Electronic Supplementary Information for *Energy and Environmental Science*

Supplementary Information:

**Releasing 17.8 wt % H₂ from Lithium Borohydride Ammoniate**

### Table of Contents

<table>
<thead>
<tr>
<th>Paragraph</th>
<th>Procedure of Synthesis</th>
<th>P.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. S1</td>
<td>Room temperature XRD pattern of 2Li(NH₃)BH₄·MgCl₂ sample collected after heating at 90°C for 5 min.</td>
<td>p. 3</td>
</tr>
<tr>
<td>Fig. S2</td>
<td>NH₃ desorption at the equilibrium of liquid-state Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ samples as a function of temperature. Profile of Li(NH₃)₄/₃BH₄ upon heating to 200°C was also included.</td>
<td>p. 5</td>
</tr>
<tr>
<td>Fig. S3</td>
<td>Hydrogen release from the Co-doped Li(NH₃)₄/₃BH₄ sample at a) 140°C for 3 hours and b) 180°C for 7 hours, respectively.</td>
<td>p. 6</td>
</tr>
<tr>
<td>Fig. S4</td>
<td>¹¹B NMR spectrum of the solid residue collected after the Li(NH₃)₄/₃BH₄ sample dehydrogenated at 250°C.</td>
<td>p. 7</td>
</tr>
<tr>
<td>Fig. S5</td>
<td>Room temperature XRD patterns of a) 2LiBH₄·Li₄BN₃H₁₀ after held at 70°C for 2 hours and then cooled to room temperature, b) Li₃BNH₆ after held at 90°C for 10 hours and then cooled to room temperature.</td>
<td>p. 7</td>
</tr>
</tbody>
</table>
1. Procedure of Synthesis

The synthesis and volumetric apparatus were composed of NH₃ vessel, LiBH₄ vessel and a digital pressure gauge. Co-LiBH₄ (0.1046 g, 4.121 mmol) and NH₃ (0.0939 g, 5.524 mmol) are stored in two vessels separately. To make LiBH₄/NH₃ molar ratio ¾, the amount of NH₃ in the vessel should be more than the theoretical value due to the NH₃ equilibrium pressure of LiBH₄ ammoniate. NH₃ was gradually introduced to LiBH₄ vessel at room temperature. After absorption, the NH₃ vessel was weighed and the mass loss was the exact content of the LiBH₄ ammoniate (usually should be LiBH₄/NH₃ molar ratio ¾). Then the volumetric release was conducted in the small LiBH₄ vessel (6.7 ml), and the pressure change inside the volumetric apparatus was recorded by a digital pressure gauge (J. Mater. Chem. 2009, 19, 8426.).
Fig. S1 XRD patterns of 2Li(NH₃)BH₄-MgCl₂ sample collected after heating at 90 °C for 5 min.

The 2Li(NH₃)BH₄-MgCl₂ sample was prepared by mixing fresh Li(NH₃)BH₄ with anhydrous MgCl₂ in the molar ratio of 2:1, after hand milling for 5 min, the mixture was heated to 90 °C for 5 min in a sealed bottle and then cooled down slowly.¹

**Calculation procedures of NH₃ contents remaining in the Li(NH₃)₁₂BH₄ and Li(NH₃)₁₄BH₄ samples as a function of temperature:**

Since the Co-doped Li(NH₃)₄/₃BH₄ sample converts to liquid state at temperature around 55 °C, in addition, hydrogen evolution took place at ca. 135 °C and 200 °C (Fig. 1B) for the Co-doped and neat samples, respectively, therefore, our calculation of NH₃ remaining in the sample as a function of temperature focused on temperatures above 55 °C. When the sample is put in a closed vessel, the amounts of NH₃ released from the sample at given temperatures were calculated from the free volume of gas
and NH₃ vapor pressure at equilibrium. By referencing to the previous work on pressure-composition-isothermal properties of LiBH₄-NH₃ system,² the equilibrium pressure (P) of NH₃ at given temperature (T) can be determined from Clausius-Clapeyron equation (Equation S1),

\[
\log P(\text{mm}) = -\frac{A}{T} + B \quad \text{(S1)}
\]

where A and B were empirical constants determined by Sullivan and Johnson (shown in Table S1).² As there is no thermodynamic data available for the composite of Li(NH₃)₁.₂BH₄, [²] we calculated the temperature dependences of NH₃ equilibrium pressure of the liquid-state Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄. Once the P and T are known, the specific numbers of NH₃ can be determined through the Van der Waals equation (Equation S2) which takes into account the molecular stickiness and the molecular size of gas,³ and the NH₃ content detached in the gas phase (equiv.) and remaining in the vicinity of the sample (%) can be calculated from Equation S3 and S4, respectively,

\[
(P + \frac{an^2}{V^2})(V - nb) = nRT \quad \text{(S2)}
\]

\[
\text{NH}_3(\text{Equiv.}) = \frac{n}{m} \quad \text{(S3)}
\]

\[
\text{NH}_3(\%) = (1 - \frac{n}{c \times m}) \times 100\% \quad \text{(S4)}
\]

Where P is the pressure of the gas (atm), V the free volume of gas (L), n the number of moles, R the universal gas constant (0.08206 L·atm/(mol·K)), T the absolute temperature (K), a and b are the Van der Waals constants which reflect the attraction between the molecular particles and the volume of a mole of gas molecule at rest, respectively. For NH₃, a and b are 4.170 L²·atm/mol² and 0.03707 L/mol, respectively.
m is sample loading amount (mol) and c is the molar ratio of NH₃/LiBH₄, for Li(NH₃)₁.₂BH₄ or Li(NH₃)₁.₄BH₄, c is 1.2 or 1.4, respectively. The temperature-dependent equivalent numbers of NH₃ release from Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ samples, and our Li(NH₃)₄/₃BH₄ sample heating to 200 °C were shown in Fig. S2, it can be seen that at temperatures below 200 °C the slight pressure increase in Li(NH₃)₄/₃BH₄ is probably due to NH₃ release. Table S2 presents the percentage of NH₃ remaining in the Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ samples at 55, 135 and 200 °C, the corresponding values for our Li(NH₃)₄/₃BH₄ sample should be in-between.

**Table S1.** Values of A, B for Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(NH₃)₁.₂BH₄</td>
<td>2415</td>
<td>8.709</td>
</tr>
<tr>
<td>Li(NH₃)₁.₄BH₄</td>
<td>2276</td>
<td>8.528</td>
</tr>
</tbody>
</table>

**Fig. S2** Temperature-dependent NH₃ desorption at the equilibrium of liquid-state Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ samples. Profile of the Li(NH₃)₄/₃BH₄ sample upon
heating to 200 °C was also included.

**Table S2.** Percentage of NH₃ remaining in Li(NH₃)₁.₂BH₄ and Li(NH₃)₁.₄BH₄ at varied temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>55 °C</th>
<th>135 °C</th>
<th>200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(NH₃)₁.₂BH₄</td>
<td>99.9%</td>
<td>96.7%</td>
<td>81.2%</td>
</tr>
<tr>
<td>Li(NH₃)₁.₄BH₄</td>
<td>99.8%</td>
<td>95.9%</td>
<td>79.1%</td>
</tr>
</tbody>
</table>

**Fig. S3** Hydrogen release from the Co-doped Li(NH₃)₄/₃BH₄ sample at (A) 140 °C for 3 hours and (B) 180 °C for 7 hours, respectively.
Fig. S4 $^{11}$B NMR spectrum of the solid residue collected after the Li(NH$_3$)$_4$/3BH$_4$ sample dehydrogenated at 250 °C.

Fig. S5 Room temperature XRD patterns of (A) 2LiBH$_4$-Li$_4$BN$_3$H$_{10}$ after held at 70 °C for 2 hours and then cooled to room temperature, (B) Li$_2$BNH$_6$ after held at 90 °C for 10 hours and then cooled to room temperature.

In both cases, Li$_2$BNH$_6$ could be observed after the samples were cooled to room
temperature, which evidences the recombination of Li$_4$BN$_3$H$_{10}$ and LiBH$_4$ to Li$_2$BNH$_6$ during the sample cooling process is possible.

![Diagram](image.png)

**Fig. S6** (A) Volumetric release curve of the ball milled post-140 °C dehydrogenated Li(NH$_3$)$_{4/3}$BH$_4$ sample, (B) Temperature profile.

The post-140 °C dehydrogenated sample was ball milled at 200 rpm for 2 hours, and was heated to 140 °C at a heating rate of 0.5 °C/min.

![TEM Image](image.png)

**Fig. S7** TEM image of the Co-doped LiBH$_4$ sample after ball milling.
**Fig. S8** Co K-edge XAFS spectra of CoCl$_2$, metallic Co and Co-doped LiBH$_4$ sample after ball milling and the Co-doped Li(NH$_3$)$_{4/3}$BH$_4$ samples after dehydrogenation at 180 and 250 °C, respectively.

**References**

