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Xuebin Yu

Fudan University, Shanghai, China, xyu@uow.edu.au

Guanglin Xia

Fudan University, Shanghai, China

Zaiping Guo

University of Wollongong, zguo@uow.edu.au

Hua-Kun Liu

University of Wollongong, hua@uow.edu.au

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Abstract

LiBH₄/Al mixtures with various mol ratios were prepared by ball milling. The hydrogen storage properties of the mixtures were evaluated by differential scanning calorimetry/ thermogravimetry analyses coupled with mass spectrometry measurements. The phase compositions and chemical state of elements for the LiBH₄/Al mixtures before and after hydrogen desorption and absorption reactions were assessed via powder x-ray diffraction, infrared spectroscopy, and x-ray photoelectron spectroscopy. Dehydrogenation results revealed that LiBH₄ could react with Al to form AlB₂ and AlLi compounds with a two-step decomposition, resulting in improved dehydrogenation. The rehydrogenation experiments were investigated at 600 °C with various H₂ pressure. It was found that intermediate hydride was formed firstly at a low H₂ pressure of 30 atm, while LiBH₄ could be reformed completely after increasing the pressure to 100 atm. Absorption/ desorption cycle results showed that the dehydrogenation temperature increased and the hydrogen capacity degraded with the increase of cycle numbers.

Keywords

Dehydrogenation, rehydrogenation, mechanism, aluminum, destabilized, lithium, borohydride

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Dehydrogenation/rehydrogenation mechanism in aluminum destabilized lithium borohydride

Xuebin Yu^{a)}

Department of Materials Science, Fudan University, Shanghai 200433, China; Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia; and CSIRO National Hydrogen Materials Alliance, CSIRO Energy Centre, Mayfield West, NSW 2304, Australia

Guanglin Xia

Department of Materials Science, Fudan University, Shanghai 200433, China

Zaiping Guo and Huakun Liu

Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia; and CSIRO National Hydrogen Materials Alliance, CSIRO Energy Centre, Mayfield West, NSW 2304, Australia

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LiBH₄/Al mixtures with various mol ratios were prepared by ball milling. The hydrogen storage properties of the mixtures were evaluated by differential scanning calorimetry/thermogravimetry analyses coupled with mass spectrometry measurements. The phase compositions and chemical state of elements for the LiBH₄/Al mixtures before and after hydrogen desorption and absorption reactions were assessed via powder x-ray diffraction, infrared spectroscopy, and x-ray photoelectron spectroscopy. Dehydrogenation results revealed that LiBH₄ could react with Al to form AlB₂ and AlLi compounds with a two-step decomposition, resulting in improved dehydrogenation. The rehydrogenation experiments were investigated at 600 °C with various H₂ pressure. It was found that intermediate hydride was formed firstly at a low H₂ pressure of 30 atm, while LiBH₄ could be reformed completely after increasing the pressure to 100 atm. Absorption/desorption cycle results showed that the dehydrogenation temperature increased and the hydrogen capacity degraded with the increase of cycle numbers.

I. INTRODUCTION

In order to use hydrogen as one of the clean fuels of the future, it is necessary to develop high-performance hydrogen-storage materials.^{1,2} Most of the complex hydrides, such as sodium alanate systems,^{3–5} the amide system,^{6–8} the borohydride system,^{9–13} and so on inevitably possess a high hydrogen storage capacity, so systematic investigations have vigorously been in progress in the past few years. Among them, lithium borohydride, LiBH₄, is presently one of the most promising solid-state hydrogen-storage materials, because of its high hydrogen storage capacity of 18.5 wt%. However, the main evolution of gas starts at 380 °C, and only half the hydrogen is released before 600 °C.¹⁴ Recently, Züttel et al.¹⁴ reported that SiO₂ may be used to destabilize the dehydrogenation of LiBH₄, lowering the temperature of hydrogen evolution to 300 °C. Pinkerton et al.¹⁵ also reported that LiBH₄ could react with LiNH₂ to form

quaternary hydride Li–B–N–H. This quaternary hydride released hydrogen at just above 250 °C.

More recently, new approaches modify the hydrogenation/dehydrogenation reaction of LiBH₄ by using additives to form compounds or alloys in the dehydrogenated state that are energetically favorable with respect to the products of the reaction without additives. This concept is known as destabilization. The principle underlying this concept is that having a stabilized dehydrogenated state reduces reaction enthalpy. For example, LiBH₄ may be reversibly dehydrogenated and rehydrogenated by the addition of MgH₂,^{16–18} resulting in complete dehydrogenation of the borohydride phase and the formation of Li–Mg alloy and MgB₂. Furthermore, it was also demonstrated by experiment and computation that Al addition can destabilize LiBH₄, resulting in improved dehydrogenation.^{19–24} However, in these references, the LiBH₄/Al mixture was investigated only with a mol ratio of 2:1 and no detailed dehydrogenation/rehydrogenation mechanism was described. To understand the role of Al in destabilizing the decomposition of LiBH₄, especially for the intermediate process of dehydrogenation, further investigations are necessary.

^{a)}Address all correspondence to this author.

e-mail: yuxuebin@fudan.edu.cn
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In this paper, the hydrogen storage properties of LiBH_4/Al mixtures with various mol ratios are studied. The results are reported here.

II. EXPERIMENTAL

The LiBH_4 (95%, Alfa Aesar, USA) and Al (J&K Chemical Ltd., Shanghai, China) were obtained commercially and used without further purification. All handling procedures were conducted under an inert atmosphere. LiBH_4

was mixed with Al powder in various mol ratios in a glove box (oxygen and water content each below 1 ppm), and then the mixtures were mechanically milled for 2 h (planetary QM-1SP2, Nanjing, China) under an inert gas (argon).

Hydrogen release property measurements were performed by differential scanning calorimetry/thermogravimetry (DSC-TG; Netzsch STA 449C, Selb, Germany) equipment connected to a mass spectrometer (MS; Hiden, Warrington, UK), using a heating rate of $10^\circ\text{C}/\text{min}$ under 1 bar argon with a purging rate of $100\text{ cm}^3/\text{min}$. Typical sample quantities were 5–10 mg for pure LiBH_4 and 20–30 mg for LiBH_4/Al mixtures. The rehydrogenation of LiBH_4/Al samples was carried out on a Sievert's apparatus under 600°C and various H_2 pressure for 24 h. Powder x-ray diffraction (XRD; X'Pert-MPD) measurements were conducted to confirm the phase structure. All the XRD results for the dehydrogenated samples were obtained after cooling down to room temperature. Powders were spread and measured on a Si single crystal. Polymer film was used to cover the surface of the powder to avoid oxidation during the XRD measurement. LiBH_4 and LiBH_4/Al mixtures were pressed with KBr for Fourier transform infrared (FTIR; Magna-IR 550 II, Nicolet USA) analysis. The chemical state of lithium and boron in LiBH_4 and LiBH_4/Al mixtures were analyzed with x-ray photoelectron spectroscopy (XPS; XR5, VG, UK) with Al $\text{K}\alpha$ radiation ($h\nu = 1486.6\text{ eV}$). The binding energy values correspond to the carbon C1s core level at 285.0 eV .

III. RESULTS AND DISCUSSION

The hydrogen desorption properties of LiBH_4/Al mixtures and LiBH_4 after 2 h milling with various mol ratios are shown in Fig. 1. Descriptions of the individual samples are presented in Table I. The onset of hydrogen desorption from LiBH_4 (S1) was at about 380°C . The main desorption peak appeared at 440°C . In the case of LiBH_4/Al with a mol ratio of 2:1, the onset hydrogen desorption started at 310°C and the first hydrogen release peak appeared at 379°C . On further heating, a strong peak at 480°C was observed. This suggests that the desorption process in S2 consists of two steps below 500°C , indicating its different decomposition pattern compared with pure LiBH_4 . With increasing Al content, the main desorption peak became broader and shifted to lower temperature. In particular, the

FIG. 1. (a) MS and (b) TG results for the evolution of hydrogen ($m/e = 2$) from LiBH_4 (S1) after 2 h milling and LiBH_4/Al mixtures with mol ratios of 2:1 (S2), 1:1 (S3), 2:3 (S4), and 1:3 (S5).

TABLE I. Comparison of hydrogen desorption capacities for 2 h milled LiBH_4 (S1) and LiBH_4/Al mixtures with mol ratios of 2:1 (S2), 1:1 (S3), 2:3 (S4), and 1:3 (S5) after heating to 500°C . The rehydrogenation conditions are 100 atm H_2 pressure and 600°C .

Composition	S1 LiBH_4	S2 LiBH_4/Al (2:1)		S3 LiBH_4/Al (1:1)		S4 LiBH_4/Al (2:3)			S5 LiBH_4/Al (1:3)	
	Cycle 1	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2
H_m (wt%)	6.5	7.7	5.1	6.4	5.4	5.1	5.1	3.8	3.6	3.6
H_c (wt%)	18.5	11.3	11.3	8.2	8.2	6.4	6.4	6.4	3.9	3.9

H_m , measured hydrogen desorption capacity from the LiBH_4/Al mixtures; H_c , calculated theoretical hydrogen capacity in the LiBH_4/Al mixtures.

main desorption peak at 379 °C was observed for the LiBH_4/Al with a mol ratio of 1:3 (S5). To investigate the potential by-products released from the LiBH_4/Al mixtures, MS for various gas evolutions from the S1 and S3 samples were measured as shown in Fig. 2. Clearly, there is no significant BH_3 or B_2H_6 released, suggesting that all the weight loss from the LiBH_4 and LiBH_4/Al mixtures can be ascribed to hydrogen release. Figure 1(b) displays TG results for samples S1 to S5, and the total weight loss from them is listed in Table I. The weight loss of 6.5 wt% for LiBH_4 suggests that only 35.1% of the hydrogen was released before 500 °C. However, the measured hydrogen release capacities from the S2, S3, S4, and S5 samples are 7.7, 6.4, 5.1, and 3.6 wt%, respectively, which correspond to 68.1%, 78%, 79.7%, and 92.3% of the hydrogen in their respective mixture. This represents a significant improvement compared with the pure LiBH_4 . The fact that around

three-fourths of the hydrogen was released from sample S2 suggests that the LiBH_4 was probably decomposed to LiH . Meanwhile, part of the LiH was decomposed further in the S3, S4, and S5 samples.

To identify the hydrogen desorption mechanism of the LiBH_4/Al mixtures, XRD of the mixtures before and after dehydrogenation was conducted, as shown in Fig. 3. Compared with the pattern of S1, it can be seen that the patterns for S2 to S4 before dehydrogenation show a mixture of LiBH_4 and Al , suggesting that the milled reactants are a physical mixture, and no new phase appears to have formed. In the case of S5, no apparent LiBH_4 was observed [Fig. 3(a)]. However, the FTIR results in Fig. 4 clearly identified the presence of B–H bond ($2200\text{--}2400\text{ cm}^{-1}$), suggesting that the disappearance of LiBH_4 peaks from the XRD might be the result of its low concentration and the nanocrystallinity/disorder

FIG. 2. MS results for the gas evolution of H_2 ($m/e = 2$), O_2 ($m/e = 32$), H_2O ($m/e = 18$), BH_3 ($m/e = 14$), and B_2H_6 ($m/e = 24$) from the (a) S1 and (b) S3 samples.

FIG. 3. XRD patterns for 2 h milled LiBH_4/Al mixtures. (a) Before dehydrogenation. (b) After dehydrogenation to 500 °C XRD for all the dehydrogenated samples were measured after cooling down to room temperature. The broad amorphous peaks at 20 to 25° resulted from the amorphous polymer tape.

FIG. 4. FTIR result of (a) S1 and (b) S5 samples after ball milling for 2 h.

produced by the ball-milling process. After heating to 500 °C, the S1 sample still showed the LiBH₄ phase and no LiH phase was observed. This is different from the previously reported results, in which the LiH was formed after heating the LiBH₄ to 470 °C.⁹ The different observations might result from the lower heating rate of 5 °C/min in the reference, which increase the decomposition of LiBH₄. In the case of S2 to S5 samples, new diffraction patterns were detected [Fig. 3(b)]. From comparison with the XRD database, the new patterns correspond to a mixture of residual Al, AlB₂, LiH, and AlLi. This suggests that the Al reacted with LiBH₄ to form AlB₂ and AlLi, resulting in improved hydrogen release.

Figure 5 shows the XPS spectra of the decomposed S1 and S5 samples with positions of the B1s and Li1s peaks. For boron, two peaks centered on 188.2 and 187.2 ± 0.3 eV are observed for S1 and S5 sample, respectively, which correspond to B (1s) formed with boride. Given the XRD results in Fig. 3(b), it can be concluded that the peak at 188.2 eV is ascribed to the B (1s) in LiBH₄ and the peak at 187.2 ± 0.3 eV results from the B (1s) in AlB₂. Furthermore, the peaks of Li1s are located at 55 and 56.3 eV for S1 and S5 samples, which correspond to LiH (LiBH₄) in S1 and LiAl in S5.

Figure 6 presents the results from further XRD investigation after sample S2 to S5 was heated to various temperatures. In the case of S2 [Fig. 6(a)], the XRD patterns at 350 and 400 °C showed Al and LiBH₄. No apparent AlB₂ or AlLi formed. The AlB₂ peaks appeared at 450 °C, suggesting the prior formation of AlB₂. After heating to 500 °C, the LiBH₄ peaks disappeared and strong LiH peaks appeared. It figures out a reaction of $2\text{LiBH}_4 + \text{Al} \rightarrow 2\text{LiH} + \text{AlB}_2 + 4\text{H}_2$ as described in Refs. 21 and 22. However, in the cases of S3 to S5 [Figs. 6(b), 6(c), and 6(d)], a new phase of AlLi started to form after 450 °C and its intensity increased with the

FIG. 5. (a) B1s and (b) Li 1s XPS spectra of decomposed S1 and S5 samples.

increasing temperature. Simultaneously, the LiH peaks weakened or disappeared. It suggests that the formation of AlLi is correlated with the decomposition of LiH. The aforementioned results suggest that the dehydrogenation mechanism of the LiBH₄/Al system could be two steps; firstly, Al reacts with LiBH₄ to form AlB₂ and LiH, and then the Al reacts with LiH to form AlLi. The two-step decomposition in LiBH₄/Al system may also be demonstrated from the MS results in Fig. 1, in which the second step with small hydrogen evolution peaks at 450 to 500 °C can be observed for S3 to S5 samples.

Therefore, the reaction process is postulated to be:

The total equation is:

FIG. 6. XRD patterns for (a) S2, (b) S3, (c) S4, and (d) S5 dehydrogenated to various temperatures. XRD patterns for all the samples were measured after cooling down to room temperature. The broad amorphous peaks at 20 to 25° resulted from the amorphous polymer tape.

From Eqs. (1) to (3), the decomposition of S2 is based on Eq. (1), which has a calculated hydrogen capacity 9.9 wt%. In the case of S3, part of LiH decomposed from LiBH₄ will react with Al based on Eq. (2). It possesses a theoretical hydrogen capacity of 7.2 wt%. Furthermore, the decomposition of S4 and S5 are based on Eq. (3) with two-step hydrogen release (75% hydrogen for the first step and 25% hydrogen for the second step), in which the calculated hydrogen capacities are 6.4 and 3.9 wt%, respectively. However, the practical desorption capacities in S2 to S5 are 7.7, 6.4, 5.1, and 3.6 wt%, which correspond to 77.8%, 88.9%, 79.7%, and 92.1% of their theoretical capacities, respectively. It indicates that, besides S5 sample, the proposed reactions in S2 to S4 did not implement completely during the heating, which can be demonstrated by the residual Al element peaks after dehydrogenation to 500 °C [see Figs. 6(a)–6(c)]. The fact that enhancing hydrogen desorption rate and lowering desorption temperature from S2 to S5 suggests that the increase of Al content in LiBH₄/Al system is effective on accelerating the full decomposition of LiBH₄, which might result in more sufficient contact between LiBH₄ and Al.

The improvement of dehydrogenation in LiBH₄/Al system could be explained by the decreased enthalpy compared with pure LiBH₄. The enthalpy for the LiBH₄/Li + B and LiBH₄/LiH + B systems are esti-

mated to be 194 and 69.2 kJ/mol.¹⁴ However, the formation of stable compounds of AlB₂ and AlLi, which have large formation enthalpy, might result in a decrease of hydrogenation/dehydrogenation enthalpy in LiBH₄/Al system. For example, the formation enthalpy in LiBH₄ + 1/2Al → LiH + 1/2AlB₂ + 3/2H₂ system is decreased to 28.9 kJ/mol.²² The reduced enthalpy led to an increase of absorption/desorption plateau pressure or a decreased absorption/desorption temperature.

It was reported that LiBH₄ could be subsequently rehydrogenated at 600 °C and >150 bar of hydrogen.^{11,25} Obviously, this is too rigorous. Previous work on LiBH₄/Al showed that the reversible conditions of LiBH₄ could be reduced by Al addition. Yang et al. reported that the LiBH₄/Al (mol ratio of 2:1) system has a reversible capacity of 6.7 wt% when rehydrogenated at 350 °C and 150 atm hydrogen pressure.²⁰ Kang et al. claimed that about 5 wt% hydrogen capacity was achieved for dehydrogenated LiBH₄/Al (mol ratio of 2:1) sample first rehydrogenated at 400 °C and 100 atm H₂.²¹ Here, our results showed that the S2 to S5 samples could be reversed completely under 600 °C and 100 atm H₂. However, at a low hydrogen pressure of 30 atm, intermediate hydride was formed first. LiBH₄/Al samples (S2–S5) that had been dehydrogenated under vacuum for 30 min at temperatures up to 600 °C was rehydrogenated at 600 °C under 30 and 100 atm hydrogen pressure for 24 h. Figure 7 showed the XRD results

FIG. 7. XRD patterns for dehydrogenated S2 to S5 samples rehydrogenated at 600 °C and under 100 a.m. hydrogen for 24 h. XRD for all the rehydrogenated samples were measured after cooling down to room temperature. The broad amorphous peaks at 20 to 25° resulted from the amorphous polymer tape.

FIG. 8. DSC results for the rehydrogenated S2 to S5 samples. The rehydrogenation conditions are 100 atm H_2 pressure and 600 °C.

for the S2 to S5 samples rehydrogenated under 600 °C and 100 atm H_2 , in which the AlB_2 and $AlLi$, formed during the dehydrogenation, disappeared, and Al and $LiBH_4$ peaks were presented. It suggests that the AlB_2 and $AlLi$ were reversed to Al and $LiBH_4$. In addition, the DSC results (Fig. 8) presented two endothermic peaks at 115 and 270 °C, corresponding the phase transformation and melting point of $LiBH_4$, also demonstrated the formation of $LiBH_4$.

Figure 9 shows the TG–MS results for hydrogen evolution from the rehydrogenated $LiBH_4/Al$ samples with a heating rate of 10 °C/min. The main hydrogen desorption peaks for the rehydrogenated S2 to S5 are located at 508, 456, 449, and 415 °C, which are shifted to high tempera-

FIG. 9. (a) MS and (b) TG results for the evolution of hydrogen ($m/e = 2$) from S2 to S5 samples rehydrogenated at 100 atm H_2 pressure and 600 °C.

ture compared with the as-prepared samples, suggesting that the dehydrogenation–rehydrogenation process has degraded the kinetics of $LiBH_4$. It is accordant with the results in Ref. 19, but different with Refs. 20 and 21, in which the kinetics was improved for the rehydrogenated sample. The possible reasons might result from the different experimental conditions, most notably the presence of Ti^{3+} catalyst in the references. The total weight loss for the rehydrogenated S2 to S5 samples are about 5.1, 5.4, 5.0, and 3.6 wt%, respectively. The dehydrogenation capacities in the rehydrogenated S4 and S5 are the same with their first dehydrogenation capacity. The decrease of dehydrogenation capacity in the rehydrogenated S2 and S3 is caused by their increased decomposing temperature. In fact, after heating to 550 °C, the dehydrogenation capacities for the two samples were increased to 7.4 and 5.8 wt% [Fig. 9(b)], comparable to their first capacities. The above results suggest that the reverse reaction was complete at 600 °C and 100 atm hydrogen pressures.

FIG. 10. (a) MS and (b) TG results for the evolution of hydrogen ($m/e = 2$) from S4 sample with increasing charge-recharge cycles. The rehydrogenation conditions are 100 atm H_2 pressure and 600 °C.

Furthermore, hydrogen desorption properties for S4 sample with three charge-recharge cycles were investigated as shown in Fig. 10. It can be seen that the hydrogen desorption temperature for the sample at the third cycle is similar to that of the second cycle. However, the hydrogen capacity at 500 °C was decreased to 3.8 wt%. The decrease of the dehydrogenation capacity with the hydrogen charge-recharge cycles is similar to the results in Refs. 20 and 21.

Figure 11 displays the TG-MS results of S2 to S5 rehydrogenated under 600 °C and 30 atm. Compared with Fig. 9, the peak temperature of S3 to S5 did not change, but the temperature of S2 sample dropped about 35 °C. TG results in Fig. 11(b) revealed that the hydrogen capacities for S2 to S5 samples decreased to 3.2, 3.0, 2.9, and 2.1 wt%, respectively, suggesting that it is not a complete rehydrogenation. XRD results in Fig. 12 shows that the rehydrogenated samples consist of Al and new reformed phase, while no $LiBH_4$, AlB_2 , or $AlLi$ were observed, indicating an alternative rehydrogenation mechanism. At low

FIG. 11. (a) MS and (b) TG results for the evolution of hydrogen ($m/e = 2$) from S2 to S5 samples rehydrogenated at 30 atm H_2 pressure and 600 °C.

FIG. 12. XRD patterns for dehydrogenated S2 to S5 samples rehydrogenated at 600 °C and under 30 a.m. hydrogen for 24 h. XRD for all the rehydrogenated samples were measured after cooling down to room temperature. The broad amorphous peaks at 20 to 25° resulted from the amorphous polymer tape.

H₂ pressure, the intermediate hydride was formed first. However, the limited XRD data in the current study could not display a full understanding of the reversible mechanism. Detailed investigation on the relationship between reversibility of LiBH₄/Al with rechargeable conditions (temperature and H₂ pressure) is in progress.

IV. CONCLUSIONS

In summary, our study of the LiBH₄/Al system has led to the discovery of a new dehydrogenation/rehydrogenation mechanism. We have demonstrated that LiBH₄/Al mixture could be decomposed completely, resulting from a two-step reaction: first, Al reacts with LiBH₄ to form AlB₂ and LiH, and then the Al further reacts with LiH to form AlLi. Furthermore, the rehydrogenation experiments revealed that intermediate hydride was formed firstly at 600 °C and 30 atm H₂ pressure, and the LiBH₄ could be reformed completely when increasing the pressure to 100 atm. The new results illustrate that the strategy of using elements to form stable compounds with Li or B upon dehydrogenation can be used to destabilize the LiBH₄. However, further study is still required to screen various elements and alloys, in order to find some satisfactory candidates that could not only destabilize the decomposition of LiBH₄ at lower temperature, but also form reversible compounds with LiBH₄ under moderate conditions.

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