Structural evolution upon decomposition of the LiAlH4 + LiBH4 system

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\textbf{A B S T R A C T}

In the present work we focus the attention on the phase structural transformations occurring upon the desorption process of the LiBH4 + LiAlH4 system. This study is conducted by means of manometric–calorimetric, in situ Synchrotron Radiation Powder X-ray Diffraction (SR-PXD) and ex situ Solid State Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) measurements. The desorption reaction is characterized by two main dehydrogenation steps starting at 320 and 380 °C, respectively. The first step corresponds to the decomposition of LiAlH4 into Al and H2 via the formation of Li3AlH6, whereas the second one refers to the dehydrogenation of LiBH4 (moltens state). In the range 328–380 °C, the molten LiBH4 reacts with metallic Al releasing hydrogen and forming an unidentified phase which appears to be an important intermediate for the desorption mechanism of LiBH4–Al-based systems. Interestingly, NMR studies indicate that the unknown intermediate is stable up to 400 °C and it is mainly composed of Li, B, Al and H. In addition, the NMR measurements of the annealed powders (400 °C) confirm that the desorption reaction of the LiBH4 + Al system proceeds via an amorphous boron compound.

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1. Introduction

In the field of the hydrogen-based fuel cells technology, enormous efforts have been devoted to the development of materials capable to reversibly store high amounts of hydrogen with favorable thermodynamic and kinetic properties [1–3]. Currently, large interest is addressed towards a class of materials defined as tetraborohydrides, due to their high gravimetric hydrogen storage densities [4]. Among them, LiBH4 is considered one of the most attractive and promising materials for automotive application, because of its high hydrogen gravimetric capacity of 18.5 wt.\% [2,5,6]. However, due to its high thermodynamic stability \( (T_{\text{des}} > 500 \, ^{\circ}\text{C}) \) and sluggish sorption kinetics, LiBH4 does not meet the requirements set for on-board hydrogen storage [7]. Recently, in order to tailor the thermodynamics and the kinetics of LiBH4 de-hydrogenation process, different approaches were proposed which can be classified in three categories: the addition of catalysts, the nanoconfinement into scaffolds and the destabilization of the tetrahydroborate by combination with a hydride phase.

Doping with several additives including halides, oxides and pure metals effectively reduces the dehydridding temperature of LiBH4 [8–12]. For example, Au et al. verified that the halides TiF3, TiCl3 and ZnCl2, when added to LiBH4, form unstable transition metal borohydride species which contribute to drastically reduce the thermal desorption temperature of the doped LiBH4 from 300 °C to less than 100 °C [9]. Destabilization of LiBH4 was also achieved by the addition of different oxides with the following order of efficiency: Fe2O3 > V2O5 > Nb2O5 > TiO2 > SiO2 [10]. More recently, Pendolinio and coauthors demonstrated that the desorption temperature of LiBH4 can be decreased from 500 °C to 350 °C by the addition of boron [12].

Another method is represented by the confinement of LiBH4 in mesoporous scaffolds, nanotubes and carbon aerogels [13–17]. LiBH4 was successfully infiltrated into the mesoporous channels of SBA-15 under hydrogen pressure [13]. For the as-prepared LiBH4/SBA-15 nanocomposite, the initial desorption temperature was 150 °C [14]. Vajo et al. reported that fast desorption kinetics of LiBH4 was achieved (50 times at 300 °C) when it was confined within a nanoporous carbon scaffold. However, despite recent progress, the employment of scaffolds drastically decreases the hydrogen storage density of the whole system.
The third approach concerns with the opportunity to tailor the thermodynamic properties of complex hydrides by incorporating a second or a third compound in the reacting mixture to stabilize the reaction products [18–23]. Bösenberg et al. mixed LiBH4 and MgH2 aiming to modify the thermodynamics for the de/rehydrogenation process of LiBH4. By this approach, MgB2 is formed during dehydrogenation [24]. The LiBH4/MgH2 composite system decomposes at lower temperature compared to pure LiBH4 and good reversibility was achieved under milder conditions. Fichtner et al. prepared, by ball milling, a TiF3-doped LiBH4-LiAlH4 (2:1) mixture that starts to decompose between 177 and 247°C and can reversibly absorb hydrogen up to 5.1 wt.% [25]. In addition, Pressure–Composition–Temperature (PCT) experiments pointed out a reduction of the decomposition enthalpy of LiBH4 from 74 kJ/mol H2 (pristine LiBH4) to 60.4 kJ/mol H2 for the TiF3-doped composite system [26]. More recently, Walker et al. demonstrated that the destabilization of LiBH4 induced by a synergic effect of Ti and LiAlH4 can be improved by longer milling times of the starting materials [27]. Nevertheless, despite the long list of works on the LiBH4/LiAlH4 system, up to our knowledge, no experimental investigation is reported for the nominal stoichiometry 1:1.

In this study, the desorption reaction for the binary LiBH4-LiAlH4 (1:1) composite system has been investigated in detail by means of combining manometric calorimetric measurements, in situ Synchrotron Radiation Powder X-ray Diffraction (SR-PXD) and ex situ solid-state MAS Nuclear Magnetic Resonance (NMR).

2. Experimental details

Commercial powders of LiBH4 (95% purity) and LiAlH4 (97% purity) were purchased from Sigma–Aldrich and Alfa Aesar, respectively. The binary mixture of LiBH4-LiAlH4 in a molar ratio 1:1 was prepared by high-energy ball milling using a Spex Mix. 8000. 5 g of powders were sealed in a stainless steel vial and the milling was performed under argon atmosphere with 2 balls (10 g each one), for 30 h with a rotation speed of 875 rotation per minute, rpm. The powders were manipulated inside a glove box (MBraun-20-G) with high-purity argon atmosphere and O2 and H2O levels below 0.1 ppm.

Structural evolution of the milled powders was characterized by means of in situ Synchrotron Radiation Powder X-ray Diffraction (SR-PXD), performed at the beamline D3 of the HASYLAB, DESY, Hamburg. A high-pressure sample cell provided with a sapphire capillary and specifically designed for in situ monitoring of solid/gas reactions was used [24]. The in situ measurement was performed at 1 bar of Ar pressure. The powders were heated from 30 to 400°C with 5°C/min as heating rate and then kept for 40 min at 400°C. Each X-ray diffraction (XRD) pattern was collected with an exposure time of 30 s using a wavelength (λ) of 0.49902 angstrom (Å). The FIT2D program was used to convert the two-dimensional images into the one-dimensional powder patterns [28]. Phase abundance and microstructural parameters were evaluated by fitting the XRD patterns by Rietveld method with the software MAUD [29].

Coupled manometric calorimetric measurements were performed on the as-milled powders: a high-pressure cell of Sensys DSC (Setaram) was charged with 50 mg of powder under Ar atmosphere in a glove box and was directly connected to the manometric instrument (PCTPro-2000 by Setaram & Hy-Energy; pressure sensors accuracy: 1% of reading) by a 1/8” stainless steel tube. Thermal programmed desorption steps (TPD) were performed by heating the samples from room temperature to 450°C at 5°C/min under an atmosphere of 0.5 bar of hydrogen.

Solid-state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker Advance 400 MHz spectrometer with a wide bore 9.4T magnet and by employing a boron-free Bruker 4 mm CPMAS probe. The spectral frequencies were 128.33 MHz for the 11B nucleus, 155.33 for the 7Li nucleus and 104.28 for the 27Al nucleus. The NMR chemical shifts were reported in parts per million (ppm) internally referenced to BF3(O(CH2)3)2, LiCl and Al(NO3)3, respectively. The powder materials were packed into 4 mm ZrO2 rotors in an argon-filled glove box and were sealed with tight fitting Kel-F caps. MAS experiments were performed at room temperature at sample rotation frequencies of 12 kHz using dry nitrogen gas. Spectra were acquired at 20°C and the temperature was controlled by a BRUKER BCU unit.

3. Results and discussion

The coupled manometric calorimetric profile recorded on the as-milled sample is reported in Fig. 1. The manometric analysis of the reacting LiBH4-LiAlH4 mixture reveals a multistep desorption path: the first desorption step starts at ca. 120°C with a release of about 3.9 wt.% of H2 while the second step takes places at 380°C and corresponds to a release of 2.9 wt.% of H2. Full dehydrogenation is not achieved at 430°C. At this temperature, 6.8 wt.% H2 is measured which does not match the theoretical gravimetric capacity of the system (10.12 wt.%) associated with the following reaction:

\[
\text{LiBH}_4 + \text{LiAlH}_4 \rightarrow \frac{1}{2}\text{AlB}_2 + 2\text{LiH} + \frac{1}{2}\text{Al} + 3\text{H}_2(\text{g})
\] (1)

The composite shows a complex calorimetric profile. The measurement, reported in Fig. 1 (black solid line), reveals six thermal events during heating: five endothermic peaks with onset temperature of 95°C (A), 114°C (B), 183°C (D), 271°C (E) and 380°C (F) and one exothermic peak at 120°C (C).

In order to further investigate the desorption reaction, in situ SR-PXD was performed on the LiBH4-LiAlH4 mixture using the same experimental conditions applied for the coupled manometric calorimetric analysis.

Fig. 2 shows a series of XRD patterns collected in the range of temperature between room temperature and 400°C with 5°C/min as heating rate while Fig. 3 displays the patterns, with Rietveld fitting profiles, relevant to samples thermally treated at the temperature of the peaks in the DSC analysis. At room temperature, reflections of the starting material correspond to the α-LiBH4 and LiAlH4 are visible. Small traces of metallic Al (<4 wt.%) are also

![Fig. 1.](http://dx.doi.org/10.1016/j.jallcom.2013.12.027)
formation of Li$_3$AlH$_6$ is confirmed by the Rietveld refinement of the pattern collected at 115 °C (Fig. 3C). This result suggests that LiAlH$_4$ melts and subsequently exothermically decomposes to Li$_3$AlH$_6$, Al, and H$_2$. Observation of these two characteristic events (peaks B and C in Fig. 1) is in accordance with previous works, which reported that the as-received LiAlH$_4$ melts around 170 °C (endothermic event) and quickly decomposes (exothermic event) to Li$_3$AlH$_6$ at 194 °C. The onset thermal events are shifted to lower temperatures for the milled material [30,31]. The decomposition of LiAlH$_4$ to Li$_3$AlH$_6$ is also endorsed by a sharp intensification of the diffraction peaks of Al (Fig. 2) and a slight increase of the pressure inside the cell (blue line in Fig. 2) associated to hydrogen release during this step. This is in agreement with the first desorption step at about 120 °C (Fig. 1).

Around 170 °C, the Bragg reflections related to Li$_3$AlH$_6$ start to disappear followed by an increase of the cell pressure and a further growth of intensity of the Al peaks. As reported in literature [32], Li$_3$AlH$_6$ decomposes forming LiH, Al, and hydrogen. However, since Al and LiH crystallize in the same space group (Fm-3m) and with similar unit cell parameters (4.0494 Å and 4.0609 Å, respectively), their diffraction peaks overlap, making complicate both the qualitative and quantitative evaluation of the phases. The Al/LiH and h-LiBH$_4$ phases still exist over 223 °C (Fig. 3D) and, in particular, the intensity of the Al/LiH reflections increases significantly over this temperature, as shown in Fig. 2. Note that LiBH$_4$ does not seem to influence the LiAlH$_4$ decomposition step. In fact, the amount of hydrogen released during the first step (3.9 wt.% H$_2$ – Fig. 1) is close to the theoretical hydrogen storage capacity of LiAlH$_4$ in the whole system (5.06 wt.% H$_2$), if decomposes to LiH, Al, and H$_2$ (as proved by XRD measurements).

At ca. 262 °C h-LiBH$_4$ starts to melt and its diffraction peaks vanish, given rise to a diffuse halo shown in Fig. 2 in the region marked as 2. According to the literature [33], the melting occurs without evolution of hydrogen and it is characterized by an endothermic event which is confirmed by the DSC analysis reported in Fig. 1 (peak E).

Around 328 °C, the intensities of the Al/LiH peaks decrease and some signals belonging to an unknown phase show up. The formation of the unknown phase is accompanied by an increase of the pressure inside the cell, therefore the reaction between Al and molten LiBH$_4$ leads to release of hydrogen at temperature lower than pristine LiBH$_4$. The unidentified phase (denoted by the symbol ? in Fig. 2) is stable up to 400 °C as evidenced by pattern E in Fig. 3. At this temperature, four distinct peaks show up: $d_{obs} = 2.601$ Å ($I_{obs} = 100$), 1.844 Å ($I_{obs} = 87$), 1620 Å ($I_{obs} = 57$), 1502 Å ($I_{obs} = 66$). Similar indexation was found by Ravnsbaek et al. for an identified phase formed at 390 °C during the thermal desorption of the LiBH$_4$ + Al (1:1.5) system [34]. More recently, Jensen et al. reported that the decomposition of the LiBH$_4$ + Al system occurs via two intermediate compounds observed below 500 °C which could be a new phase mainly composed by Li–Al–B species [35].

At the end of the annealing process ($T = 400$ °C), only the Al/LiH and the unknown phase are observed in the XRD, as emerged by Fig. 3E. In addition, no traces of AlB$_2$ are visible.

The as-annealed powders were then characterized by solid-state MAS NMR technique to identify the unknown species. In Fig. 4A, $^1$H (dark line) NMR spectrum of the mixture treated at 400 °C is displayed. A sharp peak at 0.5 ppm is observed which cannot be directly associated to LiH (+1.5 ppm). In addition, chemical shift of $+19.4$ ppm is measured, in accordance with the typical chemical shift of LiAl [36]. Note that the broadening of the centerband line width of LiAl suggests that the size of the LiAl crystals is very small and its integrated signal is less than 5% close to the XRD detectable limits. Regarding $^{27}$Al [1H] measurement, the pattern is reported in Fig. 4B. More than half of the observed $^{27}$Al signal is due
to Al metal (1640 ppm), confirming that aluminum is the major product of the mixture annealed at 400 °C. The broad peak at ~+400 ppm and the doublet at +11.9 and +77.7 ppm (inset in Fig. 4B) can be attributed to Al nucleus in the LiAl and LiAlO2 phases, respectively. In Fig. 4C, $^{11}$B ($^1$H) (dark line) and $^{11}$B (red line) MAS NMR spectra are shown. Residual LiBH4 is detected at −37 ppm (signal 5.6%), whereas the broad peak centered around 0 ppm results difficult to assign. This asymmetric peak can be interpolated by two peaks placed at −2.94 ppm (signal 44.3%) and +15.03 ppm (signal 50.1%). The peak at −2.94 ppm could overlap that of AlB2 signal (+2.84 ppm), but, as confirmed by XRD analysis, its formation could not be detected up to 400 °C.

Composite-pulse decoupling (CPD) is a very useful technique to distinguish among species that contain B–H bonded atoms [37]. In the spectrum acquired without decoupling the proton (red line), a decrease of the signal relative to the B–H unit is observed in the peak centered at −2.94 ppm. This proves that the boron based species associated to the signal at −2.94 ppm contains hydrogen. In addition, it is worth to claim that Al atoms is contained within this phase because during heating, the Al XRD peaks decrease drastically their intensity leading to the formation of the unknown phase. However, no $^{27}$Al signal which could be associated to that phase is observed in Fig. 4B. The peak at +15.03 ppm is not influenced by decoupling proton, probably because contains B atoms which are not bonded to hydrogen. On the basis of $^{11}$B MAS NMR studies in the literature, this resonance could be assigned to amorphous boron (+18 ppm) [38]. Summarizing, the in situ XRD and MAS NMR results suggest that the unknown phase is mainly composed by Li–Al–B–H atoms and, together with metal Al and amorphous boron, it represents a crucial intermediate in the decomposition mechanism of the LiBH4 + LiAlH4 system. Nevertheless, more efforts are still required in order to definitely clarify its chemical nature and its influence on the reversibility of the system.

4. Conclusions

In this work, we investigated the thermal decomposition of the LiBH4–LiAlH4 system. It is reported that the desorption of the 1:1 mixture reveals a multi-step reaction with a total weight loss of 6.8 wt.% of H2 at 430 °C. In order to characterize the decomposition products evolved during heating, in situ SR-PXD experiment were performed. It is observed that the onset decomposition temperature of molten LiBH4 takes place around 328 °C namely 50 °C less than pure LiBH4. The molten LiBH4 reacts with Al particles (produced by the decomposition of LiAlH4 and Li3AlH6) forming an unidentified phase, already reported in the literature and releases hydrogen as confirmed by the variation of the pressure monitored during the in situ XRD experiments. As evinced by ex situ solid state MAS NMR, the unknown phase seems to be mainly composed by Li–B–Al–H atoms. This study represents a further progress in the full characterization of the reaction mechanism of the LiBH4/Al-based system.

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