

Electronic Supplementary Information

Effect of soluble sulfur species on electrochemical behavior of lithium–sulfur batteries with dual-phase electrolytes

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Experimental details

Preparation of Li–S cells

The catholyte-based Li–S cells are composed of two glass cylinders for the positive electrode and negative modules, respectively. A Li⁺-ion conductive glass-ceramic membrane, Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂ (LATP, thickness = 150 μm, ionic conductivity ≈ 10⁻⁴ S cm⁻¹ at 298 K, Ohara Corporation), is inserted between the positive electrode and negative modules. The preparation and assembly of the cells was conducted in an Ar-filled glovebox (<1 ppm of H₂O and O₂, Mikrouna). For the positive module, a current collector of Super P carbon (Timcal)-loaded Ti foil (99.5%, 0.2 mm in thickness, Nilaco) was stuck on one open end of each glass cylinder. The geometric area of the cast carbon was 9 mm in diameter. The tetrahydrofuran (THF, stabilizer free, 99.9%, Aladdin) solution containing soluble Li₂S_n and 1 M LiClO₄ (99.9%, Sigma Aldrich) is employed as catholyte. If not specially mentioned, Li₂S_n is prepared from reaction of 0.2 M S (99%, Wako Chemicals) with excess of metallic lithium (2Li + n/8S₈ → Li₂S_n) in THF. For the negative module, the Li-metal foil is immersed in 70 μL of ethylene carbonate/dimethyl carbonate (EC/DMC, 3/7, v/v) with 1 M of LiPF₆. The metallic Li foil in contact with on Cu mesh (Nilaco) was bonded with copper (Cu) foil. For a control experiment, the catholyte solution with soluble S₈ was prepared from a dissolution of 0.2 M sulfur (S) (99 %, Wako Chemicals) and 1m LiClO₄ (99.9 %, Aldrich) into THF. The total volume of the catholyte solution added into the positive glass module is 150 μL.

Electrochemical measurements

If not specially mentioned, the electrochemical measurements were performed at the room temperature of 25 °C. All electrochemical measurements were examined using a VMP3 battery tester (Biologic Claix) and the specific capacity values were calculated on the basis of mass of sulfur. Cyclic voltammogram (CV) and charge-discharge curves were acquired in the voltage range of 1.5–3 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy measurements were examined in the frequency range of 10⁻² to 10⁶ Hz at a voltage of 5 mV and displayed to Nyquist plot.

Characterization

The morphological information of carbon current collectors was attained from scanning electron microscopy (SEM, S-4800, HITACHI). Ultraviolet-visible absorption spectroscopy (UV-vis, UV-3600 spectrophotometer, Shimadzu) was used to examine the dissolved electrochemically active species in

electrolytes. The elemental analysis of catholyte solution containing Li_2S_n polysulfide and LiClO_4 was conducted on a inductive coupled plasma emission spectrometer (Shimadzu Corporation, ICPS-8100). The ^1H NMR was conducted on a Varian 600 MHz spectrometer at ambient temperature. To convert the sulfur species into Bz_2S_x ($x \geq 1$), the carbon current collectors after the 1st discharge were immersed in the mixture of BzCl/DME (1/1, v/v) and sonicated for 1 hour. It should be note that the cycled carbon current collectors were washed by DME to only preserve the solid products. Each sample was then allowed to sit for four days to be completely converted. After the solvent was evaporated, the samples were then mixed with chloroform-d and filtered out of polymer matrix. Finally, the filtrate was used for ^1H NMR analysis. As a control, commercial Li_2S powder was added to the mixture of BzCl/DME in the same manner and tested by ^1H NMR.

Table. S1 The elemental analysis of catholyte solution containing Li_2S_n polysulfide and LiClO_4 .

Element	Content (mg mL^{-1})	Sample amount (mL)
S	10.33	0.1
Li	10.02	
Cl	42.05	

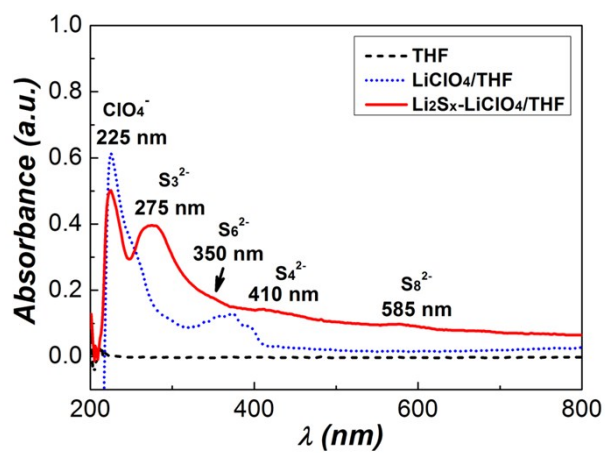


Fig. S1 UV-visible absorption spectra of LiClO_4 -THF solution (blue dot line) and the catholyte of Li_2S_x - LiClO_4 /THF solution (with dilution to allow the absorbance to reach an appropriate range). The pure THF solvent is used as a reference sample.

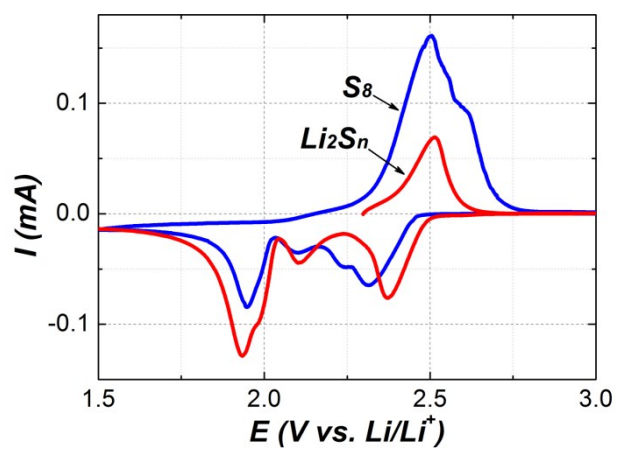


Fig. S2 The 1st cycle of cyclic voltammogram (CV) curves of Li-S cells with Li_2S_n (red line) and S_8 (blue line) catholytes in voltage range of 1.5–3 V (vs. Li/Li^+) at a sweeping rate of 0.01 mV s^{-1} .

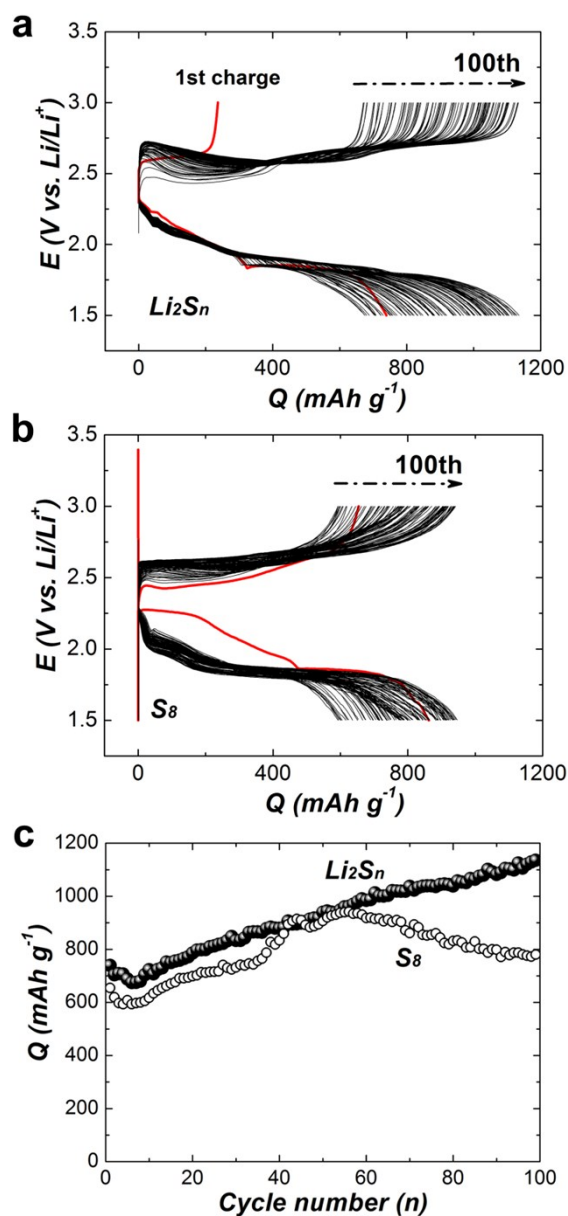


Fig. S3 Cyclic performance of Li-S cells with Li_2S_n catholyte or S_8 catholytes in voltage range of 1.5–3 V (vs. Li/Li^+) at a current rate of 0.2 C (1 C = 1672 mA g^{-1}). (a, b) Charge-discharge curves for 100-times cycling with (a) Li_2S_n and (b) S_8 catholyte. The initial cycles are marked in red. (c) Corresponding cycling profiles with respect to specific capacity. The specific capacity is calculated on the basis of mass of sulfur (S).

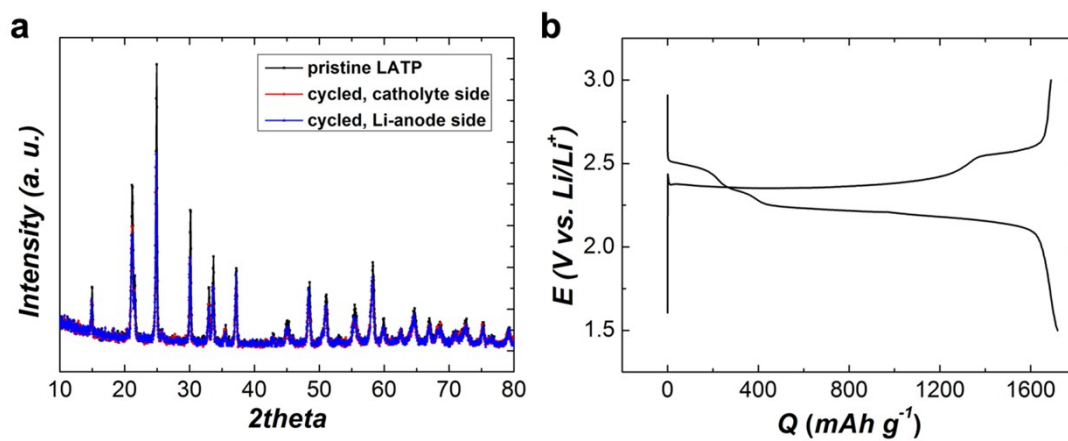


Fig. S4 (a) XRD patterns of LATP communicating with cathode (red) and anode (blue) electrolytes for 100 cycles accompany with the pristine one (black). (b) The typical galvanostatic charge/discharge profile of as-prepared Li-S cell with the recycled catholyte at a current density of 0.025 C.

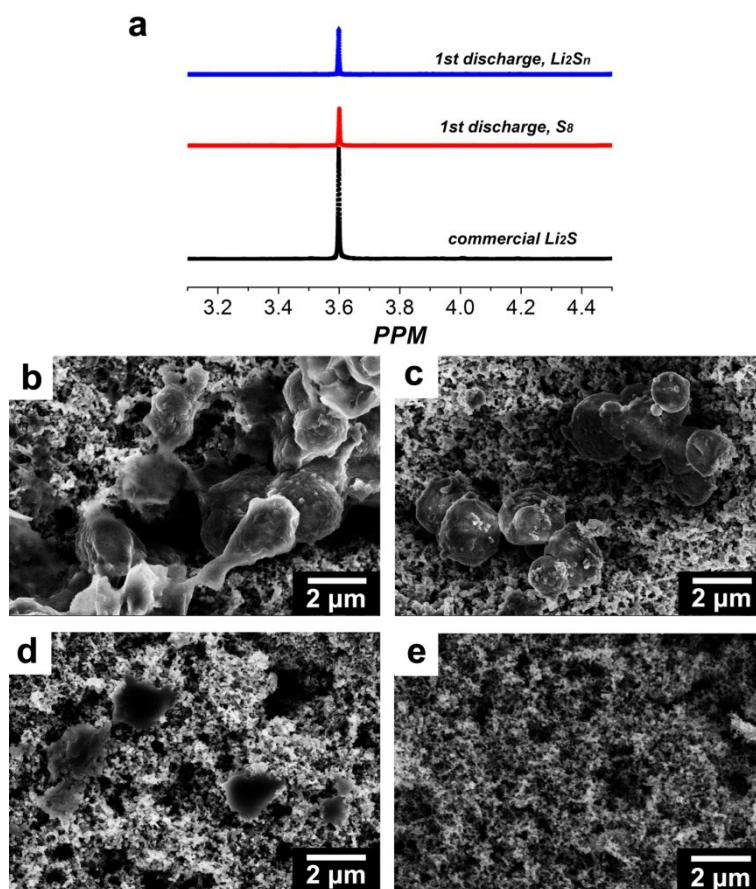


Fig. S5 (a) ^1H NMR spectra of the converted BzPS from commercial Li_2S powder, carbon current collectors for S_8 (red) and Li_2S_n (blue) after the 1st discharge. SEM images of carbon current collectors for the catholyte of (b, d) S_8 and (c, e) Li_2S_n . (b, c) After the 1st discharge. (d, e) After the subsequent recharge.

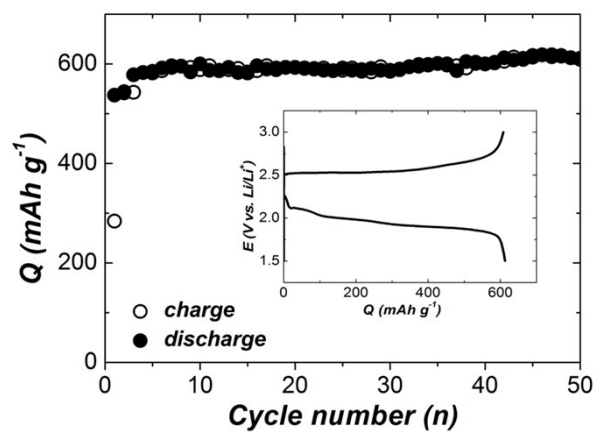


Fig. S6 Electrochemical cycling performance of the Li-S cell with a THF solution containing 1 M LiClO_4 and 1/8 M Li_2S_8 at 0.1 C for 50 cycles. The inset is representative charge-discharge profile upon the 50th cycle.