

Supplementary Information

Fast-charging and durable all-solid-state lithium-sulfur batteries enabled by pre-embedded solid-solid redox mediator

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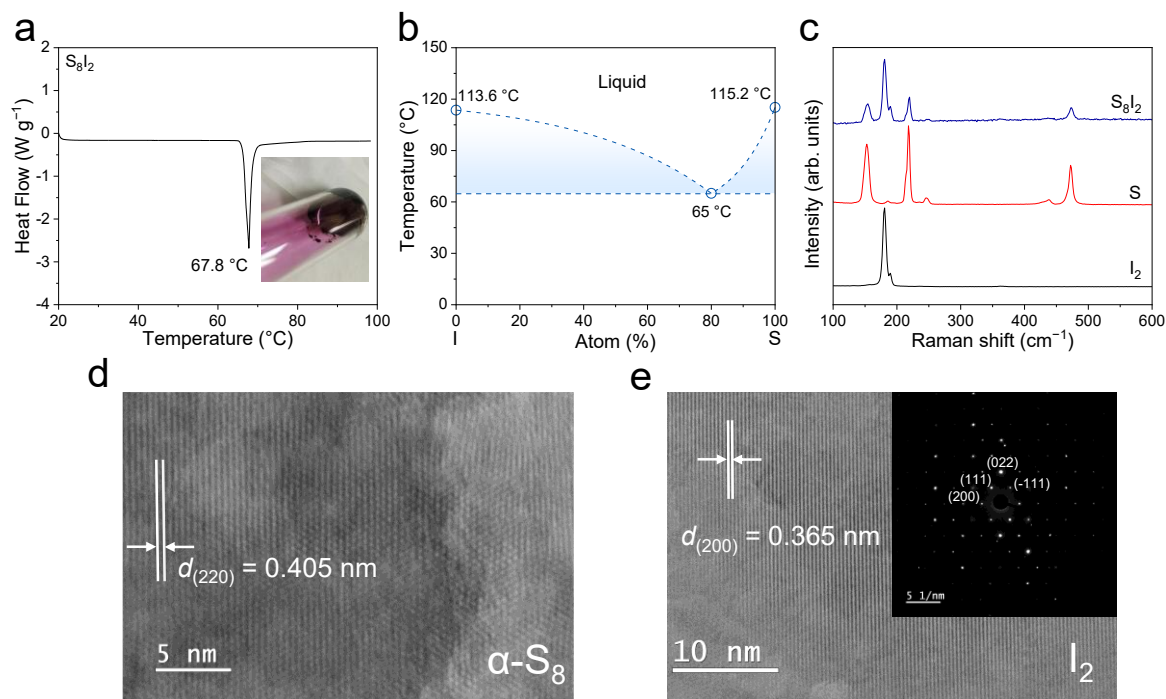
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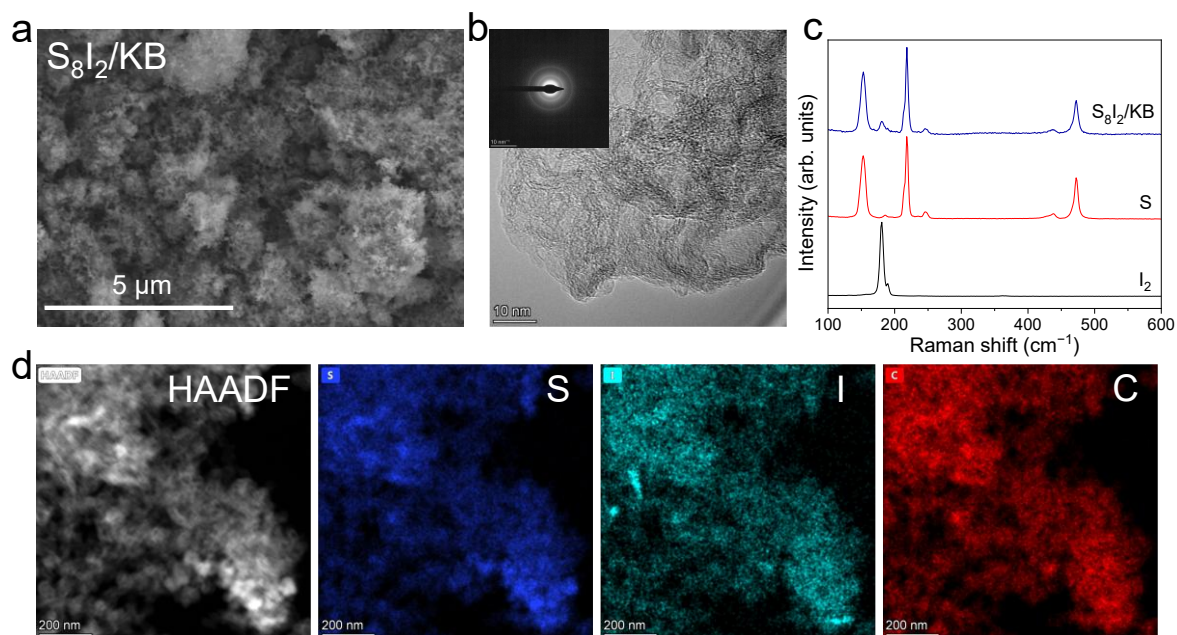
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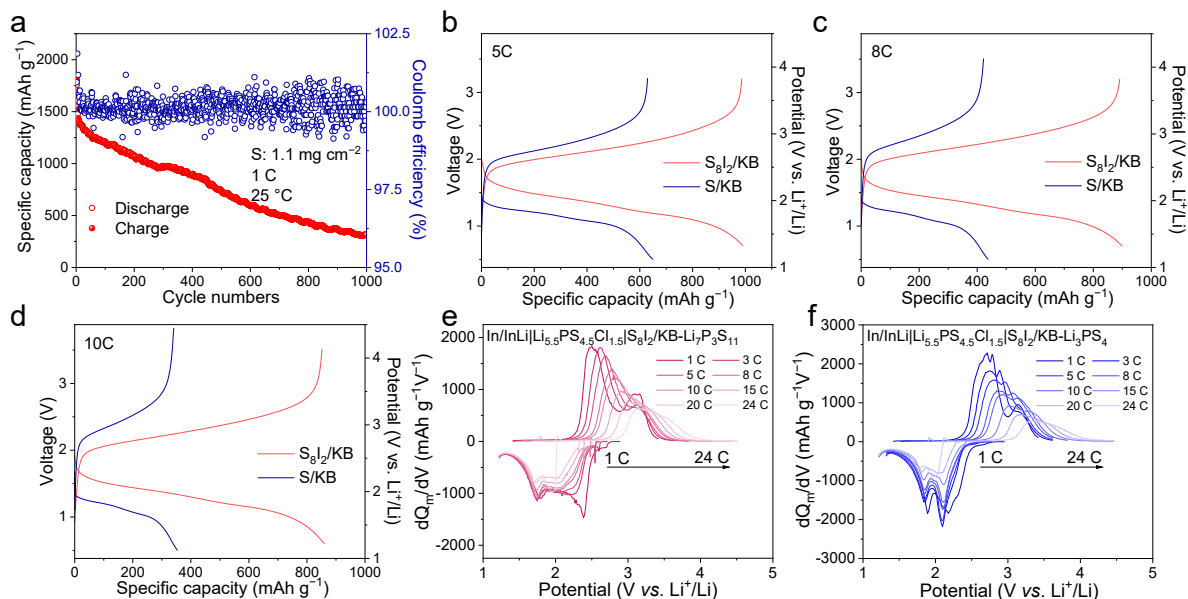
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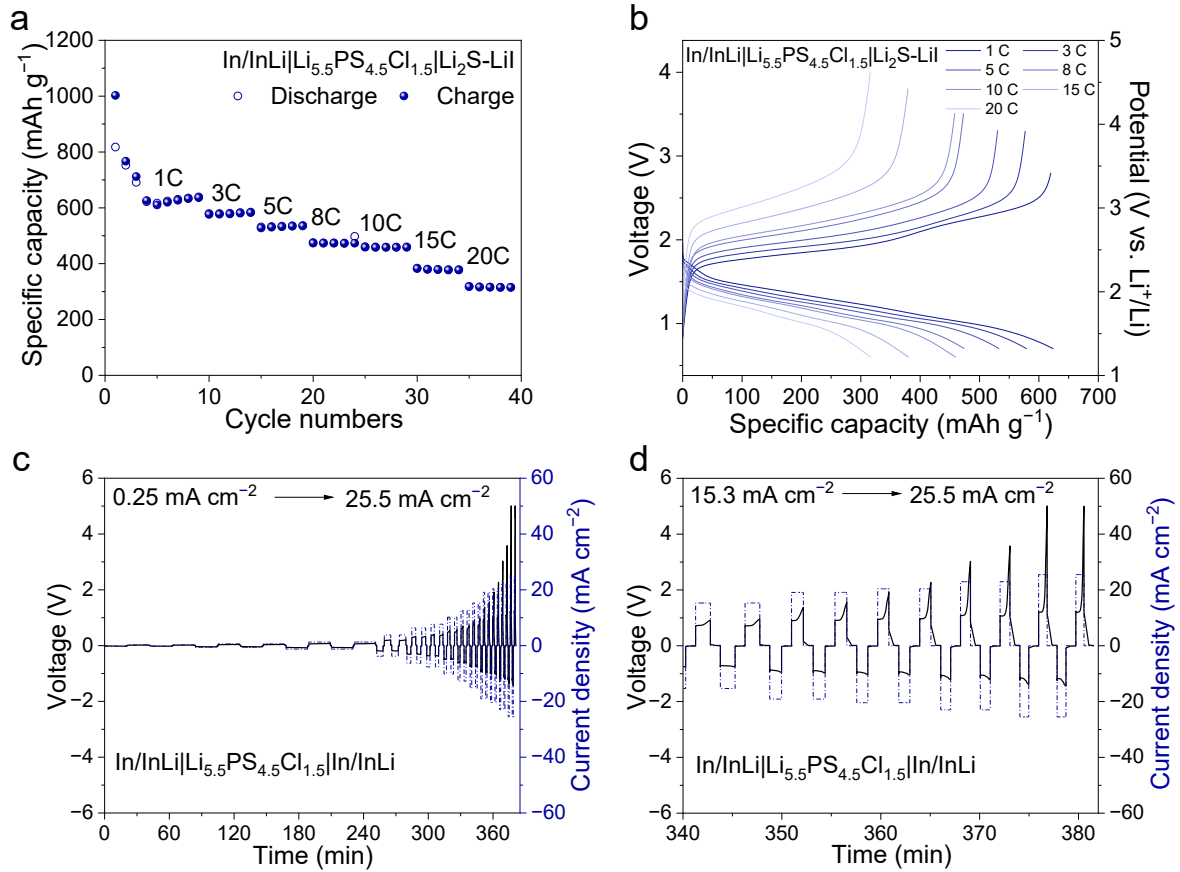
Supplementary Fig. 1 | Characterization of the non-carbon-encapsulated composite of the stoichiometric S_8I_2 eutectic. **a**, Differential scanning calorimeter (DSC) curve of a eutectic S_8I_2 (the inset shows the liquid melt of S_8I_2 at $80\ ^{\circ}C$). **b**, The schematic binary S-I phase diagram¹. **c**, Raman spectra of the S_8I_2 composite along with I_2 and S as references. **d**, **e**, Cryo-transmission electron microscopy images of the S_8I_2 eutectic composite showing the areas corresponding to $\alpha-S_8$ (**d**) and to I_2 (**e**) (inset shows the selected area electron diffraction pattern corresponding to I_2), clearly indicating the phase separation nature of the composite.



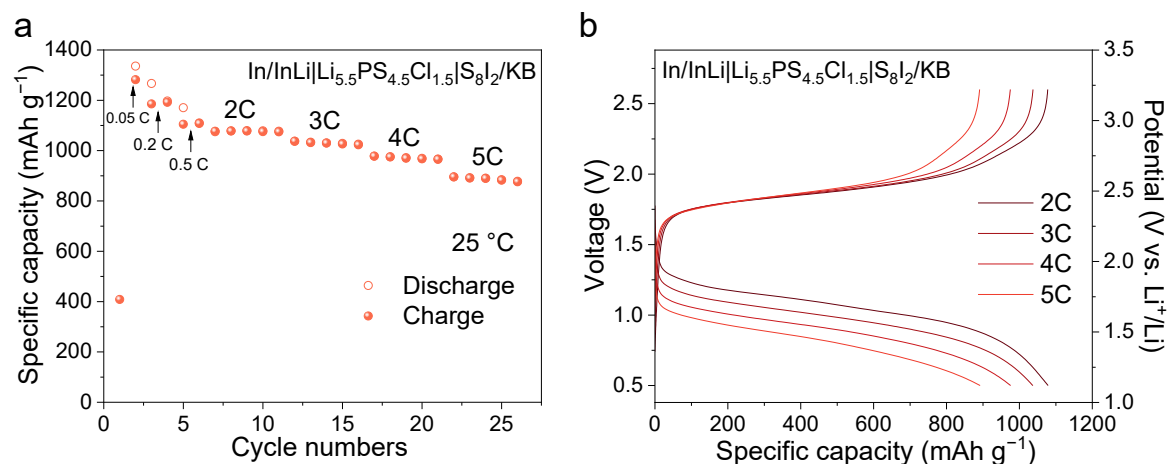
Supplementary Fig. 2 | Characterization of the carbon-encapsulated amorphous S_8I_2/KB nanocomposite. **a**, Representative scanning electron microscopy image of the amorphous S_8I_2/KB nanocomposite showing that the S_8I_2 melts into the mesopores of KB carbon so that the particle morphology resembles that of pristine KB. **b**, Representative high-resolution transmission electron microscopy (HRTEM) image of S_8I_2/KB . The inset shows the selected area electron diffraction (SAED) pattern, confirming the amorphous nature of the composite. **c**, Raman spectra of the amorphous S_8I_2/KB nanocomposite and the reference spectra of I_2 and S, confirming the presence of S and I_2 in the composite. **d**, The representative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of S_8I_2/KB and its energy-dispersive X-ray spectroscopy (EDX) mapping. This image is another area of the S_8I_2/KB nanocomposite with a larger scale than the one shown in **Fig. 1d** (i.e. scale bar here is 200 nm).



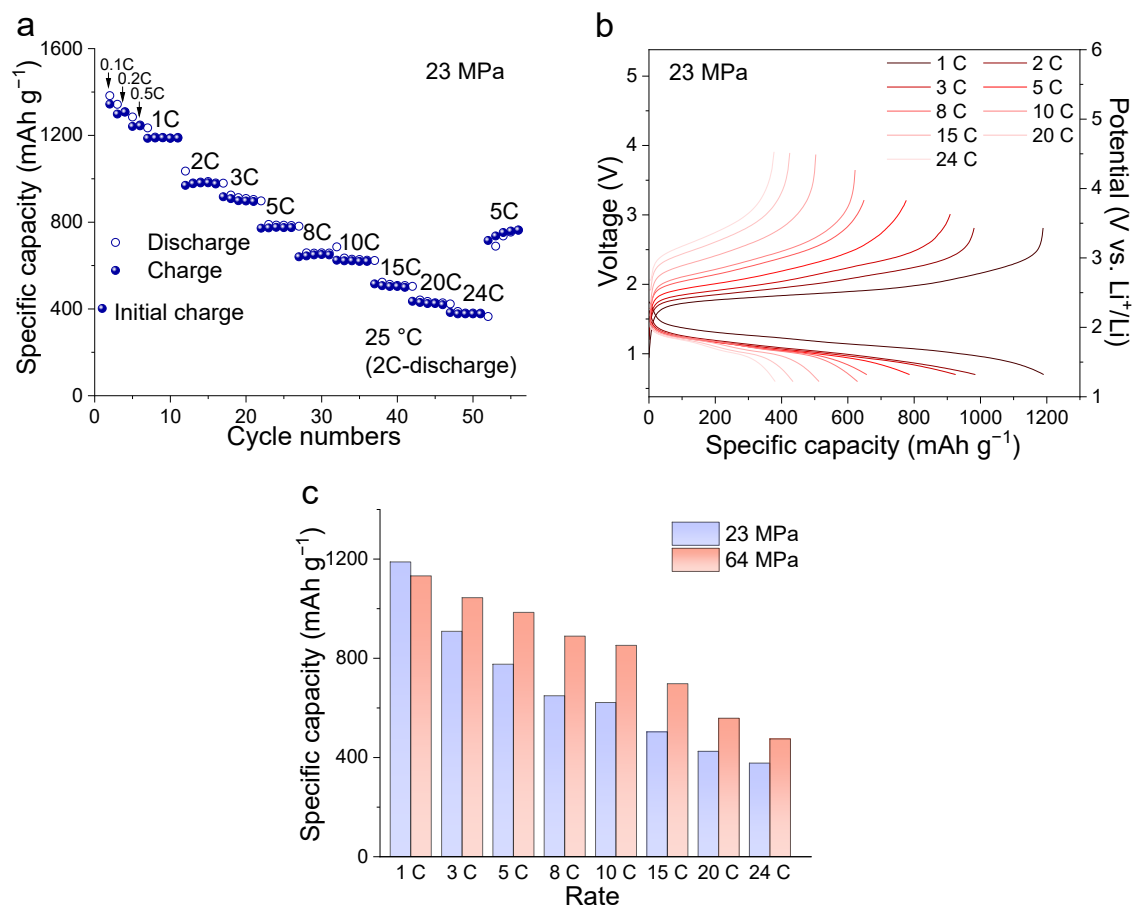
Supplementary Fig. 3 | Fast-charging performance of all-solid-state lithium-sulfur batteries at 25 °C. **a**, Long-term cycling of the cell with S/KB composites at 1 C. The cell was activated at 0.03-0.5 C prior to 1 C. **b-d**, Voltage profiles for the cells using S₈I₂/KB or S/KB composites (shown in **Fig. 2a**) at charging rates of 5C (**b**), 8C (**c**), and 10C (**d**). The voltage profiles of the S₈I₂/KB cell at these rates clearly show lower polarization compared to the cell with S/KB. **e, f**, The corresponding differential capacity (dQ_m/dV) plots for the cells using S₈I₂/KB nanocomposite with Li₇P₃S₁₁ catholyte (**e**) and Li₃PS₄ catholyte (**f**) for charging rate capability measurements as shown **Figs. 2g, i**, respectively. Cells were tested in a custom pressure cell configuration.



Supplementary Fig. 4 | Charging rate capability of the cell using the milled Li₂S-LiI composite and galvanostatic cycling of the In/InLi|Li_{5.5}PS_{4.5}Cl_{1.5}|In/InLi symmetric cells at 25 °C. **a, b,** Charging rate capability of the cell using the milled Li₂S-LiI composite with Li_{5.5}PS_{4.5}Cl_{1.5} catholyte with varied charging rates (labelled) and constant discharging rate of 1 C (**a**) and the discharge-charge voltage profiles (**b**); the mass for calculation of the rate and capacity is based total mass of iodine and sulfur (not Li₂S-LiI) for better comparison with other cells. The loading of S/I is 0.82 mg cm⁻² and the cell was activated at 0.1- 0.5 C for the first four cycles. 1 C = 945 mA g⁻¹_{S/I}. **c, d,** Galvanostatic cycling of the In/InLi|Li_{5.5}PS_{4.5}Cl_{1.5}|In/InLi symmetric cell with the current density increased stepwise from 0.25 mA cm⁻² to 25.5 mA cm⁻², wherein (**d**) is the enlarged section at high currents. The Li plating/stripping was set to be a constant time of 20 min for cycling at currents from 0.25 mA cm⁻² to 1.3 mA cm⁻², and a constant areal density of 0.38 mA h cm⁻² at currents from 3.8 mA cm⁻² to 25.5 mA cm⁻². The In/InLi counter electrode shows greatly increased overpotential at high current densities; this is due to the limited lithium diffusion kinetics in the surface and bulk of In/InLi electrode, and the accompanying volume change and interfacial reaction with the solid electrolyte, as observed previously^{2,3}. Moreover, the observed polarization (> 4V) at 25.5 mA cm⁻² is contributed by both electrodes of the cell, that is, the plating reaction polarization and stripping reaction polarization. The stripping reactions generally experience higher polarization than the plating reactions⁴, due to the formation of voids between the negative electrode and electrolyte and limited Li diffusion in InLi. Therefore, at high charging rates at **Fig. 2** (faster lithium plating), the polarization from In/InLi negative electrode would not increase as significantly as seen in the symmetric cells.

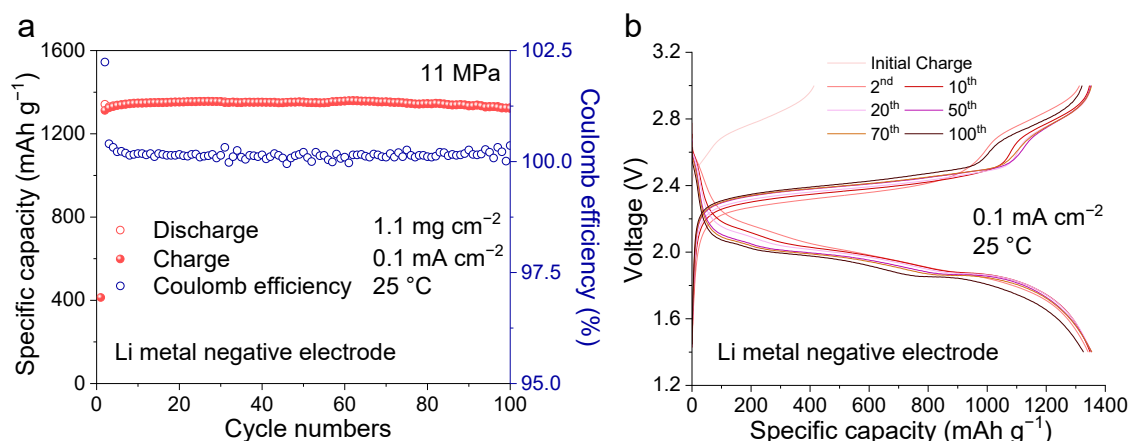


Supplementary Fig. 5 | Discharging rate capability of the $\text{S}_8\text{I}_2/\text{KB}$ cell at 25 °C. a, b Discharging rate capability of the cell using the $\text{S}_8\text{I}_2/\text{KB}$ nanocomposite with $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ catholyte with varied discharging rates (labelled) and constant charging rate of 1 C at 25 °C (a), and the corresponding discharge-charge voltage profiles (b). The loading of S_8I_2 is 1.0 mg cm^{-2} , and the cell was activated at 0.05-0.5 C. 1 C = $945 \text{ mA g}^{-1}_{\text{S/I}}$.



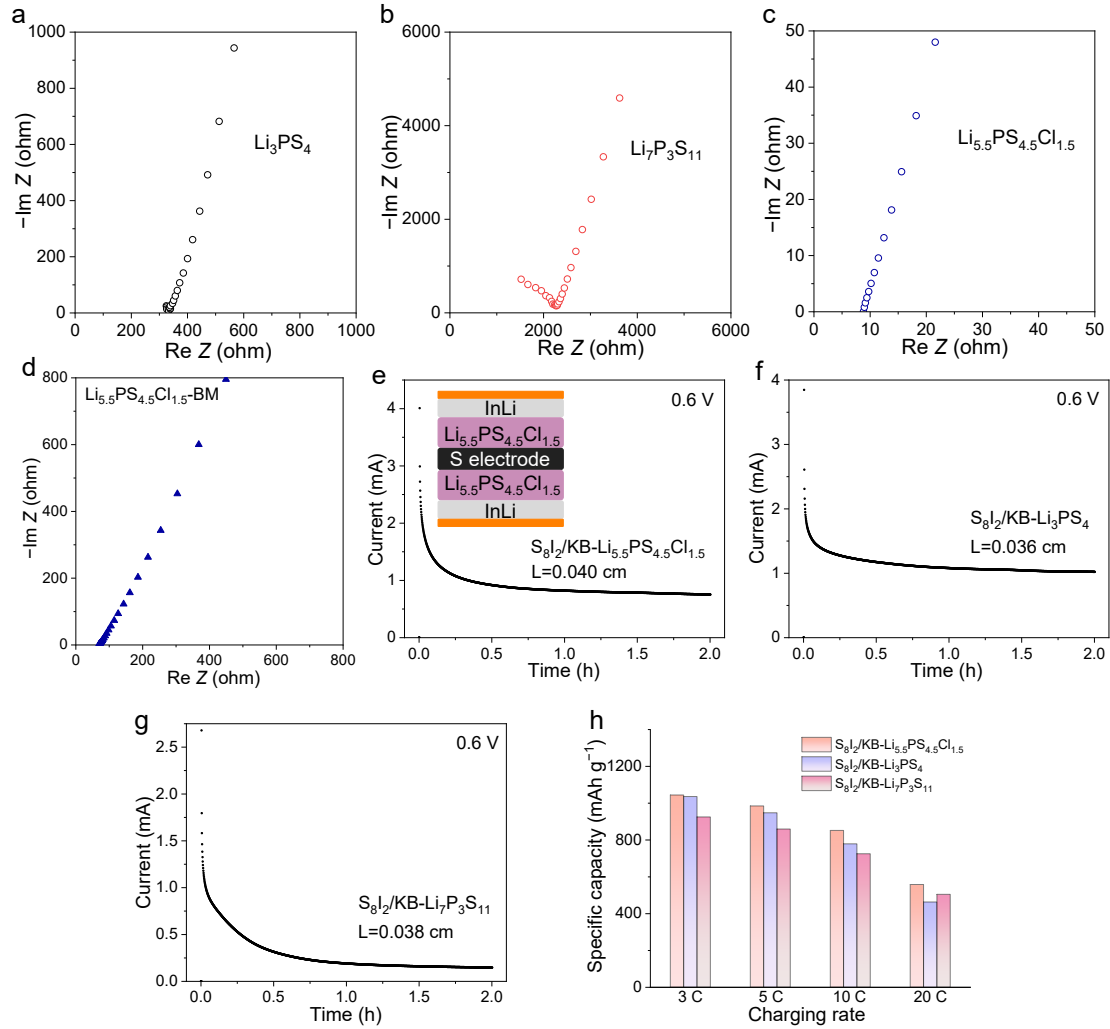
Supplementary Fig. 6 | Charging rate capability under different pressures at 25 °C. a, b, Charging rate capability of the S₈I₂/KB cell with Li_{5.5}PS_{4.5}Cl_{1.5} catholyte and an applied pressure of 23 MPa (discharge rate is 2C, 2.0 mA cm⁻²) (**a**), and the corresponding voltage profiles (**b**). The cell has a S₈I₂ loading of 1.1 mg cm⁻² and was activated by cycling at 0.1-0.5 C rates prior to rate capability measurements. **c,** The comparison of charging rate performance of the two cells with applied pressure of 23 MPa and 64 MPa, respectively. 1 C = 945 mA g⁻¹_{S/I}.

Notes: Charging rate capability of the In/InLi|Li_{5.5}PS_{4.5}Cl_{1.5}|S₈I₂/KB-Li_{5.5}PS_{4.5}Cl_{1.5} cell with In/InLi negative electrode with a lower pressure of 23 MPa is shown to highlight the influence of applied pressure. It can be seen that the cell shows a specific capacity of 1188.8 mA h g⁻¹_{S/I} and 899.1 mA h g⁻¹_{S/I} at the charging rate of 1 C (1.0 mA cm⁻²) and 3 C (3.0 mA cm⁻²), respectively (**a,b**). The exhibited capacity at all examined rates for the cells at 23 MPa is compared with the cell shown in the **Fig. 2a** in the main text (**c**). It shows that at higher rates, high stacking pressure seems to be more important for achieving high capacity than at low rates. This is likely due to the contact issues at higher rates.

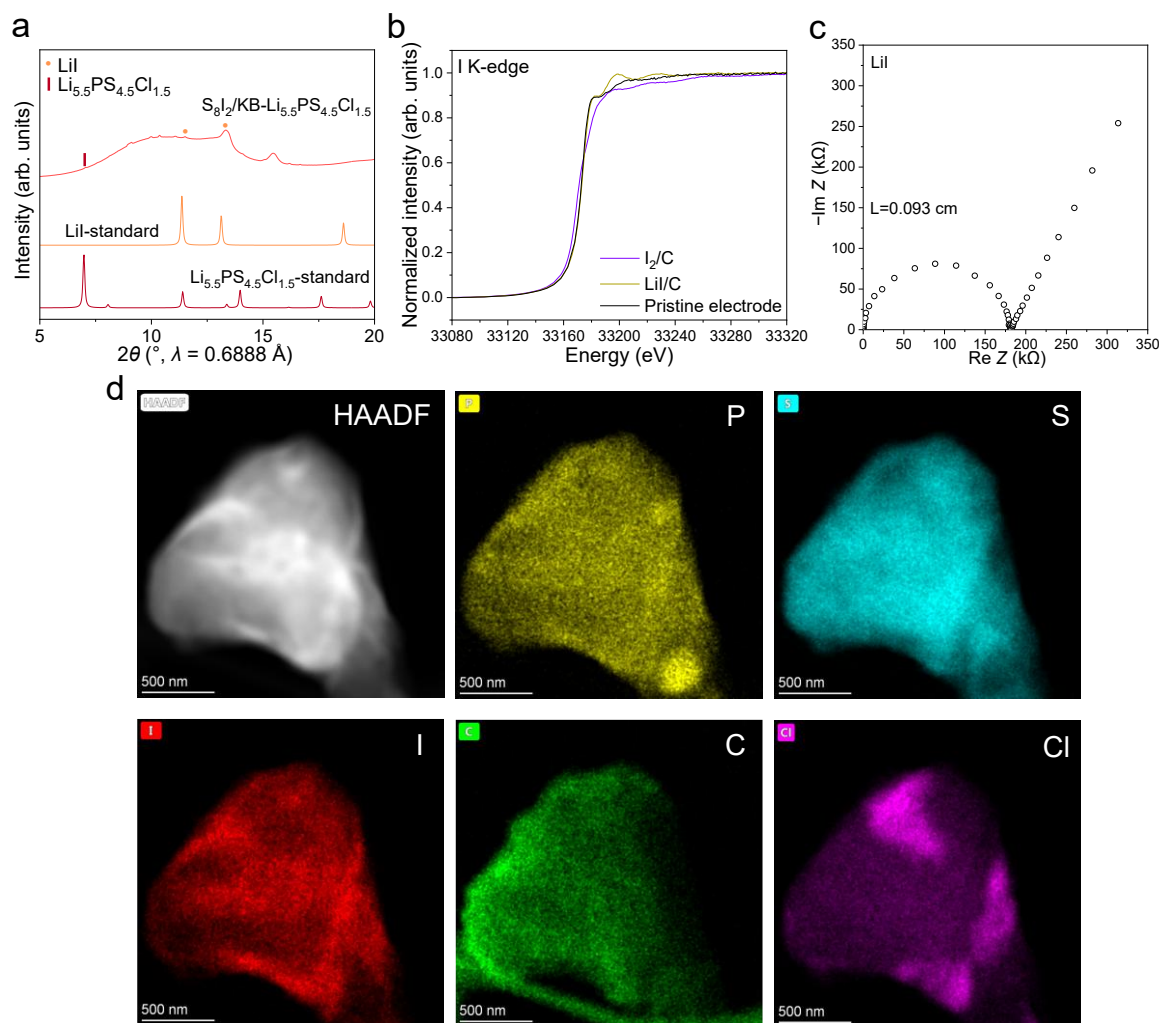


Supplementary Fig. 7 | Long-term cycling of the S_8I_2/KB cell with Li negative electrode. a, b, Long-term cycling of the S_8I_2/KB cell with Li negative electrode at a 0.1 C (discharging /charging) rate (S_8I_2 loading: 1.1 mg cm^{-2}) at 25°C using an applied pressure of 11 MPa (a) and the corresponding discharge-charge voltage profiles (b). The Cell was tested in a custom pressure cell configuration.

Notes: The $S_8I_2/KB\text{-}Li_{5.5}PS_{4.5}Cl_{1.5}$ cell with Li metal negative electrode was examined with an applied stacking pressure of 11 MPa. Even under the low operating pressure, the $S_8I_2/KB\text{-}Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode can still show a high specific capacity of $1312.5 \text{ mA h g}^{-1}_{S/I}$ (1.5 mAh cm^{-2}) at a rate of 0.1 C (0.1 mA cm^{-2}). The cell shows very stable cycling retaining $1321.4 \text{ mA h g}^{-1}_{S/I}$ over 100 cycles with marginal variation of the voltage polarization.

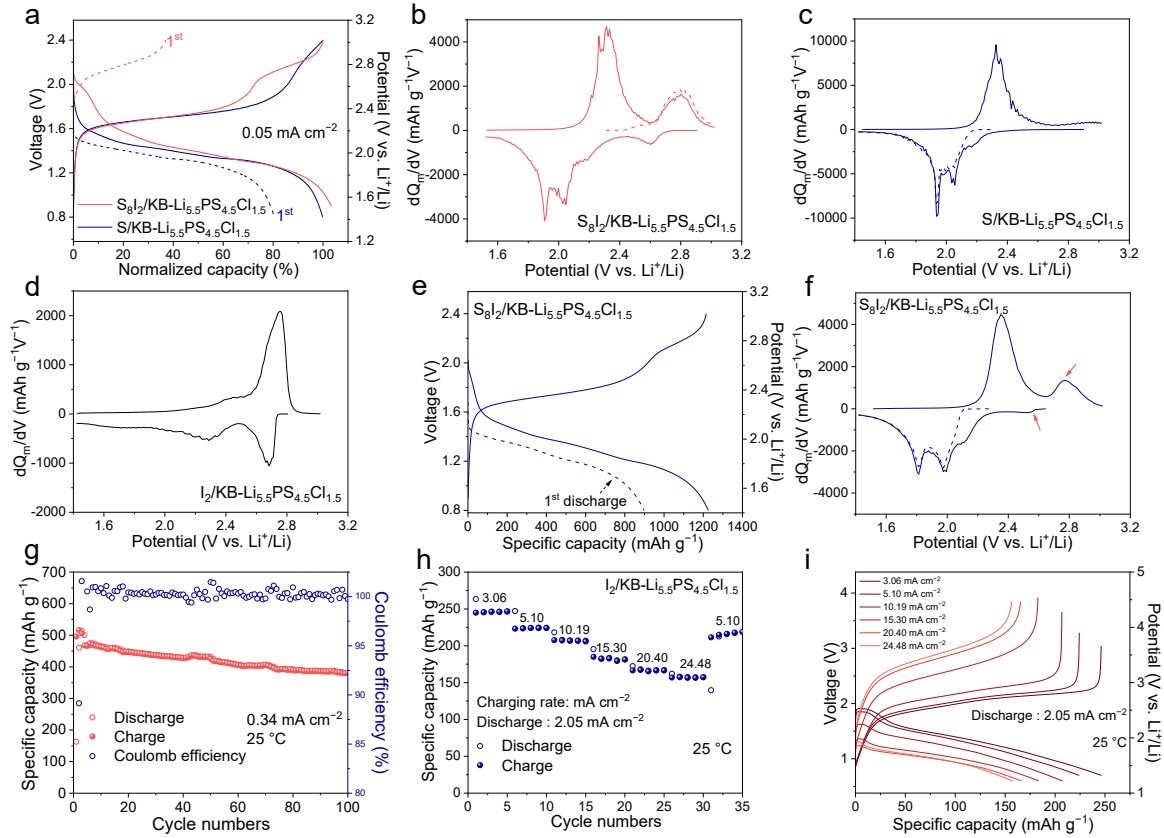


Supplementary Fig. 8 | Ionic conductivity measurements of the three sulfide catholytes and the corresponding S_8I_2/KB electrodes. a-c, The Nyquist plots for measuring the ionic conductivity of synthesized Li_3PS_4 (synthesized by mere ball milling) (a), $Li_7P_3S_{11}$ (synthesized by mere ball milling) (b), and $Li_{5.5}PS_{4.5}Cl_{1.5}$ (c) electrolytes by electrochemical impedance spectroscopy (EIS). The ionic conductivities for Li_3PS_4 , $Li_7P_3S_{11}$, and $Li_{5.5}PS_{4.5}Cl_{1.5}$ in the current form are $1.8 \times 10^{-4} \text{ S cm}^{-1}$, $3.0 \times 10^{-5} \text{ S cm}^{-1}$, and $7.5 \times 10^{-3} \text{ S cm}^{-1}$, respectively. d, Ionic conductivity measurement of the ball-milled $Li_{5.5}PS_{4.5}Cl_{1.5}$ electrolyte, showing an ionic conductivity of 1.7 mS cm^{-1} . This indicates that ball milling tends to decrease the conductivity of solid electrolyte to some extent upon preparation of electrodes⁵. The resistance was determined from the intercept on the real axis or from the intersection between the semicircle and the low-frequency tail. e-g, Measurements of the ionic conductivity of the S_8I_2/KB -catholyte electrodes by DC polarization with an electron-blocking configuration of $Cu|LiIn|Li_{5.5}PS_{4.5}Cl_{1.5}|S_8I_2/KB-SE|Li_{5.5}PS_{4.5}Cl_{1.5}|InLi|Cu$. The ionic conductivity for the three S_8I_2/KB -catholyte composites prepared with $Li_{5.5}PS_{4.5}Cl_{1.5}$, Li_3PS_4 and $Li_7P_3S_{11}$ catholyte is 0.064 mS cm^{-1} , 0.078 mS cm^{-1} , and 0.012 mS cm^{-1} , respectively. Measurements were performed at 25°C . h, The summarized data of specific capacity achieved with the three catholytes at different currents (3 C, 5 C, 10 C and 20 C) as shown in Figs. 2a, f, h. The variations in the values of the capacity among the three positive electrodes are relatively small. Nevertheless, for high-loading (thick) positive electrodes, the ionic conductivity of the catholyte would play more important roles in the specific capacity.

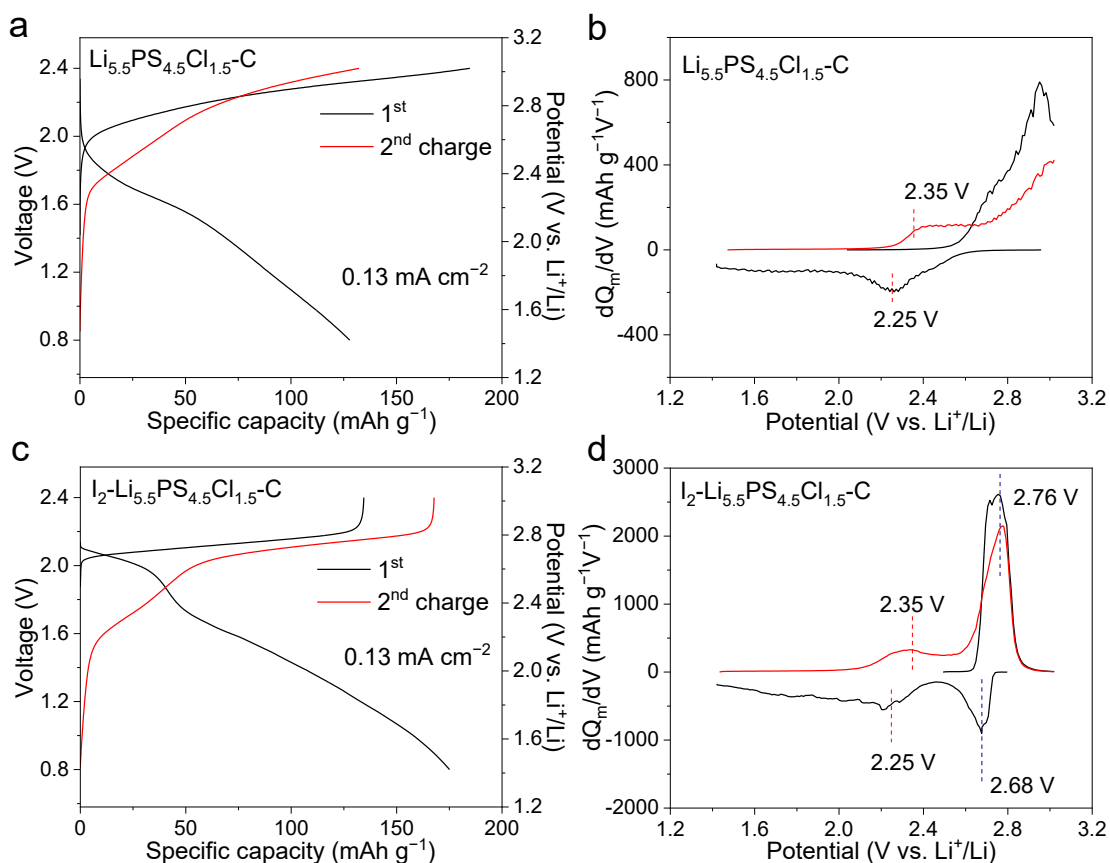


Supplementary Fig. 9 | Further characterization of the $S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ electrode composite.

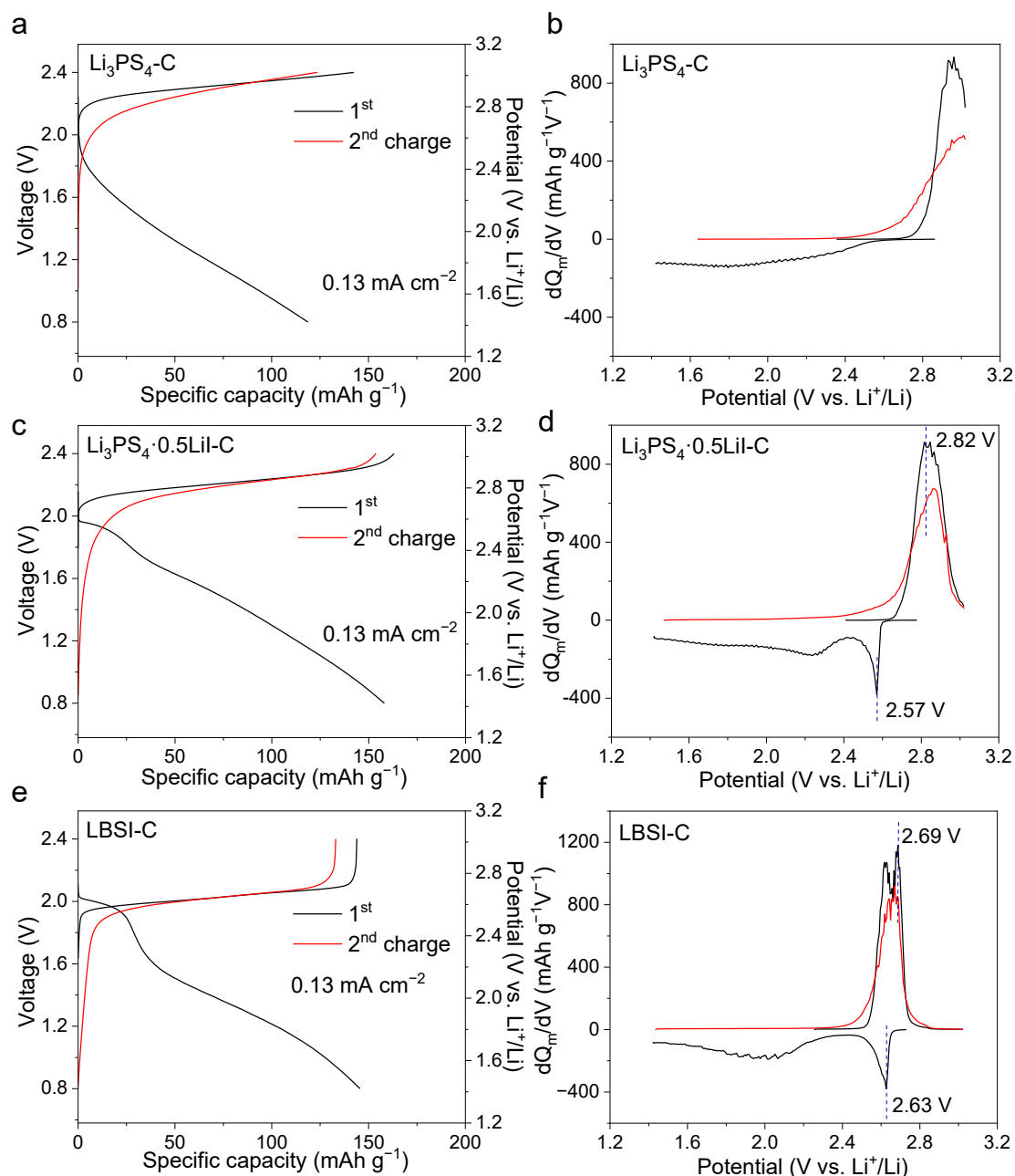
a, Synchrotron X-ray diffraction patterns of the $S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode composite (30 wt% of S_8I_2) with standard patterns of $Li_{5.5}PS_{4.5}Cl_{1.5}$ and LiI . **b**, The I K-edge X-ray absorption near edge structure (XANES) spectra of the pristine S_8I_2/KB electrode ($S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$; 30 wt% of S_8I_2), with the spectra of I_2/C and LiI/C measured as references. **c**, Nyquist plot for measuring the conductivity of LiI ; the ionic conductivity of LiI is measured to be 6.5×10^{-4} mS cm^{-1} at $25^\circ C$. The resistance was determined from the intersection between the semicircle and the low-frequency tail. **d**, The high-angle annular dark-field (HAADF) scanning transmission electron microscopy image and the corresponding energy dispersive X-ray mapping of $S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode composite (50wt% of S_8I_2), which shows the distribution of I within the bulk and on the edge of the particle and its uniform presence with elements of P, S, Cl, and C.



Supplementary Fig. 10 | Detailed electrochemical behavior of all-solid-state lithium-sulfur batteries during initial cycles and further characterization of $I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode at 25 °C. **a-c**, The charge-discharge voltage profiles of the cell of $S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ (current: 0.05 mA cm⁻²) started with charging, and of the cell of pure sulfur $S/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ (current: 0.05 mA cm⁻²) started with discharging (**a**); the corresponding dQ_m/dV plots of the $S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ cell (**b**) and the $S/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ cell (**c**). **d**, The dQ_m/dV plot of the $I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ cell as shown in **Fig. 3d**. **e, f**, The initial discharge (dashed line) and first full cycle (solid line) voltage profiles of the S_8I_2/KB cell at 0.35 mA cm⁻² between 1.4 – 3.0 V (vs Li⁺/Li) (cell starts with discharging first) (**e**), and the corresponding differential capacity (dQ_m/dV) plots (**f**). The $Li_{5.5}PS_{4.5}Cl_{1.5}$ electrolyte is used in these cells. **g**, Long-term cycling of the cell using I_2/KB composite with $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte in the positive electrode (mass based on I_2 and I_2 loading of 1.7 mg cm⁻²). **h, i**, Charging rate performance of the cell with $I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode (**h**) and the corresponding discharge-charge voltage profiles (**i**) (mass based on I_2 and I_2 loading of 1.5 mg cm⁻²). Cells were tested in a custom pressure cell configuration.



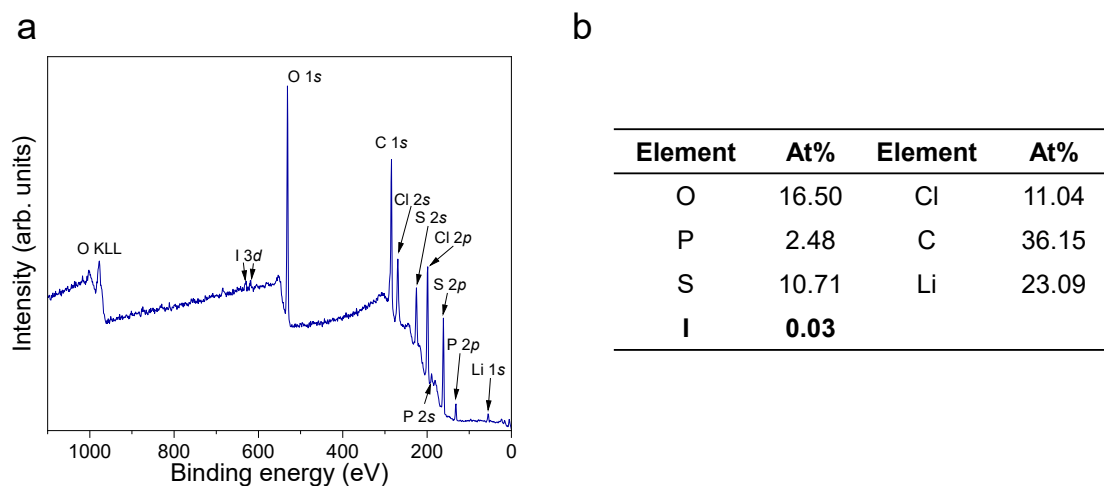
Supplementary Fig. 11 | Electrochemical behavior of the sulfide SEs as electrodes in all-solid-state cells at 25 °C. **a,b,** Voltage profiles (**a**) and the corresponding differential capacity (dQ_m/dV) plots (**b**) of the cell with a $\text{Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}\text{-C}$ positive electrode (without active sulfur; a $\text{Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ loading of 6.3 mg cm^{-2}). **c,d,** Voltage profiles (**c**) and the corresponding dQ_m/dV plots (**d**) of the cell with a $\text{I}_2\text{-Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}\text{-C}$ positive electrode (mixture of I_2 and $\text{Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ by milling without active sulfur; a $\text{I}_2\text{-Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ loading of 6.3 mg cm^{-2}). The mass of active material for calculating capacity is based on $\text{I}_2\text{-Li}_{0.5}\text{PS}_{4.5}\text{Cl}_{1.5}$.



Supplementary Fig. 12 | Electrochemical behavior of the sulfide electrolytes as electrodes in all-solid-state cells at 25 °C. a, b, Voltage profiles (a) and the corresponding differential capacity (dQ_m/dV) plots (b) of the cell with a $\text{Li}_3\text{PS}_4\text{-C}$ positive electrode (without active sulfur; a Li_3PS_4 loading of 6.3 mg cm^{-2}). **c, d,** Voltage profiles (c) and the corresponding dQ_m/dV plots (d) of the cell with a $\text{Li}_3\text{PS}_4 \cdot 0.5\text{LiI-C}$ positive electrode (without active sulfur; a $\text{Li}_3\text{PS}_4 \cdot 0.5\text{LiI}$ loading of 6.4 mg cm^{-2}). **e, f,** Voltage profiles (e) and the corresponding dQ_m/dV plots (f) of the cell with a LBSI-C positive electrode (without active sulfur; LBSI: $3\text{Li}_2\text{S}-2.5\text{B}_2\text{S}_3-4.5\text{LiI}$, mol ratio; a LBSI loading of 6.4 mg cm^{-2}).

Notes of Supplementary Fig. 11 and Supplementary Fig. 12: The working electrodes were prepared by mixing the solid electrolyte (SE) with carbon to fully manifest the decomposition of the SE. The separator was made using the $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ solid electrolyte and the In/LiIn foil was used as the counter electrode. These cells were subjected to galvanostatic cycling at similar loading and current density of 0.13 mA cm^{-2} to examine the redox behavior (protocol: 1st charge, 1st discharge and 2nd charge). The $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ -C electrode shows a slope-type charging profile (2.4-3.0 V vs. Li^+/Li) for the first charge, and a poorly defined plateau behavior with characteristic potential of 2.25/2.35V for the following discharge/charge (**Supplementary Figs. 11a, b**). This plateau is ascribed to the S^{2-} - S_x^{2-} - S^0 redox^{6,7}. Further, there is significant loss of capacity upon first discharge, indicating a considerable irreversibility of the sulfur redox in the $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ (**a**). $\text{Li}_6\text{PS}_5\text{Cl}$ is oxidized to Li_3PS_4 , S and LiCl species at the potential less than 2.9V. The PS_4^{3-} is further oxidized to $\text{P}_2\text{S}_7^{4-}$ and S^0 at the potential above 2.9 V⁶. The reaction at beyond 3 V is avoided. In contrast, upon milling with I_2 , the I_2 - $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ -C electrode shows a well-defined first-charge plateau at 2.76 V, and a first-discharge voltage plateau at 2.68 V (**Supplementary Fig. 11c**), in addition to the pair of poorly defined plateau at 2.25/2.35 V (dQ_m/dV plot in **d**). The well-defined plateau at 2.68/2.76V is accounted for the redox of iodine (LiI/I_2) (**Supplementary Fig. 11d**).

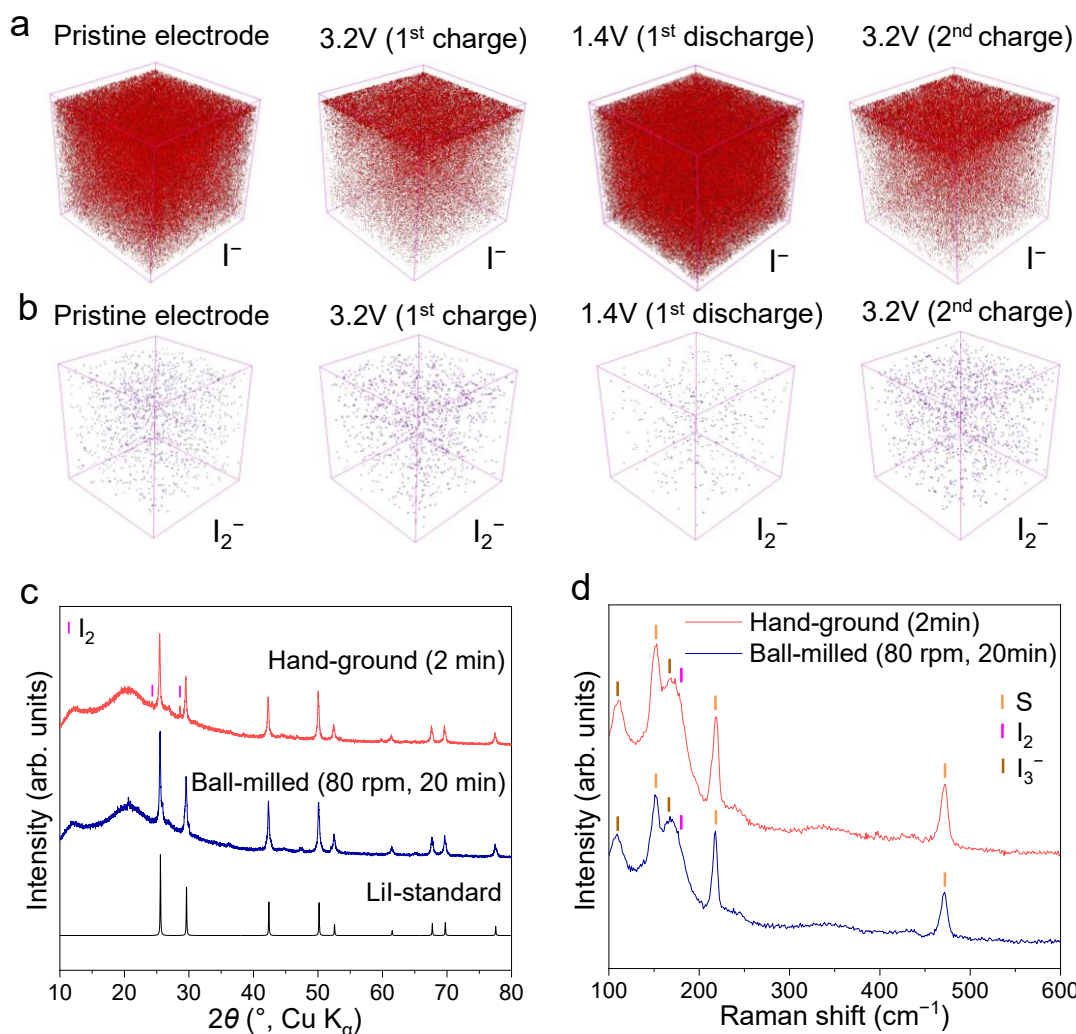
In addition, the Li_3PS_4 -C electrode shows a slope-type charge/discharge voltage profiles and no apparent plateau is found in the dQ_m/dV plot (**Supplementary Figs. 12a,b**), suggesting a slightly different sulfur redox mechanism than that in $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$. In contrast, the $\text{Li}_3\text{PS}_4 \cdot 0.5\text{LiI}$ -C electrode shows well defined plateaus on the first and second charge (and the first discharge) with the potential of 2.57/2.82V, which is attributed to the LiI/I_2 redox (**Supplementary Figs. 12c,d**). Note that a fraction of the capacity is from the sulfur redox for $\text{Li}_3\text{PS}_4 \cdot 0.5\text{LiI}$ -C, particularly shown by the slope behavior at the later stage of discharge and beginning of charge. Therefore, the $\text{Li}_3\text{PS}_4 \cdot 0.5\text{LiI}$ -C electrode exhibits coexistence of the S^{2-}/S^0 and the I^-/I_2 redox. To avoid the influence of the PS_4^{3-} group, the LBSI is prepared (LBSI: $3\text{Li}_2\text{S}$ - $2.5\text{B}_2\text{S}_3$ - 4.5LiI , mol ratio) as the electrode material. The LBSI-C electrode shows a well-defined charge/discharge plateau at 2.69 V/2.63 V (**Supplementary Figs. 12e,f**), which is related to the redox of iodine (LiI/I_2).



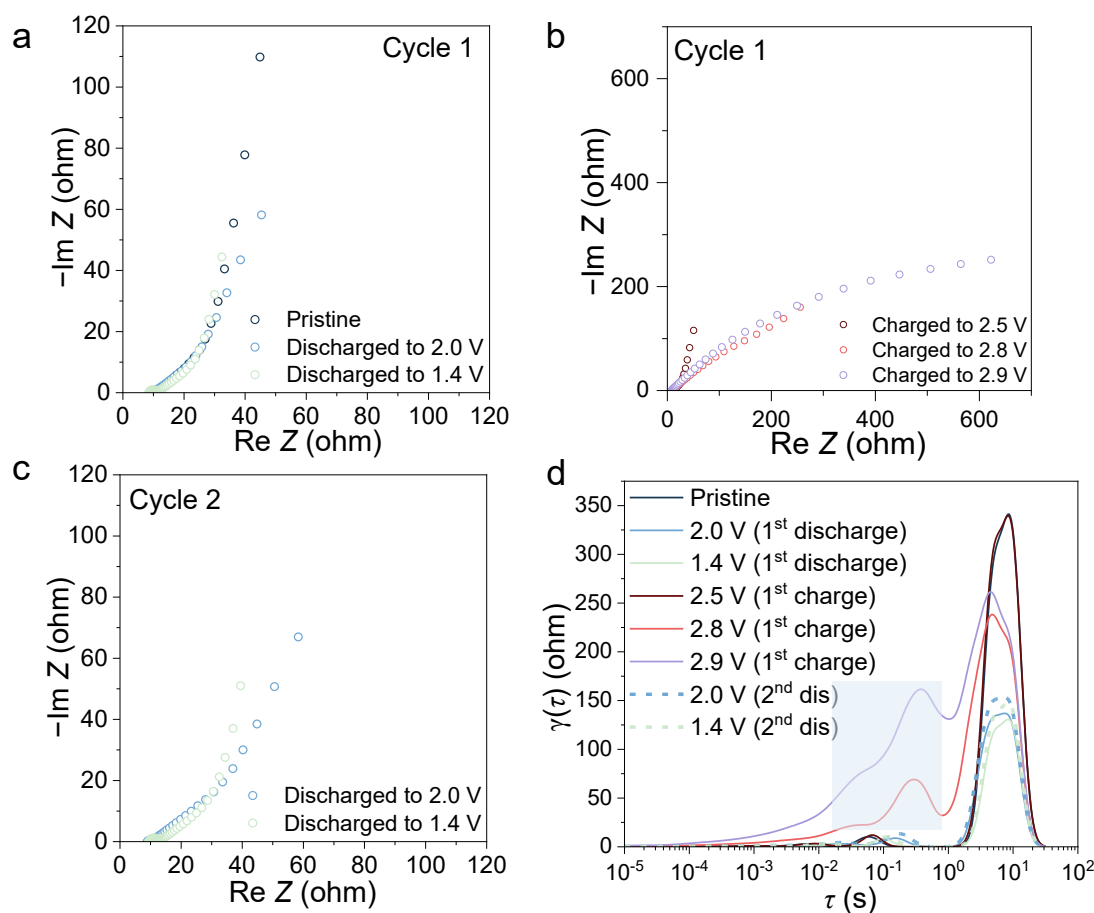
Supplementary Fig. 13 | X-ray photoelectron spectroscopy (XPS) survey spectrum of the In/InLi negative electrode surface in the In/InLi|Li_{5.5}PS_{4.5}Cl_{1.5}|S₈I₂/KB cell. a,b, XPS survey spectrum (a) and the resulted elements analysis (b) of the In/InLi negative electrode surface close to the L_{5.5}PS_{4.5}C_{1.5} electrolyte in the In/InLi|Li_{5.5}PS_{4.5}Cl_{1.5}|S₈I₂/KB cell after 10 cycles at 3 C and 25 °C. The survey spectrum indicates that the content of I is very small (0.03 at%), confirming that there is essentially no cross-diffusion of iodine to the negative electrode surface.



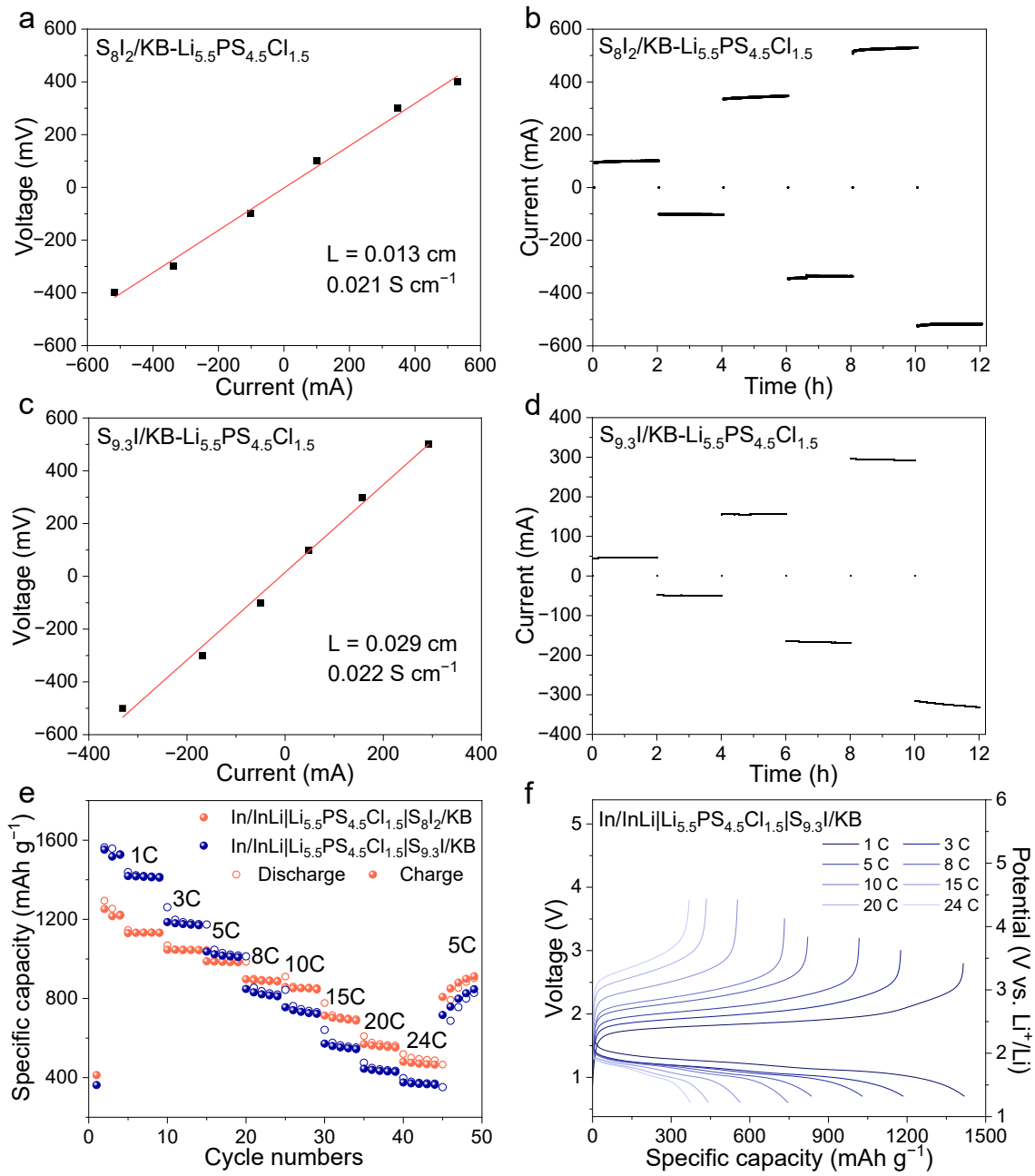
Supplementary Fig. 14. Digital image of the cell setup for operando I K-edge X-ray absorption spectroscopy measurement.



Supplementary Fig. 15 | Mechanistic studies of the solid-solid redox mediation (SSRM) effect for S_8I_2/KB positive electrodes. **a**, 3D time-of-flight secondary-ion mass spectrometry (TOF-SIMS) representations of I^- for the S_8I_2/KB positive electrode at varied states obtained by depth profiling. **b**, 3D TOF-SIMS representations of I_2^- for the S_8I_2/KB positive electrode at varied states obtained by depth profiling. The three cells were separately charged and discharged according to the labelled protocols (first charged to 3.2 V (100% SOC), then discharged to 1.4 V (100% DOD), and then second charged to 3.2 V). Cells were cycled at 0.05 C and 25 °C before disassembly. Solid electrolyte (SE) used for these cells is $Li_{5.5}PS_{4.5}Cl_{1.5}$. Note that owed to the resolution limits from the TOF-SIMS instrument for heavy fragments, the absolute values of I_2^- counts seem small in general; nevertheless, the relative change of I_2^- counts as a function of varied discharging/charging states is clearly conveyed. **c**, **d**, Characterization of the reaction of Li_2S and I_2 by a gentle 20-minutes' ball-milling at 80 rpm or by simple 2-minute hand grinding: the XRD pattern (**c**) and Raman spectrum (**d**) of the products. The XRD pattern of LiI is shown as a reference.

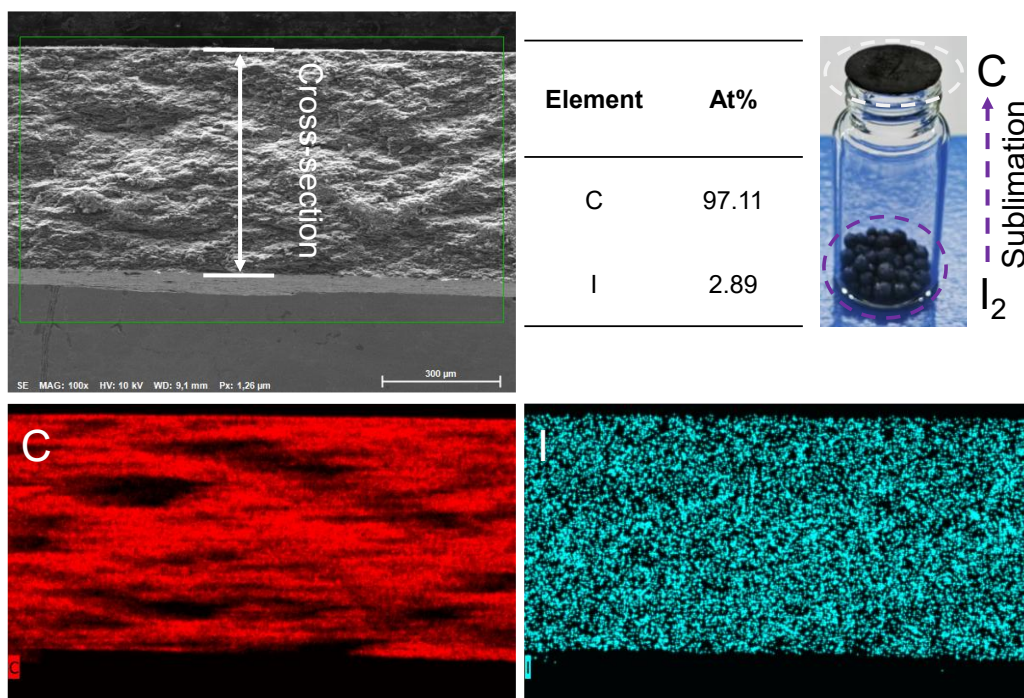


Supplementary Fig. 16 | In situ electrochemical impedance spectroscopy (EIS) studies on the S_8I_2/KB cell. **a-c**, the Nyquist plots at some representative states during the first discharge (**a**), first charge (**b**), and second discharge (**c**). The cell is cycled at a rate of 0.2 C (0.18 mA cm^{-2}) and 25°C . **d**, The distribution of relaxation time (DRT) analyses of the corresponding Nyquist plots shown in **a-c**. The DRT analysis shows the appearance of a new relaxation distribution (γ) at the characteristic time constant (τ) between $10^{-2} \sim 10^0$ (shadowed area) upon charging to 2.8 V, further confirming the formation of a new interface ascribed to oxidation of LiI forming I_2 (**d**). The disappearance of the interface during the second discharge indicates the reversible behavior.



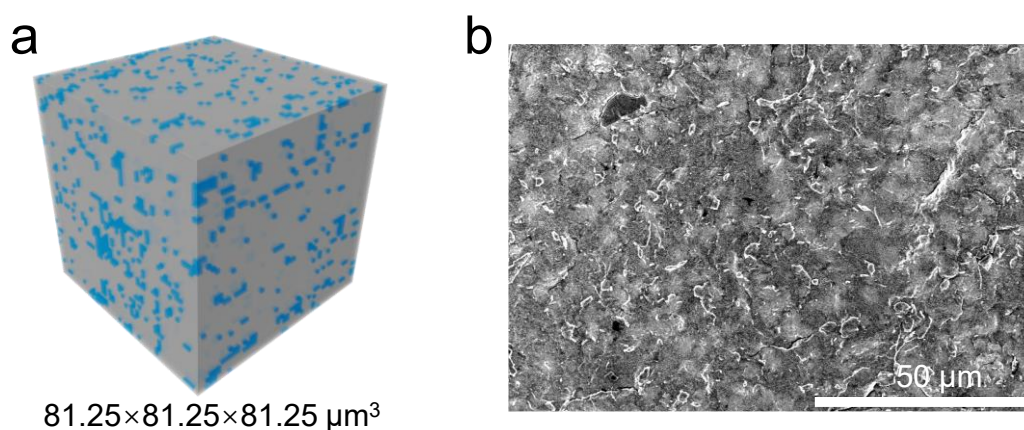
Supplementary Fig. 17 | Electronic conductivity measurements of $S_{9.3I}/KB$ and S_{8I_2}/KB composites with $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte and charging rate capability comparison of the corresponding cells at 25 °C. a,b, Current-voltage (a) and DC polarization curves (b) of the $S_{8I_2}/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ composites with an ion-blocking configuration of $Ti|S_{8I_2}/KB-Li_{5.5}PS_{4.5}Cl_{1.5}|Ti$. c,d, Current-voltage (c) and DC polarization curves (d) of the $S_{9.3I}/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$ composites with an ion-blocking configuration of $Ti|S_{9.3I}/KB-Li_{5.5}PS_{4.5}Cl_{1.5}|Ti$. e, Charging rate capability of $S_{9.3I}/KB$ and S_{8I_2}/KB cells with $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte at varied charging rates (labelled; discharging rate of 2C). The loading of $S_{9.3I}$ and S_{8I_2} in the positive electrodes is 1.1 mg cm^{-2} . f, The discharge-charge voltage profiles for the cell using $S_{9.3I}/KB$ composites. The $S_{9.3I}/KB$ positive electrode is synthesized in the same form as S_{8I_2}/KB positive electrode using $Li_{5.5}PS_{4.5}Cl_{1.5}$ as catholyte.

Notes: The electronic conductivities of the two positive electrodes of S_8I_2/KB and $S_{9.3}I/KB$ using $Li_{5.5}PS_{4.5}Cl_{1.5}$ as catholyte were measured to be very close: 0.021 S cm^{-1} and 0.022 S cm^{-1} , respectively, as shown in **a-d**. The theoretical capacity of the $S_{9.3}I$ stoichiometric compound is calculated to be $1236\text{ mA h g}^{-1}_{S/I}$ and thus 1C is defined as $1236\text{ mA g}^{-1}_{S/I}$ (that of the S_8I_2 is $945\text{ mA h g}^{-1}_{S/I}$). As shown in **e,f**, the $S_{9.3}I/KB$ positive electrode shows a generally high charging rate capability with $1017.0\text{ mA h g}^{-1}_{S/I}$ when charged at 5C and $434.2\text{ mA h g}^{-1}_{S/I}$ at 20C; Clearly, the $S_{9.3}I/KB$ positive electrode benefits from the iodine-based solid-solid redox mediation effect enabled by the nanometric S/I homogenization within the pores of carbon.

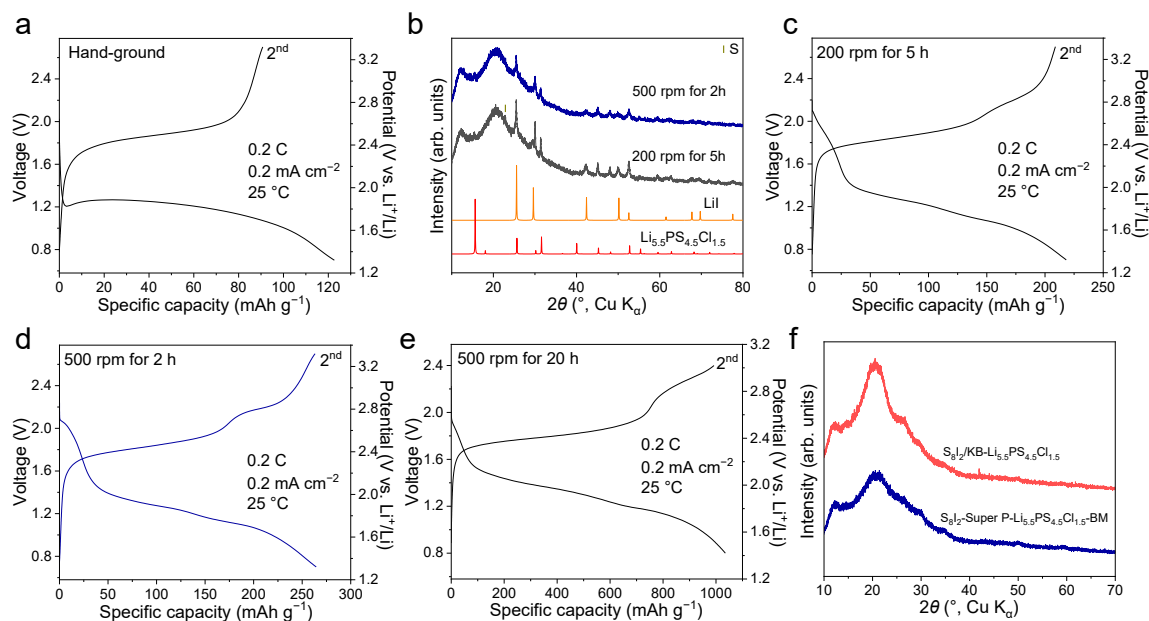


Supplementary Fig. 18 | Energy dispersive X-ray (EDX) mapping of the vertical cross-section of KB carbon pellet after indirect contact with I₂.

Notes: A dense KB carbon pellet of about 500 micrometer thickness was prepared by cold pressing under 867 MPa for 1 hour to ensure compactness. Then, the KB carbon pellet was placed above the bottle containing I₂. After resting for 18 hours, the carbon pellet was retrieved and the elemental distribution was measured over the cross-section by EDX. The result shows that iodine is uniformly distributed over the cross-section with a fraction of 2.89 at%, which proves the rapid diffusion of I₂ along the carbon surface.

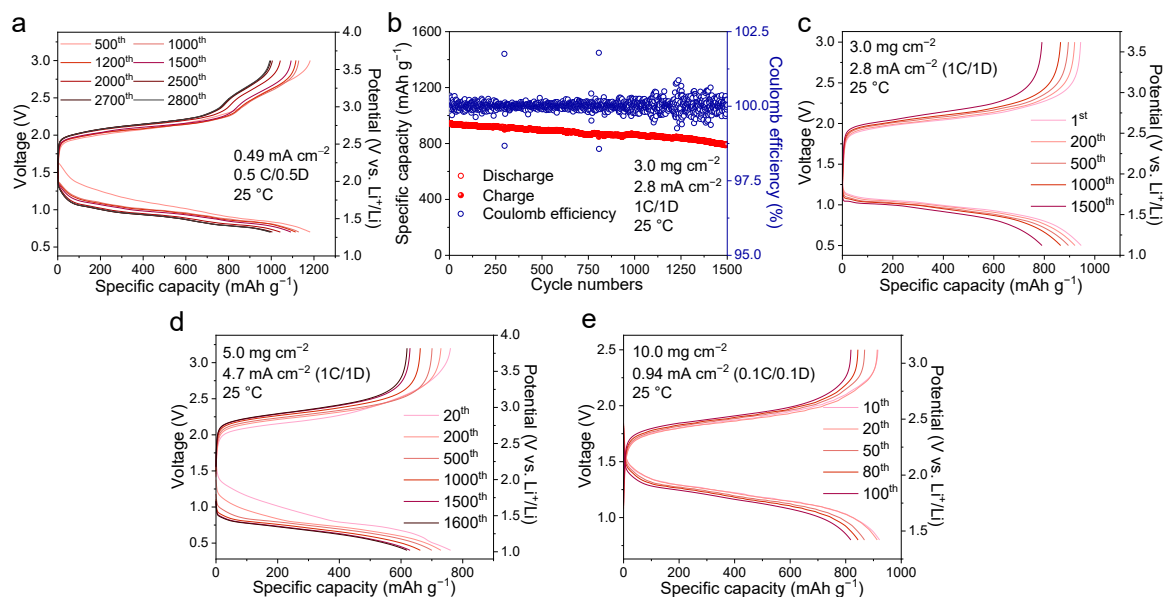


Supplementary Fig. 19 | Pore distribution of $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ composite pellet. **a**, 3D volume rendering image of $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ composite pellet from synchrotron X-ray computed tomography (XCT). The $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ (30 wt% of S_8I_2) positive electrode pellets were fabricated by cold pressing under 433 MPa for 1 min. The blue regions represent the voids. The porosity of $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ composite pellet is quantified to be 12.9%. **b**, Scanning electron microscopy image of $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ composite pellet. Although the $\text{S}_8\text{I}_2/\text{KB-Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ composite pellet is compact, some voids are still present and so that the iodine may diffuse along the voids in the positive electrode. In addition, nano- and micro-voids are expected to also form upon cycling of sulfur positive electrode because of the volume breathing effect of sulfur⁸⁻¹⁰. This is expected to contribute to the channels for the diffusion of iodine in the positive electrode.

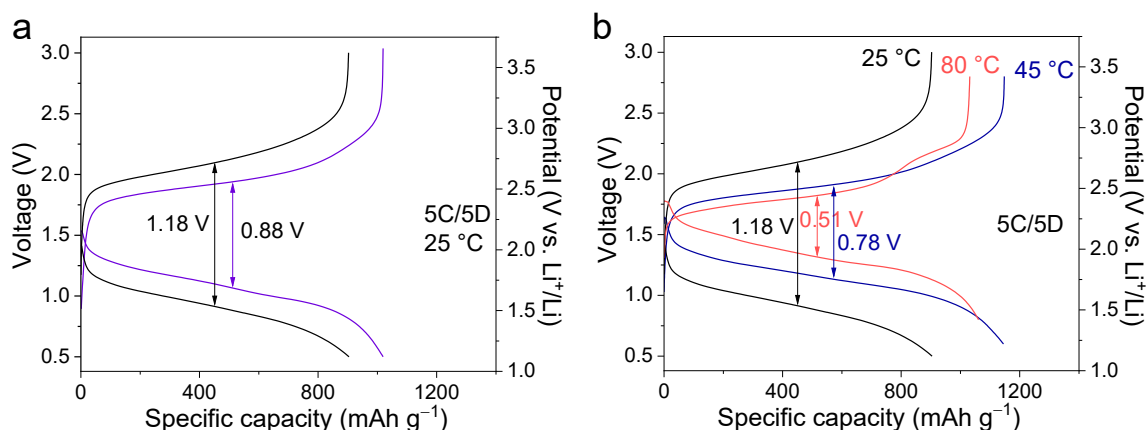


Supplementary Fig. 20 | Characterization of S_8I_2 positive electrodes prepared from low-surface-area carbons with different mixing methods. **a**, Voltage profiles of the S_8I_2 cell of positive electrode made by hand grinding S_8I_2 , Super P, and $Li_{5.5}PS_{4.5}Cl_{1.5}$ with a weight ratio of 3:2:5 for one hour (S_8I_2 loading: $1.1\ mg\ cm^{-2}$). **b**, XRD patterns of the S_8I_2 positive electrode made by ball-milling S_8I_2 , Super P, and $Li_{5.5}PS_{4.5}Cl_{1.5}$ with a weight ratio of 3:2:5 at 200 rpm for 5 hours and 500 rpm for 2 hours. XRD patterns of $Li_{5.5}PS_{4.5}Cl_{1.5}$ and LiI are shown as references. **c,d,e**, Voltage profiles of the S_8I_2 cell of positive electrode made by ball-milling S_8I_2 , Super P, and $Li_{5.5}PS_{4.5}Cl_{1.5}$ with a weight ratio of 3:2:5 at 200 rpm for 5 hours (S_8I_2 loading: $1.1\ mg\ cm^{-2}$) (**c**), 500 rpm for 2 hours (S_8I_2 loading: $1.0\ mg\ cm^{-2}$) (**d**), and 500 rpm for 20 hours (S_8I_2 loading: $1.1\ mg\ cm^{-2}$) (**e**), respectively. **f**, XRD patterns of the S_8I_2 positive electrode made by ball-milling S_8I_2 , Super P, and $Li_{5.5}PS_{4.5}Cl_{1.5}$ with a weight ratio of 3:2:5 at 500 rpm for 20 hours (S_8I_2 -Super P- $Li_{5.5}PS_{4.5}Cl_{1.5}$ -BM), along with the S_8I_2/KB positive electrode composite ($S_8I_2/KB-Li_{5.5}PS_{4.5}Cl_{1.5}$) for comparison. All electrochemical measurements are conducted at 25 °C.

Notes: The positive electrodes prepared by directly mixing S_8I_2 with a low-surface-area carbon (Super P) and the $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte were evaluated. The use of low-surface-area carbon is expected to minimize the electrochemical reactions of the electrolyte while offering sufficient electronic conductivity. However, the positive electrode does not show meaningful capacity by hand grinding of the S_8I_2 -Super P- $Li_{5.5}PS_{4.5}Cl_{1.5}$ composite (**a**), even if the grinding was performed for one hour (which is typically used for the all-solid-state LMO positive electrodes¹¹). We therefore performed the mixing of the composite respectively by ball-milling at 200 rpm for 5 h, and at 500 rpm for 2 h, respectively. The two positive electrodes both show clear formation of LiI , as confirmed by XRD (**b**). However, still the two milled positive electrodes both deliver rather low capacity even at the low rate of 0.2C (**c,d**). This is primarily due to insufficient contact, and is evidence of the essence of nanometric S/I homogenization by the encapsulation with nanoporous carbon. Further, S_8I_2 -Super P- $Li_{5.5}PS_{4.5}Cl_{1.5}$ positive electrode by ball-milling for a longer-term (20 h) were performed. The cell fortunately shows appreciable capacity of $992.0\ mAh\ g^{-1}_{S/I}$ at 0.2C (**e**), which is due to the better mixing. The XRD pattern (**f**) shows that the sulfur in the positive electrode prepared by ball-milling is amorphous.

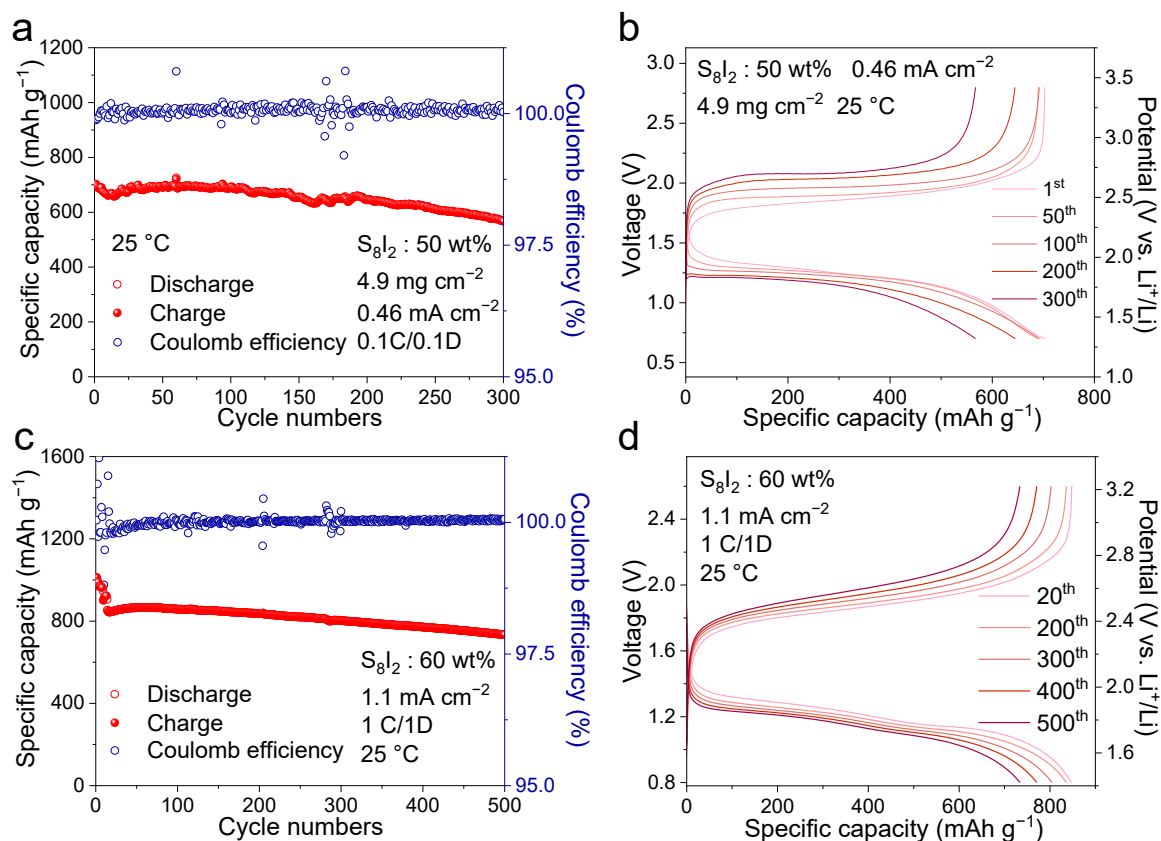


Supplementary Fig. 21 | Additional long-term cycling performance data of S_8I_2/KB based all-solid-state lithium-sulfur batteries at 25 °C. a, Discharge–charge voltage profiles of the S_8I_2/KB cell with Li_3PS_4 catholyte at a 0.5 C rate (S_8I_2 loading: 1.0 $mg\ cm^{-2}$). **b, c**, Long-term cycling (**b**) and discharge–charge voltage profiles (**c**) of the S_8I_2/KB cell with a $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte at a 1 C rate with a high S_8I_2 loading of 3.0 $mg\ cm^{-2}$. **d**, Discharge–charge voltage profiles of the S_8I_2/KB cell (shown in Fig. 6a) with a $Li_{5.5}PS_{4.5}Cl_{1.5}$ catholyte at a 1 C rate with a S_8I_2 loading of 5.0 $mg\ cm^{-2}$. **e**, Discharge–charge voltage profiles of S_8I_2/KB cell with a high S_8I_2 loading of 10.0 $mg\ cm^{-2}$ (30 wt% S_8I_2) at a 0.1 C rate (shown in Fig. 6b). Cells were tested in a custom pressure cell configuration.

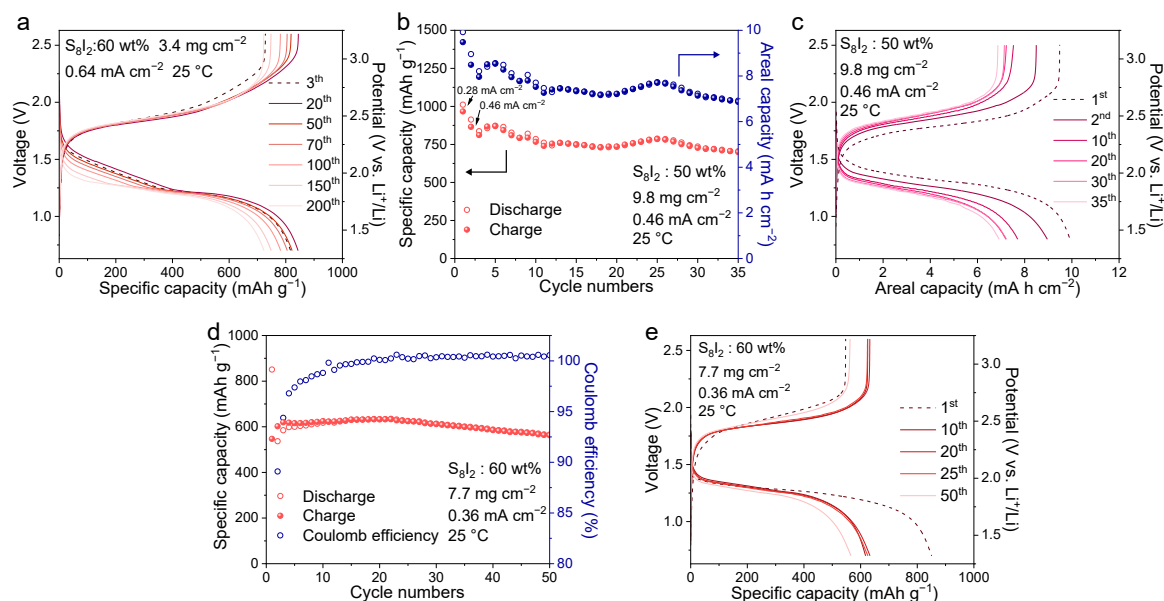


Supplementary Fig. 22 | Electrochemical performance of all-solid-state lithium-sulfur batteries at a 5 C rate. a, The comparison of voltage profiles of S_8I_2 /KB cells with different separators and separator thickness (450 μm ; 230 μm) at 25 $^{\circ}\text{C}$. **b,** The voltage profiles of S_8I_2 /KB cells at the temperature of 25 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$, and 80 $^{\circ}\text{C}$, respectively. The S_8I_2 loading is 1.1 mg cm^{-2} , 1.2 mg cm^{-2} and 1.5 mg cm^{-2} for the cell at 25 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$, respectively. The current density is 5.2 mA cm^{-2} , 5.6 mA cm^{-2} and 7.0 mA cm^{-2} at 25 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$, respectively.

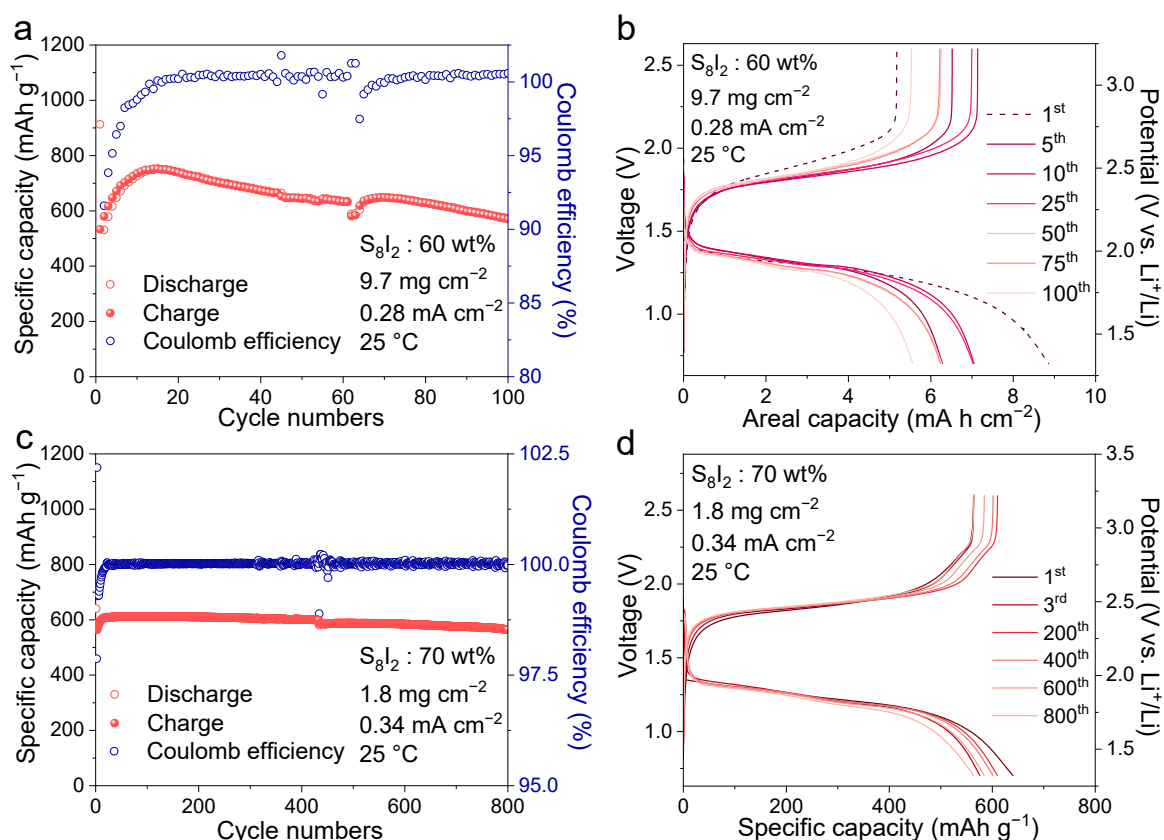
Notes: **Supplementary Fig. 22** shows how to reduce the polarization of the cell under high rates. The cell with a separator electrolyte of higher ionic conductivity ($\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$) and smaller thickness shows a much reduced polarization of 0.88 V vs 1.18 V (**a**). A more important direction to reduce the polarization would be to find even higher-conductivity solid electrolyte materials. Further, the performance of cells at elevated temperatures was examined at 45 ± 1 $^{\circ}\text{C}$ and 80 ± 1 $^{\circ}\text{C}$. As shown in **b**, the voltage polarization of the cells at 45 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ at a high rate of 5 C (discharge/charge rate) is significantly lower than the cell at 25 $^{\circ}\text{C}$ (0.78 V, 0.51 V vs. 1.18 V). Also, the cell shows a much increased specific capacity at 45 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ (1145 $\text{mA h g}^{-1}_{\text{S/I}}$, 1061 $\text{mA h g}^{-1}_{\text{S/I}}$ vs 904 $\text{mA h g}^{-1}_{\text{S/I}}$). Therefore, operation at elevated temperature can be a key advantage of all-solid-state batteries.



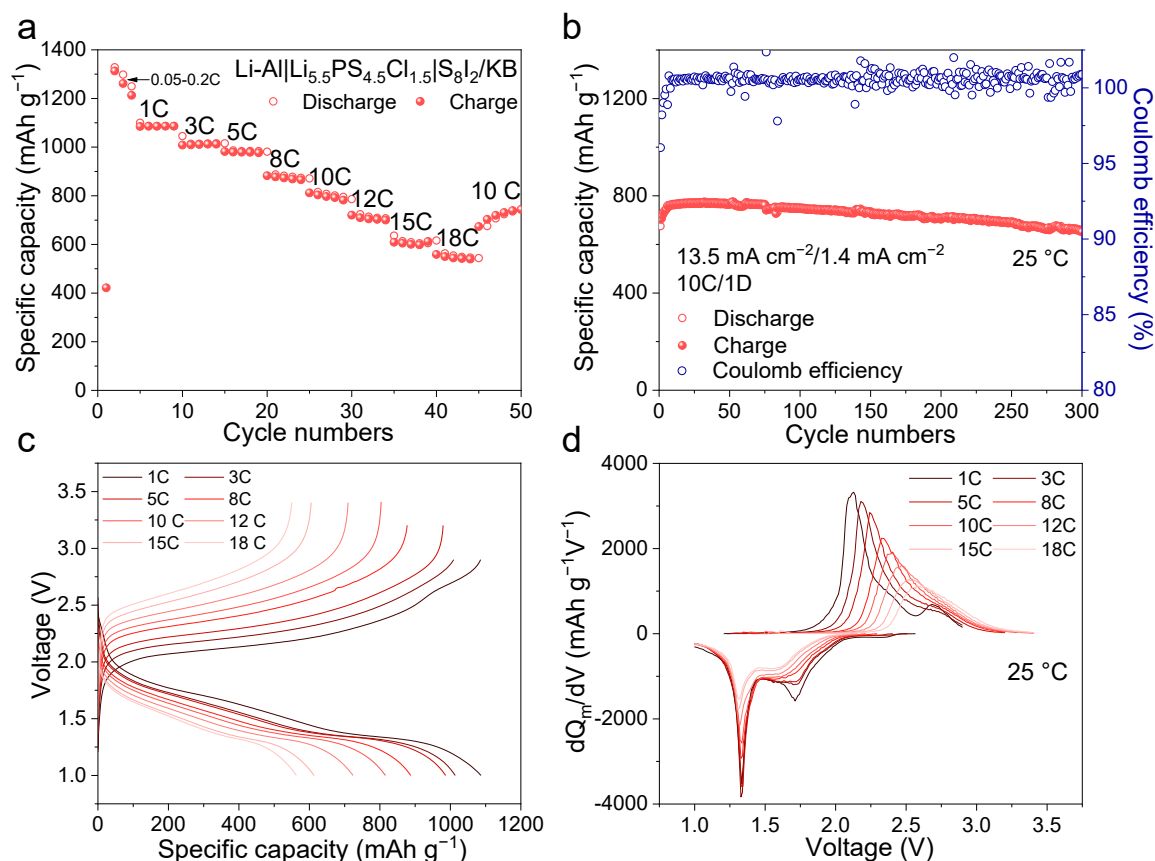
Supplementary Fig. 23 | Additional long-term cycling performance data of S_8I_2/KB based all-solid-state lithium-sulfur batteries at 25 °C. **a, b,** Long-term cycling (**a**) and corresponding discharge-charge voltage profiles (**b**) of the S_8I_2/KB cell with a high S_8I_2 fraction of 50 wt% in positive electrode and a high S_8I_2 loading of 4.9 mg cm⁻² at 0.1 C. **c, d,** Long-term cycling stability (**c**) and voltage profiles (**d**) of the S_8I_2/KB cell with 60 wt% S_8I_2 and a S_8I_2 loading of 1.1 mg cm⁻² at 1 C (25 °C). The cell was activated at 0.1-0.5C prior to cycling. Cells were tested in a custom pressure cell configuration.



Supplementary Fig. 24 | Additional cycling performance measurements of high-loading positive electrodes at 25°C . **a**, Voltage profiles of the S_8I_2 /KB cell with 60 wt% S_8I_2 and a S_8I_2 loading of 3.4 mg cm^{-2} at 0.64 mA cm^{-2} (25°C). **b,c**, Cycling performance (**b**) and voltage profiles (**c**) of the S_8I_2 /KB cell with 50 wt% S_8I_2 and a S_8I_2 loading of 9.8 mg cm^{-2} at 0.46 mA cm^{-2} . **d, e**, Cycling performance (**d**) and voltage profiles (**e**) of the S_8I_2 /KB cell with 60 wt% S_8I_2 and a S_8I_2 loading of 7.7 mg cm^{-2} at 0.36 mA cm^{-2} . Cells were tested in a custom pressure cell configuration.



Supplementary Fig. 25 | Additional cycling performance measurements of high-loading positive electrodes at 25 °C. **a, b,** Cycling performance (**a**) and the corresponding voltage profiles (**b**) of the S_8I_2 /KB cell with 60 wt% S_8I_2 and a S_8I_2 loading of 9.7 mg cm^{-2} at 0.28 mA cm^{-2} . **c, d,** Long-term cycling of the S_8I_2 /KB cell with 70 wt% S_8I_2 and S_8I_2 loading of 1.8 mg cm^{-2} at 0.34 mA cm^{-2} (**c**) and the corresponding voltage profiles (**d**). Cells were tested in a custom pressure cell configuration.



Supplementary Fig. 26 | Fast-charging performance of $\text{S}_8\text{I}_2/\text{KB}$ based all-solid-state lithium-sulfur batteries with Li-Al negative electrode at 25 °C. $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ is used as the separator electrolyte for the cell. **a, b**, Charging rate performance with varied charging rates (labelled) and a constant discharging rate of 1 C (1.4 mA cm^{-2}) (**a**), and the long-term cycling performance with a charging rate of 10 C (13.5 mA cm^{-2}) (**b**) (S_8I_2 loading: 1.4 mg cm^{-2}). The cell was activated by cycling at 0.05~0.2 C for the first four cycles. **c, d**, The voltage profiles with charging rates from 1 C (1.4 mA cm^{-2}) to 18 C (24.2 mA cm^{-2}) (**c**) and the corresponding dQ_m/dV plots (**d**). Cells were tested in a custom pressure cell configuration.

Supplementary Table S1. Comparison of cycling stability, rate capability (upper) and areal capacity (bottom) with some reported all-solid-state Li-S or LMOs-based batteries

Positive electrode	Negative electrode	Cycling stability	Rate capability	T^a (°C)	P^b (MPa)	Ref.	
		Cycle #/ Capacity retention (%) (current density)	Rate/Capacity (~1mg cm ⁻² active material)				
Se _{0.05} S _{0.95} @pPAN/CNT / Li ₁₀ GeP ₂ S ₁₂	In/InLi	150/81% (0.33 mA cm ⁻²)	1 C/434.6 mA h g ⁻¹	RT ^c	- ^d	12	
S/CNT/ Li ₁₀ GeP ₂ S ₁₂	Li-Al	200/93.3% (0.36 mA cm ⁻²)	0.5 C/914 mA h g ⁻¹ 1 C/514 mA h g ⁻¹	RT	-	13	
Li ₂ S/LiI/ VGCF/Li ₃ PS ₄	In/InLi	2000/ discharge capacity-limiting (~2.3 mA cm ⁻²)	2 C/970 mA h g ⁻¹	25	-	14	
S/CNT/Li ₆ PS ₅ Cl	In/InLi	100/84% (0.18 mA cm ⁻²)	0.5 C/1008 mA h g ⁻¹	25	2~5 ^e	15	
S _{9.3} I/VGCF/LPS	SP/Li	400/87% (~0.19 mA cm ⁻²)	~0.1 C/811.8 mA h g ⁻¹	25	30	16	
S ₈ I ₂ /KB/Li _{5.5} PS _{4.5} Cl _{1.5}	In/InLi	9000/75.8% (2.45 mA cm ⁻² ; 2C) 5000/80.6% (12.7 mA cm ⁻²)	10 C/851.9 mA h g ⁻¹ 24 C/474.7 mA h g ⁻¹	25	64	Our work	
°Temperature, °bPressure applied during cycling, °cRoom temperature, °dNot provided, °cell with solid-state electrolyte film							
Positive electrode	Negative electrode	Current (mA cm ⁻²)	1 st capacity (mA h cm ⁻²)	Cycle #/ Capacity retention (%)	T^a (°C)	P^b	Ref.
Li ₂ S/LiVS ₂ / Li _{5.5} PS _{4.5} Cl _{1.5}	In/InLi	1	2.6	50/-	RT	10.7 N m	17
S/Co ₃ O ₄ @NC/Li ₇ P ₃ S ₁₁	In/InLi	0.2	5.2	100/88.9%	30	-	18
Li ₂ S/VGCF/ Li ₇ Sb _{0.05} P _{2.95} S _{10.5} I _{0.5}	In/InLi	0.06	2.2	15/2.4 mA h cm ⁻²	RT	-	19
S/CNT/Li ₁₀ GeP ₂ S ₁₂ /LiI	In/InLi	0.12	4.1	50/~68%	60	150MPa	20
S _{9.3} I/VGCF/LPS	SP/Li	1.3	~4.5	50/~90%	100	30MPa	16
NCM811/Li ₆ PS ₅ Cl	Si	5	2	500/80%	RT	50MPa	2
F@NMC811/Li ₆ PS ₅ Cl	Mg ₁₆ Bi ₈₄ /Li	2.6	7.64	40/80%	80	2.5MPa	21
LSO@NMC811/ Li ₆ PS ₅ Cl	LiNI-Mg/Li	1.1	2.2	350/82.4%	60	1MPa	22
NCM85/Li ₂ In _{1/3} Sc _{1/3} Cl ₄	In/InLi	0.49	4.1	80/4.1 mA h cm ⁻²	RT	250MPa	11
S ₈ I ₂ /KB/Li _{5.5} PS _{4.5} Cl _{1.5}	In/InLi	4.7 0.94	3.9 9.3	1,600/80.3% 100/87.9%	25 25	64MPa	Our work

Supplementary Table S2. The cell parameters for calculating the specific energy of the two cells based on pouch cell configuration including the positive electrode, negative electrode, separator, packaging and tabs.

Parts	Components	Cell 1	Cell 2
Positive electrode	Specific capacity (mA h g^{-1})	1000	900
	Content of active materials (wt%)	50	60
	Content of carbon (wt%)	21.7	19
	Content of solid catholyte (wt%)	28.3	21
	Single side areal loading ($\text{mg cm}^{-2}_{\text{SA}}$)	9.8	9.7
	Positive electrode area (mm^2/mm)	55/79	
	Total weight of composite current collector (PET/Al) (g)	1.22	
Negative electrode	Lithium metal negative electrode thickness (μm)	190	169
	N/P ratio	2.0	
	Total weight of negative electrode (g)	12.05	10.71
Layers number	positive electrode / negative electrode	24/25	
Separator	Thickness of solid electrolyte separator (μm)	30	
	Solid electrolyte density (g cm^{-3})	1.50	
	Total weight of solid electrolyte (g)	11	
Weight of	Packaging material (g)	0.66	
Packaging and Tabs	Tabs (g)	0.2	
Energy parameters of the pouch	Total capacity (mAh)	20438.88	18207.29
	Cell voltage (V)	1.9	1.9
	Specific Energy (Wh kg^{-1})	588.34	601.49

Supplementary Table S3. Comparison regarding positive electrode specific energy and positive electrode specific power with some reported all-solid-state Li-S or LMOs-based batteries.

Positive electrode	AM ^a content (wt%)	m _{AM} ^b (mg cm ⁻²)	Current (mA cm ⁻²)	Capacity (mA h g ⁻¹ _{AM})	Specific Energy ^c (Wh kg ⁻¹)	Specific Power ^d (W kg ⁻¹)	T ^e (°C)	Ref.
S/CNT/ Li ₁₀ GeP ₂ S ₁₂	26.25	1.07	0.36	1237	617	167.8	RT	13
S _{9.3} I/VGCF/ LPS	40	1.2	0.19	811.8	568	112	25	16
S ₈ I ₂ /KB/ Li _{5.5} PS _{4.5} Cl _{1.5}	60	1.1	1.1	852.5	936	1098	25	Our work
LSO@NMC81 1/Li ₆ PS ₅ Cl/C	70	12	1.1	~185	486	241	60	22
NCM85/ Li ₂ In _{1/3} Sc _{1/3} Cl ₄	90	6.26	0.226	~220	772	127	RT	11

^aActive material; ^bMass loading of active material; ^cPositive electrode specific energy; ^dPositive electrode specific power; ^eTemperature

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