

LiFSI-LiTFSI binary-salt electrolyte to achieve high capacity and cycle stability for Li-S battery**

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Preparation and characterization of the sulfur-based composite. High sulfur contented composite was employed as the active substance of the testing electrode with a polypyrrole (PPy) coated carbon matrix as sulfur carrier. The matrix was prepared by anolyte electropolymerization inspired by the literature.¹ Carbon (BPX70, Cabot Corporation) and multiwalled carbon nanotubes (Nanjing XF Nano Inc.) were dispersed in an aqueous solution containing 1 M H₂SO₄ and pyrrole monomer under ultrasonic to form the anolyte. The catholyte was 1 M H₂SO₄. A separator was applied between the anolyte and the catholyte. A current of 400 μA was applied to initiate the polymerization. The resultant was washed and dried, then mixed with sublimed sulfur (chemical grade) in a weight ratio of 1:4 by a planetary ball miller at 180 rpm for 1 h. The as-prepared composite was characterized by Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker), powder X-ray diffraction (XRD, Rigaku MiniFlex II), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, FEI Tecnai G2 F20). The sulfur content was measured by thermogravimetry (TGA, Mettler Toledo, TGA/DSC 1) in 50 mL·min⁻¹ Ar flow at a heating rate of 10 °C·min⁻¹ from 30 to 500 °C. The cycled anodes and cathodes were retrieved from cells after 100 cycles at 200 mA·g⁻¹-composite, scoured with DOL/DME (1:1 by volume) and dried in an argon-filled glove box. The resultants were cut into pieces, pasted on the sample holder and transferred under argon atmosphere into the transfer vessel for SEM observation.

Preparation and characterization of the electrolytes. Different electrolytes were prepared by dissolving proper amount of bis(fluorosulfonyl)imide (LiFSI, Guotaihuarong, Zhangjiagang) or/and bis(trifluoromethanesulfonyl)imide (LiTFSI, Acros) in the mixture (1:1 in volume) of 1,3-dioxolane (DOL, J&K) and 1,2-dimethoxyethane (DME, J&K) in an argon-filled glove box. The testing electrolytes were 1 M, 1.5 M, 2 M, 2.5 M, 3 M LiFSI (DOL/DME), 1 M, 1.5 M, 2 M, 2.5 M, 3 M LiTFSI (DOL/DME), and two ether-mixtures containing 1 M LiFSI + 0.5 M LiTFSI, and 0.5 M LiFSI + 1 M LiTFSI, respectively. The ionic conductivity of electrolyte was measured by a conductivity meter (Shengbang, Tianjin) at 25 °C. The shear viscosity (η) of the electrolyte was measured on a viscometer (Brookfield, DV2T) at 25 °C. All the measurements were performed more than twice to insure the reliability.

Electrochemical measurement. The active substance was blended with carbon black (Super P Li) and poly(vinylidene difluoride) (PVdF) in a weight ratio of 7:2:1 under vigorous stir for 10 h with N-methyl-2-pyrrolidone (NMP) as the dispersant. The obtained slurry was cast on carbon-coated Al foil then dried overnight at 60 °C. The resultant cathode was cut into small round pieces (12 mm in diameter). The testing cells (model R2032) were assembled in an argon-filled glove box, with metallic lithium foil as the counter and reference electrode, microporous polypropylene film (Celgard 2300) as the separator and the as-prepared sulfur electrode (lithium foil for the potential stair-step measurement) as the cathode. The galvanostatic discharge/charge measurements were conducted at different current density between 1.0~3.0 V on a LANHE-CT2001A battery testing

system (Wuhan Jinnuo, China). The cyclic voltammetry (CV) was operated on a Solartron SI 1287 electrochemical interface with a scan rate of 0.1 mV s^{-1} in the potential range of 1.0~3.0 V vs. Li/Li⁺. The electrochemical impedance spectroscopy (EIS) measurements were performed using a Zahner IM6Ex electrochemical workstation in the frequency range of 100 kHz to 100 mHz with an exciting potential amplitude of 5 mV.

Reference:

1. M. Duduta, B. Ho, V. C. Wood, P. Limthongkul, V. E. Brunini, W. C. Carter and Y. M. Chiang, *Adv. Energy Mater.*, 2011, **1**, 511.

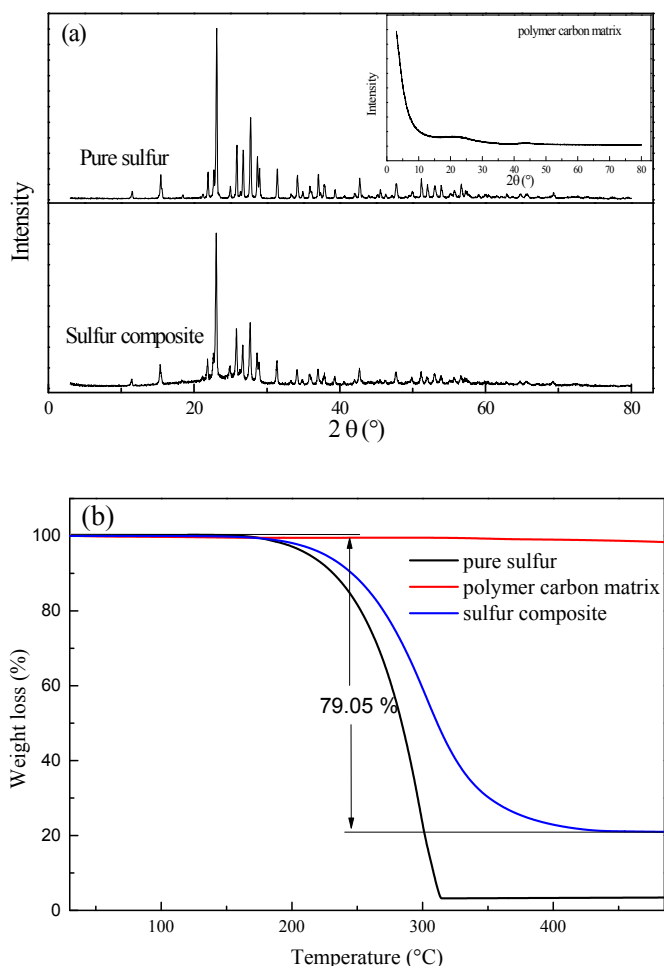


Fig. S1. (a) XRD patterns and (b) TG of sulfur, the polymer coating carbon matrix and the sulfur based composite.

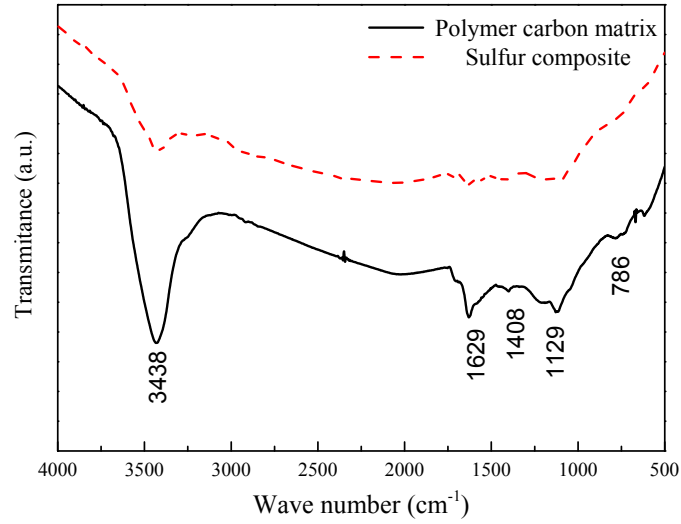


Fig. S2. FTIR of the polymer coating carbon matrix and the sulfur based composite.

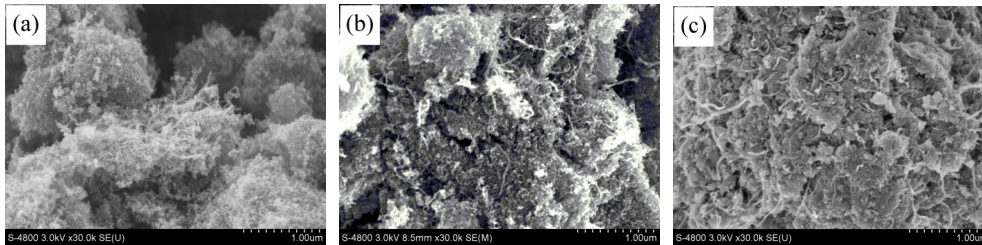


Fig. S3. SEM images of (a) the conductive mixed carbon matrix, (b) the polymer coating carbon matrix and (c) the sulfur based composite.

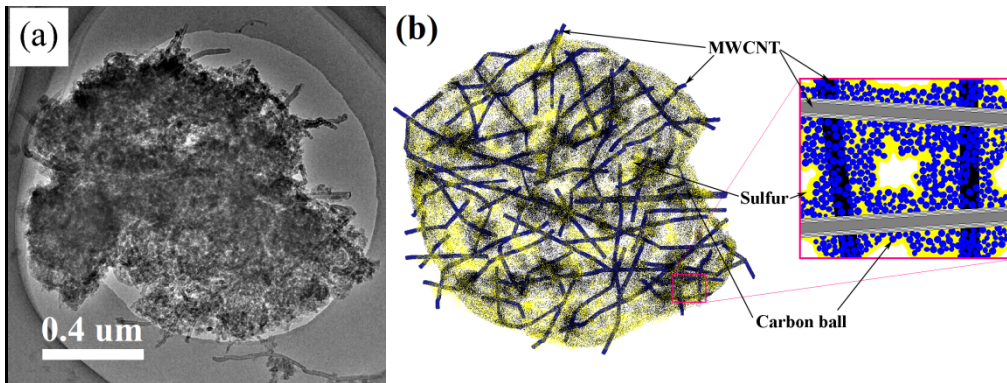


Fig. S4. (a) TEM image and (b) the schematic structure of the sulfur based composite.

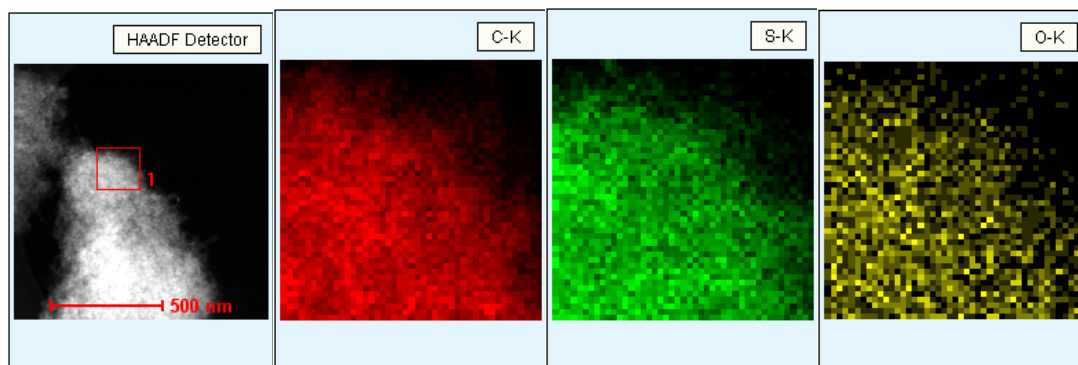


Fig. S5. STEM image and elemental mapping images of carbon, sulfur and oxygen of the region as noted by the red square in the sulfur based composite.

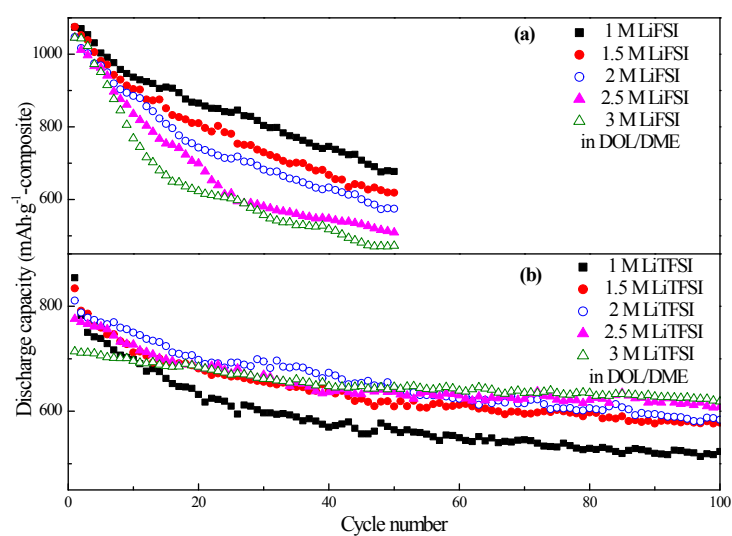


Fig. S6. The cycle performance of the sulfur cathode in different concentrated electrolytes with (a) LiFSI and (b) LiTFSI at 200 mA g⁻¹-composite.

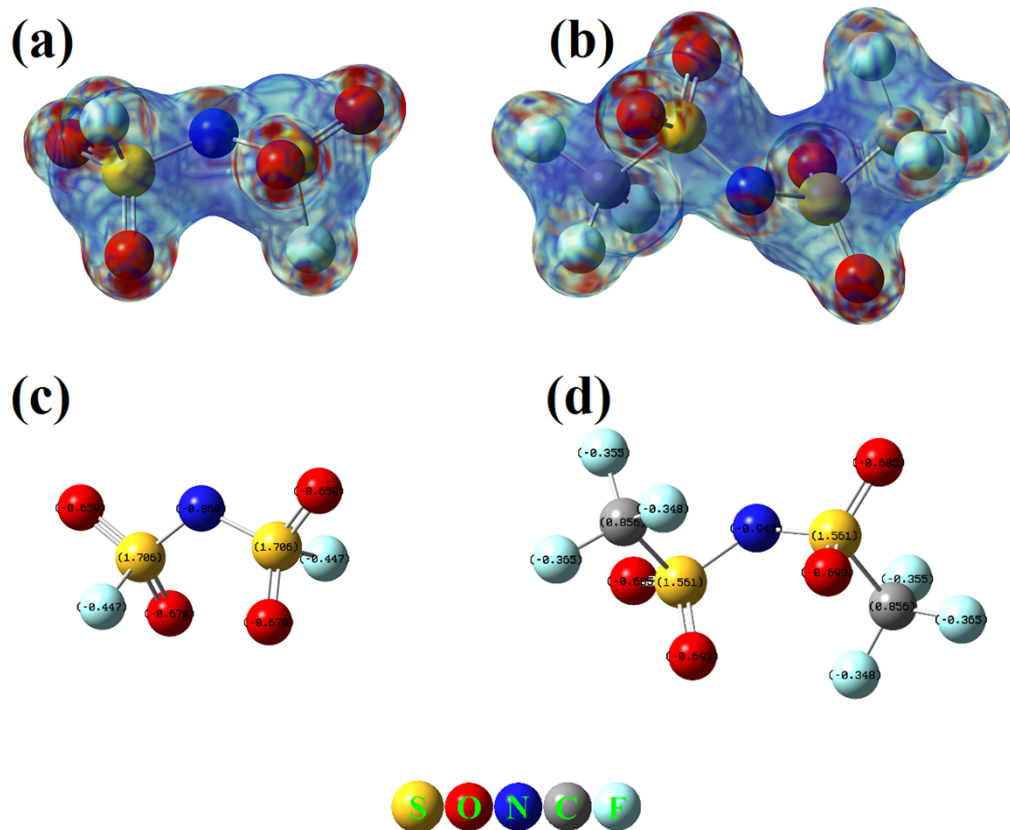


Fig. S7. Calculated Electronic Static Potential (ESP) and charges of sulfur and nitrogen atoms of (a) [FSI]⁻ and (b) [TFSI]⁻ by Gaussian. The blue coating regions (ESP) indicate positive charge distribution and the red ones suggest negative. Mulliken atomic charges of (c) [FSI]⁻ and (d) [TFSI]⁻ calculated from a Gaussian software.

Table S1. The electrochemical parameters simulated from EIS in Fig. 2.

electrolyte	R_s (ohm*mg)	R_1 (ohm*mg)	R_{ct} (ohm*mg)	W_o-R (ohm*mg)
1.5 M LiFSI				
1st	2.98	6.68	19.37	13.87
10th	4.04	17.76	20.87	23.34
50th	5.97	37.42	24.51	38.06
100th	6.67	77.82	44.05	86.08
1M LiFSI +0.5M LiTFSI				
1st	3.91	76.95	5.00	21.09
10th	4.45	36.23	4.16	32.13
50th	5.78	35.50	3.81	28.03
100th	6.54	34.88	4.78	25.47
0.5 M LiFSI + 1 M LiTFSI				
1st	4.01	32.22	5.71	26.92
10th	4.79	32.88	8.17	28.25
50th	6.65	25.36	8.39	82.69
100th	6.99	31.18	12.66	91.93
1.5 M LiTFSI				
1st	5.11	25.97	5.31	11.52
10th	6.42	18.15	9.61	25.23
50th	6.81	15.71	19.58	30.54
100th	7.40	12.59	27.50	74.13



The fitting equivalent circles in which R_s is solution resistance, R_{ct} is charge-transfer resistance, CPE is constant phase element, R_1 is the resistance from the insoluble Li_2S/Li_2S_2 film, and W_o is assigned to the semi-infinite Warburg diffusion.

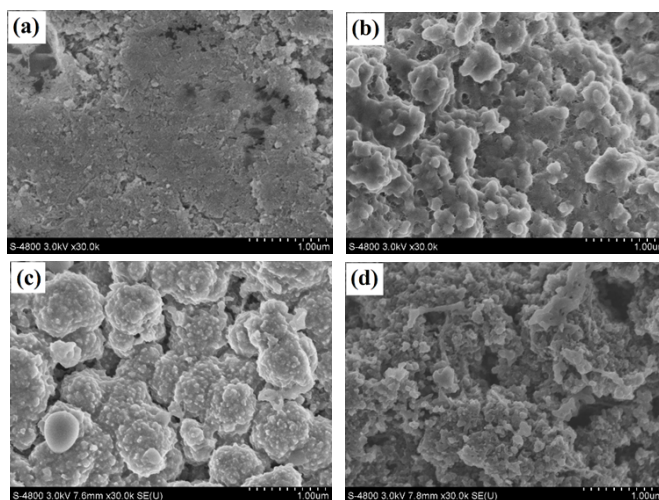


Fig. S8. SEM images of the sulfur cathode surface. (a) fresh cathode, and cycled cathodes after 100 cycles in (b) 1.5 M LiFSI electrolyte, (c) 1 M LiFSI + 0.5 M LiTFSI electrolyte, and (d) 1.5 M LiTFSI electrolyte.

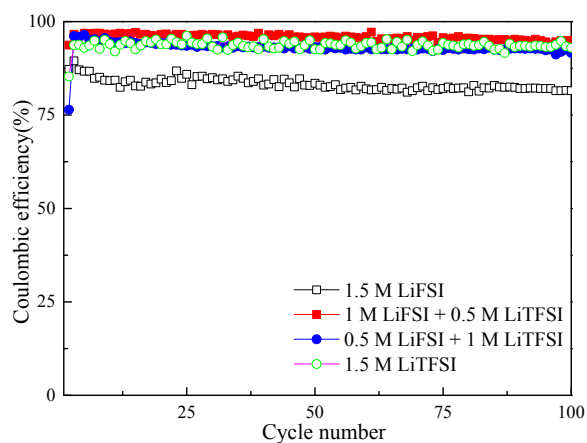


Fig. S9. The Coulombic efficiency of the sulfur cathode in various electrolytes

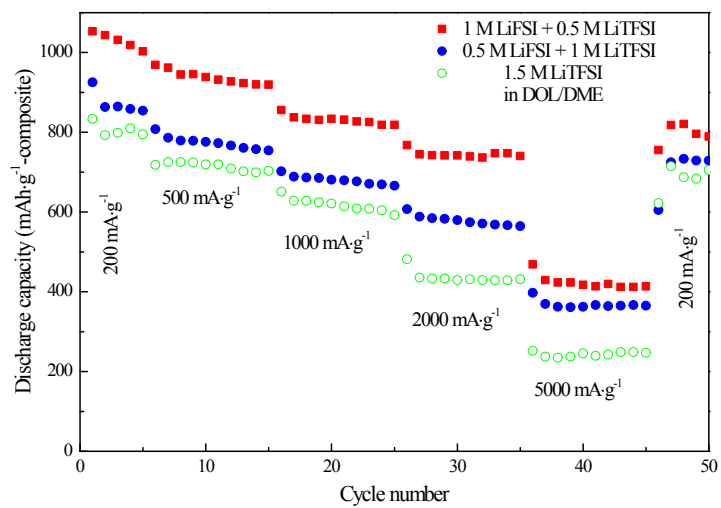


Fig. S10. The high-rate capability of the sulfur cathode in various electrolytes