Electronic Supplementary Information (ESI) for

Converting H⁺ from Coordinated Water into H⁻ Enables Super Facile

Synthesis of LiBH₄

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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 colature was transferred into a new glass bottle and evaporated under sliding vane rotary vacuum pump, while the solvent vapor (Et$_2$O) 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:

\[
\text{Yield (LiBH}_4\text{)} = \frac{\text{obtained mass of LiBH}_4}{\text{theoretical mass of LiBH}_4} \times 100\% \tag{1}
\]

Notably, the LiBH$_4$ yield is referred to as a ratio of the mass of LiBH$_4$ actually converted by 1 mol of LiBO$_2$·2H$_2$O 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$_2$O 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 compared to oxide-type or sulfide electrolyte systems. However, LiBH$_4$ acts as an electrical insulator with LT (low-temperature) Li$^+$ conductivity $< 10^{-7}$ S cm$^{-1}$, 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 could improve Li$^+$ conductivity of LiBH$_4$. Especially, we succeeded in synthesizing LiBH$_4$·NH$_3$ from the regenerated LiBH$_4$ and the commercial one, respectively. Ionic conductivity of LiBH$_4$·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 °C) to 45 °C. In addition, LiBH$_4$·NH$_3$ was prepared by exposing the as-purified LiBH$_4$
or commercial LiBH₄ 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 h⁹⁻¹⁰.

The XRD patterns of LiBH₄·NH₃ 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 LiBH₄·NH₃ acquired from the as-purified LiBH₄, 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:

\[ \sigma = \frac{d}{AR} \]  

wherein, σ, A, d, and R correspond to the conductivity, area of pellet, thickness and resistance of electrolytes, respectively. Nevertheless, LiBH₄ 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). NH₃ was introduced to increase the defects and change the atomic arrangement of LiBH₄-based crystal structure, for improving its LT Li⁺ conductivity.

The Arrhenius plots of lithium borohydride mono-ammoniate (LiBH₄·NH₃) are shown in Fig. S6b, it is found that LiBH₄·NH₃ obtained from the as-purified LiBH₄
exhibits similar conductivity increasing with the ramping temperature as the commercial one and shows higher conductivity of up to $1.20 \times 10^{-3}$ S cm$^{-1}$ near room temperature (43 °C), 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 °C 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.
Supporting Figures

Fig. S1 XRD patterns of raw materials. (A) PDF card of LiBO$_2$·2H$_2$O (JCPDS 01-074-1509), (B) PDF card of Mg (JCPDS 00-035-08), (C) As-prepared LiBO$_2$·2H$_2$O 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$_2$·2H$_2$O mixtures (in 5.0:1 mole ratio) for 15h. b, Solution-state (Tetrahydrofuran-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$_2$·2H$_2$O 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$_2$·2H$_2$O 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$_2$O/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$_4$·NH$_3$ from (A) as-purified product and (B) commercial LiBH$_4$. b, Arrhenius plots of the ionic conductivities for LiBH$_4$·NH$_3$ obtained by as-purified LiBH$_4$ in heating process (black), cooling process (red), and LiBH$_4$·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$_4$·NH$_3$ from commercial LiBH$_4$ under different temperatures. b, LiBH$_4$·NH$_3$ from as-purified LiBH$_4$ in heating process under varied temperatures.
3 Supporting Table

Table S1. Material cost of LiBH₄ produced by ball milling Mg and LiBO₂·2H₂O and commercial method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Cost (US $/ ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball milling Mg and LiBO₂·2H₂O</td>
<td>34670ᵃ</td>
</tr>
<tr>
<td>Commercial method</td>
<td>171818ᵇ</td>
</tr>
</tbody>
</table>

ᵃThe calculation is based on the yield of 38.7% LiBH₄ when Mg and LiBO₂·2H₂O 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 LiBH₄. 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.

ᵇThe price is from a commercial company in China. Commercial method refers to wet chemical reaction method [17-18]: NaBH₄ + LiCl 75% LiBH₄ + NaCl. According to a yield of 75% in current industrial production, 2.59 tons of LiCl and 2.32 tons of NaBH₄ are needed for production of 1 ton LiBH₄. Then the total cost of raw materials is $171818 due to the prices of LiCl and NaBH₄ being $25769/ton and $45291/ton, respectively [19].
4 Supporting References


