Supplementary Information

To mitigate self-discharge of lithium–sulfur batteries by optimizing ionic liquid electrolytes

Lina Wang, Jingyuan Liu, Shouyi Yuan, Yonggang Wang* and Yongyao Xia*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China.

E-mail: ygwang@fudan.edu.cn; yyxia@fudan.edu.cn.

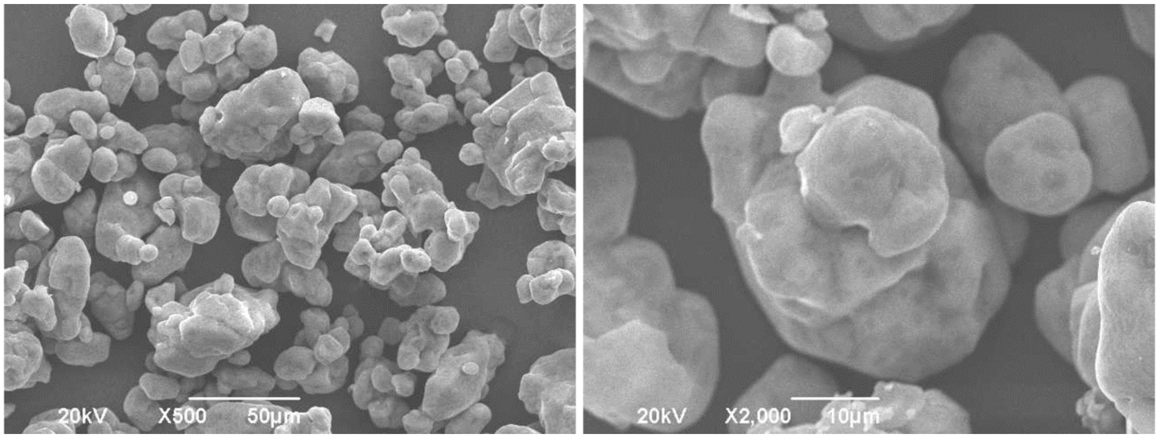

Fig. S1 SEM images of commercial pristine sulfur with low (left) and high (right) magnification.

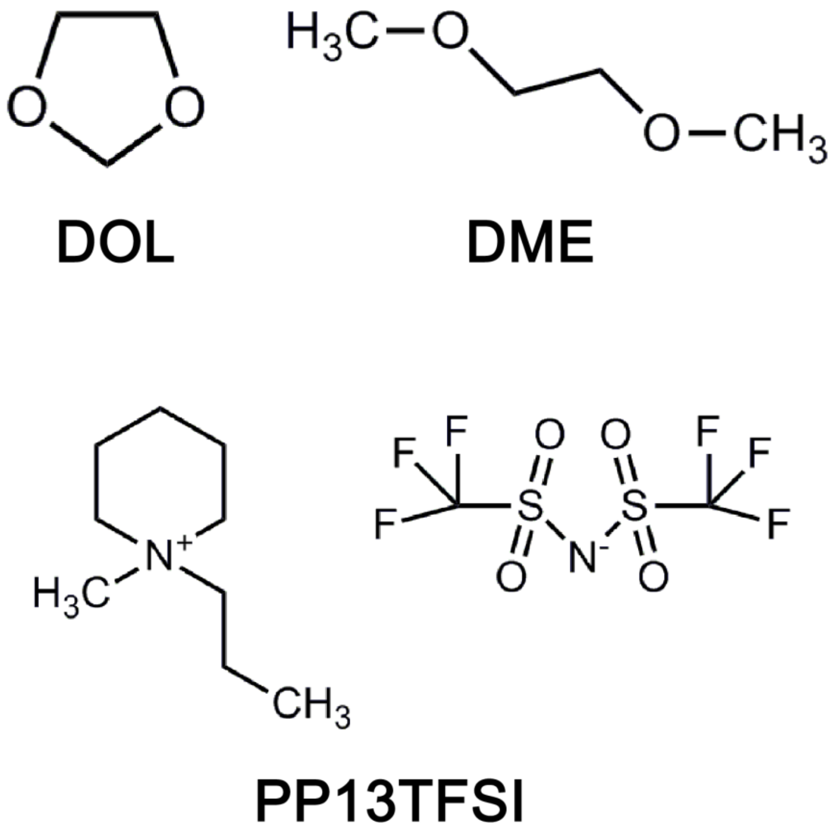

Fig. S2 Chemical formula of DOL, DME and PP13TFSI.

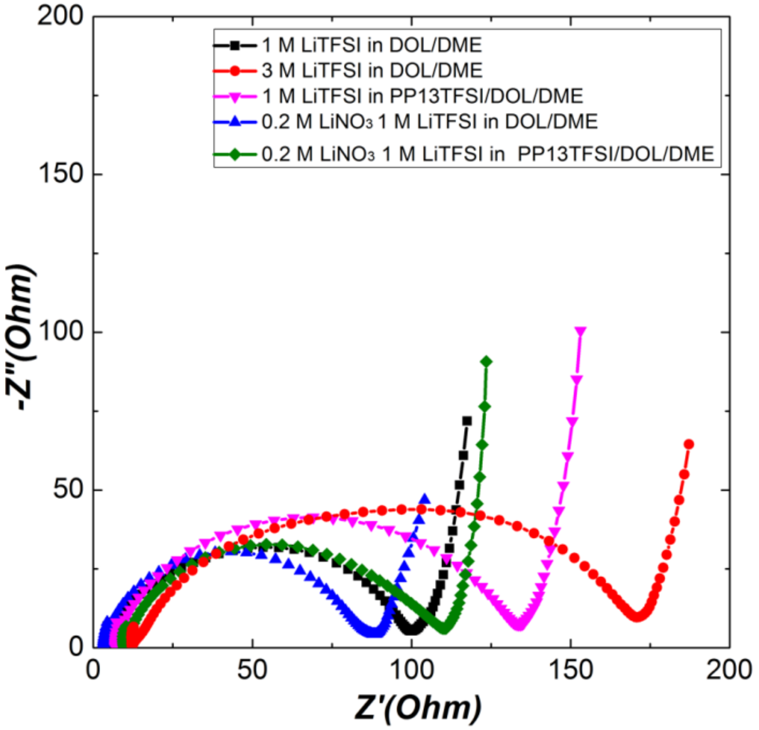

Fig. S3 Electrochemical impedance spectra (EIS) of as-prepared Li–S cells with electrolytes of DOL/DME (1/1, v/v)–1 M LiTFSI (black), DOL/DME (1/1, v/v)–3 M LiTFSI (red), PP13TFSI/DOL/DME (2/1/1, v/v)–1 M LiTFSI (magenta), DOL/DME (1/1, v/v)–0.2 M $LiNO_3$–1 M LiTFSI (blue), or PP13TFSI/DOL/DME (2/1/1, v/v)–0.2 M $LiNO_3$–1 M LiTFSI (olive).

The spectra in Fig. S3 comprise flat semicircles at the high medium frequencies as their main feature and a straight or slightly curved line at the low frequencies. The Z' values in these spectra, measured at the highest frequencies (i.e., the extrapolated intercept of the high frequency semicircle with the Z' axis), reflecting the solution impedance. The interfacial resistance in the Nyquist plot, indicated by the intersection of semicircles with the real (Z') axis at lower frequency, should be attributed to multilayer surface films that are formed in solutions on the active metallic Li due to its continuous reactions with solution species.

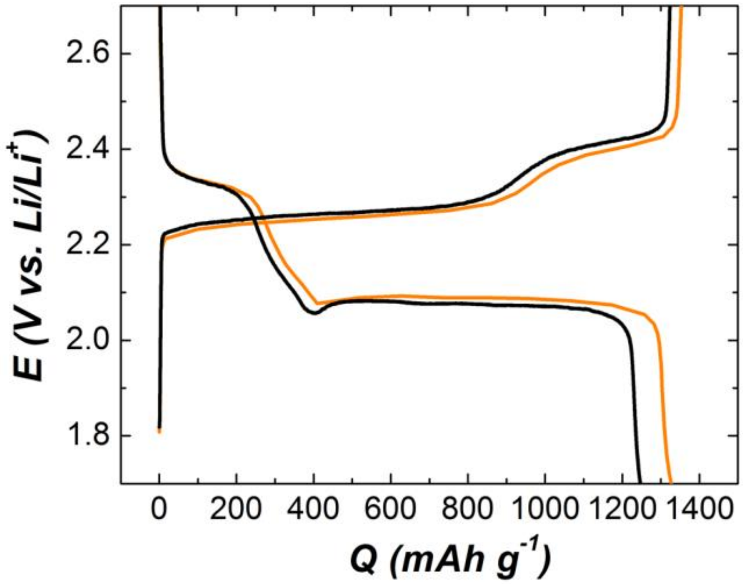

Fig. S4 Charge–discharge voltage profile of Li–S cell with a treated Li-metal electrode (orange line). Before integrated into the cell, the Li-electrode was immersed in solution of DOL/DME (1/1, v/v)–0.2 M $LiNO_3$–1 M LiTFSI, and then was rinsed by DME. The voltage profile of another cell using as-received Li-metal without pretreatment is also presented for comparison (black line). Both of the cells use DOL/DME (1/1, v/v)–1 M LiTFSI as electrolyte and operate at 0.2 C (1 C = 1672 mA g^{-1}).

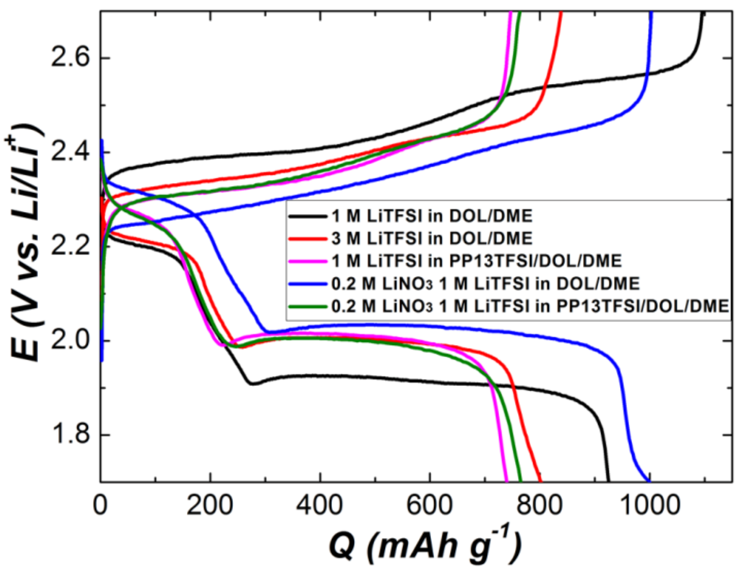

Fig. S5 Charge–discharge voltage profiles of Li–S cells at the 10th cycles with various electrolytes at the current rate of 0.5 C in voltage range of 1.7–2.7 V.

For comparation, a same discharge cutoff voltage of 1.7 V was applied to all the cell types. It has been reported $LiNO_3$ may be irreversibly reduced on positive electrode surface at lower potentials in DOL/DME.[1] Because the reduction products adversely affect the reversibility and capacity of Li−S battery, therefore, to raise the discharge cutoff voltage is always favorable for the long cycle life of the high energy density Li−S batteries.

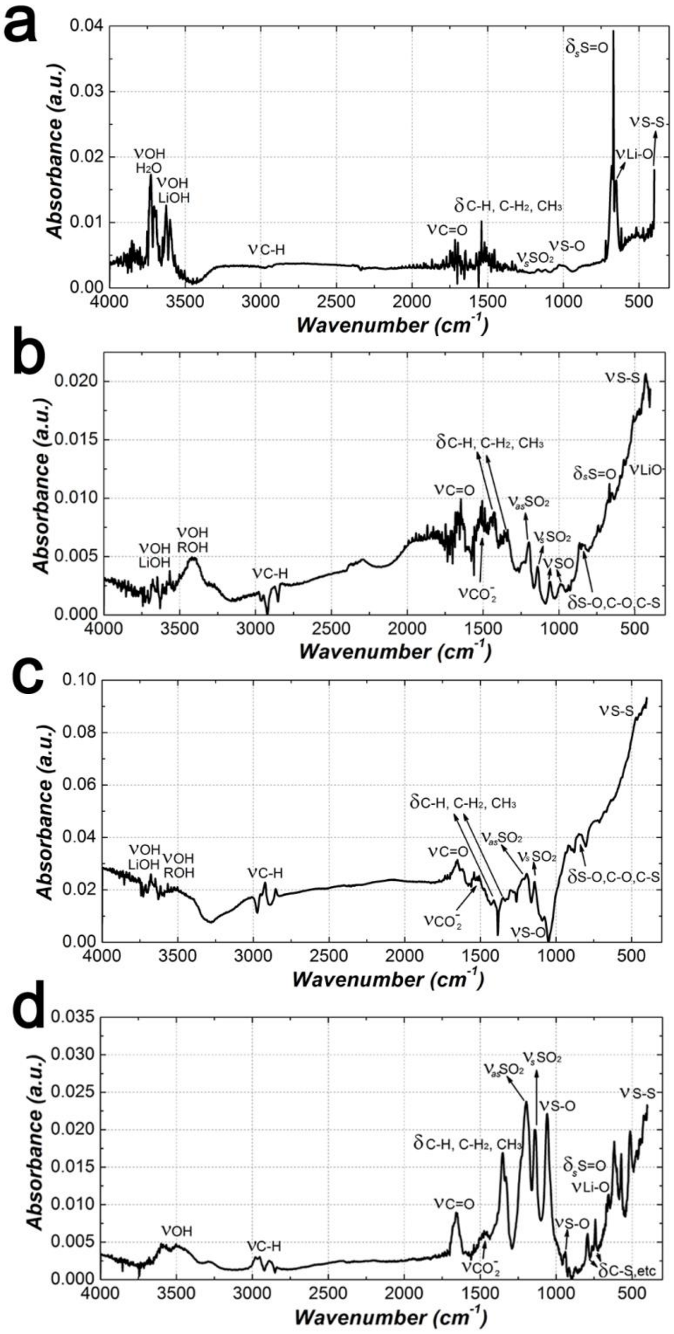

Fig. S6 FTIR spectra of Li-electrodes from cells cycled 10 times with (a) DOL/DME (1/1, v/v)–1 M LiTFSI, (b) PP13TFSI/DOL/DME (2/1/1, v/v)–1 M LiTFSI, (c) DOL/DME (1/1, v/v)–0.2 M $LiNO_3$–1 M LiTFSI, and (d) PP13TFSI/DOL/DME (2/1/1, v/v)–0.2 M $LiNO_3$–1 M LiTFSI.

Solubility measurements of Li_2S_8

The preparation of Li_2S_8 solutions was adopted from a method of Rauh et al.[2] Li_2S (99.9% purity, Alfa Aesar) and elemental sulfur (S_8) powders were mixed with a stoichiometric molar ration of 8:7 ($8Li_2S + 7S_8 \rightarrow 8Li_2S_8$) in a solvent of DOL/DME (1/1, v/v) or PP13TFSI/DOL/DME (2/1/1, v/v) in an Ar-filled glove box. The solutions were maintained at 25 ℃ for 24 h and then were centrifuged. To estimate the solubility of Li_2S_8 in DOL/DME, the precipitation was dried in vacuum for the evaporation of DOL/DME. The solubility of Li_2S_8 was estimated based on the weight difference of the precipitation and the reactants. To estimate the solubility of Li_2S_8 in PP13TFSI/DOL/DME, the weight of the supernatant liquid dissolved with Li_2S_8 was measured. The approximate solubility of Li_2S_8 was calculated based on the weight difference of solutions before and after dissolution of Li_2S_8 per volumetric 1 mL.

Reference

1. S. S. Zhang, *Electrochimica Acta*, 2012, **70**, 344–348.
2. R. D. Rauh, F. S. Shuker, J. M. Marston and S. B. Brummer, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1761−1766.