

Electronic Supplementary Information (ESI)

Realizing fast Li-ion conduction of Li_3PO_4 solid electrolyte at low temperature by mechanochemical formation of lithium-containing dual-shells†

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MATERIALS AND METHODS

LiBH₄ (purity > 95% from Aladdin) was used as received without further purification, and Li₃PO₄ (purity > 99% from Aladdin) was dried under dynamic vacuum at 300 °C for 5h prior to use. xLiBH₄-Li₃PO₄ mixtures were prepared with five different kinds of mixed mass, ratios ranging from x=40, 50, 70, 80 to 90. For each experiment, 1g of the mixture was loaded into a custom-designed milling jar in a glove box filled with argon. The ball-to-sample weight ratio was kept at 40:1. Two mixtures with compositions of LiBH₄ and LiPO₄ were mechanically milled at 400 rpm for 2H with a planetary ball mill (QM-1SP4, Nanjing). All samples prepared were milled for four periods of 30 min each separately. Breaks of 5 min have been used between each period in order to overcome heating effects. All samples were mechano-chemically treated within argon atmosphere. After milling treatment, the mixtures were collected in an Argon-filled glove-box for further structural and property characterizations. All manipulations of the samples during the experiment were conducted within an Argon atmosphere in a glove box ($\rho(\text{O}_2) < 0.1 \text{ ppm}$, $\rho(\text{H}_2\text{O}) < 0.1 \text{ ppm}$).

CHARACTERIZATION

X-ray diffraction (XRD) analysis was performed on a MiniFlex 600 XRD unit (Rigaku, Japan) by using Cu K α radiation ($\lambda = 0.154056 \text{ nm}$) at 40 kV and 15 mA. The 2θ angle was from 10° to 90° with a 0.02° increment. The samples were placed in homemade dies and sealed with polyimide thin-film tape, which ensured that the powder samples were within an Argon atmosphere during the process of measurement. Micro-structure and morphology were characterized by using scanning electron microscope (SEM) Zeiss Sigma 300 operating at 3 kV and Transmission Electron Microscope (TEM) FEI Talos F200X operating at 200 kV, coupled with Energy Dispersive Spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo Fisher Scientific Spectrometer with the Al K α X-ray source. The powder sample was inside an argon-filled glove box and then mounted on a sample holder which was transferred by using a special container from the glove-box to the XPS facility to avoid air exposure. Argon-ion sputtering was used for in-depth profile analysis. Differential scanning calorimeter (DSC) was conducted on a Netzsch DSC 200 F3 unit. Approximately 3 mg of sample was heated in an Al₂O₃ crucible at temperatures ranging from room temperature to 300 °C at 2 °C min⁻¹. For the LiBH₄/Li₃PO₄

composites, Specific surface areas and pore volumes of the samples were characterized on Micro-metrics ASAP2020 by using the Brunauer–Emmett–Teller (BET) methods.

Electro-chemical measurement: The ionic conductivity of pure LiBH_4 , $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ was measured, respectively, by electro-chemical impedance spectroscopy (EIS), which was conducted by using a Solartron impedance analyzer. These composite powders were pressed into pellets with the diameter of 14 mm and thickness of 0.7-0.9 mm approximately under the pressure of 10 MPa, using a homemade battery mold. The symmetric battery consisting of $\text{SUS}|\text{LiBH}_4\text{-Li}_3\text{PO}_4|\text{SUS}$ (SUS: stainless steel) were used to evaluate their EIS spectra, the frequency of which varied from 0.1 Hz to 1 MHz. All measurements were carried out within the temperature range from 35 °C to 125 °C at an interval of 20 °C. Each temperature point was required for a holding time of 60 minutes in order to ensure data reproducibility of the measurement. Direct Current polarization was conducted by applying a constant voltage of 10 mV for 1500 s. The Cyclic Volta-metry (CV) and the critical current density were obtained by using Li/SUS batteries and Lithium symmetrical batteries respectively with an electrolyte with a diameter of 14 mm and a thickness of approximately 1 mm. The electro-chemical window was examined by performing CV on $\text{SUS}|\text{SSE}|\text{Li}$ cells from 0.5 to 5 V at 105 °C when the scan rate was 5 mV s^{-1} . The galvanostatic plating-stripping cycling was tested on $\text{Li}|\text{SSE}|\text{Li}$ symmetric cells by using Neware battery test systems (CT-3008W-5V20A-S4, Shenzhen, China).

The temperature-dependent lithium ionic conductivity of the $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composites was measured by using electro-chemical impedance spectroscopy (EIS), which was performed on electrolytes to yield a Nyquist plot. As shown in Fig. 3a, S2, ESI†, each Nyquist plot is composed of a semicircle in the high frequency region and a line tailing in the low frequency region. The electrolyte conductivities σ can be evaluated by the following equation:

$$\sigma_{\text{Li}^+} = \frac{d}{SR}$$

where d denotes the thickness of the pressed pellet of electrolytes, S denotes the cross-sectional area of the pellet, and R denotes the pellet resistance, which corresponds to the intersection of the semicircle with the Z' axis in the low-frequency limit of the Nyquist plot (Arrhenius diagram of ionic conductivity of LiBH_4 , Li_3PO_4 , different mixing ratios $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composites are shown in Fig. S3, ESI†).

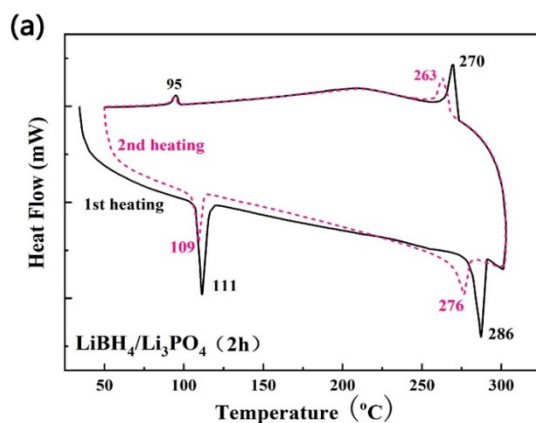


Fig. S1. In-situ DSC curves of 50 wt% $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composite by heating/cooling for (a) 2h.

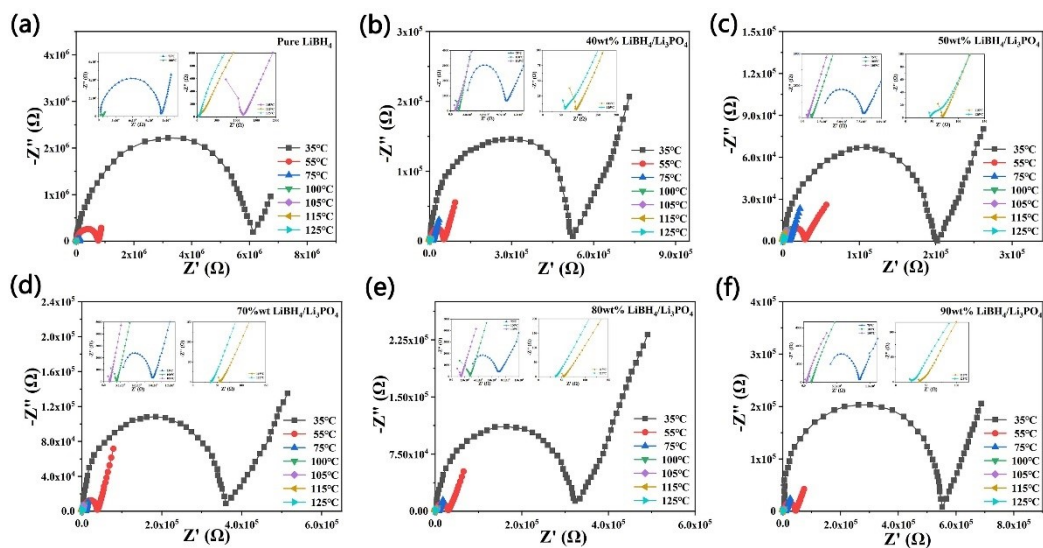


Fig. S2. (a-f) EIS of $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composite solid electrolytes with different mass fractions.

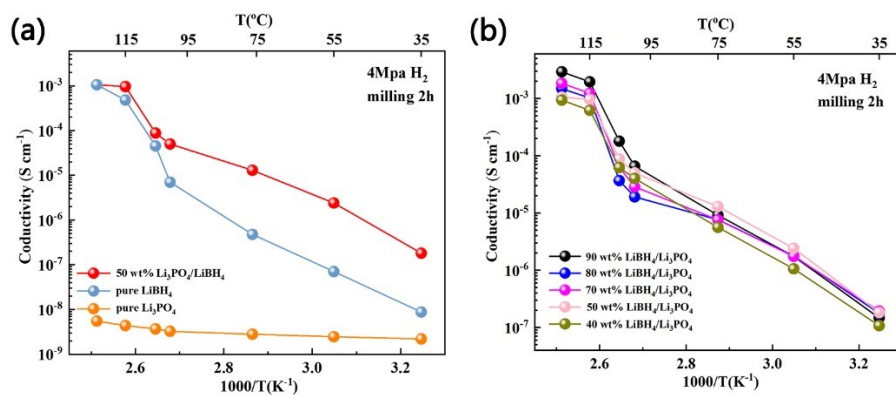


Fig. S3. Arrhenius diagram of ionic conductivity of (a) Pure LiBH_4 , Li_3PO_4 and 50wt% $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composite solid electrolyte and (b) $\text{LiBH}_4/\text{Li}_3\text{PO}_4$ composite solid electrolyte with different mass fractions.

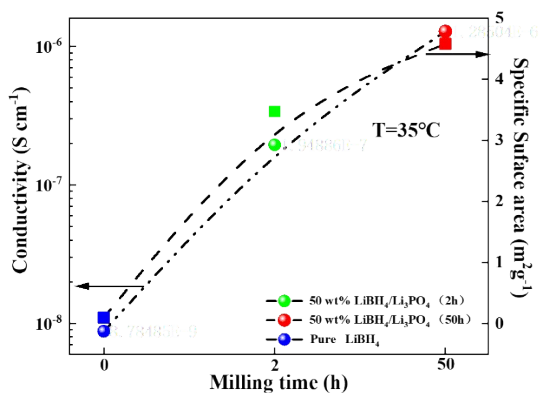


Fig. S4. The functional relationship between specific surface area, ionic conductivity ratio and ball milling time at 35°C .