Supporting Information

High-Areal-Capacity and Long-Cycle-Life All-Solid-State Battery Enabled By Freeze Drying Technology

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Experimental Procedures

Preparation of the Li₃**InCl**₆ **SSE through freeze-drying:** Lithium chloride (LiCl, Aladdin, 98%) and indium chloride (InCl₃, Aladdin, 99.9%) were weighed to the stoichiometric molar ratio and dissolved in deionized water in an ambient environment (outside of the glovebox). To obtain the precursor hydrate, the solution was quickly frozen to solid and then dried through sublimation. The Li₃InCl₆ SEs were obtained by heating the precursor at different temperatures for 4 h (200–400 °C) under vacuum.

Preparation of the Li₃InCl₆ SSE through water removal route: Lithium chloride (LiCl, Aladdin, 98%) and indium chloride (InCl₃, Aladdin, 99.9%) were weighed to the stoichiometric molar ratio and dissolved in deionized water in ambient environment (outside of the glovebox). The solution was dried at 50°C in air to obtain the precursor hydrate. The Li₃InCl₆ SE was obtained by heating the precursor at (200 °C) for 4 h under vacuum.

Preparation of the Li₃InCl₆ SSE through ball milling route: Lithium chloride (LiCl, Aladdin, 98%) and indium chloride (InCl₃, Aladdin, 99.9%) were weighed to the stoichiometric molar ratio. The mixtures were mechanically mixed in a ZrO_2 pot with ZrO_2 balls. The mixing process was performed using a planetary ball milling apparatus at 500 rpm for 24 h. Several hundreds of milligrams of the ball-milled Li₃InCl₆ was pelletized at 200 MPa, sealed in a glass tube under vacuum, annealed at 260°C for 5h.All the preparation processes were carried out with an Ar atmosphere.

Synthesis of Li₆PS₅Cl: Li₆PS₅Cl powder was prepared by mechanochemical milling of stoichiometric mixture of Li₂S (Alfa, 99.9%), P_2S_5 (Macklin, 99%), and LiCl (99.9%, Aladdin) at 400 rpm for 20 h, followed by heat-treatment at 550 °C for 5 h in a sealed glass ampoule.

Preparation of ASSBs: All of the cell preparation processes were conducted inside an Ar-filled glove box. For cathode composites fabrication, commercial NCM90 and asprepared Li_3InCl_6 were hand-milled for 10 min. For cell fabrication, 60 mg Li_3InCl_6 powder was pressed at 2 ton. Subsequently,the cathode composite powder were

dispersed on one side of the electrolyte and pressed again at 1 ton. Before attaching Li-C anode on the other side of the electrolyte layer, a thin layer of $\text{Li}_6\text{PS}_5\text{Cl}$ (60 mg) that stable toward Li-C alloy was set on the surface of Li-C anode to avoid possible influence of redox conversion. The cells were cycled in the voltage range of 2.5-4.2 V (vs. Li⁺/Li) using a Land cycler (Wuhan, China).

Characterizations: X-ray diffraction (XRD) patterns were performed on a Bruker AXS D8 Advance with a Cu K α radiation ($\lambda = 1.54178$ Å) at room temperature with fresh keeping film to avoid air exposure. The morphologies of the samples were examined using a Hitachi S-8100 field emission scanning electron microscopy (SEM) operated at 5 kV equipped with energy dispersive spectroscopy (EDS).



Figure S 2 Schematic illustration of the ASSB configuration, with Li-C as the negative electrode,Li₆PS₅Cl as the separator and Li3InCl6 as the solid electrolyte for the cathode composite and separetor.



Figure S 3 The initial charge-discharge curves of ASSBs at various C rates with different Li₃InCl₆ (a)Freeze drying-200. (b)Freeze drying-300. (c)Freeze drying-400.



Figure S 4 Charge-discharge voltage profiles of long-term cycling of the ASSBs with different Li₃InCl₆ (a)Freeze drying-200. (b)Freeze drying-300. (c)Freeze drying-400.



Figure S 5 (a) Charge-discharge voltage profiles of long-term cycling of the ASSBs with FD200 solid electrolyte at 2C rate.(b) the corresponding charge-discharge capacity and the coulombic efficiency.



Figure S 6 SEM images of with different Li₃InCl₆ under 300 Mpa. (a)Freeze drying-200.(b)Hydration method.(c)Ball milling.



Figure S 7 XRD patterns of the Li₃InCl₆ samples with different synthesized methods.



Figure S 8 Impedance spectra of the Li₃InCl₆ samples with different synthesized methods at 25 °C.



Figure S 9 The initial charge-discharge curves of ASSBs at various C rates with different Li₃InCl₆.(a)Freeze drying-200.(b)Hydration method.(c)Ball milling,



Figure S 10 Charge-discharge voltage profiles of long-term cycling of the ASSBs with different Li₃InCl₆. (a)Freeze drying-200.(b)Hydration method.(c)Ball milling,



Figure S 11 Charge-discharge voltage profiles of long-term cycling of the ASSBs with different Li₃InCl₆. (a)Freeze drying-200.(b)Hydration method.



Figure S 12 (a) Charge-discharge voltage profiles of long-term cycling of the ASSBs with FD200 solid electrolyte at 5C rate.(b) the corresponding charge-discharge capacity and the coulombic efficiency.



Figure S 13 (a) Charge-discharge voltage profiles of long-term cycling of the ASSBs with FD200 solid electrolyte at 1C rate.(b) the corresponding charge-discharge capacity and the coulombic efficiency.