

Crystal structure and stability of LiAlD₄ with TiF₃ additive

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Abstract

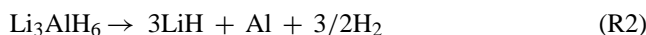
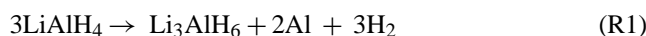
LiAlD₄ samples with TiF₃ additives have been investigated by synchrotron X-ray diffraction, neutron diffraction and a Sieverts-type apparatus. Directly after ball milling there are no signs of any Ti-containing phases, and the unit-cell of LiAlD₄ and Al give no indication of any solid solutions. Hence it is concluded that the Ti is in an amorphous state directly after ball milling. Furthermore, no LiF was observed in the samples. Based on Sieverts-type measurements the plateau pressure at 80 °C has been proved to be higher than 85 bar. Samples stored in a glove box are slowly desorbed, and after 6 months for a LiAlD₄ + TiF₃ sample, the reaction to LiD + Al is nearly finished.

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1. Introduction

Bogdanovic and Schwickardi [1] revealed that addition of Ti compounds, and other transition metal compounds, enhances the desorption kinetics of NaAlH₄ and, furthermore, that re-hydrogenation is possible under moderate conditions. This finding has led to a considerable attention to complex hydrides based on Al as promising reversible hydrogen storage media. One of the candidates is LiAlH₄. The gravimetric storage capacity is higher than for NaAlH₄, and the desorption of hydrogen is at lower temperatures for the first two reactions [2]:



At present, there is no experimental data showing that (R1) is rechargeable. However, Chen et al. [3] have, based on high-pressure DSC experiments, claimed a partial reversibility of (R2) at 160 °C and 40 bar. This is very interesting since (R2) releases 5.6 wt.% in one reaction.

Ti and V have been introduced to LiAlH₄ by ball milling with the chlorides. Addition of TiCl₄ resulted in complete

decomposition to Li₃AlH₆ and Al during ball milling [4]. Addition of VCl₃ and 3TiCl₃·AlCl₃ results in decreased re-activation temperatures when heated in dynamic vacuum for both (R1) (50 °C) and (R2) (20 °C) [3,5,6].

At the moment, there is no detailed mechanistic explanation of why additives improve the kinetics for alanates. There are two main hypotheses of the nature of the additives: either as a secondary phase (Ti or Ti compound) on the surfaces that somehow enhances the reactivity of Al in (R1) and (R2); or a solid solution (doping) of Ti/V into either Na or Al positions that destabilizes the alanates. For NaAlH₄, there are no indications from diffraction studies of any solid solution of Ti in bulk, but on the other hand, no Ti or Ti compound was detected after ball milling [7,8]. After some cycles, however, a crystalline phase interpreted as an Al_{1-x}Ti_x solid solution with $x < 1/4$ is observed [7]. For NaAlH₄, TiF₃ and TiCl₃ additives react apparently differently, evidenced by no crystalline NaF in the former case whereas broad reflection of NaCl was seen by powder X-ray diffraction (PXRD) in the latter case [7].

The aims of the present study was to carry out structural investigations of LiAlD₄ with TiF₃ additives to improve the understanding of the nature of fluorine additives and furthermore to investigate the stability of LiAlD₄ and Li₃AlD₆.

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2. Experimental

The samples were synthesized by ball milling pure LiAlD₄ (Sigma–Aldrich, >95% chemical purity and >99.8% isotope purity) at 350 rpm for 30 min and then, after mixing with 2 mol% TiF₃, ball milling at 350 rpm for 20 min. Ball to sample mass ratio was approximately 20:1. All reactions and operations were performed under argon in a glove box with less than 1 ppm O₂ and H₂O.

PXD data for fresh samples at 22 °C were collected at an INEL instrument with Cu K α ₁ radiation, Bragg Brentano geometry and 120° position sensitive detector. High-resolution synchrotron-radiation (SR) PXD data of both aged and relatively fresh samples were measured at the Swiss-Norwegian beam line (station BM1B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.5 mm boron–silica–glass capillaries. Intensities were measured in steps of $\Delta(2\theta) = 0.005\text{--}0.007^\circ$. The wavelength 0.49956 Å was obtained from a channel-cut Si (111) monochromator.

Powder neutron diffraction (PND) data were collected at 22 °C with the PUS instrument at the JEEP II reactor at Kjeller, Norway. Neutrons with wavelength 1.5553 Å were obtained from a Ge (5 1 1) focussing monochromator. The detector unit consists of two banks of seven position-sensitive ³He detectors, each covering 20° in 2 θ (binned in steps of 0.05°). Data was collected from 10° to 130° in 2 θ . The sample was placed in a rotating cylindrical vanadium sample holder with 6 mm diameter.

Rietveld refinements were carried out using the program Fullprof (version 2.20) [9]. X-ray form factors and neutron scattering lengths were taken from the Fullprof library. Pseudo-Voigt profile functions were used and the backgrounds were modelled by interpolation between manually chosen points.

Thermal programmed desorption (TPD) measurements were carried out by heating the samples at constant heating rate in dynamic vacuum. The pressure was measured with a Penning-type sensor.

The hydrogen content of the samples was determined by a carefully calibrated Sieverts apparatus, using a pressure sensor from Presens (accuracy: 0.025%). The total volume used for these experiments was approximately 111 ml, and the temperature stability was $\pm 0.02^\circ\text{C}$, except for the sample holder and its 2 ml connection line. For the experiment with H₂ atmosphere the compressibilities of Hemmes et al. was used [10], whereas compressibilities of McLennan and Gray were used for D₂ [11].

3. Results and discussion

LiAlD₄ samples with TiF₃ additive levels of 2, 5 and 15 mol% (samples 1, 2 and 3) were prepared by ball milling and investigated by diffraction techniques (PXD, PND), TPD

measurements and pressure measurements in a Sieverts-type apparatus.

PND and PXD measurements carried out within 2 weeks after the sample preparation show that the samples contain LiAlD₄ and Al. The unit-cell dimensions of LiAlD₄ are close to the values found for pure LiAlD₄ [12] and hence no signs for a solid solution of Ti in LiAlD₄ are found, e.g. SR-PXD data of a sample of 5% TiF₃ (sample 2) gives a unit-cell volume of 275.35(5) compared to 275.19(1) Å³ of pure LiAlD₄. This is similar to findings for NaAlH₄ with TiCl₃/TiF₃/Ti(OBu)₄ additives [7] and LiAlD₄ with VCl₃ additives [6]. The refined unit-cell dimension for Al is also equal to literature data for Al. The PXD diagrams after ball milling show small amounts of LiCl impurities as also observed for pure LiAlD₄.

Ti-containing phases were not observed in any of the diffraction diagrams after ball milling. Even for 15 mol% (36 wt.%) TiF₃ additive, only one extra, unexplained reflection was observed at a somewhat lower angle than the angle for the strongest reflection for TiF₃. If this is unreacted TiF₃ with deviating unit-cell dimensions, the amount is only 2 wt.%.

There are no indications of LiF after ball milling from the PND or SR-PXD data. In addition, no other crystalline F-containing phases is observed. This is different from the samples with VCl₃ additives where LiCl was formed in the reaction between LiAlD₄ and VCl₃ [6]. It is not clear whether this difference is due to smaller particle size of LiF or if the fluorides react differently than the chlorides with LiAlD₄.

In freshly prepared LiAlD₄ with 2 mol% TiF₃ (sample 1) no thermal decomposition to Li₃AlD₆ was observed by PXD. However, in samples with TiF₃ additives, that were stored several days, large amounts of Li₃AlD₆ were observed. Fig. 1

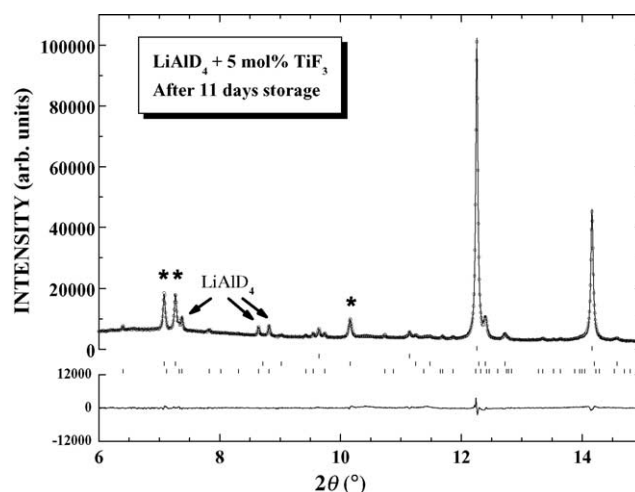


Fig. 1. Observed intensities (circles) and calculated intensities from Rietveld refinements (upper line) of LiAlD₄ with 5 mol% TiF₃ added by ball milling, measured at 22 °C at BM1B, ESRF. Positions of Bragg reflections are shown with bars for Al, LiCl, Li₃AlD₆, LiAlD₄ (from top). The difference between observed and calculated intensity are shown with the bottom line. The strongest reflections of Li₃AlD₆ are marked by *.

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