

Dehydriding and rehydriding reactions of LiBH₄

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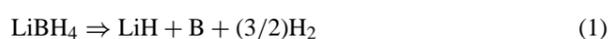
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Abstract

Structural differences in LiBH₄ before and after the melting reaction at approximately 550 K were investigated to clarify the experimental method for the confirmation of reversible dehydriding and rehydriding reactions. Since the long-range order of LiBH₄ begins to disappear after the melting reaction was achieved, investigation of the atomistic vibrations of the [BH₄]-anion in LiBH₄ was found to be effective for the confirmation of the reversibility. In the present study, LiBH₄ was successively dehydrided (decomposed) into LiH and B under 1 MPa of hydrogen at 873 K, and then rehydrided (recombined) into LiBH₄ under 35 MPa of hydrogen at the same temperature (873 K). The temperatures at the beginning and ending of the dehydriding reaction are lowered, by approximately 30 K, for LiBH₄ substituted (or mixed) with Mg (atomic ratio of Li:Mg = 9:1) as compared to those for LiBH₄ alone. This is similar to the tendency exhibited by LiNH₂.

1. Introduction

LiBH₄ is a potential candidate for hydrogen storage materials because of its high gravimetric and volumetric hydrogen densities: 18.5 mass% and 121 kg H₂/m³, respectively [1]. After the melting reaction at approximately 550 K, the dehydriding reaction accompanied by the phase decomposition proceeds mainly above 573 K according to the following equation [2]:



During the dehydriding (decomposition) reaction, 13.8 mass% of hydrogen ("3/2 mol of hydrogen" per "1 mol of LiBH₄") can be released from LiBH₄.

The dehydriding temperatures of LiBH₄ have been reported to decrease to approximately 473 K when SiO₂ is added as a catalyst [3]. Moreover, experimental studies on the physical properties of MBH₄, where M = Li, Na, K [4,5],

and the first-principles calculations of LiBH₄ [6] have indicated that an effective way to thermodynamically lower the dehydriding temperature of LiBH₄ is to suppress the charge transfer from the Li-cation to the [BH₄]-anion by the partial substitution of Li; a similar technique has already been applied for Li(-Mg)NH₂ [7-9].

In addition, the rehydriding (recombination) reaction, which proceeds as follows:



should be improved upon to functionalize LiBH₄ as a reversible hydrogen storage medium. However, until recently, it has been reported that direct synthesis of elemental Li and B yield only LiH [10], and LiBH₄ cannot be synthesized under elevated conditions: 15 MPa of hydrogen at 923 K [2,3].

Therefore, in this study, we have attempted to rehydride LiBH₄ in order to confirm the reversible reactions of Eqs. (1) and (2). Prior to that, the structural differences in LiBH₄ before and after the melting reaction at approximately 550 K were investigated to clarify the experimental method for the confirmation of the reversibility.

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2. Experimental

LiBH₄ of 95% purity was purchased from Aldrich Co. Ltd. The melting and dehydriding temperatures of LiBH₄ were measured using differential scanning calorimetry (DSC) (Bruker-AXS, PDSC 3100S, under 0.1 MPa of hydrogen at a heating rate of 10 K/min). Based on the results, LiBH₄ was dehydrided according to Eq. (1) as follows: 100 mg of LiBH₄ was placed in a Mo crucible in a glove box filled with purified argon (dew point below 180 K). The crucible containing the LiBH₄ was then sealed into a reaction-tube equipped with a connection valve for the evacuation and introduction of hydrogen. After carrying out the evacuation for 12 h, 1 MPa of hydrogen (99.99999%) was introduced into the reaction-tube and heated up to 873 K for 5 min. Subsequently, the dehydrided LiBH₄, i.e., the mixture of LiH and B, was rehydrided according to Eq. (2) in a similar method as the dehydriding reaction explained above: 35 MPa of hydrogen was introduced into the reaction-tube using the high-pressure gas reaction unit, and heated up to 873 K for 12 h.

Crystal and atomistic structures were examined at room temperature by powder X-ray diffraction measurement (PANalytical, X'Pert, Cu K α) and in situ Raman spectroscopy (Nicolet, Almega-HD with color-CCD, 532 nm laser with back scattering geometry), respectively. The dehydriding reaction was investigated using thermal desorption spectroscopy detected by gas chromatography (GL Science, GC323, at a heating rate of 10 K/min). The samples were always handled in the glove box filled with purified argon without exposure to air before and during measurements.

3. Results and discussion

3.1. Structural differences in LiBH₄ before and after melting reaction

The DSC profile of LiBH₄ is shown in Fig. 1. Two sharp and one broad endothermic reactions were observed, which correspond to the structural transition ($T_s = 380$ K) [11–13], melting reaction ($T_m = 550$ K), and dehydriding reaction ($T_d = 600$ – 700 K), respectively.

Fig. 2 shows the powder X-ray diffraction profiles of LiBH₄ at room temperature (a) before the melting reaction (as purchased) and (b) after the melting reaction under 1 MPa of hydrogen at 573 K. After the melting reaction (and then cooled down to room temperature), the diffraction peaks for LiBH₄ became smaller and broader than those before the melting reaction. These observations suggest that the long-range order of LiBH₄ began to disappear after the melting reaction was achieved.

However, the B–H atomistic vibrations of the [BH₄]-anion were clearly detected using in situ Raman spectroscopy, both before and after the melting reaction, as shown in Fig. 3. Thus, we emphasize that the investigation of the atomistic vibrations (directly affected by the short-range order or bonding)

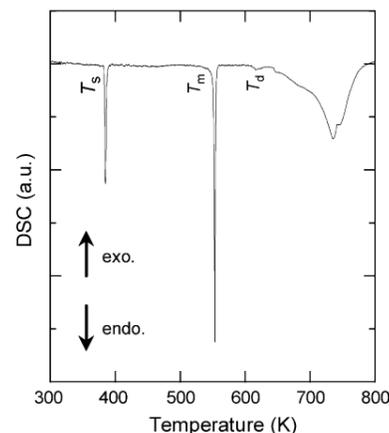


Fig. 1. DSC profile of LiBH₄. The sample was heated under 0.1 MPa of hydrogen at a rate of 10 K/min.

of the [BH₄]-anion in LiBH₄ is effective for the confirmation of the reversibility according to Eqs. (1) and (2), especially in the case of the rehydriding reaction above the melting temperature.

3.2. Rehydriding and dehydriding reactions of LiBH

The mixture of LiH and B was prepared by the dehydriding reaction of LiBH₄ under 1 MPa of hydrogen at 873 K for 5 min. As shown in Fig. 4(b), only LiH peaks were observed after the dehydriding reaction. No diffraction peak of boron was observed, indicating that boron is in an amorphous-like phase. The dehydrided LiBH₄, i.e., the mixture of LiH and B, was subsequently rehydrided under 35 MPa of hydrogen at 873 K. After the rehydriding reaction, only small diffraction peaks of LiBH₄ were observed, as shown in Fig. 4(c). This is probably due to the disappearance of the long-range order at 873 K, which is a higher temperature than that for the melting reaction mentioned above.

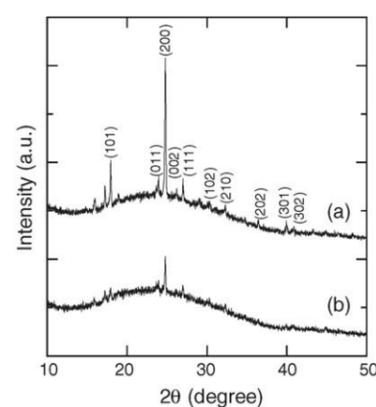


Fig. 2. Powder X-ray diffraction profiles (at room temperature) of LiBH₄ (a) before the melting reaction (as purchased) and (b) after the melting reaction under 1 MPa of hydrogen at 573 K.

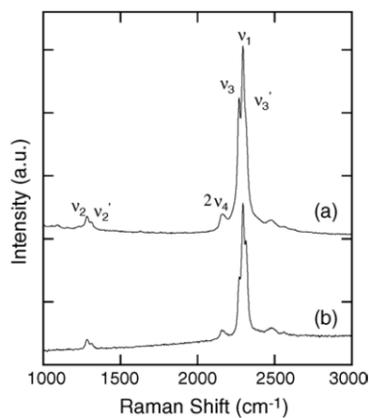


Fig. 3. Raman spectra (at room temperature) of (a) before the melting reaction (as purchased) and (b) after the melting reaction under 1 MPa of hydrogen at 573 K.

Therefore, the B–H atomistic vibrations in LiBH₄ were examined, as shown in Fig. 5. The vibration modes were clearly observed in the sample after the rehydriding reaction; this was expected from the result described in Section 3.1. From these results, LiBH₄ was confirmed to rehydride under 35 MPa of hydrogen at 873 K.

The thermal desorption profile of the rehydrided LiBH₄ is shown in Fig. 6. The dehydriding reaction of LiBH₄ begins at approximately 700 K, and a sharp peak appears at approximately 850 K. A preliminary result of the rehydrided LiBH₄ substituted (or mixed) with Mg (atomic ratio of Li:Mg = 9:1) is also shown in Fig. 6. The temperatures at the beginning and ending of the dehydriding reaction are lowered, by approximately 30 K, for LiBH₄ substituted (or mixed) with Mg as compared to those for LiBH₄ alone. A similar tendency has been reported in the case of LiNH₂ [5,8]. Detailed investi-

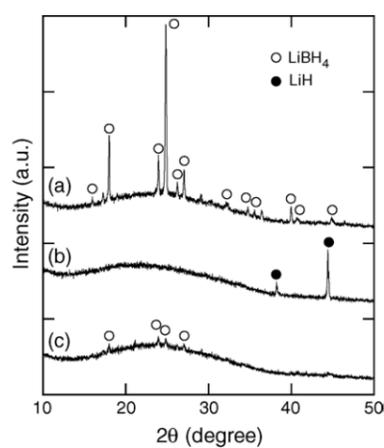


Fig. 4. Powder X-ray diffraction profiles (at room temperature) of (a) before the dehydriding reaction (as purchased), (b) dehydrided LiBH₄ under 1 MPa of hydrogen at 873 K, and (c) rehydrided LiBH₄ under 35 MPa of hydrogen at 873 K.

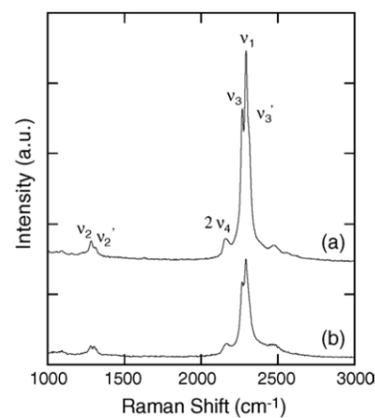


Fig. 5. Raman spectra (at room temperature) of LiBH₄ (a) before the dehydriding reaction (as purchased, same to Fig. 3(a)) and (b) after rehydriding reaction.

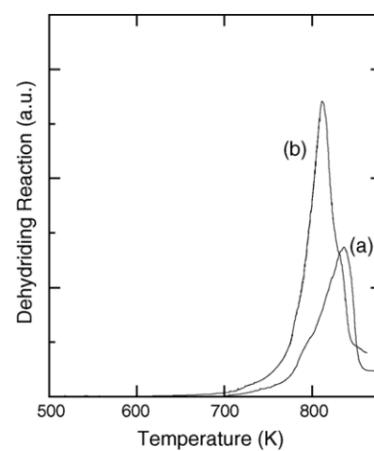


Fig. 6. Thermal desorption profiles of rehydrided (a) LiBH₄ and (b) substituted (or mixed) with Mg (atomic ratio of Li:Mg = 9:1). The sample was heated under 0.1 MPa of argon at a rate of 10 K/min.

gations of the effects of Mg substitution (or mixing) on the dehydriding and rehydriding reactions of LiBH₄ are underway.

4. Conclusions

LiBH₄, a potential candidate for hydrogen storage materials, was successively dehydrided (decomposed) into LiH and B under 1 MPa of hydrogen at 873 K, and then rehydrided (recombined) into LiBH₄ under 35 MPa of hydrogen at the same temperature (873 K). An effective way for the confirmation of the reversibility is to investigate the atomistic vibrations of the [BH₄]-anion in LiBH₄, because the long-range order of LiBH₄ began to disappear after the melting reaction was achieved. The Mg substitution (or mixing) effects for the dehydriding and rehydriding reactions of LiBH₄ have been preliminary investigated.

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