Empa
Materials Science and Technology

Supplementary information:

$Li_4B_{10}H_{10}B_{12}H_{12}$ as solid electrolyte for solid-state lithium batteries

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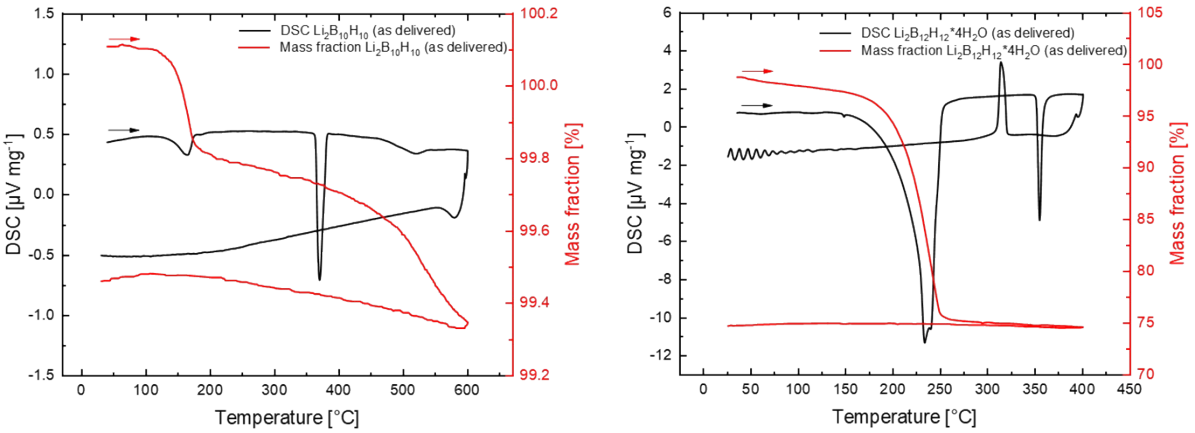

Figure S1. *DSC (black) and TG (red) signals of the as-received precursors $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$·4H_2O.*

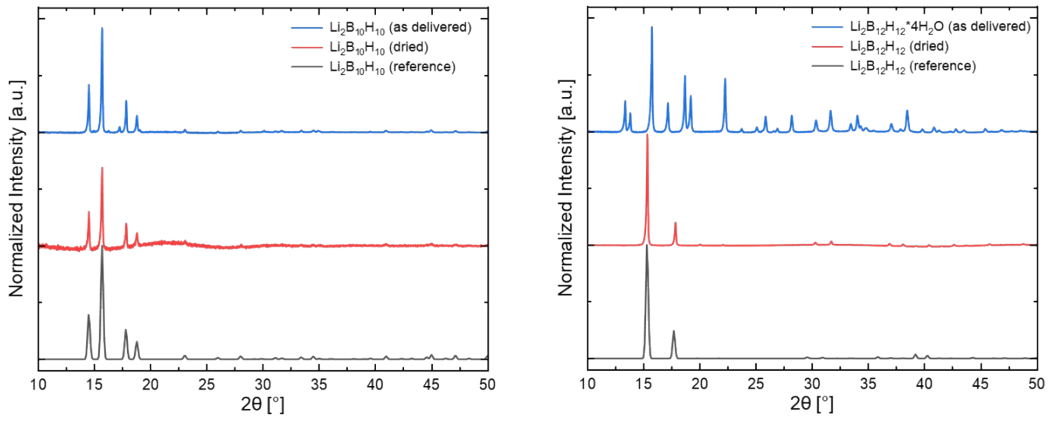

Figure S2. *XRD pattern of the as-received precursors ($Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$·4H_2O) (blue), the dried precursors (red), and the references (black)*[1].

[1] Reference pattern taken from the ICSD Database. The database refers to Wu et al., *J. Phys. Chem. C* 2015, 119, 6481 (for $Li_2B_{10}H_{10}$) [9] and Her et al., *Inorg. Chem.* 2008, 47 9757 (for $Li_2B_{12}H_{12}$) [27].

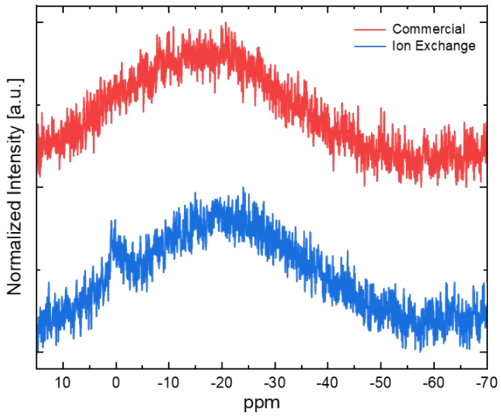

Figure S3. *^{23}Na NMR spectra of a stoichiometric mixture of $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$ prepared from the commercial precursors (red) and ion-exchanged $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ (blue).*

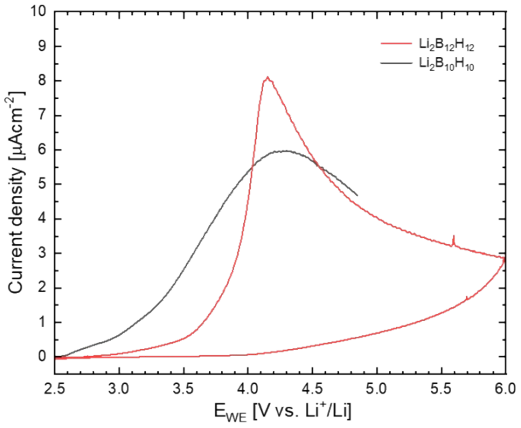

Figure S4. *Voltammograms of the Li/SE/SE-C/Pt cells at a scan rate of 10 µV s^{-1} between 2.5 V and 6.0 V vs Li^+/Li at 120 °C, using $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$ as a solid electrolyte.*

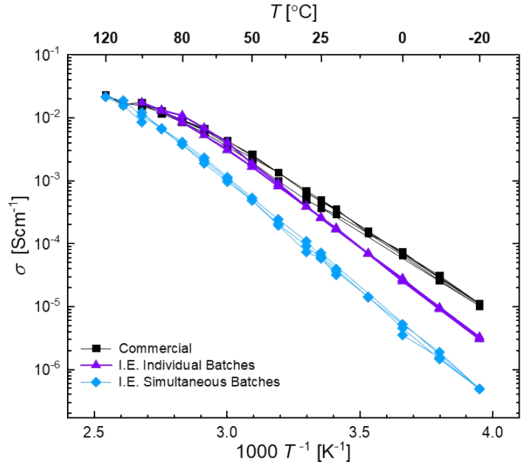

Figure S5. *Temperature-dependent lithium-ion conductivity of the dried and ball-milled 1:1 stoichiometric mixture of (i) the dried commercial precursors $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$, (ii) $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$ obtained*

by ion exchange of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ from individual batches and (iii) $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$ obtained from the simultaneous ion exchange of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$.

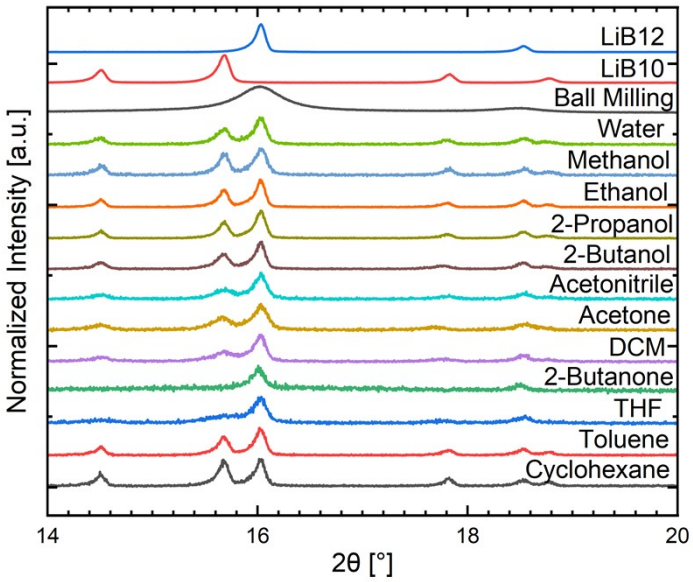

Figure S6. *XRD pattern of the $Li_2B_{10}H_{10}$ and $Li_2B_{12}H_{12}$ mixtures recovered from solutions with different solvents. Except for 2-butanone, they all show the coexistence of the initial phases.*

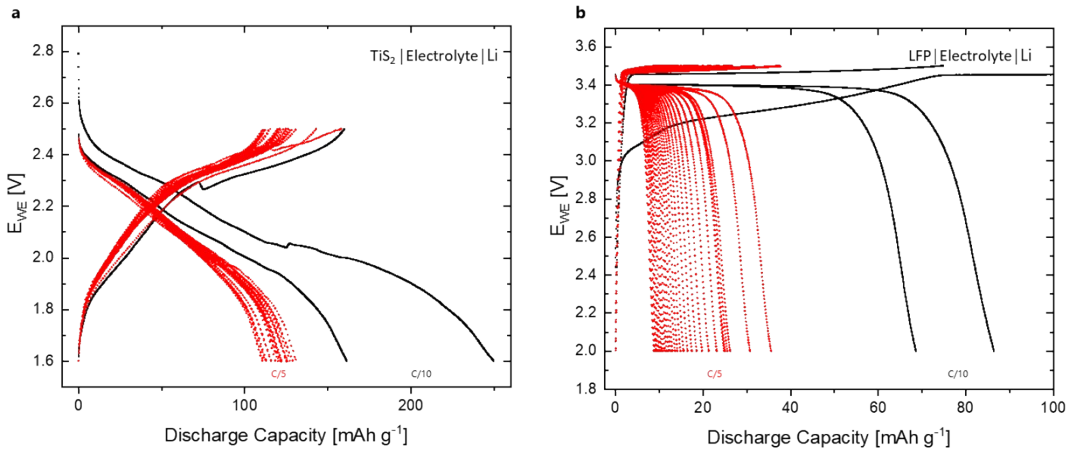

Figure S7. *a) Charge-discharge voltage profiles for 39 cycles at a C-rate of C/5 after two initial cycles at C/10, using a TiS_2|SE|Li cell under 1.71 MPa at 60 °C. The cathode composite contained 40 wt% TiS_2, 50 wt% solid electrolyte and 10 wt% carbon. The cell failed in the 39th cycle. b) Charge-discharge voltage profiles for the first 32 cycles at a C-rate of C/5 after two initial cycles at C/10, using a $LiFePO_4$|SE|Li cell under 1.71 MPa at 60 °C. The cathode composite contained 30 wt% $LiFePO_4$, 50 wt% solid electrolyte, 15 wt% carbon, and 5 wt% PVDF.*