Supporting Information

High performance All-Solid-State Li-Se Batteries induced by sulfide electrolyte

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**Methods**

**Preparation of the Se-Li$_3$PS$_4$-C cathode composite:** The commercial Se powder (99.5%, Sigma-Aldrich) was mixed with Li$_3$PS$_4$ (99.95%, MSE supplies, LLC) and acetylene black (AB) at a weight ratio of 40:40:20 by ball milling for 4 h.

**Synthesis of Li-Sn anode:** 2 g of Li metal foil were heated and melted at 250 °C in stainless steel pan inside glovebox. After melting, the surface oxide layer was removed carefully by stainless steel tweezers to obtain a bright and beaded molten lithium. Then, 6 g of Sn powder (99.8%, Aldrich) were added and the temperature of the stainless steel pan was still kept at 250 °C for 10 minute. When the temperature turn down, a soft alloy particle with white color could be achieved. The resulting alloy particle were press under 100 MPa to form the Li-Sn anode foils. Both of Li and Li$_{22}$Sn$_5$ were detected by XRD measurement in the obtained Li-Sn anode foils (Figure S10).

**Electrochemical measurements:** All-solid-state cells (Se/Li$_3$PS$_4$/Li or Se/Li$_3$PS$_4$/Li Li-Sn) were assembled to examine the electrochemical performance of Se. The commercial Li$_3$PS$_4$ powders were used as a solid electrolyte separator. Lithium or Li-Sn alloy foil was used as the negative electrode. The all-solid-state cells were fabricated as follows: 100 mg of the Li$_3$PS$_4$ was pressed successively under 240 MPa to form solid electrolyte layer. The cathode composite powder was uniformly spread onto the surface of the Li$_3$PS$_4$ electrolyte and pressed under 360 MPa. Li or Li-Sn alloy foil was subsequently pressed onto the other side of the Li$_3$PS$_4$ layer under 120 MPa. The mass loading of cathode is about 7.6 mg cm$^{-2}$, corresponding to a Se loading of 3 mg cm$^{-2}$. The three-layered pellet was sandwiched between two stainless-steel rods as current collectors for both positive and negative electrodes. All the processes were performed in an Ar-filled glove box.

All-solid-state cells were tested at different current densities by using a multichannel battery tester (LAND CT-2001A, Wuhan Rambo Testing Equipment Co., Ltd.). Rate capability and cycling stability were tested using an operating voltage window of 1.0-3.0 V (vs Li/Li$^+$). After
charging at a constant current, the cells were further charged at a constant voltage of 3.0 V until the current dropped to 10% of the constant current. All electrochemical tests were performed at room temperature unless otherwise noted. The galvanostatic intermittent titration technique (GITT) measurements were performed using LAND battery testing station, by applying a current density of 20 mA g\(^{-1}\) for 1 h followed by a 4-h relaxation. Cyclic voltammograms (CVs) were performed on a versatile multichannel potentiostation 3/Z (VMP3) under a scanning rate of 0.05 mV s\(^{-1}\) between 1.0 to 3.0 V (vs. Li/Li\(^+\)). Electrochemical Impedance Spectroscopy (EIS) measurements for all-solid-state cells were also conducted with VMP3 at different discharge/charge states with an amplitude of 10 mV and frequencies ranging from 0.1 Hz to 7 MHz.

**Characterizations:** Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS) was used to characterize the morphologies of the samples. X-ray diffraction (XRD) measurements were performed on Bruker AXS D8 Advance with Cu K\(\alpha\) radiation (\(\lambda = 1.54178\) Å). Raman spectra were measured with a HORIBA Scientific LabRAM HR Raman spectrometer operated with an incident laser beam at 532.03 nm. For X-ray photoelectron spectroscopy (XPS) analysis, the electrodes at different charge or discharge state were disassembled and transferred to XPS (Krotos AXIS Ultra Spectrometer) system using an Ar-filled glove box to avoid exposure to air or moisture.
Figure S1. Cyclic voltammogram of Se cathode in all-solid-state cell at 60 °C in the potential range from 1.0 to 3.0 V at 0.05 mV s⁻¹.

Figure S2. (a) Impedance plots of commercial Li₃PS₄ under different temperatures (-5, 5, 15, 25, 35 and 45°C). (b) Arrhenius plots of ionic conductivity for commercial Li₃PS₄.
Figure S3. (a) Impedance plots of Li$_3$PS$_4$-Se composite under different temperatures (-5, 5, 15, 25, 35 and 45˚C). (b) Arrhenius plots of ionic conductivity for Li$_3$PS$_4$-Se composite.

Figure S4. (a) Impedance plots of Li$_3$PS$_4$-S composite under different temperatures (-5, 5, 15, 25, 35 and 45˚C). (b) Arrhenius plots of ionic conductivity for Li$_3$PS$_4$-S composite.
Figure S5. (a-e) DC polarization curves of Li$_3$PS$_4$-Se, Li$_3$PS$_4$-S and Li$_3$PS$_4$ using symmetric cells at different voltages. (f) Stable current response of Li$_3$PS$_4$-Se, Li$_3$PS$_4$-S and Li$_3$PS$_4$ using symmetric cells at different voltages.
Figure S6. SEM and EDX mapping of Se-Li$_3$PS$_4$-C cathode composite after ball milling process.

Figure S7. SEM images (top view, cathode side) of Se-Li$_3$PS$_4$-C/Li$_3$PS$_4$ pellet pressed at 360 MPa.
Figure S8. SEM image (top view, cathode side) of Se-Li$_3$PS$_4$-C/Li$_3$PS$_4$ pellet pressed at 360 MPa and corresponding EDX mapping of C, P, S and Se.

Figure S9. (a) Charge/discharge curves of an all-solid-state Se/Li$_3$PS$_4$/Li cell using a lithium foil at 50 mA g$^{-1}$ at 25 °C. (b) Lithium cyclability in a symmetric Li/Li$_3$PS$_4$/Li cell. The cell was cycled at a current density of 0.05 mA cm$^{-2}$ at room temperature and 25 °C.
Figure S10. XRD pattern of the as-prepared Li-Sn alloy.

Figure S11. Lithium cyclability in a Li-Sn/Li$_3$PS$_4$/Li-Sn symmetric cell. The cell was cycled at a current density of 0.05 mA cm$^{-2}$ at room temperature.
Figure S12. SEM images (top view, cathode side) of Se-Li$_3$PS$_4$-C/Li$_3$PS$_4$ pellet after 100 cycles.

Figure S13. SEM image (top view, cathode side) of Se-Li$_3$PS$_4$-C/Li$_3$PS$_4$ pellet after 100 cycles and corresponding EDX mapping of C, P, S and Se.
Figure S14. Nyquist plots of Se/Li$_3$PS$_4$/Li-Sn all-solid-state batteries at (a) initial state before discharge/charge, (b) first discharge to 1.0 V, (c) first charge to 3.0 V and (d) charge to 3.0 V after 30 cycles.

Figure S15. (a) Raman spectra of pure Se, commercial Li$_3$PS$_4$, Li$_3$PS$_4$/C and Se/Li$_3$PS$_4$/C. (b) Raman spectra of pure Se and Se after milling process. The signal marked as “*” in the spectra should be caused by fluorescent lamp during test.

It's noticed that the peak at 252 cm$^{-1}$ might also be assigned to Se with different allotropic form$[^1]$. Thus to make sure the assignment of this new peak after ball-milling process, the Raman spectra of commercial pure Se before and after ball-milling process were also
compared as shown in Figure S14b. It could be seen that the peaks didn't show obvious change, indicating no other selenium allotropic form emerged after ball-milling process.

Figure S16. Se 3d and Li 1s XPS spectra of Se/Li$_3$PS$_4$/C cathode at different discharge/charge states. (a for fresh state, b for discharged at 1.8 V vs. Li/Li$^+$, c for discharged at 1.4 Li/Li$^+$, d
for discharge to 1.0 V Li/Li$^+$, e for charged to 2.3 V Li/Li$^+$, f for charged to 2.8 V Li/Li$^+$, and
g for charged to 3.0 V Li/Li$^+$).

Figure S17. Ex-situ XRD patterns of Se/Li$_3$PS$_4$/C cathode at different discharge/charge states.