Electronic Supplementary Information (ESI) for

Converting H^+ from Coordinated Water into H^- Enables Super Facile Synthesis of $LiBH_4$

Kang Chen[a], Liuzhang Ouyang[a,*], Hao Zhong[a], Jiangwen Liu[a], Hui Wang[a], Huaiyu Shao[b,*], Yao Zhang[c], Min Zhu[a,*]

[a] *School of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou, China.*

[b] *Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering (IAPME), University of Macau, Macau SAR, China.*

[c] *School of Materials Science and Engineering, Jiangsu Key Laboratory of Advanced Metallic Materials, Southeast University, Nanjing, China.*

*E-mail: meouyang@scut.edu.cn (L.Z. Ouyang)

*E-mail: memzhu@scut.edu.cn (M. Zhu)

*Email: hshao@um.edu.mo (H.Y. Shao)

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1 Supporting Methods

Purification and quantification of lithium borohydride. $LiBH_4$ was extracted by as-distilled diethyl ether from the ball-milling mixtures. It is worth noting that both MgO and remaining reactants are insoluble in diethyl ether. The extracted solution and undissolved side-products were separated by polytetrafluoroethylene membrane (0.45 μm). Afterward, the colatuie was transferred into a new glass bottle and evaporated under sliding vane rotary vacuum pump, while the solvent vapor (Et_2O) was captured by a cold trap placed in liquid nitrogen. Finally, the white solid powder ($LiBH_4$) was obtained through the aforementioned procedures. The amount of formed $LiBH_4$ was quantitatively determined by iodometric analysis [1-2] and the $LiBH_4$ yield was calculated in accordance with the following equation:

$$Yield\ (LiBH_4) = \frac{obtained\ mass\ of\ LiBH_4}{theoretical\ mass\ of\ LiBH_4} \times 100\% \quad (1)$$

Notably，the $LiBH_4$ yield is referred to as a ratio of the mass of $LiBH_4$ actually converted by 1 mol of $LiBO_2 \cdot 2H_2O$ to the theoretical value. In addition, to test the accuracy of the quantitative method，52.0mg of commercial $LiBH_4$ (95%), actually, 49.4mg of $LiBH_4$ was mixed into 100 mL of NaOH solution (0.25 mol/L). There was 48.7mg of $LiBH_4$ calculated by iodometric analysis. Then, the error of iodometric analysis was 1.4%, which was acceptable for quantification of $LiBH_4$. Moreover，50.1mg of commercial $LiBH_4$ (actually 47.6mg) was dissolved into 20 mL of as-distilled Et_2O and the extraction was evaporated via vacuum drying. There was 46.7mg of $LiBH_4$ quantified by iodometric analysis. The error calculation was also below 2%.

Ionic conductivity. Since the discovery of superior Li^+ conductivity in the HT (High temperature) phase, $LiBH_4$ has attracted much attention as solid-state electrolytes (SSEs) with high compatibility with Li electrode, negligible electronic conduction, and low grain boundary resistance [3] compared to oxide-type or sulfide electrolyte systems [4-5]. However, $LiBH_4$ acts as an electrical insulator with LT (low-temperature) Li^+ conductivity < 10^{-7} S cm^{-1} [6], which falls short of the commercial demand (> 10^{-3} S cm^{-1}). As expected, the structural deformation by inducing defects and changing the atomic arrangement [7-8] could improve Li^+ conductivity of $LiBH_4$. Especially, we succeeded in synthesizing $LiBH_4{\cdot}NH_3$ from the regenerated $LiBH_4$ and the commercial one, respectively. Ionic conductivity of $LiBH_4{\cdot}NH_3$ was obtained according to the following procedures.

The powder samples were loaded into a stainless-steel mould with a diameter of 13 mm and pressed into pellets as solid electrolyte with thickness of ~1 mm under a pressure of 20 MPa initially. Two metallic lithium foils of 13.5 mm diameter were then placed on the two sides of pellets to form test electrodes, and loaded in an airtight sample holder. All preparations took place in a glove box (Mikrouna, China) filled with Ar gas. Afterward, the ionic conductivity of pellets was measured by alternating current (AC) impedance spectroscopy in a frequency range from 1 Hz to 1 MHz with an electrochemical workstation (Gamry Interface 1000 and CHI604C, Chenghua, Shanghai). The airtight sample holder was placed in an oil bath and held for 30 min to control the temperature. Testing temperatures were ramped from room temperature (28 ℃) to 45 ℃. In addition, $LiBH_4{\cdot}NH_3$ was prepared by exposing the as-purified $LiBH_4$

or commercial $LiBH_4$ to an atmosphere of high-purity ammonia (99.999%) with 1 bar pressure at room temperature for 2 h and evacuated by sliding vane rotary vacuum pump for 3 h [9-10].

The XRD patterns of $LiBH_4 \cdot NH_3$ from as-purified product and commercial product are shown in **Fig. S6a**, which shows a good agreement with other's report [8]. The lithium-ionic conductivity was tested using two pieces of lithium foil electrodes in the typical Nyquist plots. **Fig. S7** shows partial of impedance plots of $LiBH_4 \cdot NH_3$ acquired from the as-purified $LiBH_4$, as well as the commercial one at different temperatures. The resistance R concerned about ionic conductivity could be obtained from the intersection of a single arc or semi-circle with the Z` axis in the low-frequency limit from the Nyquist plots [11-12]. Therefore, the conductivity σ in accordance with following equation [13-14]:

$$\sigma = \frac{d}{AR} \tag{2}$$

wherein, σ, A, d, and R correspond to the conductivity, area of pellet, thickness and resistance of electrolytes, respectively. Nevertheless, $LiBH_4$ acts as an electrical insulator with LT Li^+ conductivity < 10^{-7} S cm^{-1}, which is far from meeting the commercial demand (> 10^{-3} S cm^{-1}). NH_3 was introduced to increase the defects and change the atomic arrangement of $LiBH_4$-based crystal structure, for improving its LT Li^+ conductivity.

The Arrhenius plots of lithium borohydride mono-ammoniate ($LiBH_4 \cdot NH_3$) are shown in **Fig. S6b**, it is found that $LiBH_4 \cdot NH_3$ obtained from the as-purified $LiBH_4$

exhibits similar conductivity increasing with the ramping temperature as the commercial one and shows higher conductivity of up to 1.20×10^{-3} S cm^{-1} near room temperature (43 ℃), higher than that of $LiBH_4$ (10^{-7} S cm^{-1}) by 4 orders of magnitude [6, 15]. It should be noted that a drastic increase in ionic conductivity occurs around 37 ℃ due to the structural change resulting from the formation of Schottky defects when ammonia is desorbed and it brings position vacancy [8]. This is the reason why the conductivity in cooling process is better than that in heating process.

2 Supporting Figures

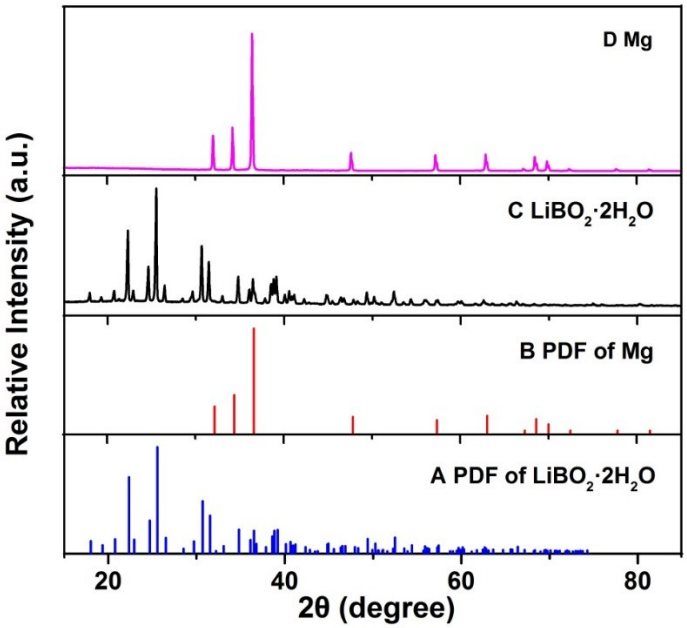

Fig. S1 XRD patterns of raw materials. (A) PDF card of $LiBO_2 \cdot 2H_2O$ (JCPDS 01-074-1509), (B) PDF card of Mg (JCPDS 00-035-08), (C) As-prepared $LiBO_2 \cdot 2H_2O$ from $LiBO_2$ aqueous solution, and (D) Pristine Mg.

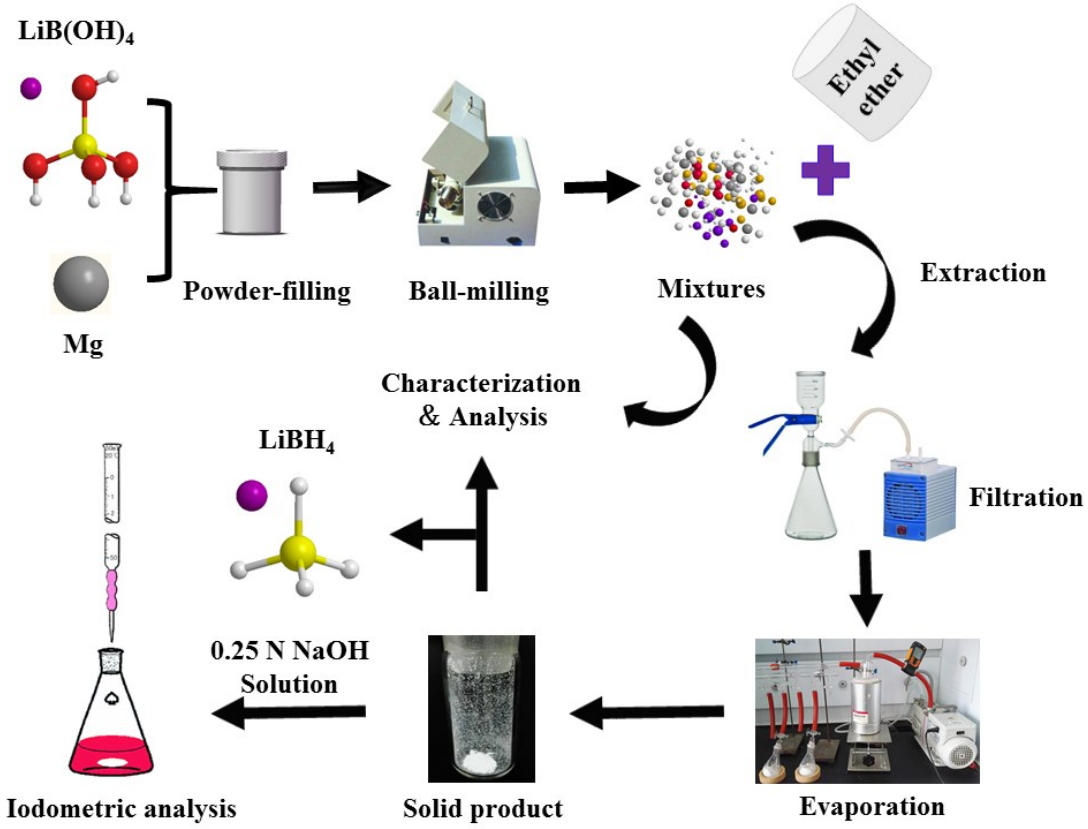

Fig. S2 Schematic flow of the experimental procedures.

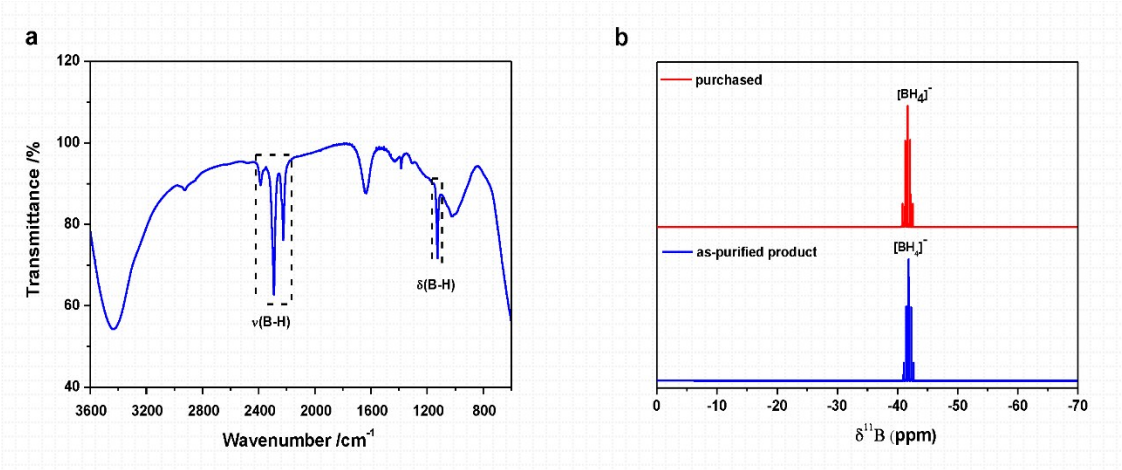

Fig. S3 FT-IR and NMR measurements. a, FT-IR spectrum of the product after ball-milling Mg and $LiBO_2 \cdot 2H_2O$ mixtures (in 5.0:1 mole ratio) for 15h. b, Solution-state (Tetrehydrofuran-d8) ^{11}B (^{1}H coupled) NMR spectra of commercial $LiBH_4$ and purified product.

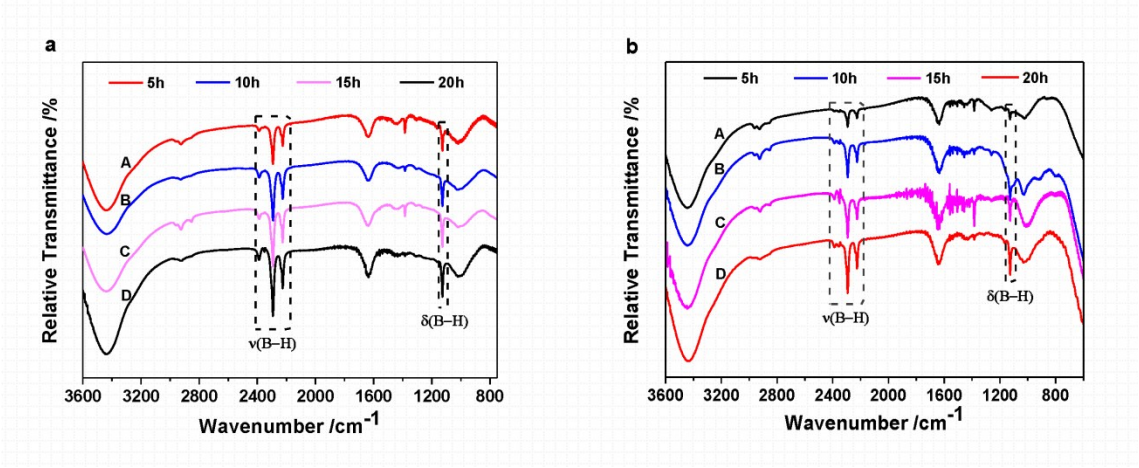

Fig. S4 FT-IR spectra. a, FT-IR spectroscopy of Mg and $LiBO_2 \cdot 2H_2O$ mixtures (in 5.0:1 mole ratio) after ball-milling for different durations: (A) 5h, (B) 10h, (C) 15h, and (D) 20h. b, FT-IR spectra of Mg and $LiBO_2 \cdot 2H_2O$ mixtures (in 5.5:1 mole ratio) under same condition: (A) 5h, (B) 10h, (C) 15h, and (D) 20h.

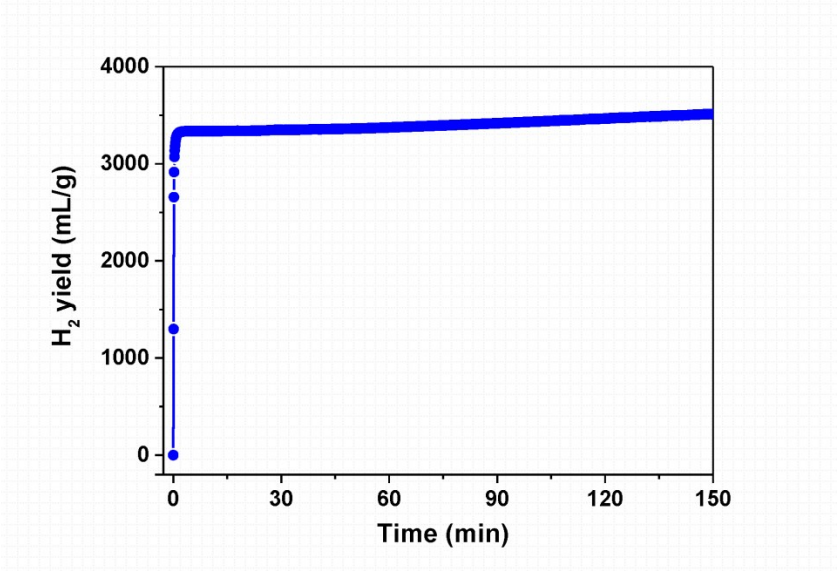

Fig. S5 Hydrolysis curve of the regenerated $LiBH_4$ in 2 wt.% $CoCl_2$ aqueous solution with a molar ratio of $H_2O/LiBH_4 = 4$. The hydrogen yield of the as-purified product is 3294 mL g^{-1} in 60s, then followed by a sluggish kinetics.

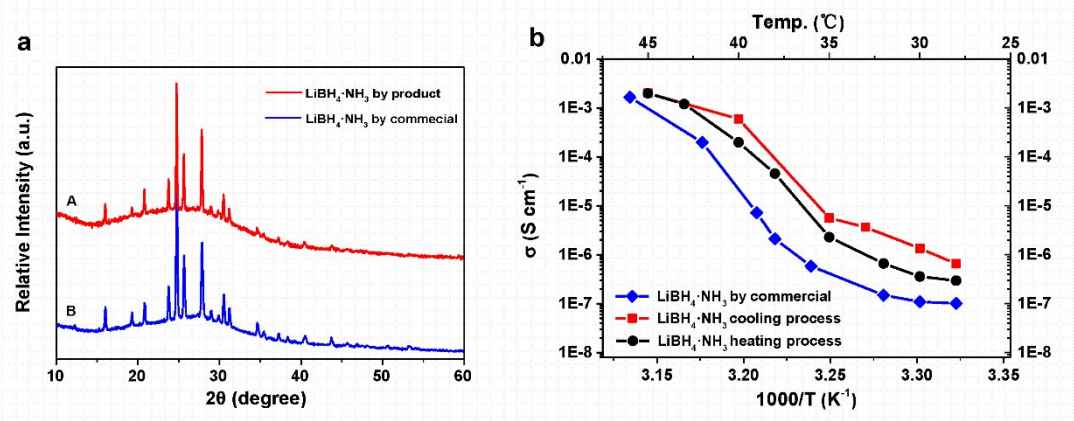

Fig. S6 Ionic conductivity tests. a, The XRD patterns of $LiBH_4{\cdot}NH_3$ from (A) as-purified product and (B) commercial $LiBH_4$. b, Arrhenius plots of the ionic conductivities for $LiBH_4{\cdot}NH_3$ obtained by as-purified $LiBH_4$ in heating process (black), cooling process (red), and $LiBH_4{\cdot}NH_3$ by commercial product (blue) at different temperatures.

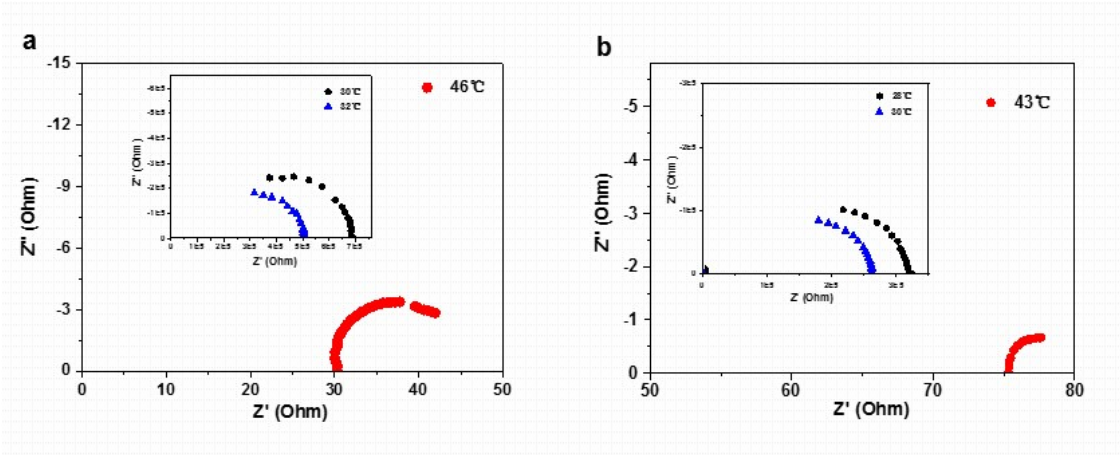

Fig. S7 Typical Nyquist plots of impedance data obtained using a lithium-metal electrode. a, $LiBH_4 \cdot NH_3$ from commercial $LiBH_4$ under different temperatures. b, $LiBH_4 \cdot NH_3$ from as-purified $LiBH_4$ in heating process under varied temperatures.

3 Supporting Table

Table S1. Material cost of $LiBH_4$ produced by ball milling Mg and $LiBO_2{\cdot}2H_2O$ and commercial method**.**

Method	Cost (US $/ ton)
Ball milling Mg and $LiBO_2{\cdot}2H_2O$	34670[a]
Commercial method	171818[b]

[a]The calculation is based on the yield of 38.7% $LiBH_4$ when Mg and $LiBO_2{\cdot}2H_2O$ mixture with a ratio of 5.0:1 is ball milled for 20h. Then 14.41 tons of Mg are required to produce 1 ton $LiBH_4$. The price of Mg is $2406/ton, which is available from China nonferrous metal network [16]. Then the total cost of raw materials is $34670/ton.

[b]The price is from a commercial company in China. Commercial method refers to wet chemical reaction method [17-18]: $NaBH_4 + LiCl \xrightarrow[75\%]{isopropylamine} LiBH_4 + NaCl$. According to a yield of 75% in current industrial production, 2.59 tons of LiCl and 2.32 tons of $NaBH_4$ are needed for production of 1 ton $LiBH_4$. Then the total cost of raw materials is $171818 due to the prices of LiCl and $NaBH_4$ being $25769/ton and $45291/ton, respectively [19].

4 Supporting References

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