

Supplementary Materials: Cross-Linked Solid Polymer-based Catholyte for Solid-State Lithium-Sulfur Batteries

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1. Cathode processing

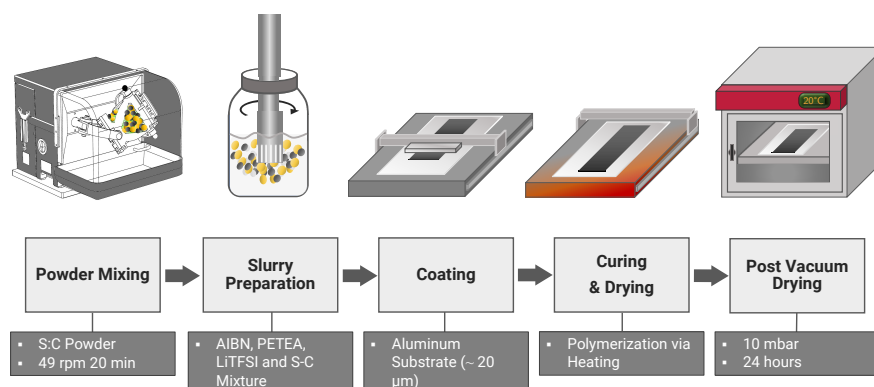


Figure S1. Cathode processing steps. The gray boxes in the second row describe fixed parameters and materials, which were used for every cathode preparation.

The cathode process route is visualized in Figure S1. The first and the last step were conducted in a dry room; the other steps were carried out in an argon-filled glove box ($\text{O}_2 < 0.1 \text{ ppm}$, $\text{H}_2\text{O} < 0.1 \text{ ppm}$). First, sulfur and carbon black were mixed in a tubular mixer. After the powder mixing, the cathode slurry was prepared. Here, PETEA, LiTFSI, and AIBN were dissolved in DMSO. The amount of AIBN was adjusted to 3 wt% of the mass of the monomers. Then, the pre-mixed S-C powder was added to the solution. DMSO content was adjusted to obtain a slurry with a final solid content of 20 wt%. The slurry mixing was conducted with a batch disperser (X 10/20- E3 Ystral GmbH) at 9500 rpm for 30 min. Afterward, the slurry was coated via a manual applicator (Proceq ZAF 2010) on a 20 μm thick aluminum current collector attached to an automatic film applicator device (Zehntner ZAA2300.H) with heatable plates. The applicator thickness was set to 300 μm and coating speed was set to 30 mm s^{-1} . Simultaneously, the coating plate of the film applicator was preheated at 60 $^\circ\text{C}$ to directly start the polymerization process for 3 h. Finally, the cathode was moved to a dry room and vacuum-dried at 10 mbar, 20 $^\circ\text{C}$ for 24 hours.

2. Electrolyte processing

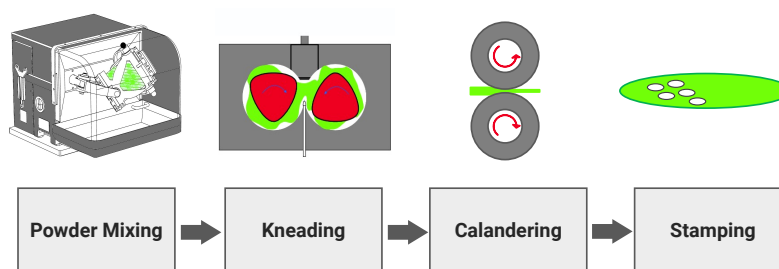


Figure S2. PEO-LiTFSI solid polymer electrolyte processing steps.

The SPE processing was performed in a dry room (dew point $< -30 \text{ }^\circ\text{C}$). The process route is visualized in Figure S2. First, PEO and LiTFSI, with a EO : Li molar ratio of $r = 14$, were mixed as powders with a turbula mixer (Willy A. Bachofen AG Maschinenfabrik). The powder was kneaded (Haake Rheomix 600 from Thermo Scientific) and a plast-like compound was formed. As the third step, the kneaded compound was calendered to form a thin membrane with a thickness of 150 μm . Finally, disks with a diameter of 16 mm were stamped out of the membrane to assemble them as the separator into coin cells.

3. Equivalent circuit used to fit EIS data

The obtained impedance spectra were fitted with constant-phase elements (CPE) and resistance (R) with an equivalent circuit composed of R_{SPE} : bulk ionic resistance of the polymer electrolyte; $CPE_{int.}$: constant phase element of the interphase layer; $R_{int.}$: resistance of the interphase layer; CPE_{DL} : double layer constant phase element at the electrode–polymer interface; R_{CT} : charge transfer resistance using the software EC-tool.

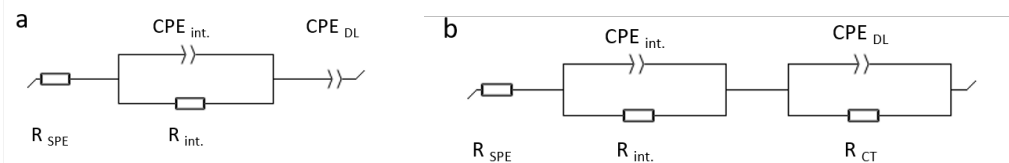


Figure S3. Equivalent circuit used to fit EIS data.

4. Coulombic efficiency and cycling results for coin cells with various catholyte contents, different sulfur to carbon ratios, and with a PP12-based cathode and PEO electrolyte separator

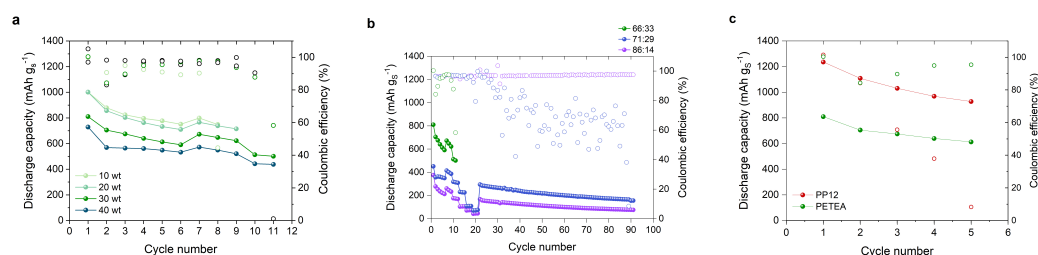


Figure S4. Coulombic efficiency and cycling results for coin cells with PEO electrolyte separator and with (a) various catholyte content, (b) different sulfur to carbon ratio, and (c) PP12-based cathode.

5. Discharge voltage profile at different C-rates for different S : C ratios

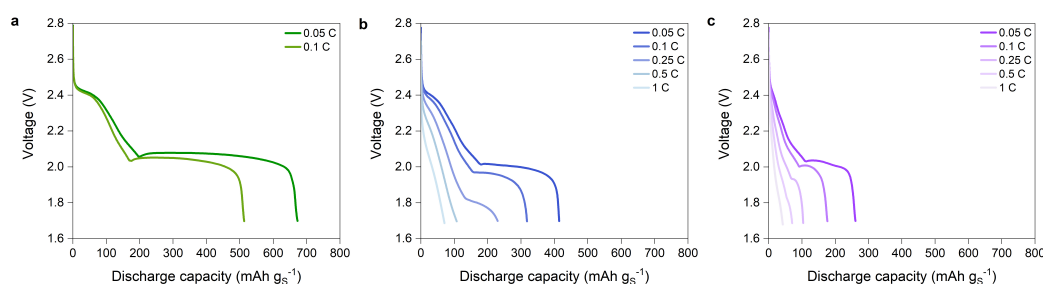


Figure S5. Discharge voltage profile at different C-rates for different S : C ratios (a) 66.66 : 33.33 (b) 71 : 29, and (c) 86 : 14.

6. Repeatability of cell data and effect of C-rate test on cell performance

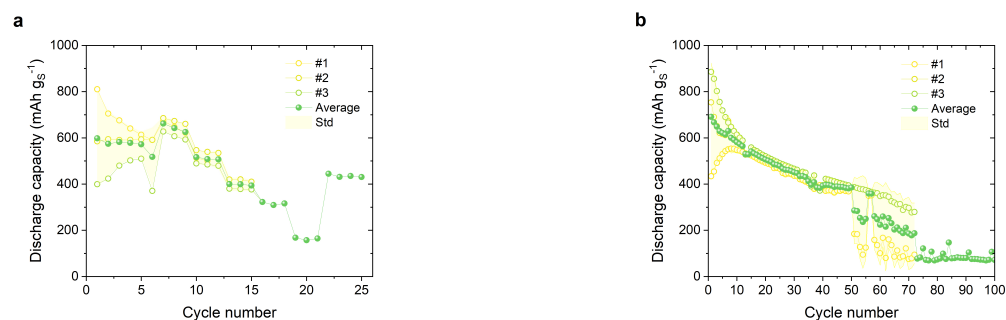


Figure S6. Discharge capacity of the full cells with lithium metal anode, PEO-based electrolyte separator, and sulfur cathodes with the sulfur to carbon ratio of 66.66 : 33.33 and PETEA catholyte content of 30 wt%, three cells are cycled (a) with a C-rate test protocol in Table 1, and (b) at a constant C-rate of 0.1.

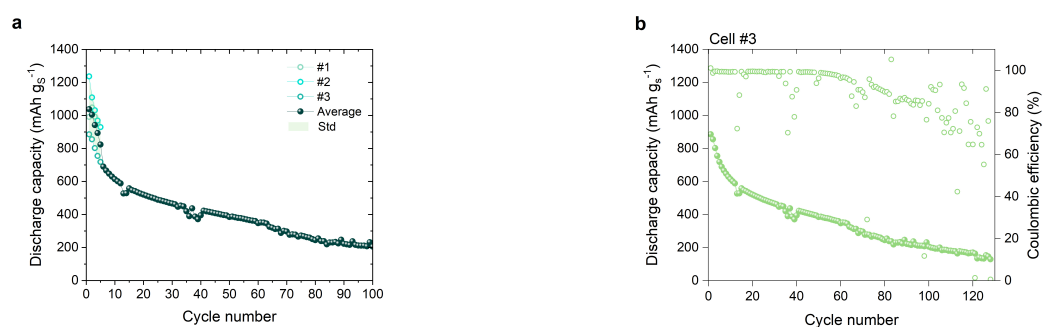


Figure S7. Discharge capacity of (a) the cells with lithium metal anode, PEO-based electrolyte separator, and sulfur cathodes with the sulfur to carbon ratio of 66.66 : 33.33 and PP12 catholyte content of 30 wt%, three cells are cycled at a C-rate of 0.1 and (b) the discharge capacity of the cell # 3.

7. PETEA and PP12 cathodes

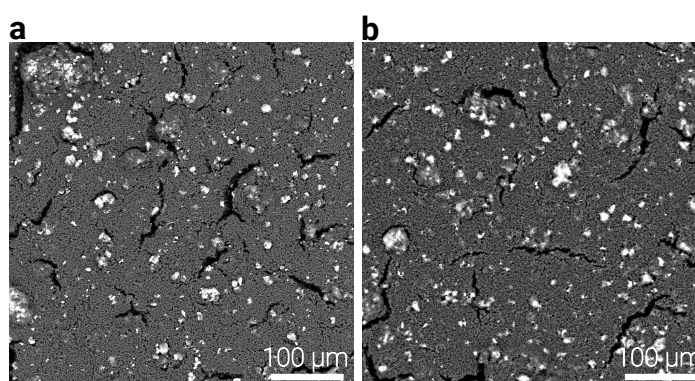


Figure S8. SEM images of the surface of cathodes with (a) PETEA and (b) PP12 catholytes.

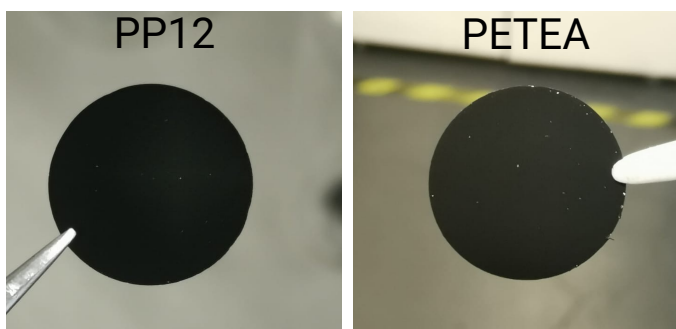


Figure S9. Real images of stamped cathodes with PP12 and PETEA.

8. Ionic conductivity of electrolyte separators at room temperature

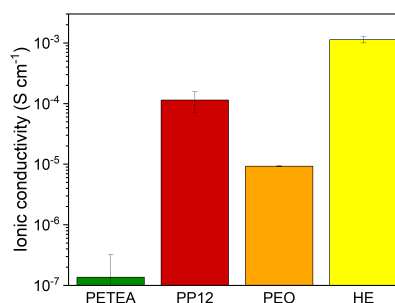


Figure S10. Ionic conductivity of pure PETEA, PP12, PEO, and hybrid electrolyte (HE) separators at 20 °C.

9. EIS of LSB cells at room temperature

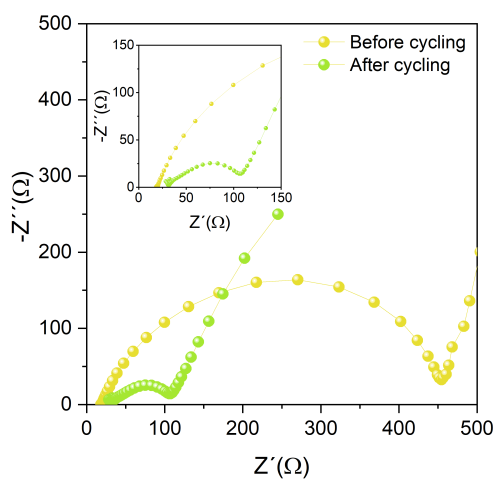


Figure S11. Nyquist plots of cells with lithium metal anode, HES, and PP12 cathode at 20 °C before and after cycling.