Supporting Information

Room-Temperature Synthesis of Methacrylate-derived Sulfurized Polymer Cathode for Rechargeable Lithium Batteries

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1.Experimental Procedures

1.1 Materials

Three methacrylate monomers, sodium thiophenolate, DMF, and carbon disulfide were purchased from Admas-beta and used without any further treatment. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.99%) was obtained from the DoDoChem official website. Dimethoxyethane (DME, 99%) and 1,3-dioxolane (DOL, 99%) were purchased from Meryer Chemical Reagent Co., Ltd. Lithium nitrate ($LiNO_3$,99.999%) was acquired from Macklin Chemical Reagent. Polypropylene separators (PP, 16±2 μm) were sourced from the Canrd official website. Lithium metal (Li, diameter is 14 mm) was supplied by China Energy Lithium Co., Ltd. A electrolyte formula with 1M concentration (1M LiTFSI in DME:DOL = 1:1 vol% with 2 wt% $LiNO_3$) was used.

1.2 Typical polymerization procedure

The sulfur 256 mg, MA-n monomer (1 mmol), and initiator (PhSNa) 6.6 mg were added into a 25 mL Schlenk flask (in the reactor was [Monomer]: [Sulfur]: [PhSNa] = 40:20:1), followed by the addition of dry DMF 2 mL, the system turned dark red quickly. The mixture degassed by three cycles of freezing-pumping-thawing with argon, then placed under room temperature and stirred for 24 h. The reaction quenched with liquid nitrogen, after recovered to the room temperature, the color turned slight yellow, filtrated the solution by 0.2 μm filter membrane and the solution could be precipitated by dropping the diluted into 50 ml methanol, then filtrated and collected the solid. The solid dissolved in 1 mL THF and then reprecipitated in methanol. The final polymer was dried in a vacuum oven at 45 °C for 24 h.

1.3 Materials characterization

Raman spectra were acquired using a HORIBA LabRAM HR Evolution S3 spectrometer. FTIR spectra were recorded by ThermoFisher Nicolet 6700. Raman spectra were recorded by DXR ThermoFisher Scientific with 532 nm laser excitation. Element Analysis was performed using Elementar Vario Micro Cube.

1.4 Preparation of SP-n (n = 1, 2, 3) cathode

The SP cathode was prepared by pressing SP film onto a titanium mesh. Specifically, 60 mg of SP-n (n = 1, 2, 3) was mixed with 30 mg Ketjen Black (KB) and then ground into uniform powder. Subsequently, the working cathode was prepared by combining the powder with a binder (PTFE) in a 9:1 mass ratio to form a film using isopropyl alcohol. The film was then pressed onto a titanium mesh and dried at 55 °C for 4 hours. The loading mass of active materials was maintained at 3.4 mg cm^{-2} (corresponding to the sulfur loading of ~1.0 mg cm^{-2}) for standard tests, with additional sample (SP-2) prepared at higher loading mass of 6.7 mg cm^{-2} (corresponding to the sulfur loading of ~2.0 mg cm^{-2}) for high-loading tests.

1.5 Electrochemical measurements

The SP materials were used as the cathodes, lithium metal served as the anode (diameter 14 mm, serving as both counter and reference electrode), and the customized electrolyte consisted of 1 M LiTFSI in DOL/DME (1:1 v/v) with 0.2 M $LiNO_3$. A Celgard 2500 membrane was employed as the separator, and the resulting configuration formed Li//SP cells. CR2032 coin cells were assembled in a glove box (Mikrouna, Super (1220/750/900)) with an argon (Ar) atmosphere to evaluate electrochemical performance. Electrochemical performance (EIS) was evaluated using an electrochemical workstation (CHI 760E) through A.C. Impedance (IMP). Constant current charge-discharge tests were conducted using a LAND battery testing system (CT3004A).

Temperature variation test: After fabricating the Li//SP battery, the cell was placed in a high-low temperature test chamber (Surui experimental equipment Co., LTD, RGD100), which allows precise control of temperature over a range of 0 to 60 °C. Once the cells were placed in the chamber, the room temperature (25 °C) was stabilized for 4 hours. Subsequently, galvanostatic measurements were initiated. After completing the room temperature test for 5 cycles, we set the temperature to 20 °C, allowing 30 minutes for stabilization before beginning the test. This procedure was replicated for other temperature variation tests, which included temperature adjustments from 10 °C to 0 °C, and then from 0 °C to 10 °C, 20 °C, 30 °C, 40 °C, 50 °C, and finally to 60 °C.

1.6 Calculation of lithium-ion diffusion coefficient

Lithium-ion diffusion coefficient D_{Li^+} ($cm^2\ s^{-1}$) is evaluated by cyclic voltammetry method and calculated according to the Randles-Sevick equation:

$$I_p = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li} v^{0.5} \qquad \text{(Eq-1)}$$

where I_p(A) is the peak current value, n represents the number of electrons of in the reaction (for Li-S batteries, n = 2), A (cm^2) indicates the electrode area (here is 1.13 cm^2), C_{Li} (mol mL^{-1}) means the lithium-ion concentration in the electrolyte, and v stands for the scanning rate (V s^{-1}).

2. Supplementary Figures

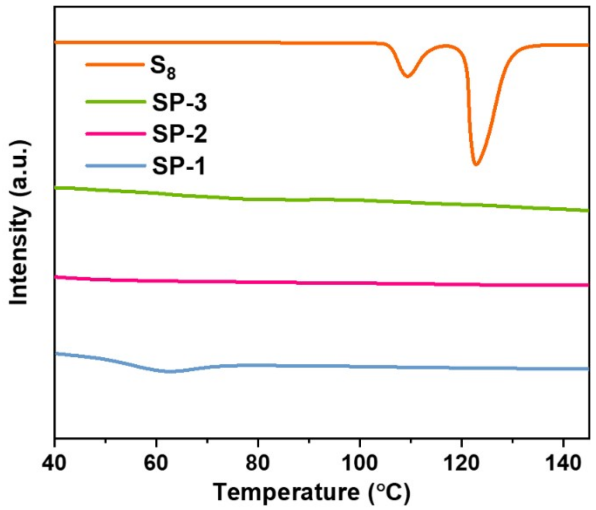

Figure S1. DSC curves of elemental sulfur and SPs.

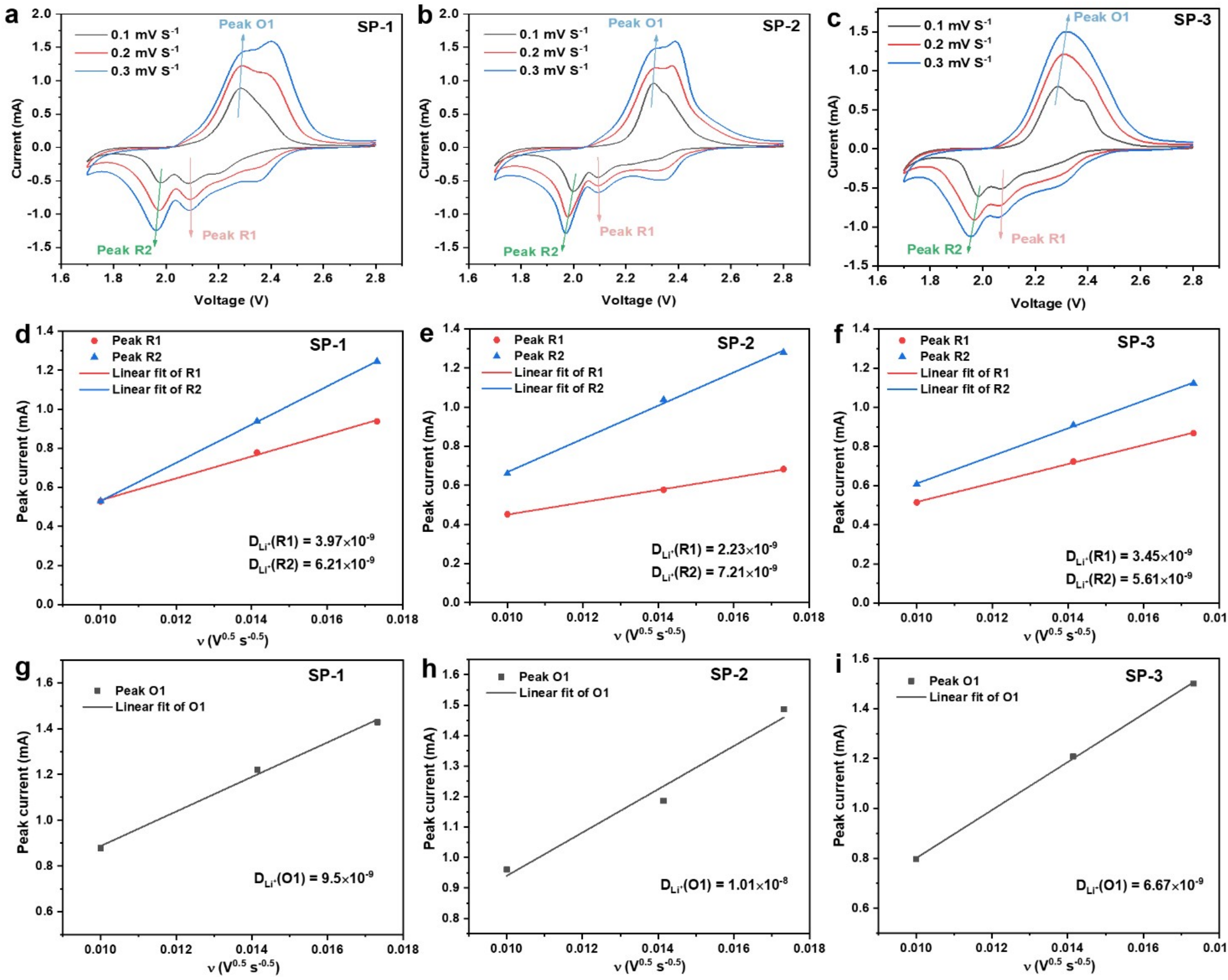

Figure S2. (a-c) CV test with different scan rates. (d-e) Li$^+$ diffusion coefficients calculation for (d-e) reduction and (g-i) oxidation peaks, respectively.

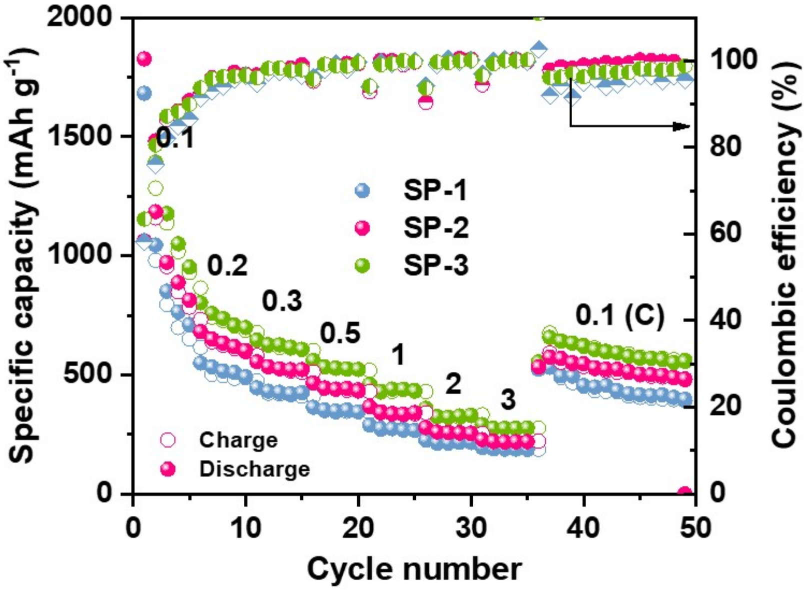

Figure S3. Rate capability of the batteries with various SP cathodes.

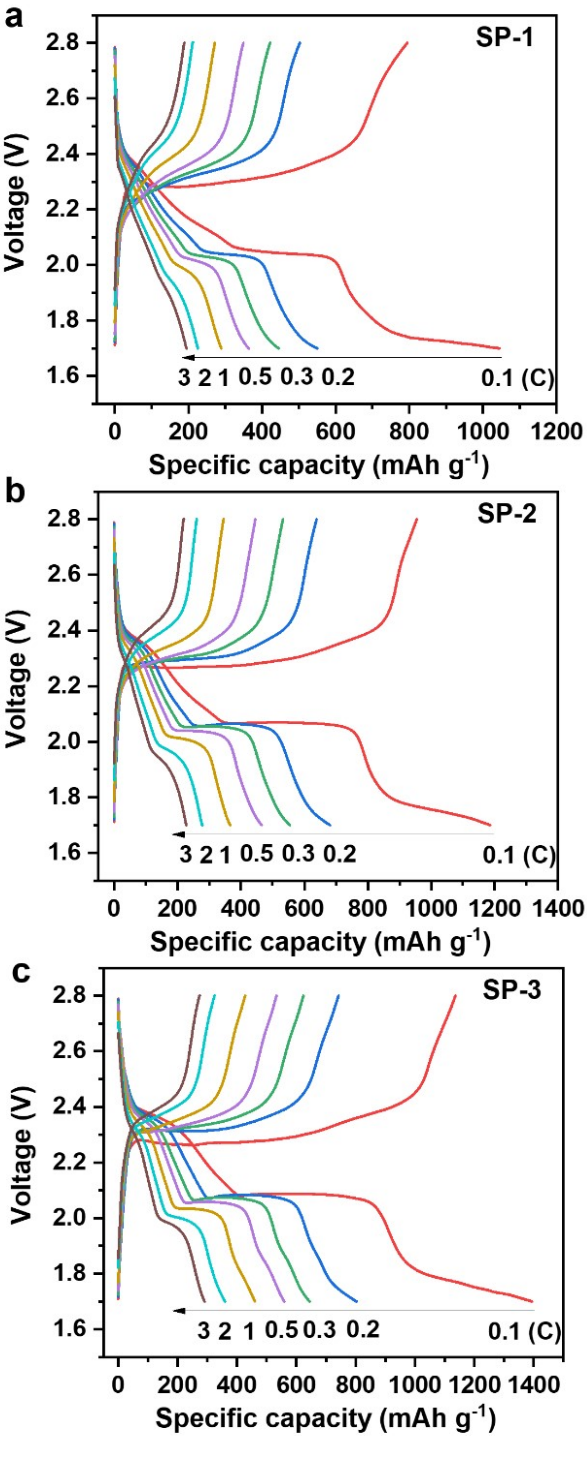

Figure S4. Charge-discharge profiles for three SP cathodes under various current density.

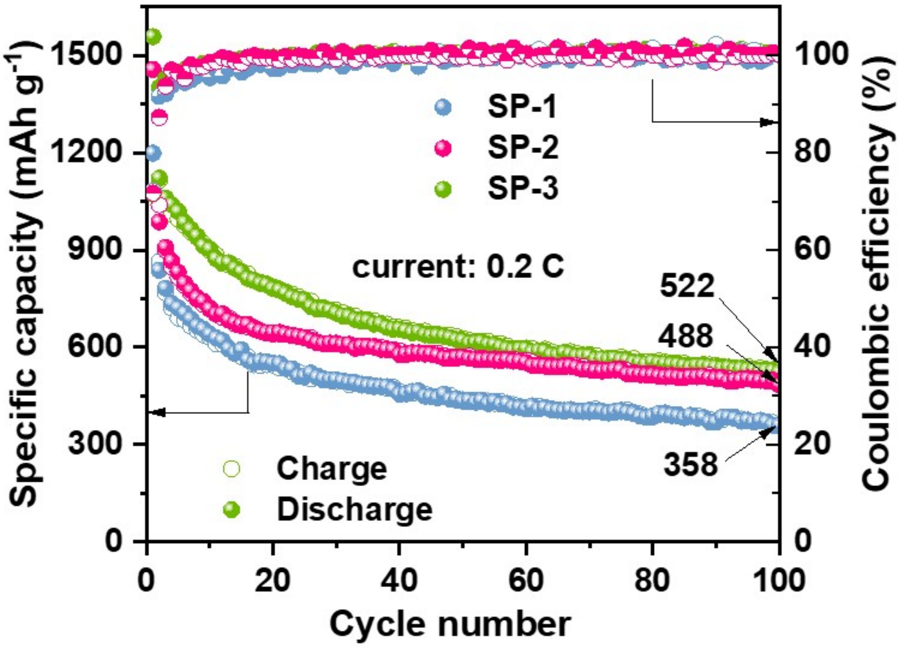

Figure S5. Cyling performance at the current of 0.2 C with various SP cathodes.

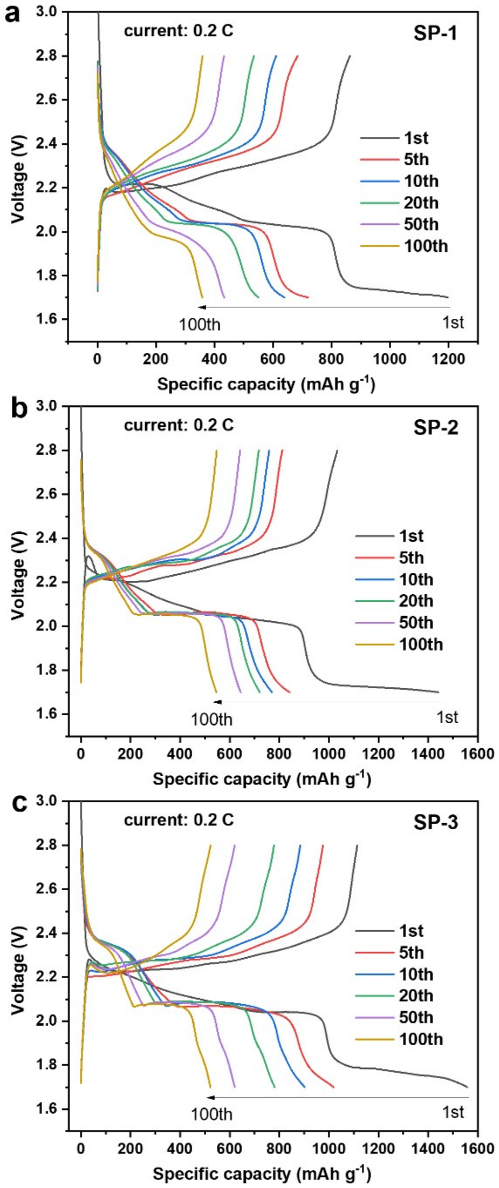

Figure S6. Different charge-discharge profiles for three SP cathodes under 0.2 C.

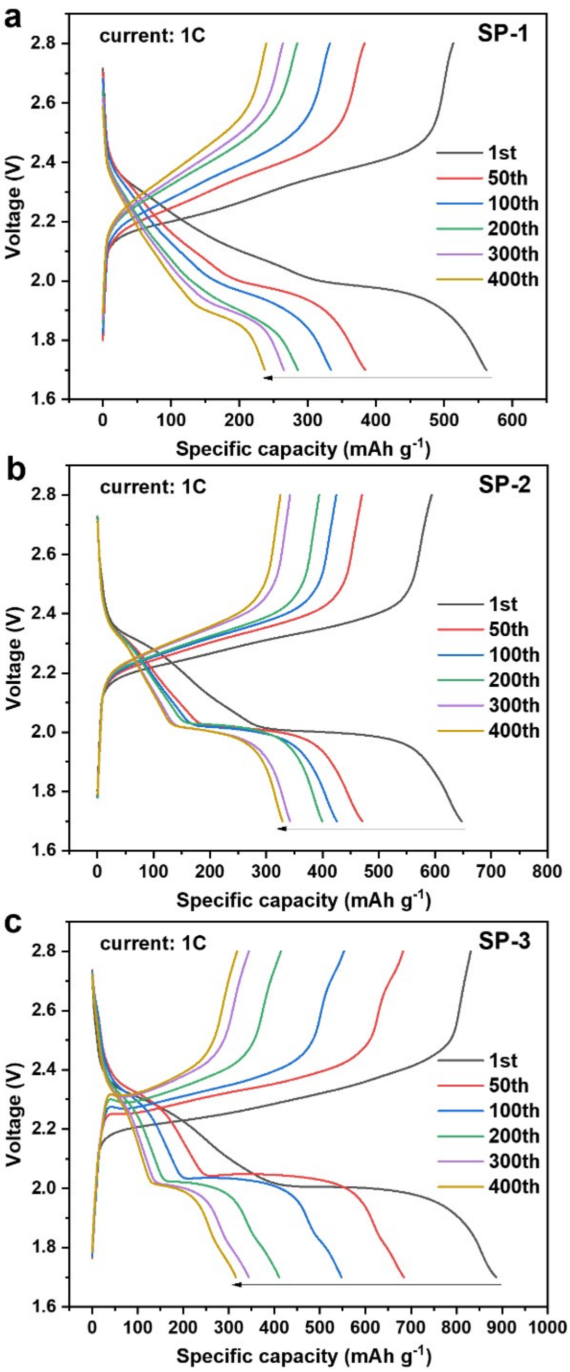

Figure S7. Different charge-discharge profiles for SP-based batteries cycled at 1 C.

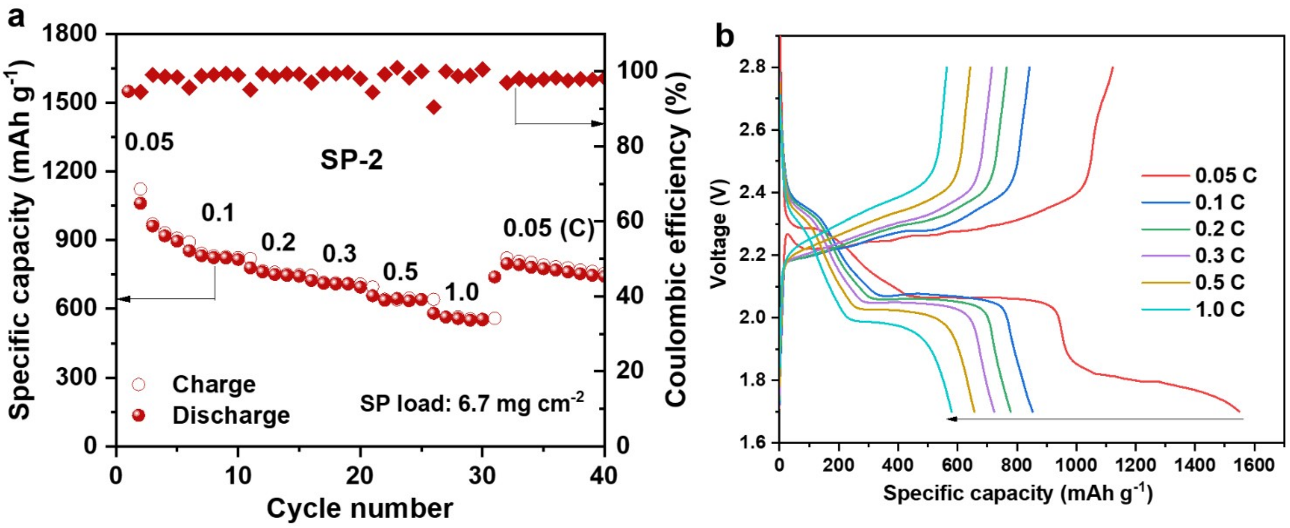

Figure S8. (a) Rate capability and (b) corresponding charge-discharge profiles for SP-2 based cell with 6.7 mg cm^{-2} loading.

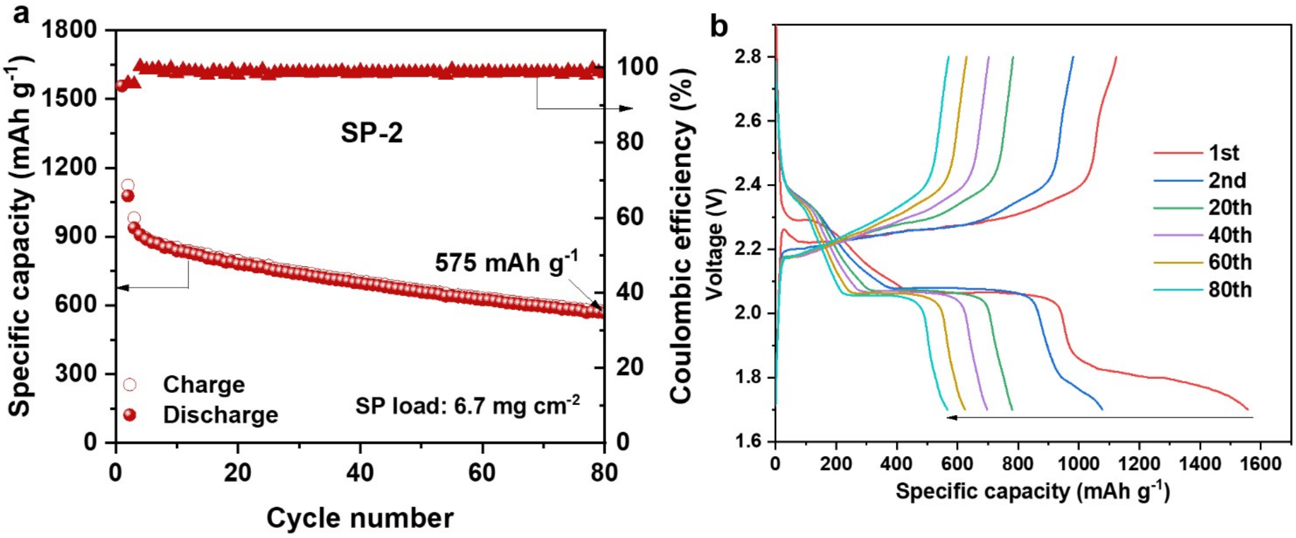

Figure S9. (a) Cycling performance at 0.1 C and (b) corresponding charge-discharge profiles for SP-2 based cell with 6.7 mg cm^{-2} loading.

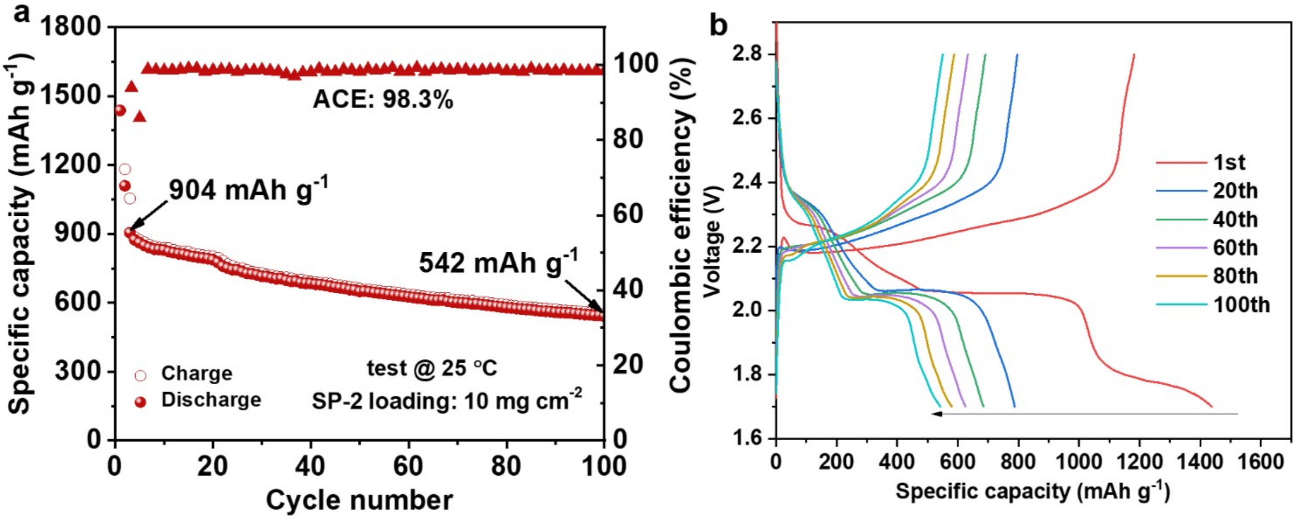

Figure S10. (a) Cycling performance at 0.2 C and (b) corresponding charge-discharge profiles for SP-2 based cell with 10 mg cm^{-2} loading.

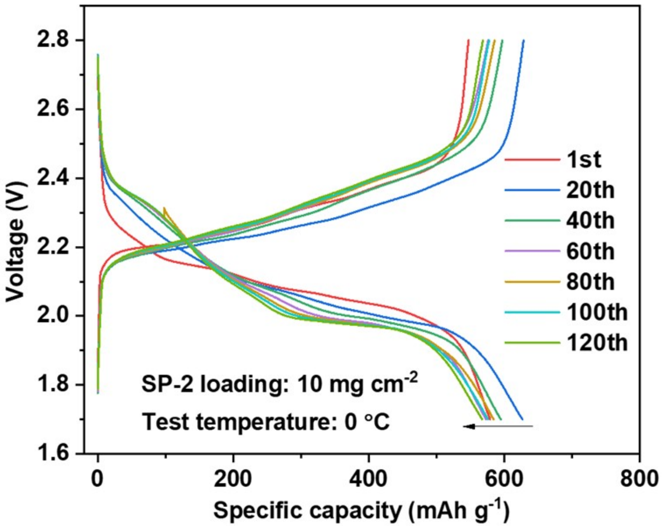

Figure S11. Charge-discharge profile for the SP-2 based cell with 10 mg cm^{-2} loading and tested at 0.2 C and low temperature of 0 °C.

Table S1. Properties of several sulfurized polymer cathodes

Sulfurized polymer	Synthetic temp. (°C)	Initial specific capacity (mAh g^{-1})	Ref. NO.[a]
S-PAN	300 °C	850	1
poly(S-r-DIB)	185 °C	1100	2
S-CTF-1	400 °C	670	3
SF-CTF-1	400 °C	1138	4
FCTF-S	400 °C	1131	5
Poly(S-TABQ)	160 °C	1346	6
COF-F-S	350 °C	1120	7
S-COP-99	400 °C	1287	8
cPpy-S-CTF	400 °C	1203	9
ZI-OS	170 °C	1550	10
Poly(S_8/TAA)	120 °C	N/A	11
SP-2	25 °C	1549	This work

[a] All the cited references are showed in the main manuscript.

Table S2. Elemental analysis results of three SP materials.

Material	N [%]	C [%]	H [%]	S [%]
SP-1	0	43.1	5.1	33.1
SP-2	0	48.9	6.1	32.5
SP-3	0.3	56.4	6.3	25.8

Table S3. Performance comparison between SP-2 and other organosulfur cathodes in lithium batteries.

Cathode	S content/ Cathode loading	Specific capacity (mAh g^{-1})	Cyclic stability (%)	Ref.
DUT-185-S_n	~30% 2.2 mg cm^{-2}	950 at 0.1 A g^{-1}	84% 500 cycles	*Adv. Mater.,***2023**, *35*, 2210151.
S-DUT-177	~25 0.55 mg cm^{-2}	720 at 0.1 A g^{-1}	76.6% 500 cycles	*J. Am. Chem. Soc.,* **2022**, *144*, 9101−9112.
F-MCDS	35% ~2.1 mg cm^{-2}	268 at 0.03 A g^{-1}	55.6% 1000 cycles	*Chem. Commun.*, **2022**, *58*, 5602–5605.
TBBT/S	50% 2 mg cm^{-2}	559.9 at 0.1 C	69% 500 cycles	*Chem. Commun.,* **2019**, *55*, 4857−4860.
PDSe-S_2	- 3.8 mg	318 at 0.1 C	73% 200 cycles	*Adv. Funct. Mater.* **2018**, *28,* 1801791.
PhS-SePh	- 0.5 M	152 at 0.2 C	52% 200 cycles	*Chem. Commun.,* **2018**, *54,* 8873−8876.
SP-2	32.5% 10 mg cm^{-2}	1118 at 0.2 C	98.3% 120 cycles	*This work*

Author contributions statement

Z. Zheng conducted material preparation and performed all electrochemical experiments under the supervision of J. Xu. X. Qian spearheaded the synthesis of all materials and corresponding characterization analyses; authored the materials synthesis section; and provided partial financial support (grant 23ZR1425100). D. Bin and Y. Wang carried out systematic analysis of electrochemical data, proposed critical revisions to the experimental methodology, and contributed substantially to manuscript refinement. J. Xu conceived and designed the study, secured major funding (grants 22309003 and 2023AH051119), and supervised project execution. The manuscript was collaboratively drafted by Z. Zheng, X. Qian, and J. Xu. All authors participated in result discussions and provided critical feedback during manuscript preparation.