Electronic Supporting Information (ESI) High-Performance All-Solid-State Li₂S Batteries Using an Interfacial Redox Mediator

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Experimental Methods

<u>Preparation of Li₂S nanoparticles.</u> Li₂S nanoparticles were synthesized by reduction of elemental sulfur with lithium naphthalenide as reported elsewhere.¹ In a typical procedure, 2.56 g naphthalene (99%, Sigma-Aldrich) was first dissolved in 15 mL monoglyme (DME, anhydrous, inhibitor-free, Sigma-Aldrich). Next, 40 mg lithium strips (Sigma-Aldrich) were added slowly to the above solution to form lithium naphthalenide. The mixture was stirred for 12 hours before slowly adding additional sulfur (160 mg; 99%, Sigma-Aldrich) to the dark-green solution. The stirred reaction was stopped after 6 days. The Li₂S powder was washed with DME via centrifugation (10 krpm, 5 min) three times, followed by drying at 150 °C for 15 h in vacuo.

<u>Preparation of the core-shell LVS (Li₂S-Li_xVS₂) nanocomposite.</u> In brief, 0.7 mmol VCl₄ (99+ %, Thermo Scientific) was introduced to a pre-dispersed solution of Li₂S (5 mmol) in THF (20 mL). The beige-coloured solution immediately turned dark purple due to the formation of VCl₄ complexes.² After stirring the mixture at room temperature for 24 h, the black solid was washed with THF via centrifugation (10k rpm, 5 min) to remove all side products (LiCl and S). THF was then evaporated *in vacuo* for 15 h at 150°C. The core-shell composite powders were pelletized, placed in a glassy carbon crucible, and sealed in a quartz tube under vacuum for crystallization at 400 °C for 2 h at a heating and cooling rate of 3 and 1.5 °C·min⁻¹, respectively.

Synthesis of Li_{5.5}PS_{4.5}Cl_{1.5} argyrodite via a solid-state reaction.³ Stoichiometric amounts of lithium sulfide (99.98%, Sigma-Aldrich), phosphorus pentasulfide (99%, Sigma-Aldrich), and lithium chloride (99%, anhydrous, free-flowing, Sigma-Aldrich) were mixed by hand grinding in an Ar filled glovebox. The solid powders were then pelletized, placed in a glassy carbon crucible, and sealed in a quartz tube under vacuum. The solid-state electrolyte (Li_{5.5}PS_{4.5}Cl_{1.5}) was obtained by heating the pellet at 520 °C for 10 hours at a ramp rate of 5.5 °C·min⁻¹.

<u>Solid-state cell assembly.</u> The cathode composite material (LVS + Li_{5.5}PS_{4.5}Cl_{1.5}) was prepared by a physical blend of the LVS core-shell composite with SSE at weight ratio of 1:1. The electrochemical performance of the all-solid-state Li-S battery was carried out using an in-house designed cell, which was assembled in an Ar-filled glovebox. A cylindrical die with an internal diameter of 10 mm was used for pellet preparation. In a typical procedure, 100±1 mg Li_{5.5}PS_{4.5}Cl_{1.5} powders were first pressed between two Ti rods under 310 MPa for 1 min. LVS/Li_{5.5}PS_{4.5}Cl_{1.5} was then added to the cathode compartment and further pressed alongside the SSE pellet for another 1 min at 430 MPa. Next, In/Li alloy supported on Cu foil was placed in the anode compartment and was further pressed for 1 min at 500 MPa. Finally, the die was placed in an air-tight stainless-steel casing capable of maintaining constant pressure on the pellet. Screws on the casing were fastened by applying a torque of 10.7 N·m. All electrochemical studies were carried out on a Bio-logic VMP3 electrochemical work station.

For comparison, a Li₂S/C/Li_{5.5}PS_{4.5}Cl_{1.5} composite cathode was also prepared using the same method, employing carbon black (Vulcan XC 72R) as the host material. The carbon-based Li₂S cathode composite was prepared by blending the as-prepared Li₂S nanoparticles, Vulcan carbon, and SSE at a weight ratio of 30:20:50.

Electronic conductivity measurements. The effective electronic conductivities of LVS, LVS cathode composite, and Li₂S cathode composite were measured with an ion-blocking symmetric cell configuration (Fig. 4A). In both cases 75 ± 1 mg of powder was loaded in a cell with a geometric area of 0.785 cm². The thickness of the pellet was measured (0.5 ± 0.02 mm for LVS and LVS cathode composites, and 0.5 ± 0.01 mm for the Li₂S cathode composite) with a micrometer after measurement. A torque of 10.7 N·m was applied on the casing to maintain the pressure in the cell. The sequence of the applied potentials for LVS were -4, -2, +2 and +4 mV whereas for the cathode composites it was -20, -10, -5, +5, +10, +20 mV with an equilibration time of 1 h.

<u>Ion conductivity measurements.</u> The effective ionic conductivities of the LVS, LVS cathode composite, and Li₂S cathode composite were measured with an electron-blocking symmetric cell configuration (Fig. 4D). The pellets used for the electronic conductivities were first loaded in the cell. Next, 100 ± 1 mg Li_{5.5}PS_{4.5}Cl_{1.5} powder was loaded in the working and counter electrode compartments, followed by an In/Li alloy supported on Cu foil. A torque of 10.7 N·m was applied on the casing to maintain the pressure in the cell. The sequence of the applied potentials was -40, -20, -10, +10, +20, +40 mV with equilibration time of 1 h. To subtract the additional resistance contributions from the separator and anode, a symmetric cell of Ti || Cu|LiIn/In || SE || In/InLi|Cu || Ti was also constructed. Impedance spectroscopy was performed on a Bio-Logic VMP3 electrochemical station, and the spectra were analyzed using RelaxIS 3 (rhd instruments) software.

<u>Physical characterization.</u> SEM studies were carried out on a Zeiss Ultra field emission SEM instrument equipped with an EDXS attachment (Oxford). TEM data was acquired at 100 KeV on a Hitachi HF-3300. XRD data were collected on a PANalytical Empyrean instrument outfitted with a PIXcel two-dimensional detector operating at 45 kV/40mA, using Cu-K α radiation (λ = 1.5405Å).

List of Supporting Figures



Fig. S1. (A) SEM image of the Li₂S aggregates and TEM image of the individual nanoparticle (inset). (B) XRD pattern of the same material.



Fig. S2. XRD pattern (upper trace) of the solid material recovered from room temperature reaction of commercial Li_2S powder and lab-prepared VS₂, identifying it as a mixture of Li_2S and $LiVS_2$, which proves that VS₂ indeed can oxidize Li_2S to yield $LiVS_2$. The inset shows the yellow-coloured mixture before the solids were separated, corresponding to the polysulfides/ sulfur dissolved in THF that result from the oxidation of the Li_2S .



Fig. S3. (A) XRD pattern of the solid-state electrolyte. All reflections correspond to those of $Li_{5.5}PS_{4.5}Cl_{1.5}$, confirming the material is single phase. (B) Nyquist plot measured at 25 °C, from which the ionic conductivity was determined to be 6 mS·cm⁻¹.



Fig. S4. EDX analysis of the Li₂S/LiVS₂/Li_{5.5}PS_{4.5}Cl_{1.5} cathode composite. (A) SEM; (B-D) elemental mapping of (b) S; (C) V; and (D) P.

Fig. S5. Electrochemical profiles of the all-solid-state LVS cell at a current density of $1 \text{ mA} \cdot \text{cm}^{-2}$ at different stages of cycling.

Fig. S6. DC polarization measurements under (A-B) ionic and (C-D) electronic blocking conditions to obtain the electronic and ionic conductivity for the (A and C) LVS and (B and D) Li_2S cathode composites, respectively. An equilibration time of 1 h was employed between cycles.

Discussion of Fig. S6. The partial electronic conductivities of the LVS ($\sigma_{e^-,LVS+SSE}$, Fig. S6A) and Li₂S cathode ($\sigma_{e^-,Li_2S+C+SSE}$, Fig. S6B) composites were obtained by measuring the electronic resistance under ion-blocking conditions (Ti || specimen || Ti). Similarly, the partial ionic conductivities of the LVS ($\sigma_{Li^+,LVS+SSE}$, Fig. S6C) and Li₂S ($\sigma_{Li^+,Li_2S+C+SSE}$, Fig. S6D) composites were obtained by measuring the total ionic resistance of the specimen under electronic-blocking conditions (Ti || Cu|LiIn/In || SSE || specimen || SSE || In/InLi|Cu Ti). However, the values obtained in Fig. S6C and D include the ionic resistance contribution from SSE ($R_{SSE} = 18 \Omega$) and anode ($R_{anode} = 50 \Omega$). Therefore, the true ionic resistance of the specimen is obtained after subtracting these contributions (Supplementary Eq. 1):

$$R_{Li^+,\text{specimen}} = R_{\text{total}} - (2R_{\text{SSE}+}R_{\text{anode}})$$
 Supplementary Eq. 1

Fig. S7: Determination of the resistance contribution from the anode: (**A**) Schematic of the symmetr cell for the experiment (top) and the equivalent circuit model used to fit the impedance data (bottom Approximately 100 mg of the solid electrolyte powder yields a pellet with a thickness of 0.78 mm in cylindrical die with a geometric area of 0.785 cm² (**B**) Nyquist plot of the resulting impedance data. Th frequency for each process is marked in the legend.

Discussion of Fig. S7. There are three major components that contribute to the separator-anode resistance. The first component is the bulk resistance that originates from the argyrodite electrolyte, and the value (18 Ω) is consistent with the ionic conductivity of the SSE material in Fig. S3B. The second component is the interfacial resistance (R_{int, anode-SSE}) between the In/InLi anode and the argyrodite electrolyte, which measured at 32 Ω . The third contribution is ascribed to the Li-ion diffusion in the In/InLi anode (R_{diff, anode}), and the value is estimated to be ~18 Ω . The R_{anode} in the main text as well as Fig. S is then referred to the sum of R_{int, anode-SSE} and R_{diff, anode} (Supplementary Eq. 2). These additional resistance contributions (R_{SSE} and R_{anode}) are subtracted from the resistance measured from DC-polarization experiments to obtain the effective ion conductivity of the LVS and cathode composite (see below).

$$R_{\text{anode}} = R_{int, anode-SSE} + R_{diff, anode}$$
 Supplementary Eq. 2

Fig. S8. (A and C) DC polarization measurement and effective (B) electronic and (D) ionic resistance for the Li₂S-LiVS₂ (LVS) core-shell active material.

Fig. S9. Electrochemical profile of the all-solid-state $Li_2S-LiVS_2$ (LVS) cell during (A) the first activation cycle (0.25 mA·cm⁻²) and (B) the second cycle (i.e., the first cycle at 1 mA·cm⁻² prior to long-term cycling at that current density) as a function of mass-specific capacity.

Fig. S10. Electrochemical profile of the all-solid-state $Li_2S-LiVS_2$ (LVS) cell at different temperatures at an active material loading of 10 mg·cm⁻² and current density of 0.25 mA·cm⁻².

Calculation of Li₂S Utilization

The highest capacity achieved for the all-solid-state LVS cell (areal capacity of 1.25 mAh.cm⁻², Fig. 3A, with a geometric cathode area of 0.785 cm²) was 0.98 mA·h at an active material loading of 1.57 mg (Li₂S+LiVS₂). EDX analysis of the LVS cathode (Fig. 2E) provides a Li₂S content of ~ 60 wt. % and LiVS₂ content of ~ 40 wt. % based on the V/S ratio. Considering the theoretical capacity of LiVS₂ is 220 mA·h·g⁻¹, assuming insertion of one Li⁺/e⁻ (LiVS₂ \rightarrow VS₂ + Li⁺ + e⁻), the capacity contributed by LiVS₂ alone is 220 mA·h·g⁻¹ × (0.40 × 1.57) mg = 0.138 mA·h. Therefore, the capacity contributed by Li₂S is at least (0.980 mA·h – 0.138 mA·h) = 0.842 mA·h, correlating to a redox contribution of 0.84 mA·h ÷ (0.60 × 1.57) mg = 895 mA·h·g⁻¹. This translates to a Li₂S utilization of 77 %.

References

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