Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information for

Influence of component molar ratios of conjugated polymers on the anode performance in lithium-ion batteries

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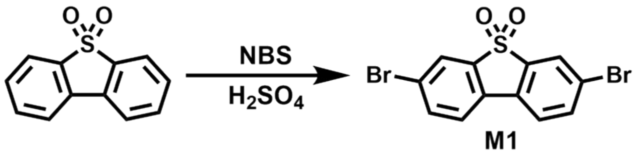
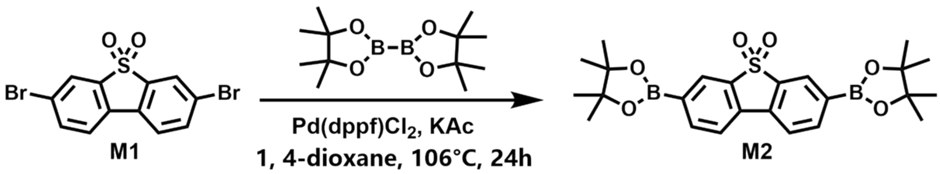
Experimental section



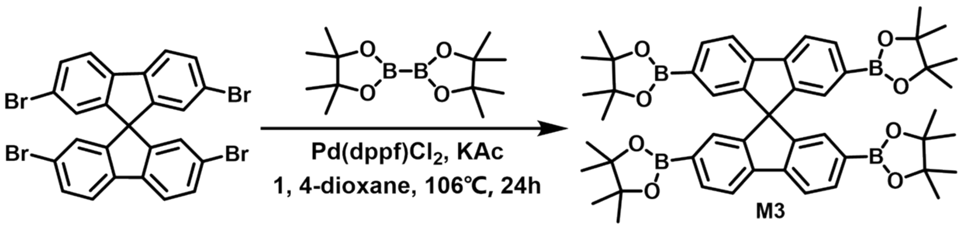
The synthetic procedures the Monomer 1 (M1):

Monomer 1 (**M1**): Synthesis of 3,7-dibromo-dibenzothiophene sulfone monomer (**M1**): Dibenzothiophene sulfone monomer (7.0 g, 32.4 mmol) was dissolved in 240 mL of concentrated sulfuric acid under argon atmosphere, and N-Bromosuccinimide (NBS) (12 g, 67.4 mmol) was added in three slow additions, and then the mixture was stirred for 24 hours at room temperature. After completion of the reaction, the reaction solution was diluted by slowly pouring it into a large amount of ice water. The solid was obtained by filtration and subsequently washed with water and saturated sodium bicarbonate solution until the pH was neutral. After drying in a vacuum drying oven, recrystallization was repeated three times with trichloromethane (150 mL×3) to give a pure white solid. Yield (5.2 g, 42.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.76-7.78 (d, J = 8.0 Hz, 2H), 7.62-7.64 (d, J = 8.0 Hz, 2H).



The synthetic procedures the Monomer 2 (M2):

Monomer 2 (**M2**): Synthesis of 3,7-diboronate-dibenzothiophene sulfone (**M2**): Under argon atmosphere, 3,7-dibromo-dibenzothiophene sulfone (4.1 g, 10.7 mmol), pinacol bis (boronic acid) ester (8.4 g, 33.0 mmol), potassium acetate (6.3 g, 85.6 mmol), [1,1'-bis (diphenylphosphino) ferrocene] palladium (II) dichloride (0.40 g, 0.5 mmol) was dissolved in 120 mL of dry 1,4-dioxane and reacted at 106 °C for 24 hours. At the end of the reaction, it was extracted with CH_2Cl_2 for 3 times, the combined organic phases were washed with water twice and dried with anhydrous magnesium sulfate. The organic solvent was removed by rotary evaporation, and the solid crude product was purified by silica gel chromatographic column ($V_{petroleum\ ether}$: $V_{dichloromethane}$ = 2:1) to obtain a white solid **M2**. yield (2.6 g, 53.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 8.04-8.06 (d, J = 8.0 Hz, 2H), 7.79-7.81 (d, J = 8.0 Hz, 2H), 1.36 (s, 24H).



The synthetic procedures the Monomer 3 (M3):

Monomer 3 (**M3**): Synthesis of 2,2',7,7'-tetraborate-9,9'-spirobifluorene (**M3**): Under argon atmosphere, 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (1.60 g, 2.53 mmol), pinacol bis(boronic acid) ester (4.50 g, 17.70 mmol), potassium acetate (3.47 g, 35.42 mmol) and [1,1'-bis (diphenylphosphino) ferrocene] palladium (II) dichloride (0.37 g, 0.46 mmol) was dissolved in 150 mL of tetrahydrofuran and reacted at 70 °C for 72 hours. After the reaction was cooled to room temperature, it was extracted with CH_2Cl_2 for 3 times, the combined organic phases were washed with water twice and dried with anhydrous magnesium sulfate. The organic solvent was removed by rotary evaporation, and the solid crude product was purified by silica gel chromatographic column ($V_{petroleum\ ether}$: $V_{dichloromethane}$ = 2:1) to obtain a white solid **M3**. yield (1.58 g, 76.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (q, J = 8.0 Hz, 8H), 7.09 (s, 4H), 1.25 (s, 48H).

The synthetic procedures the SFSO polymer:

All polymers were synthesized by the Pd-catalyzed Suzuki-Miyaura coupling method using the general procedure that the monomer, $Pd(PPh_3)_4$, K_2CO_3, were dissolved in a mixture of deoxidized N,N-dimethylformamide and water under argon atmosphere, the reaction was heated up to 130 °C for 48 hours. After cooling to room temperature, an insoluble solid was obtained by filtration and the solid product was washed with water, methanol, dichloromethane, tetrahydrofuran and acetone to remove residual palladium catalyst. Finally, it was extracted with tetrahydrofuran Soxhlet for 48 hours.

Synthesis of the polymer **SFSO-1**: monomer **M3** (0.41 g, 0.50 mmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.316 g, 0.50 mmol), K_2CO_3 (0.830 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.013 g, 8.7 μmol), 16 mL of N,N-dimethylformamide and 3 mL of water were used for this reaction. A green powdery solid was obtained, yield: 0.246 g, 85% yield.

Synthesis of the polymer **SFSO-2**: monomer **M1** (0.063 g, 0.17 mmol), monomer **M2** (0.234 g, 0.50 mmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.105 g, 0.17 mmol), K_2CO_3 (0.830 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.013 g, 8.7 μmol), 16 mL of N,N-dimethylformamide and 3 mL of water were used for this reaction. A green powdery solid was obtained, yield: 0.171 g, 83% yield.

Synthesis of the polymer **SFSO-3**: monomer **M1** (0.112 g, 0.30 mmol), monomer **M2** (0.234 g, 0.50 mmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.063 g, 0.10 mmol), K_2CO_3 (0.830 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.013g, 8.7 μmol), 16 mL of N,N-dimethylformamide and 3 mL of water were used for this reaction. A green powdery solid was obtained, yield: 0.202 g, 98% yield.

Synthesis of the polymer **SFSO-4**: monomer **M1** (0.159 g, 0.424 mmol), monomer **M2** (0.234 g, 0.50 mmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.025 g, 0.039 mmol), K_2CO_3 (0.830 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.013 g, 8.7 μmol), 16 mL of N,N-dimethylformamide and 3 mL of water were used for this reaction. A green powdery solid was obtained, yield: 0.192 g, 96% yield.

Synthesis of the polymer **SFSO-5**: monomer **M1** (0.187 g, 0.50 mmol), monomer **M2** (0.234 g, 0.50 mmol), K_2CO_3 (0.830 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.013 g, 8.7 μmol), 16 mL of N,N-dimethylformamide and 3 mL of water were used for this reaction. A green powder was obtained, yield: 0.218 g, 84% yield.

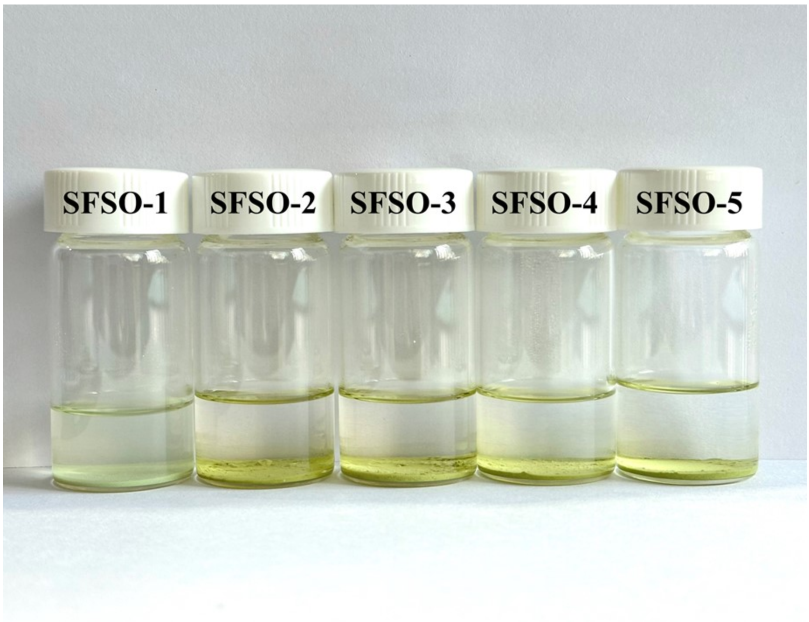


Fig. S1 The photograph of **SFSO-1** ~ **SFSO-5** in electrolyte solvent for a fortnight.

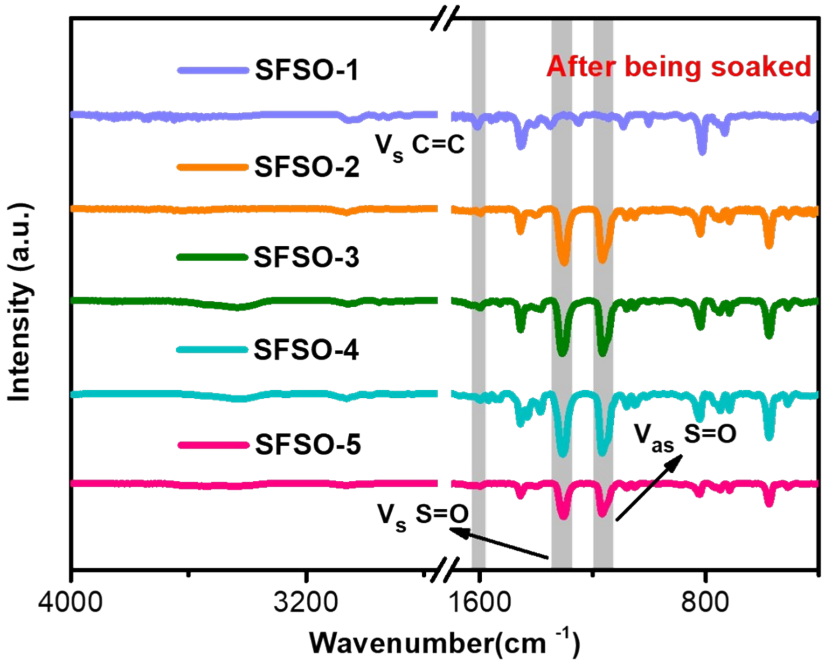


Fig. S2 The FT-IR spectra of **SFSO-1** ~ **SFSO-5** after immersion in electrolyte solvent.

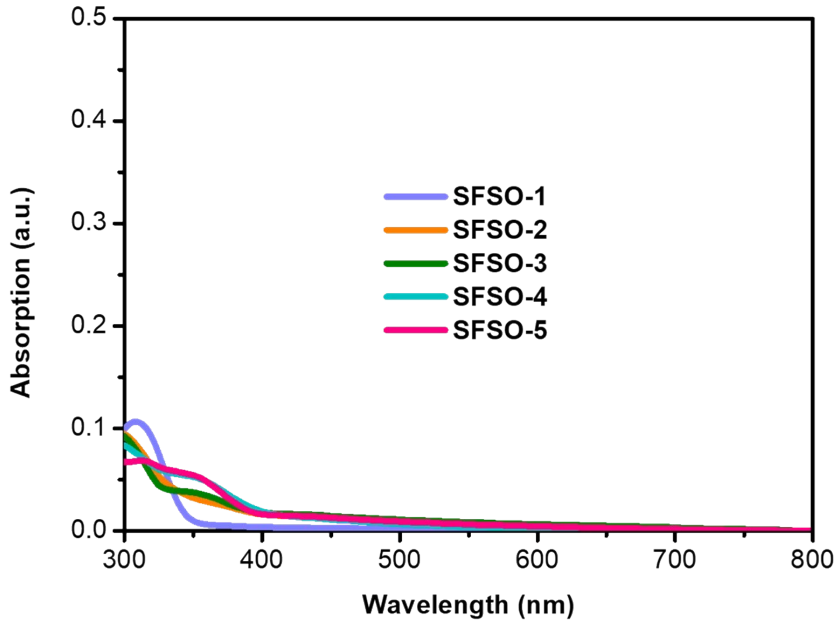


Fig. S3 UV-Vis absorption spectra of **SFSO-1** ~ **SFSO-5** in electrolyte solvent.

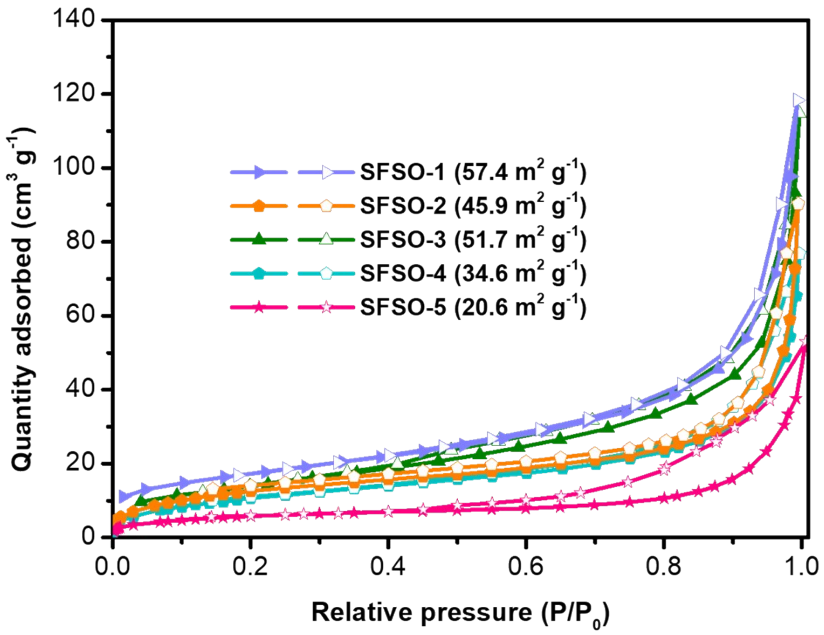


Fig. S4 Nitrogen adsorption (solid)-desorption (hollow) isotherms of **SFSO-1** ~ **SFSO-5**.

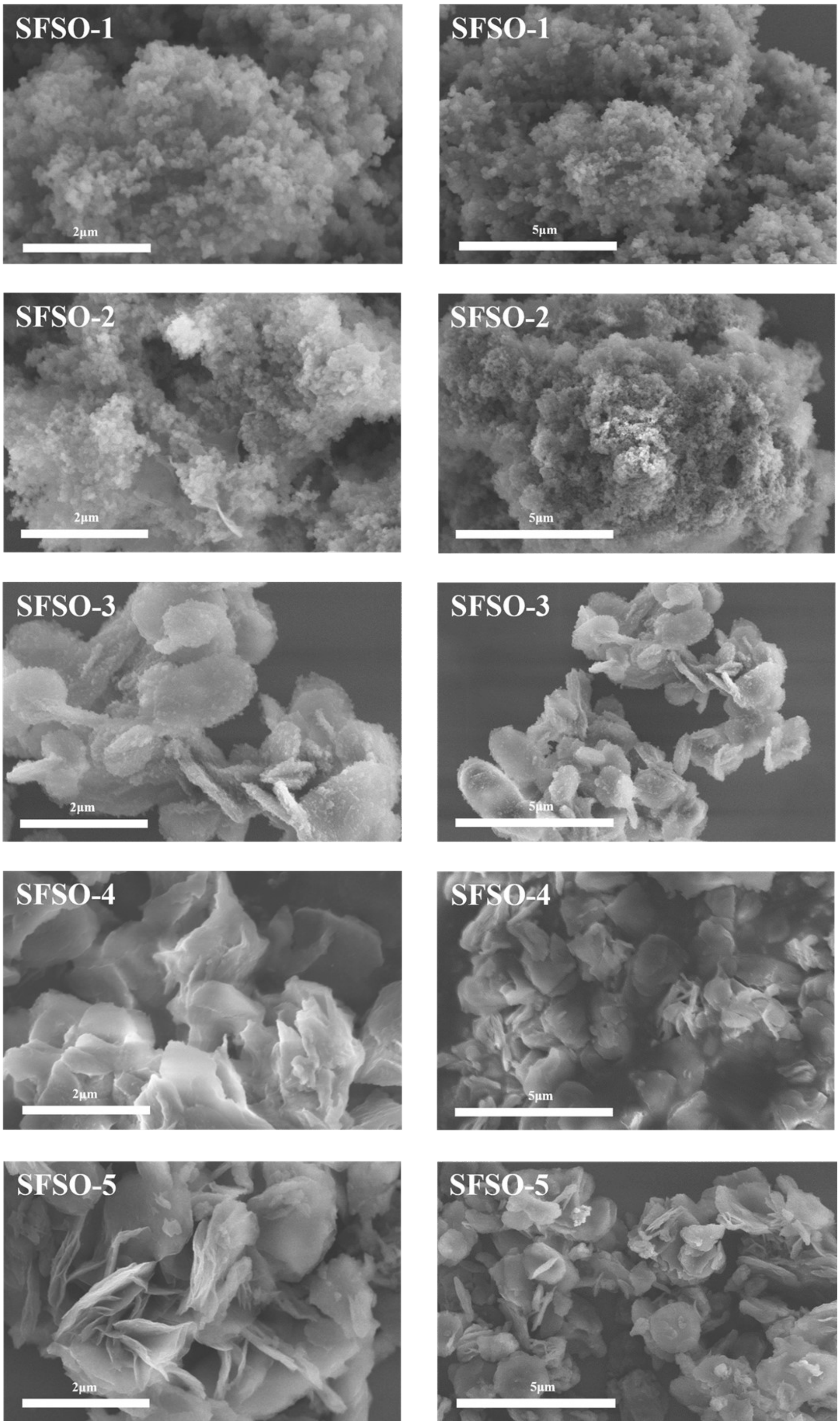


Fig. S5 The SEM images of **SFSO-1** ~ **SFSO-5**

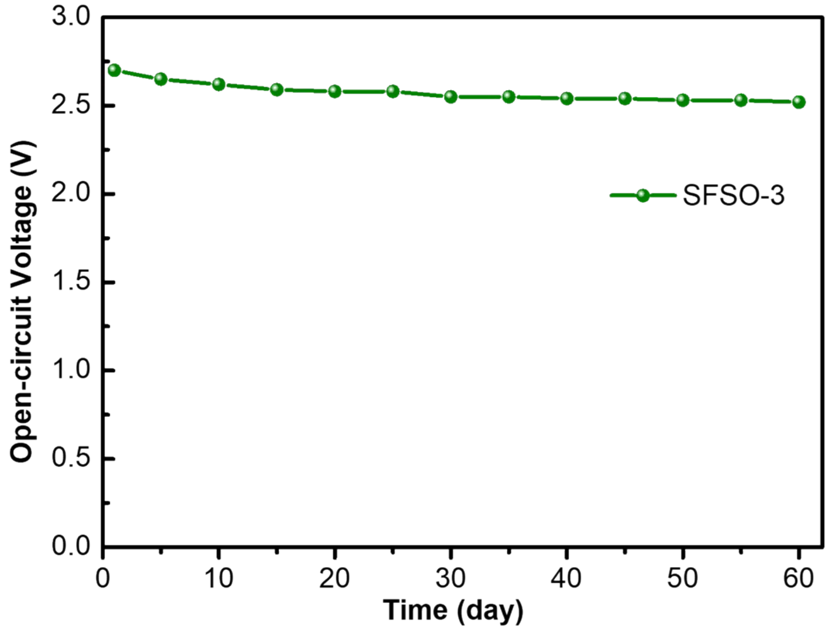


Fig. S6 Self-discharge curve of **SFSO-3** left at room temperature for two months.

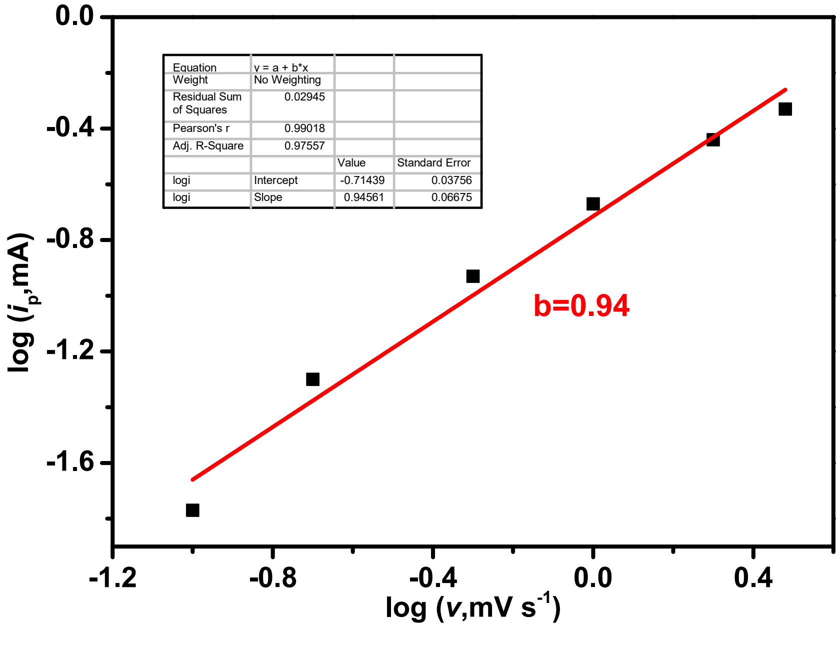


Fig. S7 The fitted linear relationship between log (scan rate) and log (peak current).

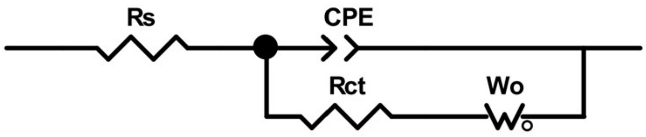


Fig. S8 The equivalent electrical circuit model to fitting EIS spectra. R_s: electrolyte resistance, R_{ct}: charge transfer resistance, CPE: constant phase element, and W_o: Warburg impedance.

Table S1 Fitted values of the elements in the equivalent circuit of the EIS data used to measure the **SFSO** electrodes.

	R_s (Ω)	CPE-T	CPE-P	R_{ct} (Ω)	W_o-R	W_o-T	W_o-P
SFSO-1	2.064	4.17×10^{-5}	0.658	206.2	289.7	0.575	0.412
SFSO-2	1.427	4.04×10^{-5}	0.714	263.5	317.4	2.624	0.418
SFSO-3	1.268	3.14×10^{-5}	0.647	138.5	273.7	2.168	0.416
SFSO-4	1.718	3.51×10^{-5}	0.716	198.1	305.7	2.331	0.417
SFSO-5	1.993	7.22×10^{-5}	0.611	362	202.2	3.683	0.413

The Li ion diffusion coefficients (D_{Li}^+, cm^2 s^{-1}) were obtained based on the EIS data through the equation:[1-3]

$$D = 0.5\left(\frac{RT}{AF^2\sigma C}\right)^2$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (298.5 K), A is the area of the electrode surface, F is the Faraday's constant (9.65×10^4 C mol^{-1}), σ is the Warburg coefficient and C is the molar concentration of Li^+.

The Warburg coefficient σ can be evaluated from equation:

$$Z_{re} = R_e + R_{ct} + \sigma\omega^{-0.5}$$

where Z_{re} is the real impedance in EIS data, R_e is the resistance of the electrolyte, R_{ct} is the charge transfer resistance, ω is the angular frequency in the low frequency region and σ is the slope for the plot of Z_{re} vs. $\omega^{-0.5}$.

Table S2 Warburg coefficients (σ) and Li ion diffusion coefficients (D_{Li^+}) obtained from EIS data

	SFSO-1	**SFSO-2**	**SFS0-3**	**SFSO-4**	**SFSO-5**
σ (s cm^{-2})	81.6	92.2	58.5	76.5	122.9
D_{Li^+} (cm^2 s^{-1})	4.18×10^{-12}	3.21×10^{-12}	1.63×10^{-11}	4.75×10^{-12}	1.84×10^{-12}

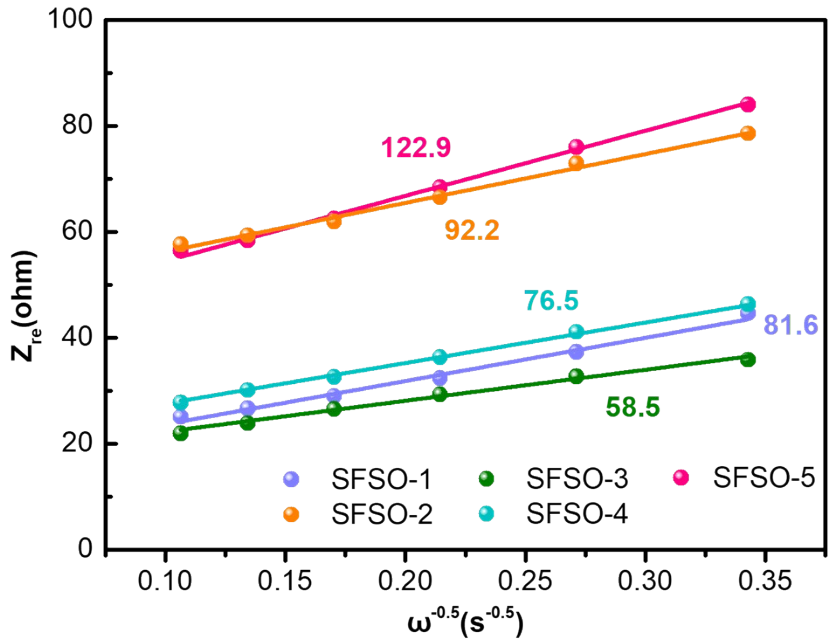


Fig. S9 The relationship between Z_{re} and $\omega^{-0.5}$ at low frequencies for **SFSO** polymers.

Sample pieces for electronic conductivity measurements were approximately 13 mm in diameter and were prepared by molding polymer powder samples at 20 MPa without any conductive carbon black or binder. The sample piece was then placed in a specific mold connected to the instrument. The resistance value (R) of the polymer material was obtained by parallel testing. The electronic conductivity (*κ*) was finally calculated by the equation:[4,5]

$$R = \frac{U}{I} = \rho\frac{L}{S}$$

$$\kappa = \frac{1}{\rho} = \frac{L}{SR}$$

Where ρ is the resistivity of the polymer material, L is the distance between two probes (cm), S is the contact surface area between the sample piece and the probe (0.29 cm^2), R is the resistance of the polymer material (Ω).

Table S3 The data obtained by the two-probe approach. The resistance of sheet polymer; the thickness of sheet polymer and calculated polymer conductivity.

	SFSO-1	**SFSO-2**	**SFS0-3**	**SFSO-4**	**SFSO-5**
R-1 (Ω)	10045.41	9124.529	5599.774	5960.755	6934.474
R-2 (Ω)	10054.82	9256.926	5621.078	5834.333	7004.642
R-3 (Ω)	10226.63	9374.738	5644.382	5897.637	7196.507
$\overline{R}$ (Ω)	10108.953	9252.206	5621.74	5897.575	7045.208
δ (cm)	0.037	0.018	0.038	0.036	0.030
κ (S cm^{-1})	1.26×10^{-5}	1.93×10^{-5}	2.33×10^{-5}	2.1×10^{-5}	6.7×10^{-6}

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