol%)	Cycle no.	Cycling temperature (°C)	Total cycling time
1	2.0	5 ^a	170–250	7 weeks
2	2.0	1	170	1 day
3	2.0	1	200	1 day
4	2.0	1	230	1 day
5	2.0	1	250	1 day
6	2.0	1	200	4 days
7	2.0	4	200	4 days
8	10.0	0	–	–

^a P – C isotherm measurements.

3. Results and discussion

SR-PXD data for $\text{Na}_2\text{LiAlH}_6$ with 10% TiF_3 (sample 8), cf. Fig. 1, clearly shows formation of Al, but no Ti- or F-containing species were detected. This is analogous to NaAlH_4 where 6% and 10% TiF_3 gave the same result [25,29]. The Ti-containing phase is either amorphous or has a small crystallite size below the detection limit of SR-PXD (about 5 nm). No NaF or LiF were found in any of the samples studied, even after cycling. A small amount of Na_3AlH_6 was also detected (~4.8 wt.%), probably due to incomplete reaction to $\text{Na}_2\text{LiAlH}_6$ in the sample preparation.

The sample after P – C isotherm measurements at five temperatures between 170 and 250 °C (sample 1) was investigated by SR-PXD. Compared to the as-prepared sample [16], extra peaks were observed at the high-angle side of the Al peaks (Fig. 2). This cubic phase with relative intensities as a fcc phase has a unit-cell dimension $a = 3.978(1)$ Å. This is smaller than for the $\text{Al}_{0.85}\text{Ti}_{0.15}$ shoulder ($a = 4.0365$ Å) earlier observed in cycled Ti-enhanced NaAlH_4 [25,29]. For comparison, $a = 4.049$ Å for Al. The present unit-cell dimension agrees well with earlier reports of Al_3Ti in the metastable L_{12} structure modification ($a = 4.00$ Å) [32,33].

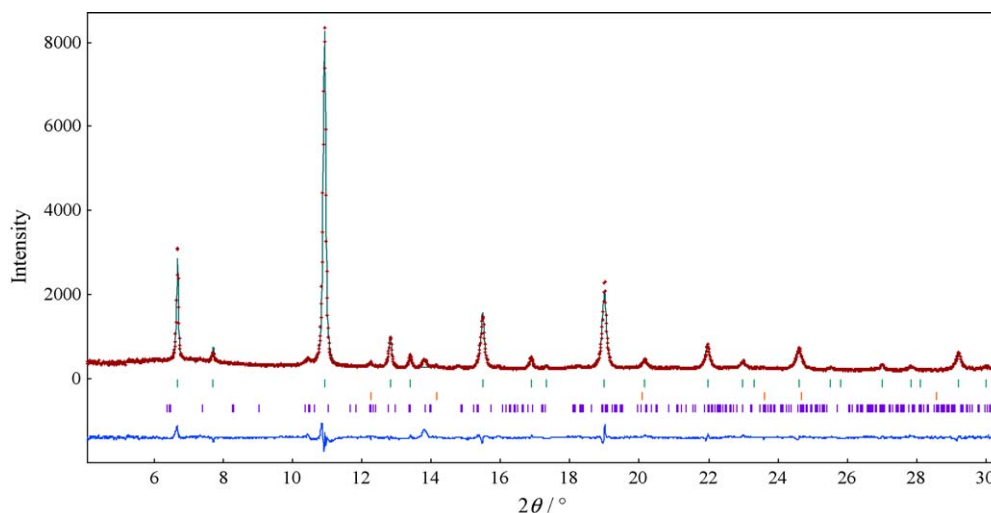


Fig. 1. SR-PXD pattern for $\text{Na}_2\text{LiAlH}_6$ ball-milled with 10% TiF_3 (sample 8) showing observed intensities (dots), calculated intensities (upper line) and differences (bottom line). Tick marks indicate the positions of the Bragg diffractions for $\text{Na}_2\text{LiAlH}_6$, Al and Na_3AlH_6 (from the top). $R_{\text{wp}} = 6.38$, $R_p = 4.65$, $S = 1.25$.

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