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Electron microscopy studies of lithium aluminium hydrides

C.M. Andrei[a], J. Walmsley[b], D. Blanchard[c], H.W. Brinks[c], R. Holmestad[a,*], B.C. Hauback[c]

[a] *Department of Physics, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*
[b] *SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway*
[c] *Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway*

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Abstract

The microstructure of $LiAlD_4$ has been studied during the decomposition process using powder X-ray diffraction (PXD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Selected area diffraction (SAD) confirmed the existence of all the decomposed phases presented in the X-ray powder diffraction data. High-resolution transmission electron microscopy confirmed the presence of the $LiAlD_4$ phase before decomposition. After the first decomposition reaction, the electron diffraction patterns were dominated by metallic Al, but significant amounts of Li_3AlD_6 were also present. Inhomogeneous distribution of the phases was confirmed by scanning electron microscopy. Most of the Al was present in discrete particles on the surface of the decomposed alanate. For the $LiAlD_4$ sample heated to 275 °C under dynamical vacuum, many of the interplanar distances for Al and LiD phase overlap. Some of the Li_3AlH_6 phase was found to remain in the material and two characteristic spacings were identified in both the electron and X-ray diffraction data. Fine scale variation in composition was observed in the backscattered scanning electron image.

Keywords: $LiAlH_4$; Alanates; Complex hydride; Electron microscopy; Diffraction pattern; TEM; SEM

1. Introduction

Hydrogen storage has been the subject of intensive research in recent years. Hydrogen is a promising alternative fuel since it is pollution-free and can readily be produced from renewable energy resources [1]. Complex hydrides containing aluminium (alanates) are attractive as hydrogen storage compounds due their high hydrogen content and low weight.

Alanates, such as, $NaAlH_4$ and $LiAlH_4$, have been known for a long time, but the work of Bogdanovic and Schwickardi [2] who demonstrated reversible hydriding behaviour in $NaAlH_4$ when Ti based additive is added, have brought these complex hydrides into focus for storage applications.

Since the first synthesis of $LiAlH_4$ in 1947 [3] several groups have further studied structural and desorption properties of this system [4–11]. $LiAlH_4$ is not reversible under moderate conditions. However, it is interesting to consider the details of the decomposition process in the material. The hydrogen storage capacity of $LiAlH_4$ is very high, 10.6 wt.% in total. Decomposition takes place in three steps upon heating [11–14] with 5.3, 2.6 and 2.6 wt.% release of hydrogen, respectively.

$$3LiAlH_4 = Li_3AlH_6 + 2Al + 3H_2 \tag{R1}$$

$$Li_3AlH_6 = 3LiH + Al + \frac{3}{2}H_2 \tag{R2}$$

$$3LiH + 3Al = 3LiAl + \frac{3}{2}H_2 \tag{R3}$$

The last reaction occurs above 400 °C and is not considered available for practical purposes. The decomposition temperatures are reported to be between 150 and 175 °C for reaction 1 (R1) and 180–220 °C for reaction 2 (R2) [13]. The temperatures can be reduced to 112 °C for R1 and 127 °C for R2 by using very slow heating rates [11].

Electron microscopy can provide key information about the microstructure of the alanates, which has not been

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[*] Corresponding author. Tel.: +47 73 59 38 80; fax: +47 73 59 77 10.
E-mail address: randi.holmestad@phys.ntnu.no (R. Holmestad).

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accessible by other techniques. However, due to the high sensitivity to air and low stability under the electron beam of the alanates, electron microscopy studies have been limited. Some work has been done using scanning electron microscopy (SEM) to study the morphology of Ti doped Li_3AlH_6 [7]. The microstructure of $NaAlH_4$ containing TiF_3 additive direct after the ball milling process and after 15 cycles has been studied recently using transmission electron microscopy (TEM) and SEM [15].

In this work, powder X-ray diffraction (PXD), TEM and SEM in conjunction with energy dispersive X-ray analysis (EDS) have been used to study undoped $LiAlD_4$. We have examined the different stages in the decomposition process with respect to microstructure and phases present. Studies of material mixed with Ti/V have been reported elsewhere [9,16].

2. Experimental

$LiAlD_4$ (Sigma–Aldrich; >95% chemical purity, >98% isotope purity) was obtained as powder and stored under Ar atmosphere. Commercial $LiAlH_4$ powders contain a significant amount of impurities and in order to avoid this problem, $LiAlD_4$ was selected for the experiments. All handling of the samples was done in Ar atmosphere in a glove box to prevent reaction with moisture and oxygen in the air. The sample contained traces of LiCl (about 0.2 wt.%).

Thermal desorption spectroscopy (TDS) experiments were carried out in dynamic vacuum at a heating rate of 2 °C/min. The background vacuum level, with empty sample holder, was approximately 2×10^{-6} mbar. In order to study the decomposition reaction at a given stage, the sample holder was removed from the furnace at the specific temperature during heating and quenched into cold water. The decomposition curves after R1 and after R2 are shown in Fig. 1. The decomposition was stopped at 185 °C for R1 and 275 °C for R2.

PXD data were collected in a flat plate geometry with an INEL MPD diffractometer equipped with a curved CPS 120 position sensitive detector covering a 2θ-range of from 1 to 120°, $\lambda = 1.540562$ Å (Cu $K\alpha_1$ radiation). The powder was uniformly spread in a thin layer on the sample holder and then covered by a thin plastic film to prevent the samples from reacting with oxygen or moisture during the measurements. Rietveld refinements were carried out using the Rietica program [17]. Structural data for $LiAlD_4$ and Li_3AlD_6 were taken from [10] and [18], respectively. Voigt profile functions were used and the background was modelled by Cheby II polynomials.

Electron microscopy samples were prepared in the glove box by mechanical grinding of the powder in a silicate crucible. The dry powder was spread on a holey carbon film supported on a copper grid. Samples were transferred into the TEM using a vacuum container and exchanged into the TEM by means of a removable glovebag device, which maintained an Ar overpressure during the transfer process. For SEM, a simple sealed transfer container has been developed that allows the sample to be placed directly into the SEM air-lock entry chamber, while still under an inert Ar atmosphere. Electron microscopy studies were performed with a Jeol 2010F TEM operated at 200 kV and a Hitachi S-4300SE SEM operated at 10 kV.

3. Results and discussion

3.1. X-ray diffraction

Fig. 2 shows the diffraction patterns of the $LiAlD_4$ during the decomposition process, determined from Rietveld refinements. The phase compositions determined from quantitative phase analysis are indicated in Table 1. Before

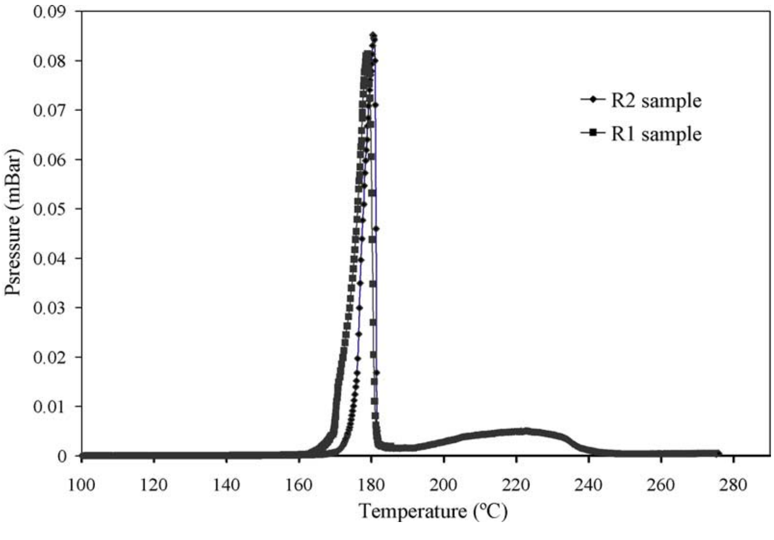

Fig. 1. Decomposition curves from TDS experiments after R1 and R2. The heating rate was 2 °C/min.