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Isothermal decomposition of $LiAlD_4$

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Abstract

A model based on the John–Mehl Avrami formalism has been successfully applied to predict the amount of deuterium released during isothermal decomposition of $LiAlD_4$, as-received or mechanically milled with Al or VCl_3. The John–Mehl Avrami parameters indicate that for $LiAlD_4$ not mixed with additives the nucleation of the new phases during its decomposition is of the continuous nucleation type while for $LiAlD_4$ ball-milled with VCl_3, the nucleation is of the site saturation type.

Keywords: Hydrogen storage materials; Alanates; John–Mehl Avrami; Metal hydrides

1. Introduction

For more than half a century, aluminium hydride and complex alkali metal aluminohydrides, "alanates", have been known and used in industrial chemistry. However, despite their high hydrogen storage capacity they were not considered as possible reversible hydrogen storage materials until Bogdanovic's breakthrough. Bogdanovic and Schwickardi [1] found that the kinetics of the dehydrogenation and hydrogenation of $NaAlH_4$ could be dramatically improved when mixed with Ti additives.

Since this discovery, there have been significant efforts to develop new additives and to synthesize new reversible alanates. However, the targets of 5–6 wt% stored hydrogen and temperature of operation around 80–100 °C have not been reached [2,3]. Despite numerous studies on alanates, the decomposition of the solid phases in these systems is still poorly understood, and the role of the additives remains a puzzle. Hence, more fundamental knowledge is needed to pursue further improvement of the alanate materials.

$LiAlH_4$ has a hydrogen content of 10.6 wt%. Hydrogen is produced by thermal decomposition in a three-step process:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + \tfrac{3}{2}H_2 \quad (2)$$

$$3LiH + 3Al \rightarrow 3LiAl + \tfrac{3}{2}H_2 \quad (3)$$

From in situ synchrotron diffraction experiments the decomposition of lithium alanate has been confirmed to follow (1) and (2) without any intermediate crystalline phases [4,5].

The thermal properties of $LiAlH_4$ have been examined extensively by Dilts et al. [6] and Dymova et al. [7,8]. It was found from differential scanning calorimetry experiments that (1) is exothermic and takes place just after melting at 165 °C. The high decomposition temperature of $LiAlH_4$ was believed to originate from kinetic constraints. Pure lithium alanate has later been found to decompose at temperatures well below its melting point when slowly heated [9]. Furthermore, the temperatures of the three reactions can be significantly decreased by mechanical grinding or by use of additives [5]. However, the role of the mechanical grinding and the additives remains poorly understood.

In the present study, the solid-state decomposition of $LiAlD_4$ is studied using the John–Mehl and Avrami (JMA) formalism [4]. Measurements of the evolved hydrogen pressure in a closed system were carried out during isothermal decomposition of $LiAlD_4$ with and without additives. A semi-empirical model based on the JMA relation is applied to describe the desorption curves. From the analysis of the JMA parameters, the mechanisms of desorption are discussed.

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In a previous study on $NaAlH_4$ [10], an attempt was made to describe the desorption curves assuming that the reactions were of the first order type. At high temperatures the model was reasonably accurate, but it failed to predict the desorption behaviour below 110 °C. The model in this work is successfully used for $LiAlD_4$ in a wide temperature range.

2. Experimental

$LiAlD_4$ (≥95% purity, containing ∼0.2 wt% LiCl) and VCl_3 (99.99%) were purchased from Sigma–Aldrich, and Al (99.99%, mean particle size 20 μm) was obtained from The Aluminium Powder Co. Ltd. All sample handling was carried out in glove box in a dry argon atmosphere to prevent any contact with oxygen and moisture.

Planetary ball milling (BM) was performed using a Fritsch Pulverisette 7 at 400 rpm. Typically, 1 g samples were used in a hardened steel vial of 12 cm^3 sealed under argon, using three steel balls each 7 g. The ball to powder mass ratio was 21:1. Prior to mixing with additives, as-received $LiAlD_4$ was ball-milled for 30 min.

Cryo milling (CM) was performed in a Spex CertiPrep 6750 Freezer mill at a frequency of 10 Hz under liquid nitrogen. Typically, 2 g samples were used, and the impactor to powder mass ratio was 15:1. Polycarbonate cylinders of 10 cm^3, sealed under argon, were used. Prior to the mixing, the filled cylinder was cooled for 15 min. CM was used instead of BM at ambient temperature in order to avoid possible thermal decomposition during the milling procedure. Table 1 describes the sample preparation for the four different samples studied in this work.

Constant temperature desorption was carried out with a Sieverts' type apparatus. Rapid heating of the sample to the set temperature was obtained by inserting the sample holder in a tight aluminium cylinder preheated in a tube furnace. Due to the excellent contact between the sample holder and the aluminium cylinder, the set temperature was reached within ∼3 min. Volumetric determination of the amount of D_2 released during the decomposition was done by measuring the pressure evolution in a calibrated volume (197 ml), after evacuation to 1×10^{-4} mbar. The sample temperature was monitored using a thermocouple in contact with the powder. The temperature of the reference volume was kept at room temperature and during continuous monitoring was used to calculate the number of moles of hydrogen released during the decomposition. As the evolved pressure remained low, 0.1 g of samples were used with a typical pressure increase of up to 0.5 bar, the ideal gas law was used to calculate the mole of D_2 released.

Phase compositions in the samples were analysed by powder X-ray diffraction (PXD) using a Bragg Brenato geometry INEL MPD diffractometer with (Cu $K\alpha_1$) radiation, and a curved CPS 120 position sensitive detector covering a 2θ range from 1° to 120°. The powder was mounted on a flat sample holder and covered by a thin polyethylene film to prevent reaction with oxygen and moisture. Rietveld refinements were carried out using the program RIETICA [11].

3. John–Mehl Avrami data analysis

Time evolved decomposition curves of solid-state reactions depend on several factors related to the mode of growth for the nucleated new phases, and in particular, on the relative rate between diffusion of the species, and nucleation and growth of the new domains [4,12]. The number of moles for the phase being studied, $y(t)$, can be expressed as sigmoidal-like curves obtained by the John–Mehl Avrami relation (JMA):

$$y(t) = 1 - \exp[-(kt)^p] \qquad (4)$$

where k is the rate of formation of the product during the decomposition and t the time.

From both theoretical and experimental considerations, p can be used to characterize the nucleation and growth processes [12,13]. Recently, Kempen et al. have investigated the limits to which the JMA can be applied in practice [14]. p can be defined either as $p = d/m + 1$ when continuous nucleation occurs or $p = d/m$ when site saturation nucleation occurs. For continuous nucleation no nuclei of the phase is present at $t = 0$, whereas for the site saturation nucleation the number of stable nuclei of the new phases is constant, and only their size increases. d represents the dimensionality of the growing phase and can take integer values from 1 to 3. m is the growth mode parameter defining whether the growth is diffusion controlled ($m = 2$) or interface controlled ($m = 1$). Hence, Eq. (4) can also bring some insight into the mechanism of the reactions in addition to determining the kinetics.

Table 1
Description of the samples preparation

Sample names	Sample treatments
A	As-received $LiAlD_4$
B	$LiAlD_4$ ball-milled 30 min
C	$LiAlD_4$ ball-milled 30 min + 6 mol% Al, ball-milled 5 min
D	$LiAlD_4$ ball-milled 30 min + 2 mol% VCl_3 cryo-milled 20 min

Here, only the reactions described by Eqs. (1) and (2) were studied. These reactions show sufficient kinetics to be observed separately in the temperature range 80–200 °C, while the reaction of Eq. (3) needs higher temperature (around 400 °C) to proceed in a practical time frame. At this high temperature, it would have been difficult to accurately resolve the first two reactions. Typical desorption curves for as-received $LiAlD_4$ at 143 °C (below the melting point: 167 °C), exhibit the sigmoidal shape of a solid-state reaction (Fig. 1). The first part of the curve (up to around 60 min) with slow production of D_2 is known as the induction period. It is characterized by a slow production rate of nuclei of the new phases. The second part with an acceleration of the decomposition is named the bulk decomposition.

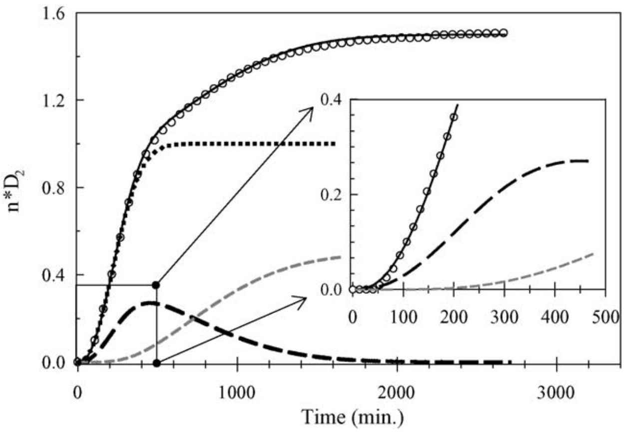

Fig. 1. Evolution of $n^*_{D_2}$ vs. time during isothermal decomposition at 143 °C of as-received $LiAlD_4$ (sample A). Comparison between experimental data and computed data obtain from the JMA model. $n^*_{D_2}$ experimental data from pressure measurements. $n^*_{D_2}$ computed using the JMA model (○); contribution from the reaction of Eq. (1) (●); contribution from the reaction of Eq. (2) (▬ ▬ ▬); total amount (Eq. (1) + Eq. (2)) (—); $n^*_{Li_3AlD_6}$ computed using the JMA model (- - -).