Supplementary Materials for

2,4-difluorophenyl isothiocyanate as a redox mediator in the electrolyte for kinetically favorable Li-S batteries

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Experimental section

Electrolyte preparation

The blank electrolyte is 1 M bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt% lithium nitrate ($LiNO_3$) dissolved in the solvent mixture of 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (v/v = 1:1). Then 0.5 wt% DPIC (TCI, 99%) was further added to prepare the experimental electrolyte. All the above operations were conducted in a glove box filled with argon.

Characterization

UV-visible absorption spectroscopy (UV-3600) and Raman spectrum (Horiba LabRAM HR Evolution) were used for examining the change of sulfur species in the solution. Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet 6700) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250XI) were used for further studying the interaction between DPIC and Li_2S_6 in the solution. The surface and cross-section morphologies of the cycled Li anode were investigated by scanning electron microscopy (SEM, Zeiss Sigma 300). The chemical composition on the Li surfaces was analyzed by XPS. Liquid nuclear magnetic resonances (NMR) of various solutions were performed on Bruker 600 MHz system.

Electrochemical performance

The DPIC/Li cell was assembled by employing commercial carbon paper (CP) as a cathode current collector in which the liquid electrolyte (1M LiTFSI and 2 wt% $LiNO_3$ in DME/DOL mixed solvent) containing 0.5 wt% DPIC (named DPIC catholyte) was dropped. The cyclic voltammetry (CV) measurement of the DPIC/Li cell was performed on an electrochemical workstation (PARSTAT MC) in different potential windows at a scan rate of 1 mV s^{-1}.

The elemental sulfur and mesoporous carbon (CMK-3, XFNano) were mixed with a mass ratio of 7:3, and then heated to 155°C for 20 h to prepare S/CMK-3 composite. The sulfur cathode was made of the S/CMK-3 composite, conductive carbon (Super P, Timcal) and poly(vinylidene fluoride) (PVDF, Solef) in a weight ratio of 8:1:1 coated on a piece of Al foil. The typical sulfur loading on the cathode was 2.0~2.2 mg cm^{-2}.

The Li-S coin cell was assembled in a glove box, which was composed of a sulfur cathode and a Li metal anode separated by a piece of PP separator. The cell was cycled galvanostaticly on a LAND tester in the voltage range of 1.7~2.8 V. CV response of the Li-S cell was monitored on the electrochemical workstation at different scan rates. Electrochemical impedance spectrum (EIS) was measured in the frequency range from 10^5 to 0.01 Hz at perturbation amplitude of 5 mV.

For redox kinetics study, a symmetrical cell was employed with two identical carbon paper as the electrodes and 30 μL 0.5 M Li_2S_6 solution as the electrolyte. Another 10 μL electrolyte without/with DPIC was dropped on the separator. CV measurement of the symmetrical cell was carried out in the potential range of -1.0~1.0 V at a scan rate of 5 mV s^{-1}. Li_2S deposition experiment was measured in a coin cell employing carbon paper as the cathode and Li foil as the anode, In the assembly process, 20 μL 0.2 M Li_2S_8 solution was added in the cathode side and another 20 μL electrolyte without/with DPIC was dropped on the separator. The cell was first discharged at a constant current to 2.06 V, and then the potential was kept at 2.05V until the current was below 10^{-5} A for nucleation and deposition of Li_2S.

Supplementary figures

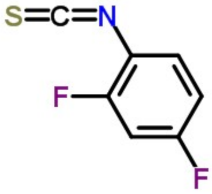

Fig.S1 The chemical structure of the DPIC

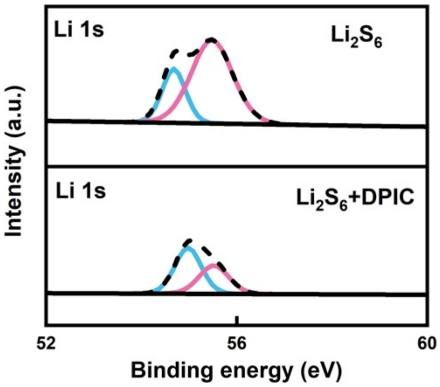

Fig.S2 Li 1s XPS spectra of Li_2S_6 solution with/without DPIC

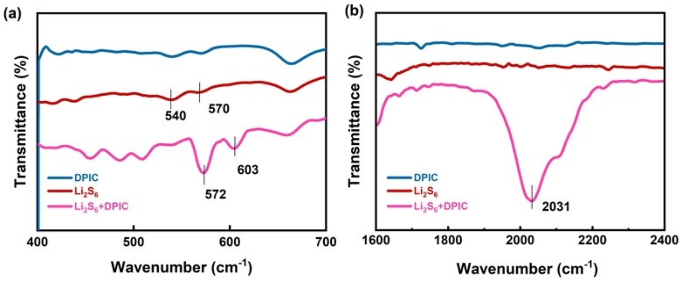

Fig.S3 FTIR spectra of the DPIC, Li_2S_6 and DPIC/Li_2S_6 mixture

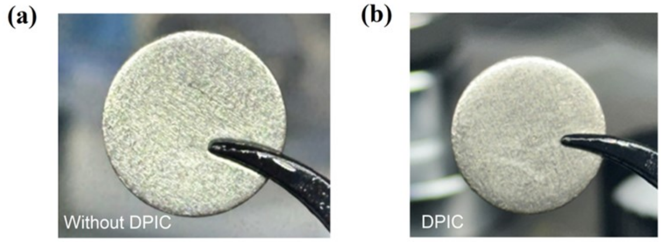

Fig.S4 Surface observation of Li metal after soaking in the electrolyte (a) without and (b) with DPIC for 7 days. The Li surface remains smooth and intact after soaking in the electrolyte with DPIC, and there is a negligible surface difference between the two cases.

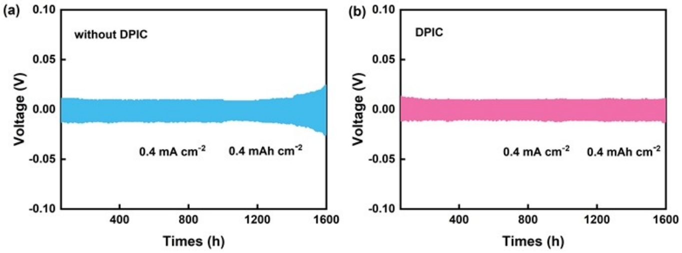

Fig.S5 Plating/stripping cycling tests of the Li symmetrical cells (a) without and (b) with DPIC. The Li symmetrical cell with DPIC delivers more stable plating/stripping cycling with a low overpotential over 1600 h at 0.4 mA cm^{-2} compared to the one without it.

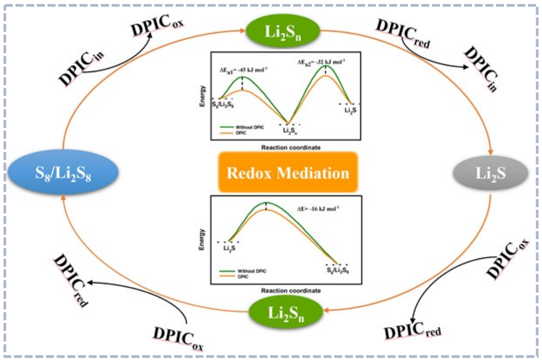

Fig.S6 Schematic diagram of DPIC mediated redox reaction in Li-S cell

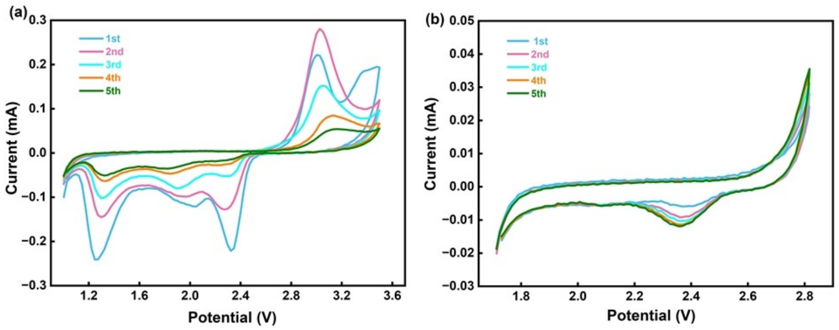

Fig.S7 CV curves of the DPIC/Li cell in the potential window of (a) 1.0~3.5 V and (b) 1.7~2.8 V, respectively (scan rate: 1 mV s^{-1})

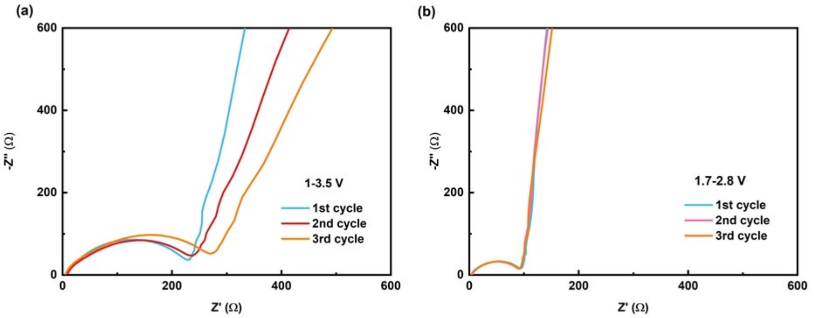

Fig.S8 EIS plots of the DPIC/Li cell during multiple CV scans in the potential window of (a) 1.0~3.5 V and (b) 1.7~2.8 V, respectively

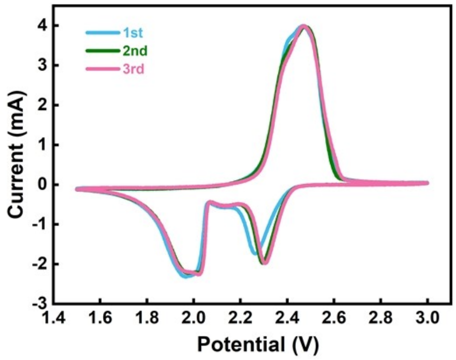

Fig.S9 CV curves of the DPIC@Li_2S_6/Li cell which employed a catholyte simultaneously containing Li_2S_6 and DPIC at a scan rate of 0.1 mV s^{-1}

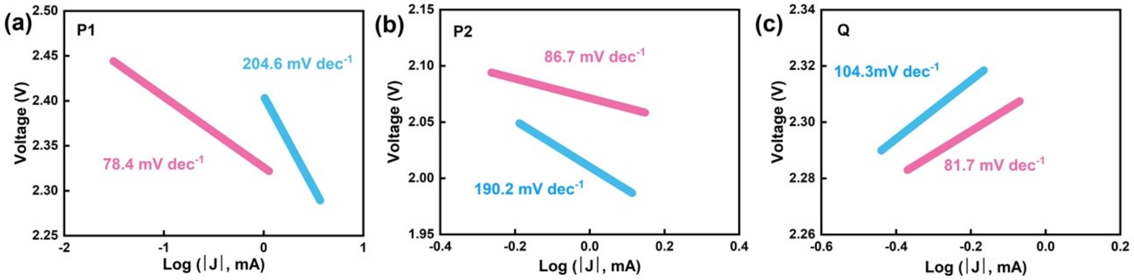

Fig.S10 Tafel plots for the redox peaks in the CV curves in Fig.2f

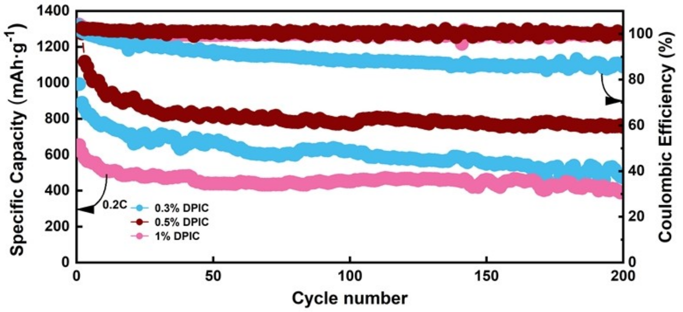

Fig.S11 Cycle performances of Li-S cells with different amounts of DPIC at 0.2C

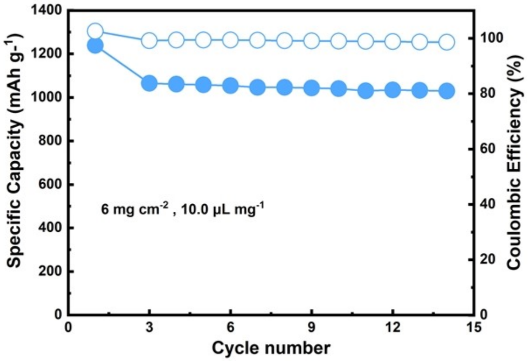

Fig.S12 Cycle test of the Li-S cell in the DPIC electrolyte at a sulfur loading of 6 mg cm^{-2} and E/S ratio of 10.0 μL mg^{-1} at 0.2C