

Electronic Supplementary Information for *Energy and Environmental Science*

Supplementary Information:

Releasing 17.8 wt % H₂ from Lithium Borohydride Ammoniate

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1. Procedure of Synthesis

The synthesis and volumetric apparatus were composed of NH_3 vessel, LiBH_4 vessel and a digital pressure gauge. Co- LiBH_4 (0.1046 g, 4.121 mmol) and NH_3 (0.0939 g, 5.524 mmol) are stored in two vessels separately. To make $\text{LiBH}_4/\text{NH}_3$ molar ratio $3/4$, the amount of NH_3 in the vessel should be more than the theoretical value due to the NH_3 equilibrium pressure of LiBH_4 ammoniate. NH_3 was gradually introduced to LiBH_4 vessel at room temperature. After absorption, the NH_3 vessel was weighed and the mass loss was the exact content of the LiBH_4 ammoniate (usually should be $\text{LiBH}_4/\text{NH}_3$ molar ratio $3/4$). Then the volumetric release was conducted in the small LiBH_4 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.).

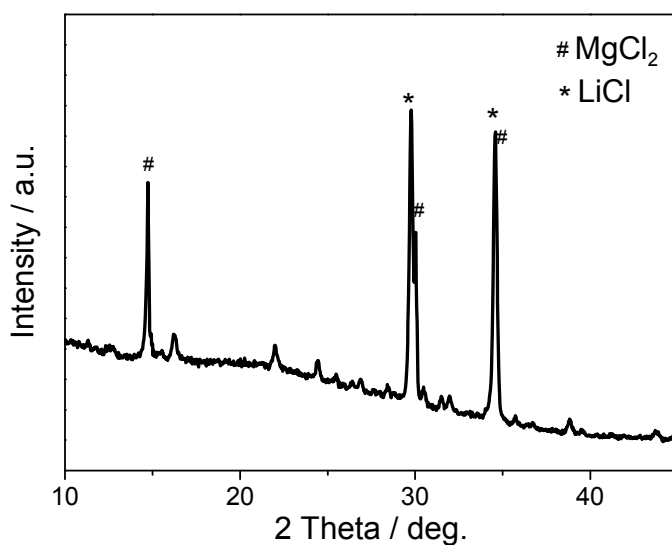


Fig. S1 XRD patterns of $2\text{Li}(\text{NH}_3)\text{BH}_4\text{-MgCl}_2$ sample collected after heating at $90\text{ }^\circ\text{C}$ for 5 min.

The $2\text{Li}(\text{NH}_3)\text{BH}_4\text{-MgCl}_2$ sample was prepared by mixing fresh $\text{Li}(\text{NH}_3)\text{BH}_4$ with anhydrous MgCl_2 in the molar ratio of 2:1, after hand milling for 5 min, the mixture was heated to $90\text{ }^\circ\text{C}$ for 5 min in a sealed bottle and then cooled down slowly.¹

Calculation procedures of NH_3 contents remaining in the $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$ samples as a function of temperature:

Since the Co-doped $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ sample converts to liquid state at temperature around $55\text{ }^\circ\text{C}$, in addition, hydrogen evolution took place at ca. $135\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ (Fig. 1B) for the Co-doped and neat samples, respectively, therefore, our calculation of NH_3 remaining in the sample as a function of temperature focused on temperatures above $55\text{ }^\circ\text{C}$. When the sample is put in a closed vessel, the amounts of NH_3 released from the sample at given temperatures were calculated from the free volume of gas

and NH_3 vapor pressure at equilibrium. By referencing to the previous work on pressure-composition-isothermal properties of $\text{LiBH}_4\text{-NH}_3$ system,² the equilibrium pressure (P) of NH_3 at given temperature (T) can be determined from Clausius-Clapeyron equation (Equation S1),

$$\log P(\text{mm}) = -A/T + B \quad (\text{S1})$$

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 $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$,^[2] we calculated the temperature dependences of NH_3 equilibrium pressure of the liquid-state $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$. Once the P and T are known, the specific numbers of NH_3 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 NH_3 content detached in the gas phase (equiv.) and remaining in the vicinity of the sample (%) can be calculated from Equation S3 and S4, respectively,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (\text{S2})$$

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

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

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 NH_3 , 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 $\text{NH}_3/\text{LiBH}_4$, for $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ or $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$, c is 1.2 or 1.4, respectively. The temperature-dependent equivalent numbers of NH_3 release from $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$ samples, and our $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ 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 $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ is probably due to NH_3 release. Table S2 presents the percentage of NH_3 remaining in the $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$ samples at 55, 135 and 200 °C, the corresponding values for our $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ sample should be in-between.

Table S1. Values of A, B for $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$ samples.

Sample	A	B
$\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$	2415	8.709
$\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$	2276	8.528

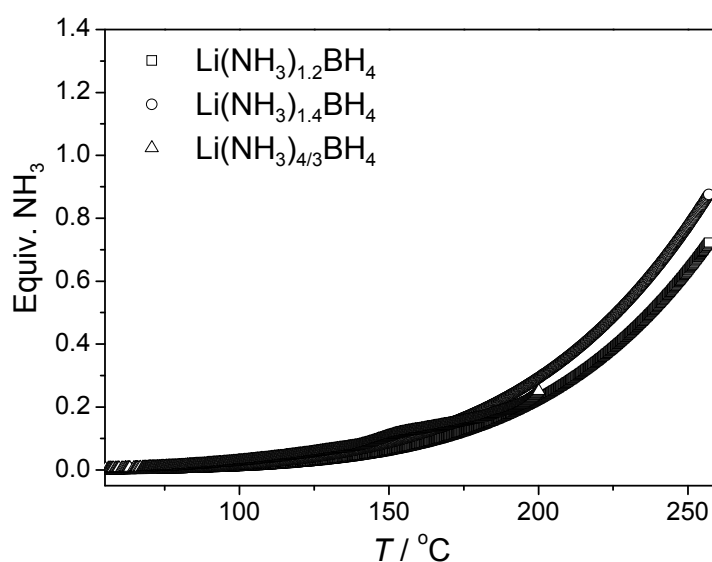


Fig. S2 Temperature-dependent NH_3 desorption at the equilibrium of liquid-state $\text{Li}(\text{NH}_3)_{1.2}\text{BH}_4$ and $\text{Li}(\text{NH}_3)_{1.4}\text{BH}_4$ samples. Profile of the $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ sample upon

heating to 200 °C was also included.

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

Sample	55 °C	135 °C	200 °C
Li(NH ₃) _{1.2} BH ₄	99.9%	96.7%	81.2%
Li(NH ₃) _{1.4} BH ₄	99.8%	95.9%	79.1%

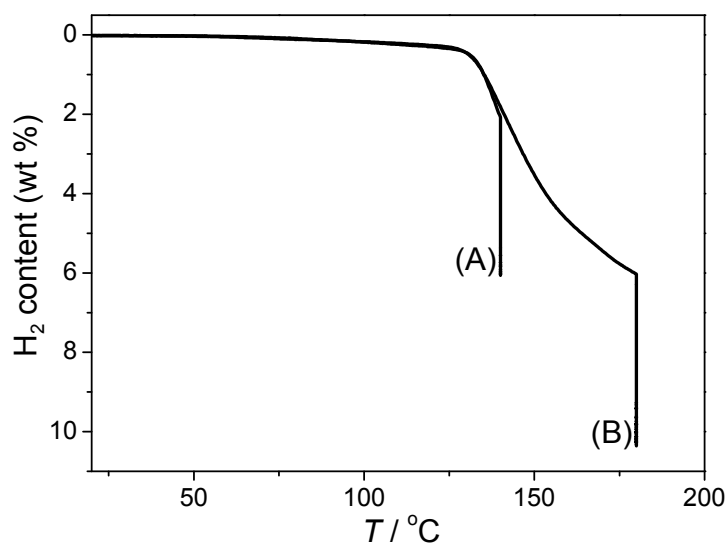


Fig. S3 Hydrogen release from the Co-doped Li(NH₃)_{4/3}BH₄ sample at (A) 140 °C for 3 hours and (B) 180 °C for 7 hours, respectively.

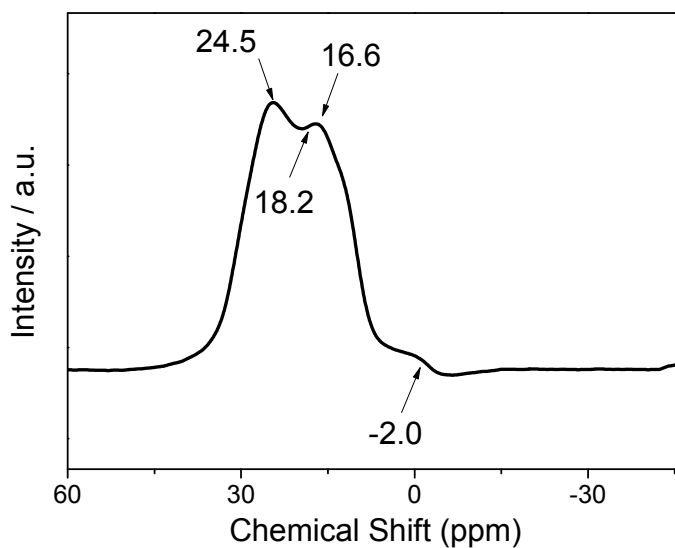


Fig. S4 ^{11}B NMR spectrum of the solid residue collected after the $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ sample dehydrogenated at 250 °C.

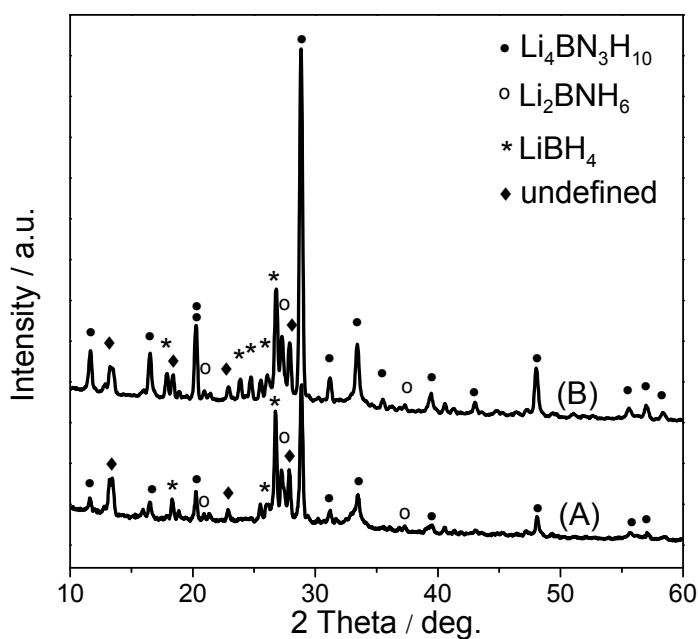


Fig. S5 Room temperature XRD patterns of (A) $2\text{LiBH}_4\text{-Li}_4\text{BN}_3\text{H}_{10}$ after held at 70 °C for 2 hours and then cooled to room temperature, (B) Li_2BNH_6 after held at 90 °C for 10 hours and then cooled to room temperature.

In both cases, Li_2BNH_6 could be observed after the samples were cooled to room

temperature, which evidences the recombination of $\text{Li}_4\text{BN}_3\text{H}_{10}$ and LiBH_4 to Li_2BNH_6 during the sample cooling process is possible.

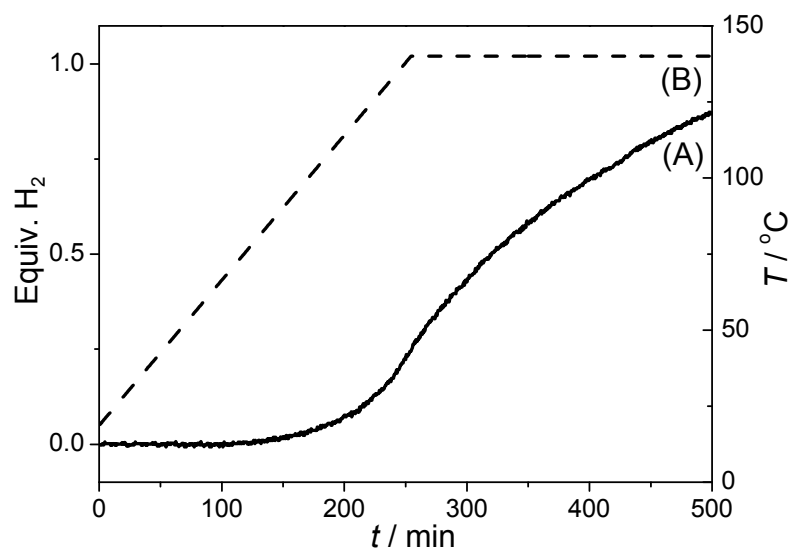


Fig. S6 (A) Volumetric release curve of the ball milled post-140 °C dehydrogenated $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ sample, (B) Temperature profile.

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.

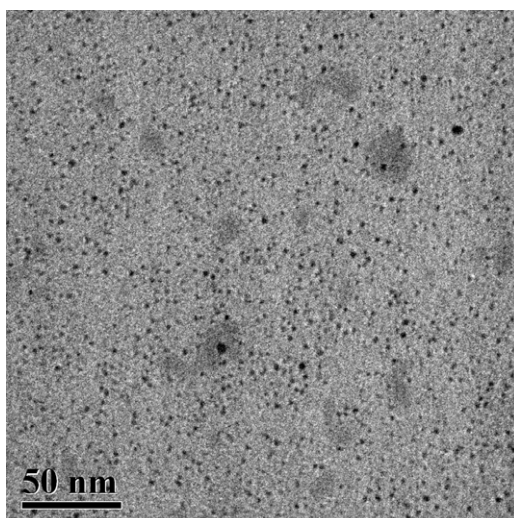


Fig. S7 TEM image of the Co-doped LiBH_4 sample after ball milling.

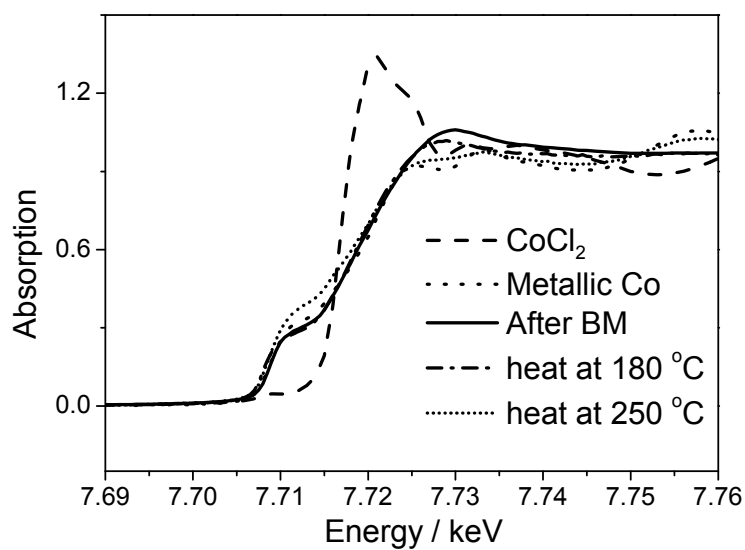


Fig. S8 Co K-edge XAFS spectra of CoCl₂, metallic Co and Co-doped LiBH₄ sample after ball milling and the Co-doped Li(NH₃)_{4/3}BH₄ samples after dehydrogenation at 180 and 250 °C, respectively.

References

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