Supporting Information For

Scalable Synthesis of Hydroxyl-Functionalized Boron Nanosheets for High Ion-Conductive Solid-State Electrolyte Application

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Experimental Section

Synthesis of hydroxyl-functionalized boron nanosheet. 10 g 70 wt.% NaOH (97%, ACS grade, Aladdin) aqueous solution was first kept in vacuum atmosphere for 1 hour to remove the soluble gas. Then 0.2 g AlB₂ powder (>99%, Sigma-Aldrich) was added into the solution with stirring. The solution was heated at 70 °C in a water bath for 12 hours. The dark black color powder changed into dark yellow. The obtained product was centrifuged and washed by DI water before redispersed into 100 mL acetonitrile (99.5%, ACS grade, Aladdin) and sonicated for 1 h. The suspension was further centrifuged at 3000 rpm for 5 min to remove the large particles. For comparison, the soluble gas removal was not carried out for solution before AlB₂ powder was added. It seems the presented oxygen in the procedure of synthesis reduces the product yield. For the oxygen-removed solution, the yield is ~ 40% and it decreases to only ~20 when the solution without gas removal was used.

Materials characterizations: X-ray diffraction (XRD, SmartLab Rigaku) was performed with Cu K α radiation ($\lambda = 1.54$ Å) as the X-ray source. The UV-vis-NIR absorption spectrum was record by LAMBDA 650S. Atomic force microscopy (AFM, Icon) and scanning electron microscopy (SEM, Hitachi S-4800) were used for the morphology analysis. To gain the crystal structure information, transmission electron microscopy (TEM, JEOL 2100F) coupled with energy dispersive X-ray (EDX) spectroscopy analyses were performed. The elemental analysis was measured by vario EL cube analyzer. N2 adsorption isotherms were measured by the Brunauer-Emmett-Teller (BET, Micrometrics ASAP2460) method. The chemical state study of the samples was carried out by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) and the binding energies were corrected for specimen charging effects using the C 1s level at 284.6 eV as the reference. The lineshapes used for XPS curve fitting were Lorentzian-Gaussian (L/G=80%) and integrated backgrounds were employed. The Raman shift was measured by a confocal Raman microscope (InVia, Renishaw, England). Thermogravimetric analysis (TGA, NETZSCH STA409) was conducted with a heating/cooling rate of 10°C min⁻¹ between 30 to 700 °C under N₂ atmosphere. X-ray total scattering data used to generate PDFs were collected using Bruker D8 Quest with Mo source.

Preparation of SSEs film. The boron nanosheet, LiTFSI (>99.9%, Aladdin) and PEO (M_w ~600k, Aladdin) were dissolved in acetonitrile, stirred for 24 h to form a homogeneous solution. The molar ratio of (EO)/Li⁺=20:1, and the quantity of the boron nanosheet was decided by the mass ratio of boron nanosheet/LiTFSI and PEO (0, 10, 20, 40 wt.%). The homogeneous solution was casted in glass sheet and dried at 120 °C in vacuum condition for 24 h. The obtained thin film with thickness of ~0.1 mm was used in performance characterization.

Assembly of the lithium-ion batteries. The PEO based batteries were assembled in 2032-type coin cells with lithium metal anode, PEO-LiTFSI-boron composite electrolyte and $LiMn_2O_4$ cathode. The cathode was composed of $LiMn_2O_4$: super P: binder=7:1:2. The slurry was coated

on Al foils and dried at 60 °C for 16 h. Then the film of PEO-LiTFSI-boron nanosheet electrolyte was placed onto cathode directly and dried at 70 °C for 24 h in order to make the complete volatilization of acetonitrile and liquid wetting of the polymer to the cathode. The batteries with lithium metal anode were sealed in a 2032-coin cell for electrochemical measurements in an Argon filled glove box.

Electrochemical measurements: The electrochemical windows were measured by the linear sweep voltammetry (LSV) profile of the electrolyte using lithium metal as the counter and reference electrode and stainless steel as the working electrode. The ionic conductivities of composite SSEs were tested via a stainless steel/SSE/stainless steel cell and evaluated by electrochemical impedance spectroscopy, in which the temperature range was set between 20-80 °C with the frequency range between 10-10⁶ Hz. The C-rates of the batteries in all of the electrochemical measurements are defined based on 1C=120 mAh g⁻¹. The batteries were charged and discharged between 2.4-4.5 V at 40 °C.



Figure S1. TEM image of the surface functionalized boron nanosheet. The cross section regions are highlighted by red circles, implying the nanosheet is multilayered. Due to the low atomic weight of element boron, the contrast of the nanosheet is very low under TEM beam and the layered image becomes blurred under magnified condition.



Figure S2. PDF analysis of the functionalized boron nanosheet and AlB₂.



Figure S3. (a) Nitrogen absorption-desorption isotherms of the boron nanosheet and its precursor AlB₂. The surface area is 140.4 m²/g and 4.1 m²/g, respectively. (b) The pore size distribution of the nanosheet calculated based on the NLDFT model.



Figure S4. Full-scale XPS survey of the hydroxyl-functionalized boron nanosheet.



Figure S5. (a) SEM and (b) High-resolution B1s spectra of the surface functionalized boron nanosheet after exposure in air for two months.



Figure S6. Density functional theory (DFT) calculations were performed by using the projector augmented wave method as implemented in the CASTEP simulation package.¹ The Perdew-Burke-Ernzerhof functional was adopted to describe the exchange-correlation term and the energy cutoff for the plane wave basis was set as 600 eV. All structures were fully optimized with the convergence criterion for the residual force and energy of 0.01 eV/Å and 10⁻⁵ eV, respectively. A 4×2 periodic slab model was constructed to simulate the monolayer hydroxylfunctionalized boron nanosheet and the data for boron nanosheet was obtained from the modification of the hydrogen boride cells and geometric optimized before use.² The vacuum slab of 15 Å was added in the simulation. The system energies were calculated based on different LiTFSI conformations where the distance of LiTFSI to the boron layer is 1.5 Å. The initial conformations of LiTFSI adsorbed on the boron nanosheet for calculation. The calculated DFT total energy for each system is (a) -17230.28 eV, (b) -17226.12 eV, (c) -

17236.93 eV, (d) -17025.86 eV. Therefore, system (c) shows the lowest energy. The electron density difference of the system was calculated then.



Figure S7. Side view of difference of charge density for the LiTFSI, in which green and yellow regions indicate electron accumulation and depletion, respectively.



Figure S8. Polarization plot measured by chronoamperometry (V=1 V) for the boron nanosheet CSSE membranes at 80 °C. Pt electron blocking electrodes were used to measure the ionic transference number (t_{ion}) of the membranes by Wagner's polarization technique. Current passing through the membranes was monitored in a 2-probe configuration using Pt electrodes attached on the surface of membranes under a constant voltage (1 V). All the measurements were carried out at 0% RH atmosphere to eliminate the ion conductivity. t_{ion} was calculated as follows:

$$t_{ion} = \frac{i_t - i_e}{i_t}$$

where i_t is the total current, and i_e is the electronic current.



Figure S9. EIS profiles of the electrolyte membrane with the boron nanosheet additive (10 wt.%) at different temperatures (20 °C, 40 °C, 60 °C, and 80 °C).



Figure S10. (a) Nyquist plot of impedance for the boron nanosheet composite SSE at 20 °C. The plot typically contains a semicircle at high frequencies which represents the Li⁺ impedance and an incline spur at low frequencies which represents the pile up of Li⁺ at the electrodes. The inset is the diagram of the equivalent circuit used to analyze the impedance data. R₁ and Q₁ correspond to the inner protonic transport resistance and the dielectric capacitance between the membrane and electrode, respectively. (b) Table of the fitting data for each element in the equivalent circuit. The conductivities were calculated by using the equation $\sigma = L/(R \cdot S)$ where σ is conductivity, *L* is the thickness of the membrane, *R* is the resistance calculated from Nyquist plots, and *S* is the area of membrane.



Figure S11. (a) Typical charge-discharge curves of $LiMn_2O_4$ -Li batteries using PEO-LiTFSI electrolyte at 40 °C. (b) Cyclic voltammogram of the $LiMn_2O_4$ -Li cell using PEO-LiTFSI electrolyte tested at 40 °C, the scan rate is 0.1 mV/s.



Figure S12. Cyclic voltammogram of the $LiMn_2O_4$ -Li cell using PEO-LiTFSI-10 wt.% boron nanosheet electrolyte tested at 40 °C, the scan rate is 0.1 mV/s.



Figure S13. Cycling performance of $LiMn_2O_4$ -Li batteries with PEO-LiTFSI-10 wt.% boron nanosheet electrolyte at 1 C and 40 °C.



Figure S14. (a) Rate performance of $LiMn_2O_4/Li$ batteries using organic electrolyte (1M LiTFSI in EC/DMC) at room temperature. (b) Cycling performance of $LiMn_2O_4/Li$ batteries with organic electrolyte (1M LiTFSI in EC/DMC) at 1C and room temperature.



Figure S15. XPS spectra of (a) B 1s, (b) O 1s, (c) F 1s and (d) S 2p for the as-prepared CSSE film (black color) and the CSSE dissembled from the batteries after 50 charge-discharge cycles (red color).

Reference

- 1. Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne,
- M. C. First Principles Methods Using CASTEP. Z. Krist. 2005, 220, 567-570.
- 2. Tominaka, S.; Ishibiki, R.; Fujino, A.; Kawakami, K.; Ohara, K.; Masuda, T.; Matsuda, I.;
- Hosono, H.; Kondo, T. Chem 2020, 6, 406-418.