Destabilization of LiBH$_4$ by mixing with LiNH$_2$

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ABSTRACT It was revealed that LiBH$_4$ is destabilized by mixing with LiNH$_2$ and the mixture desorbs a large amount of hydrogen. First-principles calculations predicted that the enthalpies of dehydrogenation for LiBH$_4$ alone and the mixture of LiBH$_4$ + 2 LiNH$_2$ are 75 kJ/molH$_2$ and 23 kJ/molH$_2$, respectively. Motivated by this prediction, we experimentally examined the dehydrogenation properties for LiBH$_4$ and the mixture under hydrogen pressure. The amounts of desorbed hydrogen from LiBH$_4$ and the mixture at 703 K and 522 K were 10.6 mass % and 7.8 mass %, respectively. The dehydrogenation pressure of the mixture was much higher than that of LiBH$_4$ alone, although the mixture was measured at approximately 180 K lower temperature. This result suggests that the mixture is much unstable as compared with LiBH$_4$ alone.

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1 Introduction

Hydrogen is considered to be one of the new clean energy sources capable of replacing fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Therefore, high volumetric and gravimetric hydrogen densities are needed for hydrogen storage materials and much attention has been paid to light-element complex hydrides such as NaAlH$_4$ [1–3], LiBH$_4$ [4–7], and Li$_2$NH/LiNH$_2$ [8–15] in recent years.

LiBH$_4$ is a potential candidate among complex hydrides because of its extremely high hydrogen capacity. The dehydrogenation reaction of LiBH$_4$ is accompanied by the decomposition as shown in the following equation [4–7];

\[
\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2 \text{H}_2 .
\] (1)

However, LiBH$_4$ is rather stable and the dehydrogenation reaction proceeds only at elevated temperatures, above the melting point of about 550 K [4–6]. The system of Li$_2$NH/LiNH$_2$ has also been reported as the hydrogen storage material with high hydrogen capacity [8–15]. The reversible reactions of Li$_2$NH/LiNH$_2$ with hydrogen are reported as follows:

\[
\text{LiNH}_2 + 2 \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{Li}_3\text{N} + 2 \text{H}_2 .
\] (2)

The reactions occur in two steps and more than 10 mass % of hydrogen is desorbed in the overall reactions. The dehydrogenation reaction proceeds mainly above 473 K in vacuum or under inert gas atmosphere [8–15]. Because the dehydrogenation temperatures for LiBH$_4$ and the system of Li$_2$NH/LiNH$_2$ are still too high for practical applications, it is required to develop the material with the less positive enthalpy for the dehydrogenation reaction.

We have focused on the mixture of LiBH$_4$ + 2 LiNH$_2$ as the hydrogen storage material with the high gravimetric hydrogen density [16]. A possible pathway on the dehydrogenation reaction of the mixture is as follows;

\[
\text{LiBH}_4 + 2 \text{LiNH}_2 \rightarrow \text{Li}_3\text{BN}_2 + 4 \text{H}_2
\] (3)

Here, 11.9 mass % of hydrogen (‘4 M of hydrogen molecule’ per ‘1 M of LiBH$_4$ and 2 M of LiNH$_2$’) is desorbed according to the above equation. In the present study, we performed the theoretical calculations to predict the enthalpy for the dehydrogenation reaction (3), and then we conducted an experiment to investigate the dehydrogenation properties of the mixture of LiBH$_4$ + 2 LiNH$_2$ under hydrogen pressure. In addition, the properties of LiBH$_4$ alone were also examined to compare with those of the mixture.

2 Theoretical predictions

We performed first-principles calculations using the ultrasoft pseudopotential method [17] based on density functional theory [18]. The generalized gradient approximation was used for the exchange-correlation energy [19]. This approach has been successfully applied for LiBH$_4$ [7] and LiNH$_2$ [11]. The computational details can be found in [7] and references therein.

The enthalpies for the dehydrogenation reactions according to (1), (2), and (3) are summarized in Table 1. Our theoretical prediction gave the enthalpy of dehydrogenation for (1) as...
The enthalpies of dehydrogenation in LiBH₄ are 75 kJ/molH₂ [7], which is in fairly good agreement with the experimental value of 69 kJ/molH₂ [5, 20]. Also, the enthalpy was predicted as 99 kJ/molH₂ for the overall dehydrogenation reaction (2), which agrees reasonably with the experimental value of 81 kJ/molH₂ [8]. The product of the dehydrogenation reaction (3), Li₃BN₂, is an existing lithium boro-nitride with tetragonal symmetry [21]. The predicted lattice parameters were $a = 0.46513$ nm and $c = 0.52281$ nm, which are in good agreement with the experimental data of $a = 0.46435(2)$ nm and $c = 0.52592(5)$ nm [21]. Since the bonds between B and N are stable in general, the enthalpy of dehydrogenation for (3) is expected to be low as compared with those for (1) and (2). In fact, our calculation predicted the enthalpy of dehydrogenation for (3) as 23 kJ/molH₂, which is encouraging for practical applications. Motivated by this theoretical prediction, we experimentally examined the dehydrogenation properties for the mixture of LiBH₄ + 2 LiNH₂.

### 3 Experimental

The starting materials of LiBH₄ and LiNH₂ both with 95% purity were purchased from Sigma-Aldrich. The mixture of LiBH₄ + 2 LiNH₂ (namely, 1 mole of LiBH₄ and 2 moles of LiNH₂) was prepared using an agate pestle and mortar by hand. The mixture of 1 g and 40 steel balls of 10 mm in diameter were placed into a steel vial of about 80 cm³ in volume. Then, the mixture was mechanically milled for 1 h under purified argon atmosphere using a planetary ball mill (Fritsch P-5).

The dehydrogenation properties of LiBH₄ and the mixture were examined by X-ray diffraction (XRD) analysis (Rigaku RINT-TTR) and the pressure-composition ($p$-$c$) isotherm measurement. The XRD measurements were carried out with Cu $K_α$ radiation at room temperature. The conventional volumetric method with a Sieverts apparatus (Suzuki Shokan Co., Ltd.) was used to obtain dehydrogenation curves of LiBH₄ and the mixture at 703 K and 522 K, respectively. All the samples were handled in a glove-box filled with purified argon (dew point below 180 K).

### 4 Results and discussion

Figure 1 shows the powder XRD profiles of LiBH₄ and the mixture of LiBH₄ + 2 LiNH₂ before and after milling. The LiBH₄ phase and the LiNH₂ phase are seen in the diffraction profile of the mixture before milling, as well as the LiBH₄ phase is seen in that of LiBH₄. On the other hand, the diffraction profile of the mixture after milling was entirely different from the above profiles. The similar profile was also observed in the mixture without milling, but with the heat treatment at 522 K under around 10 MPa of hydrogen pressure for 2 h (Fig. 1d). The diffraction peaks marked with closed squares in Fig. 1d were indexed on a cubic lattice with the parameter $a = 1.067$ nm. This cubic phase is most likely formed by the reaction of the mixture because the phase was not observed in the diffraction profiles of LiBH₄ and LiNH₂ mechanically milled independently [16].

The $p$-$c$ isotherm measurements for LiBH₄ and the mixture of LiBH₄ + 2 LiNH₂ after milling were carried out at 703 K and 522 K, respectively, to investigate their dehydrogenation reactions (Fig. 2). It has been confirmed that hydrogen is desorbed from the materials by thermal desorption spectroscopy [5, 16]. The amounts of the desorbed hydrogen for LiBH₄ and the mixture after milling were 10.6 mass% and 7.8 mass%, which correspond to 77% and 66% of those predicted from (1) and (3) (namely, 13.8 mass% and 11.9 mass%), respectively. In Fig. 2, it should be emphasized that the dehydrogenation pressure of the mixture after milling is much higher than that of LiBH₄ alone, although the mixture was measured at approximately 180 K lower temperature than LiBH₄. This much higher dehydrogenation pressure of the mixture after milling suggests that this material is much unstable as compared with LiBH₄ alone.

Figure 3 indicates the powder XRD profiles of LiBH₄ before and after $p$-$c$ isotherm measurement. Here, the amorphous-like background in the profiles, which was observed in Fig. 4, is due to the tape used to avoid the exposure of the sample to air during the XRD measurement. The sample before $p$-$c$ isotherm measurement (that is, the sample kept under around 8 MPa of hydro-

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy (kJ/molH₂)</th>
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<tbody>
<tr>
<td>Calculation</td>
<td>Experiment</td>
</tr>
<tr>
<td>(1)</td>
<td>75 [7]</td>
</tr>
<tr>
<td>(2)</td>
<td>99</td>
</tr>
<tr>
<td>(3)</td>
<td>23</td>
</tr>
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FIGURE 1 Powder X-ray diffraction profiles of (a) LiBH₄, (b) the mixture of LiBH₄ + 2 LiNH₂ before milling, and (c) the mixture after milling. Opened and closed circles show the peak positions of the LiBH₄ phase and the LiNH₂ phase, respectively. The profile of the mixture without milling, but with the heat treatment at 522 K under around 10 MPa of hydrogen pressure for 2 h is also shown as (d). The diffraction peaks of the phase indexed on a cubic lattice with the parameter $a = 1.067$ nm are marked with closed squares.

FIGURE 2 Dehydrogenation curves of LiBH₄ and the mixture of LiBH₄ + 2 LiNH₂ after milling measured at 703 K and 522 K, respectively.