## Electronic Supporting Information (ESI) High-Performance All-Solid-State Li<sub>2</sub>S Batteries Using an Interfacial Redox Mediator

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## **Experimental Methods**

<u>Preparation of Li<sub>2</sub>S nanoparticles.</u> Li<sub>2</sub>S nanoparticles were synthesized by reduction of elemental sulfur with lithium naphthalenide as reported elsewhere.<sup>1</sup> 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 Li<sub>2</sub>S 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 (Li<sub>2</sub>S-Li<sub>x</sub>VS<sub>2</sub>) nanocomposite.</u> In brief, 0.7 mmol VCl<sub>4</sub> (99+ %, Thermo Scientific) was introduced to a pre-dispersed solution of Li<sub>2</sub>S (5 mmol) in THF (20 mL). The beige-coloured solution immediately turned dark purple due to the formation of VCl<sub>4</sub> complexes.<sup>2</sup> 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<sup>-1</sup>, respectively.

Synthesis of Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> argyrodite via a solid-state reaction.<sup>3</sup> 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<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub>) was obtained by heating the pellet at 520 °C for 10 hours at a ramp rate of 5.5 °C·min<sup>-1</sup>.

<u>Solid-state cell assembly.</u> The cathode composite material (LVS + Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub>) 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<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> powders were first pressed between two Ti rods under 310 MPa for 1 min. LVS/Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> 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 Li<sub>2</sub>S/C/Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> composite cathode was also prepared using the same method, employing carbon black (Vulcan XC 72R) as the host material. The carbon-based Li<sub>2</sub>S cathode composite was prepared by blending the as-prepared Li<sub>2</sub>S 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 Li<sub>2</sub>S cathode composite were measured with an ion-blocking symmetric cell configuration (Fig. 4A). In both cases  $75\pm1$  mg of powder was loaded in a cell with a geometric area of 0.785 cm<sup>2</sup>. The thickness of the pellet was measured ( $0.5\pm0.02$  mm for LVS and LVS cathode composites, and  $0.5\pm0.01$  mm for the Li<sub>2</sub>S 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 Li<sub>2</sub>S 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,  $100\pm1$  mg Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> 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 $\alpha$  radiation ( $\lambda$  = 1.5405Å).

List of Supporting Figures



**Fig. S1**. (A) SEM image of the Li<sub>2</sub>S 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 VS<sub>2</sub>, identifying it as a mixture of  $Li_2S$  and  $LiVS_2$ , which proves that VS<sub>2</sub> 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<sup>-1</sup>.



**Fig. S4.** EDX analysis of the Li<sub>2</sub>S/LiVS<sub>2</sub>/Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub> 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 Li<sub>2</sub>S 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 Li<sub>2</sub>S ( $\sigma_{Li^+,Li_2S+C+SSE}$ , 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 cm<sup>2</sup> (**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  $\Omega$ ) is consistent with the ionic conductivity of the SSE material in Fig. S3B. The second component is the interfacial resistance (R<sub>int, anode-SSE</sub>) between the In/InLi anode and the argyrodite electrolyte, which measured at 32  $\Omega$ . The third contribution is ascribed to the Li-ion diffusion in the In/InLi anode (R<sub>diff, anode</sub>), and the value is estimated to be ~18  $\Omega$ . The R<sub>anode</sub> in the main text as well as Fig. S is then referred to the sum of R<sub>int, anode-SSE</sub> and R<sub>diff, anode</sub> (Supplementary Eq. 2). These additional resistance contributions (R<sub>SSE</sub> and R<sub>anode</sub>) 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 Li<sub>2</sub>S-LiVS<sub>2</sub> (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<sup>-2</sup>) and (B) the second cycle (i.e., the first cycle at 1 mA·cm<sup>-2</sup> 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<sup>-2</sup> and current density of 0.25 mA·cm<sup>-2</sup>.

## Calculation of Li<sub>2</sub>S Utilization

The highest capacity achieved for the all-solid-state LVS cell (areal capacity of 1.25 mAh.cm<sup>-2</sup>, Fig. 3A, with a geometric cathode area of 0.785 cm<sup>2</sup>) was 0.98 mA·h at an active material loading of 1.57 mg (Li<sub>2</sub>S+LiVS<sub>2</sub>). EDX analysis of the LVS cathode (Fig. 2E) provides a Li<sub>2</sub>S content of ~ 60 wt. % and LiVS<sub>2</sub> content of ~ 40 wt. % based on the V/S ratio. Considering the theoretical capacity of LiVS<sub>2</sub> is 220 mA·h·g<sup>-1</sup>, assuming insertion of one Li<sup>+</sup>/e<sup>-</sup> (LiVS<sub>2</sub>  $\rightarrow$  VS<sub>2</sub> + Li<sup>+</sup> + e<sup>-</sup>), the capacity contributed by LiVS<sub>2</sub> alone is 220 mA·h·g<sup>-1</sup> × (0.40 × 1.57) mg = 0.138 mA·h. Therefore, the capacity contributed by Li<sub>2</sub>S 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<sup>-1</sup>. This translates to a Li<sub>2</sub>S utilization of 77 %.

## References

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