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Supporting Information

A solid-solid biphasic conversion Li-S battery revealed by coordinated carbonate electrolyte

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EXPERIMENTAL PROCEDURES

Materials

Battery grade DME, DOL, EC, DEC and LiTFSI were purchased from Shenzhen CAPCHEM Technology Co. Ltd. Hexafluoroisopropyl methyl ether (purity 99.99%) was obtained from Braunway Technology Co., Ltd. All solvents were dried using 4Å molecular sieves until the H_2O content is less than 20 ppm, as determined by Karl-Fischer titration. Electrolyte was prepared by dissolving desired amount of LiTFSI salt in a blend solution of EC and DEC (1:1, mass).

Characterizations

Conductivity measurements were carried out using a Metrohm 644 conductor meter at 20 ^oC in a thermos-stated container. The viscosity of the electrolytes was measured on a programmable viscometer (Brookfield) at 20^oC, and the temperature was controlled within ±0.5^oC using a Brookfield TC-502 oil bath. Thermo gravimetric analysis (TGA) was measured with a STA449 F3 Jupiter thermo gravimetric analyzer (NETZSCH), at a heating rate of 10 °C min^{-1} in nitrogen atmosphere.

Li_2S_8 was prepared as reported elsewhere[1]. Li_2S_8 was mixed with the electrolytes for three days at room temperature. Then the obtained supernatants were analyzed by nuclear magnetic resonance (NMR, Bruker BioSpin) and gas chromatography (GC, Agilent 7890B-5977A). SEM images of the sulfur cathode for the surface were obtained with a scanning electron microscope (Hitachi S-3400 N). XPS analysis was conducted on a Thermo VG Scientific ESCA Lab 250 XPS Microprobe system. UV-Vis measurements were carried out on a Cary 5000 UV-Vis spectrophotometry (Varian, America). Samples for the UV-Vis measurements were obtained by soaking the cycled sulfur cathodes in their corresponding electrolyte.

Electrochemical measurements

S/KB composite was prepared by a melting diffusion at 155 °C for 12 h, with a weight ratio of 3:1 of sulfur and Ketjen black. The slurry with 80 wt% S/KB composite,10 wt% acetylene black, 5 wt% Carboxy methyl cellulose (CMC) and 5 wt% Styrene-butadiene rubber (SBR) were cast onto aluminum foil. The sulfur electrode was cut into discs with14mm diameter after dried at 60 °C under vacuum for 12 h. The average sulfur loading is about 3.0 mg cm^{-2}. CR2032 coin cells with Li counter and reference electrodes were assembled in a glove box with oxygen and water contents less than 1 ppm. Celgard 2400 was used as the separator. The Li-S batteries were tested in a LAND CT2001A battery test system in a voltage range of 1.0~3.0 V (vs. Li/Li^{+}). Galvanostatic intermit tent titrations (GITT) was performed on a CHI660E electrochemical workstation (Chenhua), by alternating 0.1 C pulses (30min) with OCV periods (60 min). Li|Li and Cu|Li cells for Li plating/stripping were cycled at 1 mAcm-2for 1 hour. The cut-off voltage for Li stripping is 0.5 V vs. Li/Li^{+} for the Cu|Li cell.

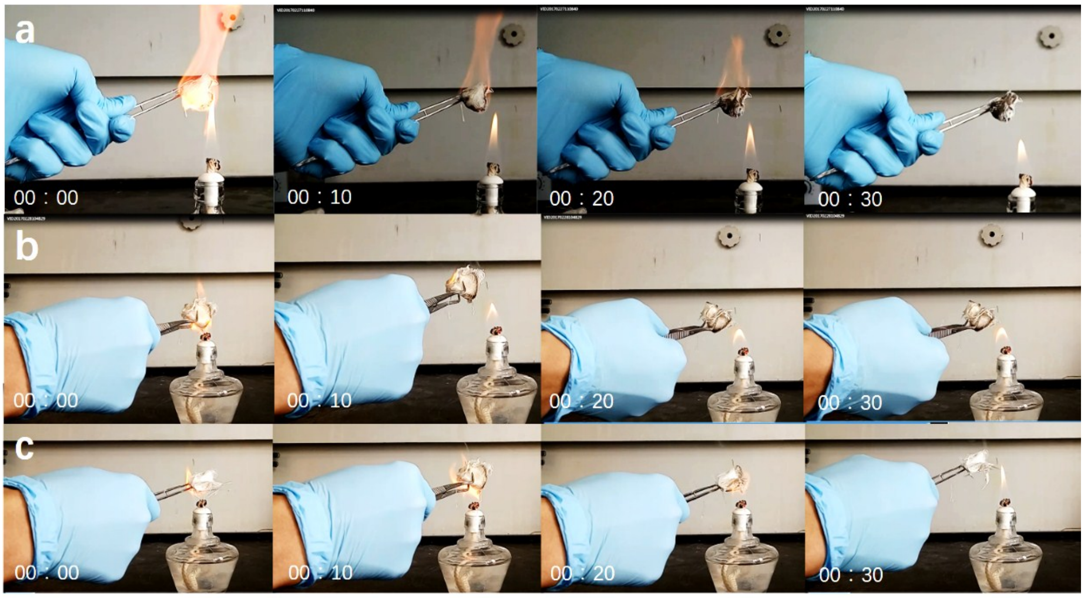

Figure S1 Flame tests of the electrolytes with the function of LiTFSI concentration. of (a) 1M electrolyte, (b) 6M electrolyte and (c) HFME-6M electrolyte. The self-extinguishing time of the dilute electrolyte is as long as 28s, which is much longer than that of the concentrated electrolyte (16s). The HFME-6M electrolyte can’t be burned completely due the introduction of the non-flammable HFME.

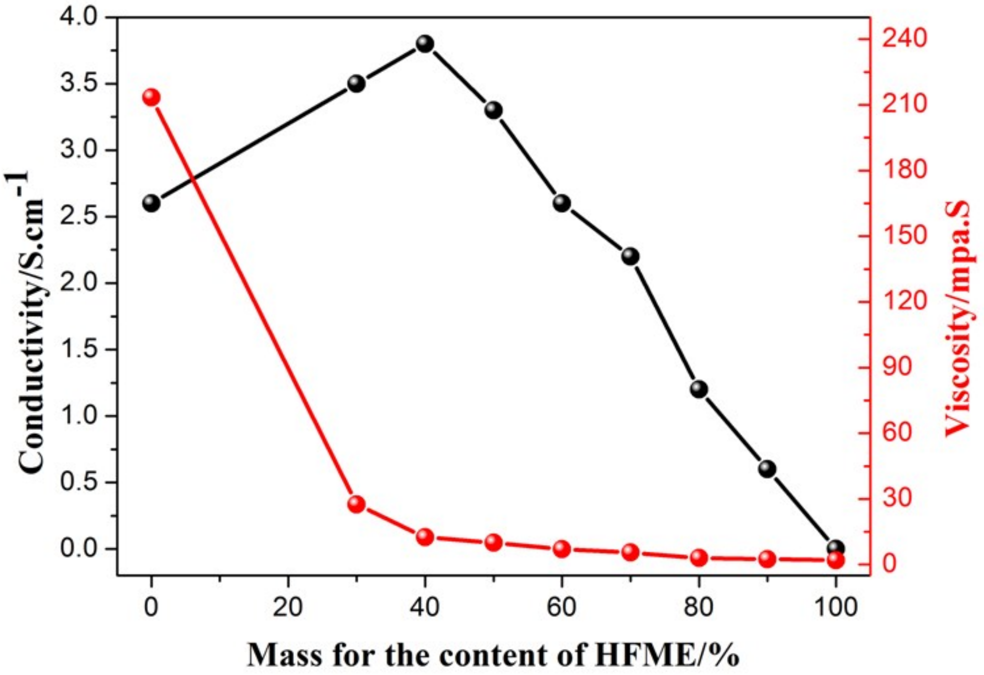

Figure S2 Conductivity and viscosity of the concentrated electrolyte with different content of HFME. Viscosity decreases evidently owing to the introduction of HFME, resulting in the improved conductivity. However, further increase of the HFME will results in a decrease in conductivity owing to the decreased concentration of Li^+.

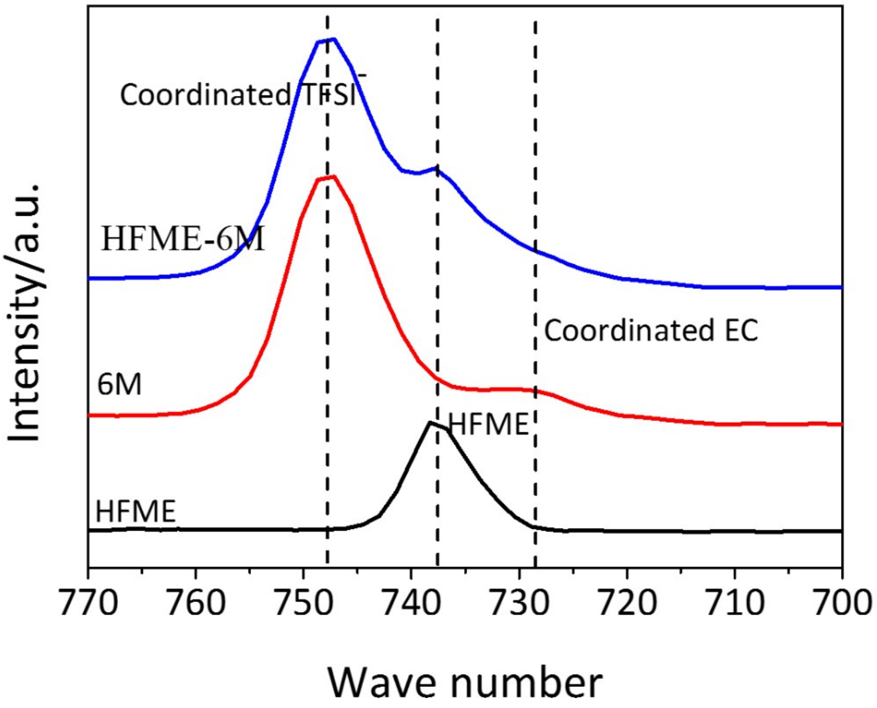

Figure S3 Raman spectra of HFME, 6M electrolyte and HFME-6M electrolyte.

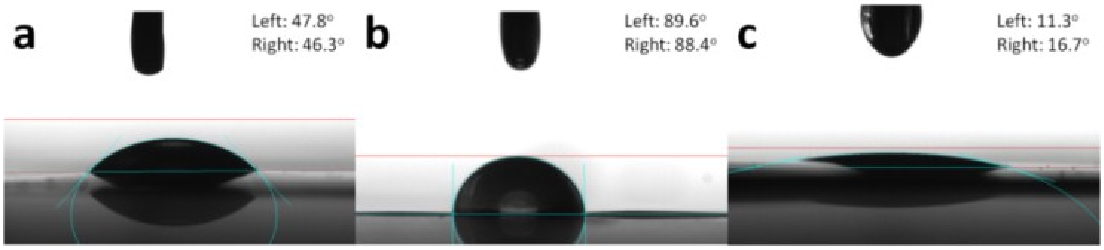

Figure S4 Contact angle measurements of the electrolyte on the Celgard 2320 separator.(a) 1M, (b) 6M and (c) HFME-6M.The contact angle of the 6 M carbonate electrolyte is poor as shown by the large contact angle (89°), which is attributed to its high viscosity. HFME provides better wettability with the separator and electrode, therefore the contact angle decreases to only around 15° for the HFME-6M carbonate electrolyte.

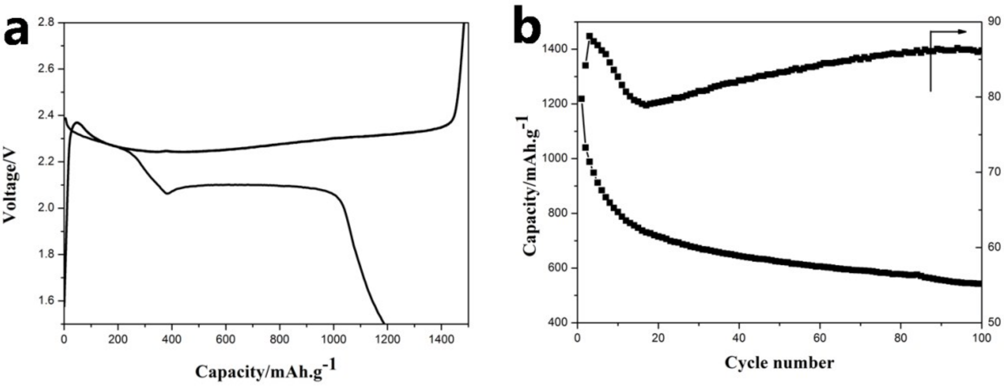

Figure S5 (a) The charge/discharge profile and (b) cycling performance of Li-S battery in 1 M LiTFSI in DOL-DME electrolyte.

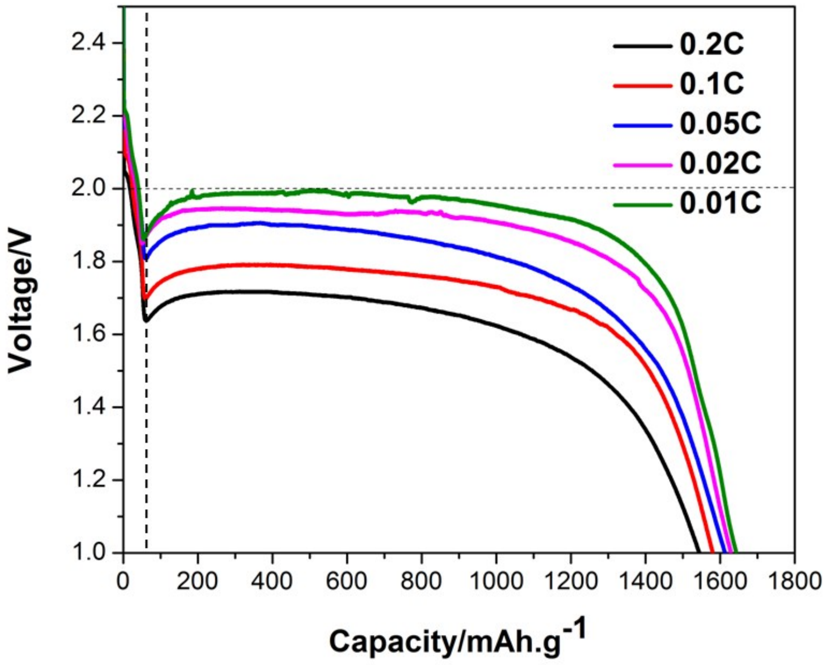

Figure S6 The first discharge profiles of Li-S battery in HFME-6M electrolyte at different rate. While the discharge plateau voltage increases evidently with the decrease of rate, the specific capacities corresponding to the plateau are similar. It is also shown that the length of the "slope" process is identical, which is independent of the rate.

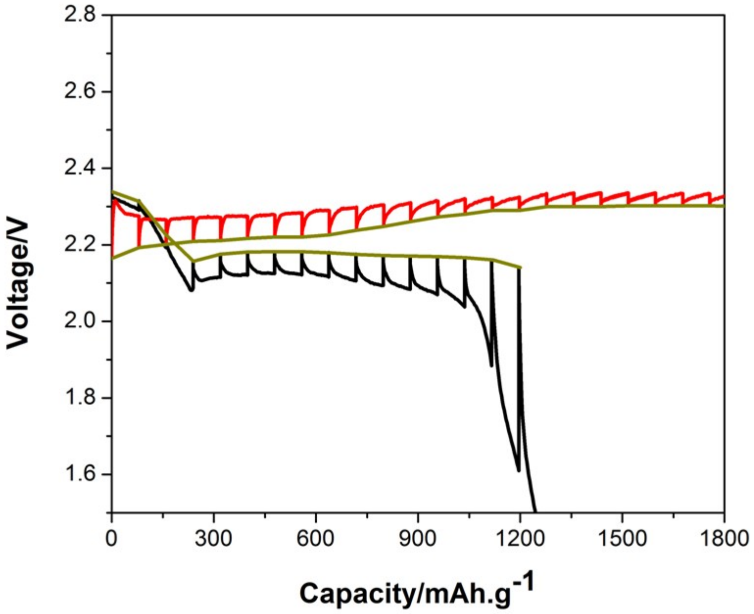

Figure S7 GITT experiments in 1 M LiTFSI in DOL-DME electrolyte. It shows two distinct plateaux profile at electrochemical equilibration. Shuttle effect is also demonstrated at the end of charge.

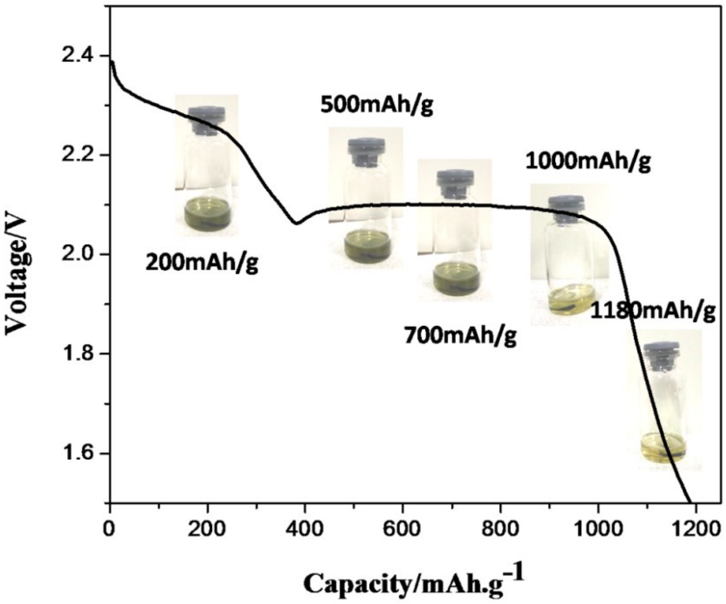

Figure S8 Pictures show the extracted polysulfides from the partially discharged electrode in the DOL/DME electrolyte. The extraction liquid is TEGDME.

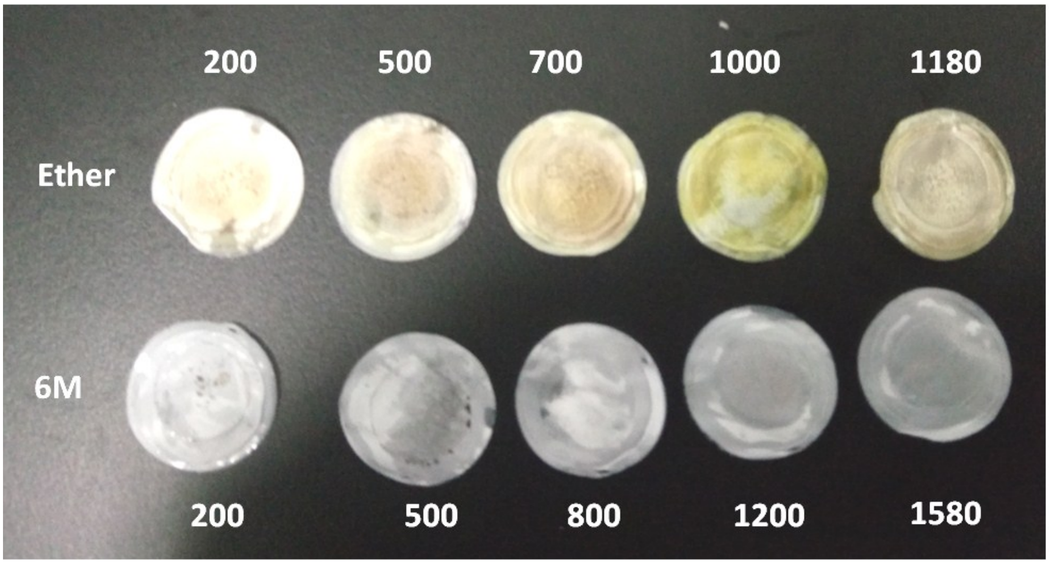

Figure S9 Pictures ofthe seperators recovered from the partically discharged cell in the DOL-DME electrolyte and 6M carbonate. Values in the picture indicate the discharge capacity, unit: mAh g^{-1}.

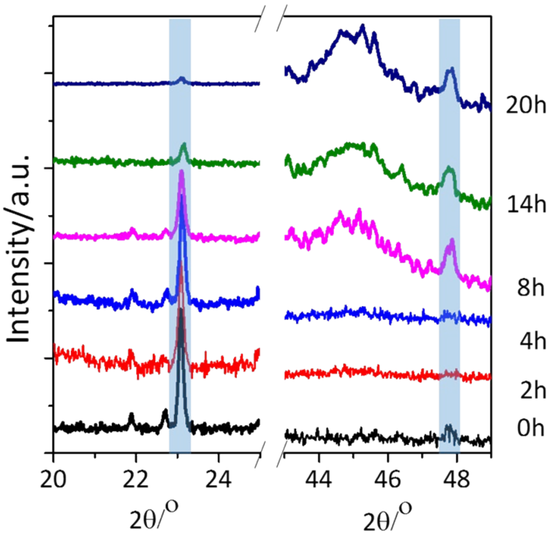

Figure S10 X-ray diffraction patterns of the electrode at different depth of discharge. Cells were discharged at a C rate of C/20, the time shown on the right stands for the discharge time.

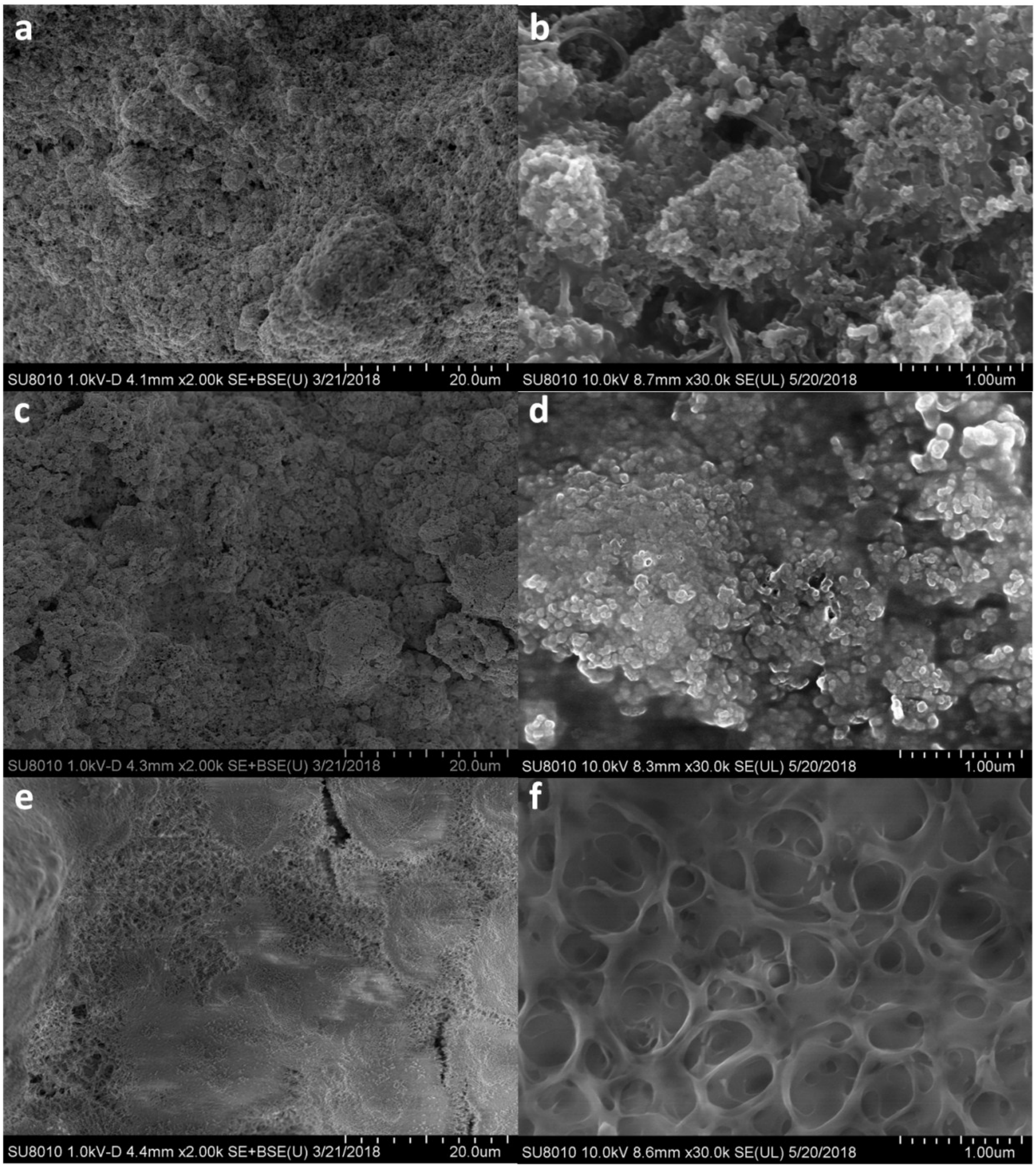

Figure S11 SME images of (a), (b) the fresh sulfur cathode, (c), (d) the cycled sulfur cathode in 6M carbonate, (e), (f) the cycled sulfur cathode in 1M carbonate.

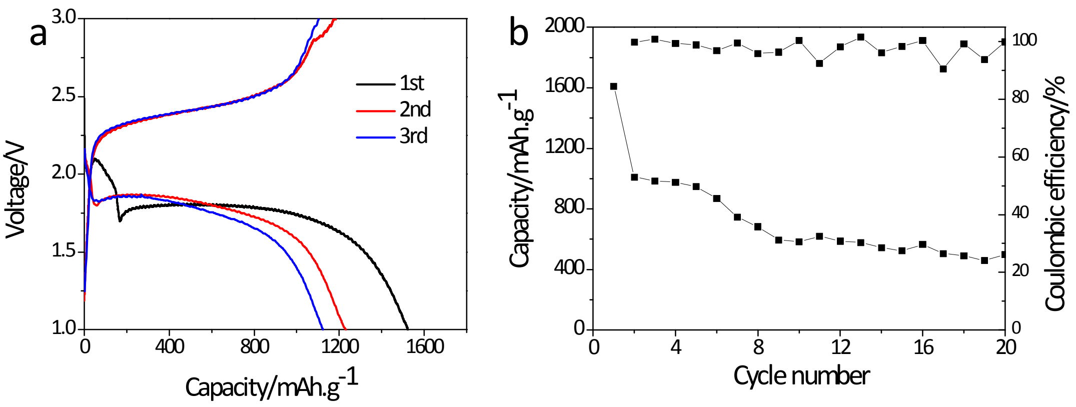

Figure S12 Electrochemical performance of the 4M $LiPF_6$ in carbonate (EC/DEC=1/1, w/w) electrolyte. (a) Voltage profile, and (b) cycling performance.

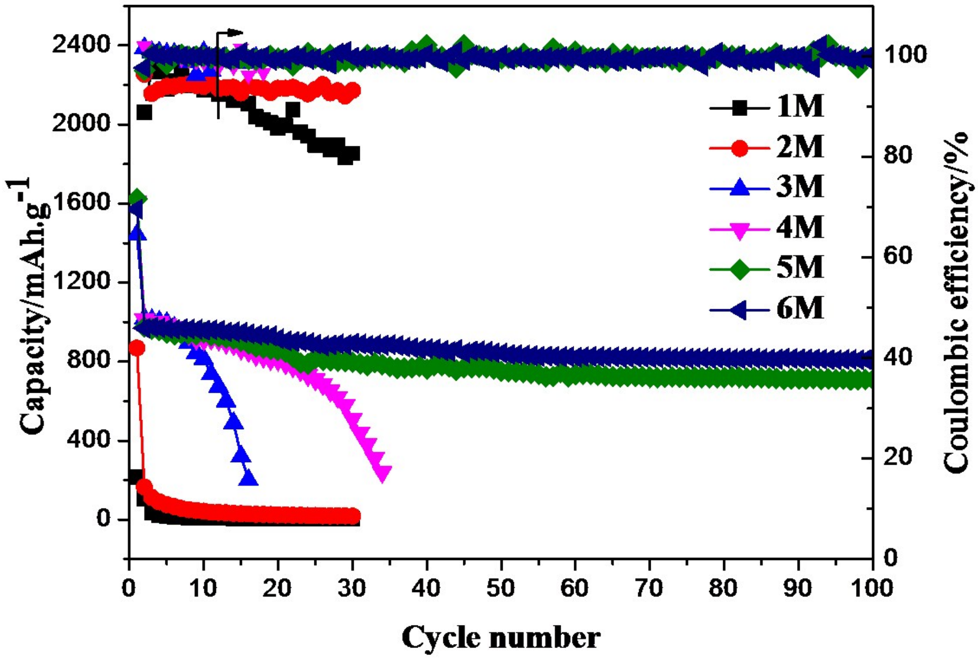

Figure S13 Cycling performance of Li-S cells at 0.2C in the various electrolytes. The E/S ratio is 12:1 μl/mg.

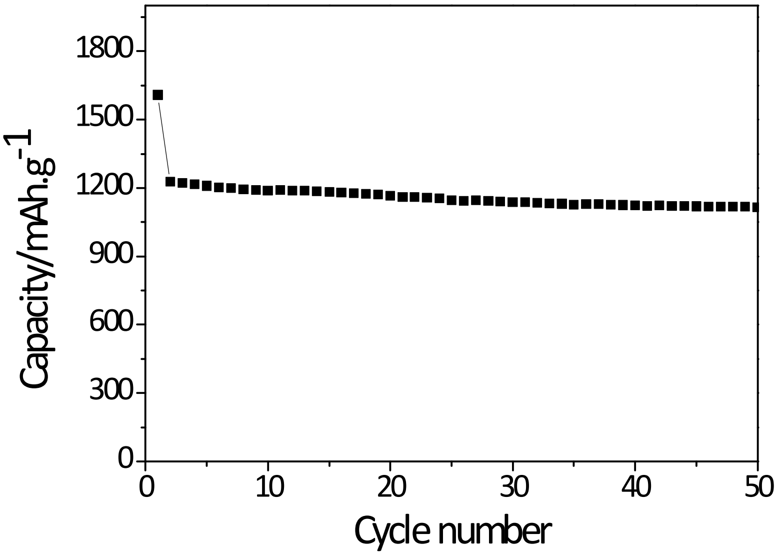

Figure S14 Cycling performance of Li-S cells in 6M carbonate, the cell was tested between 1.0 - 3.75 V.

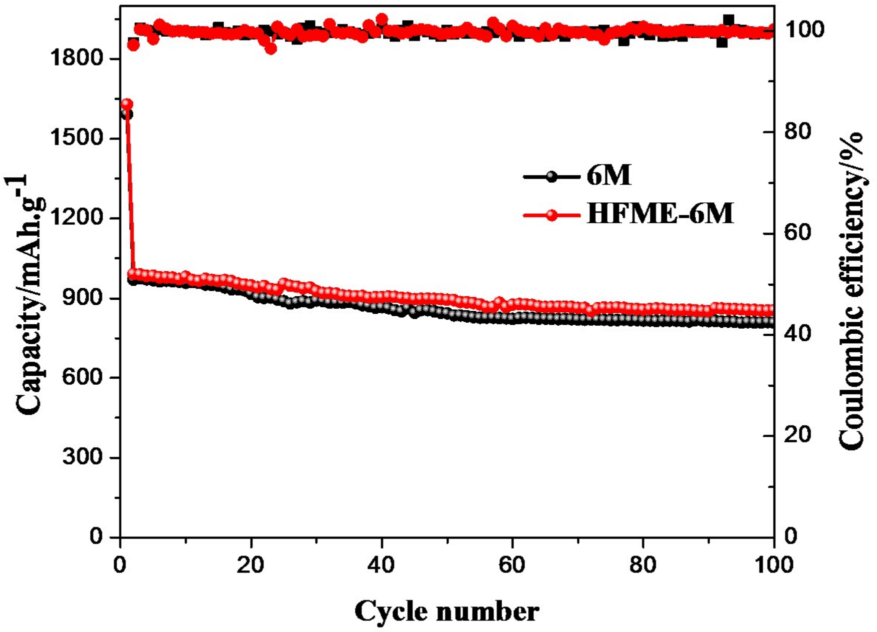

Figure S15 Cycling performance of Li-S cells in 6M and HFME-6M carbonate, the rate is 0.2C.

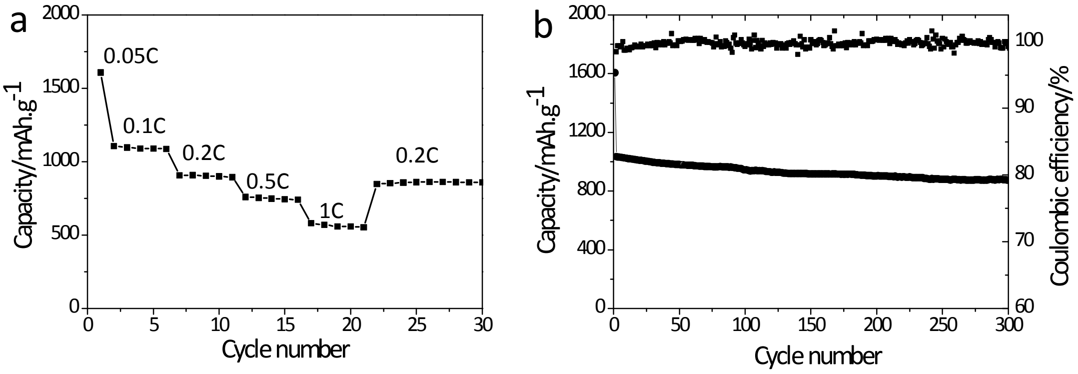

Figure S16 Cycling performance of Li-S cells in HFME-6M carbonate. (a) rate capability, and (b) long-term cycling performance at 0.1 C.

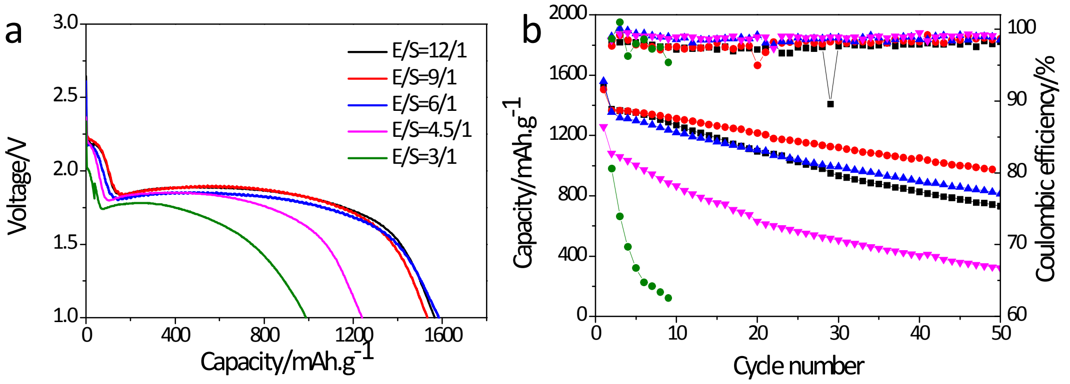

Figure S17 The cycling performance of Li-S batteries with varied E/S ratios at rate of 0.1C, the electrolyte is 7 M LiTFSI in ether (fully solvated, DOL/DME=1/1, w/w). (a) voltage profiles, and (b) cycling performance.

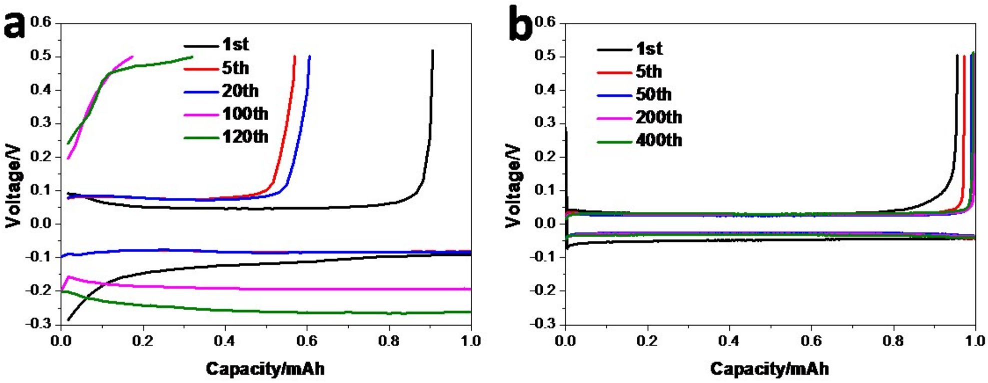

Figure S18 Voltage profiles of the Li/Cu cells cycled in 1M carbonate and HFME-6M carbonate. The current is 1 mA cm^{-1}, the cut-off voltage for Li stripping is 0.5 V vs. Li/Li^+.

1. Huang, F., Wen, G., Ma, Z., Jin, J., Xu, S., and Zhang, J. (2018). Enhancing metallic lithium battery performance by tuning the electrolyte solution structure. J. Mater.Chem. A 6, 1612.