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Supporting Information

Electrochemical reactions of lithium-sulfur batteries: an analytical study using the organic conversion technique

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Contents

Abbreviations used in this Supporting Information

Bz: Benzyl, LC: liquid chromatography, MS: mass spectrometry, NMR: nuclear magnetic resonance spectrometry, UV/Vis: ultraviolet-visible absorption, HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital,

A. Experimental and theoretical mass spectra.

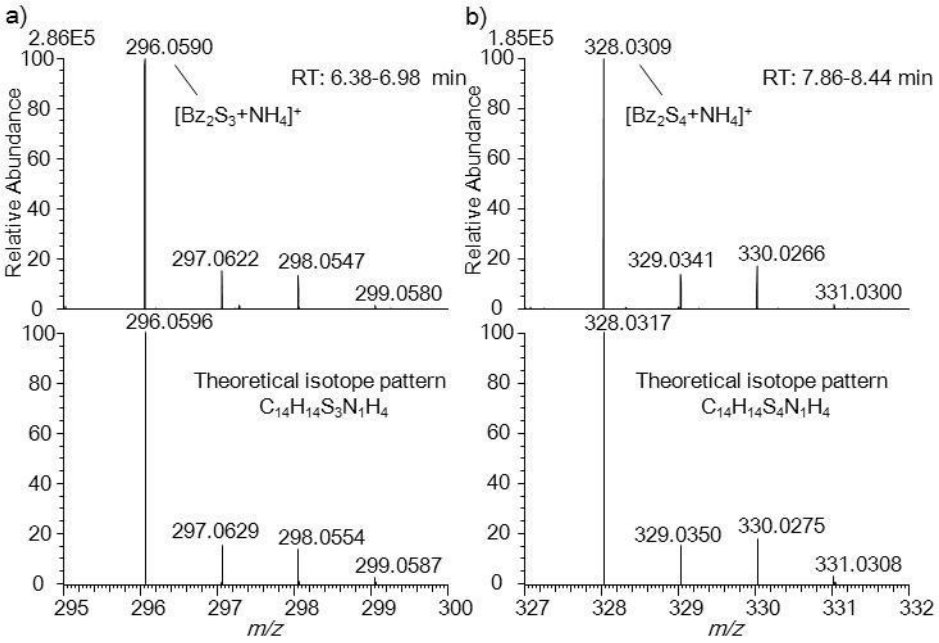

Fig. S1 Experimental mass spectra and the corresponding theoretical isotope patterns for ammonium adducts of benzylized polysulfides (a) Bz_2S_3 and (b) Bz_2S_4.

B. LC/MS results at measuring points during cell charge.

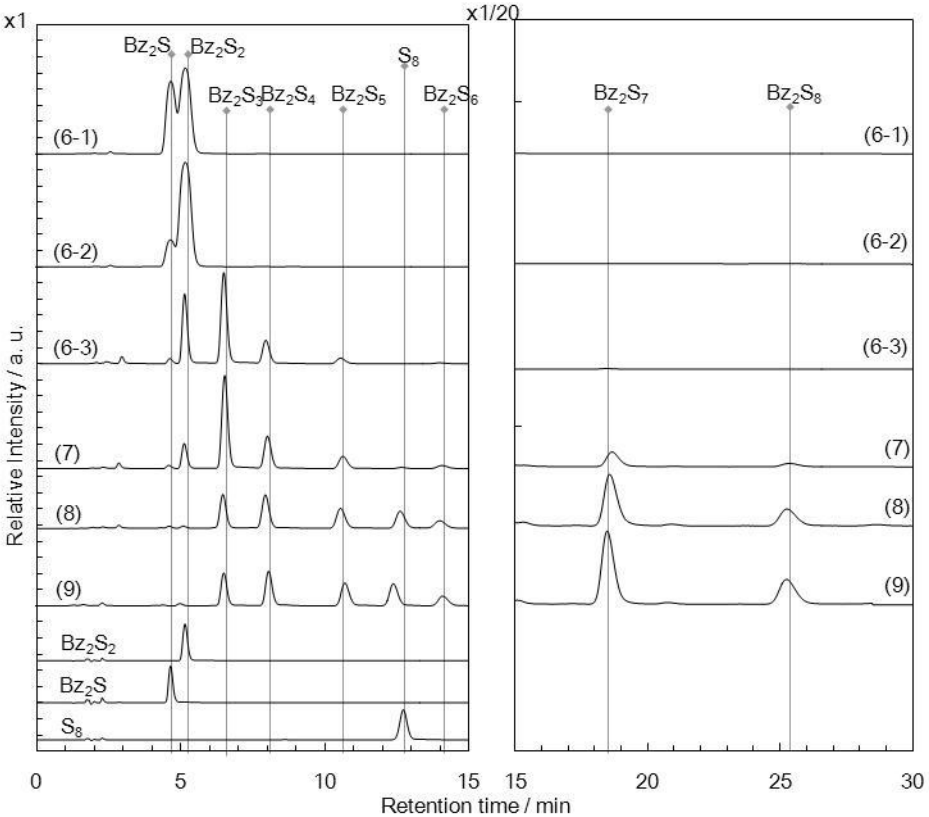

Fig. S2 LC data for points 5 to 9 with Bz_2S, Bz_2S_2 and S_8 as references.

C. Models for the calculations of ^{1}H NMR chemical shifts.

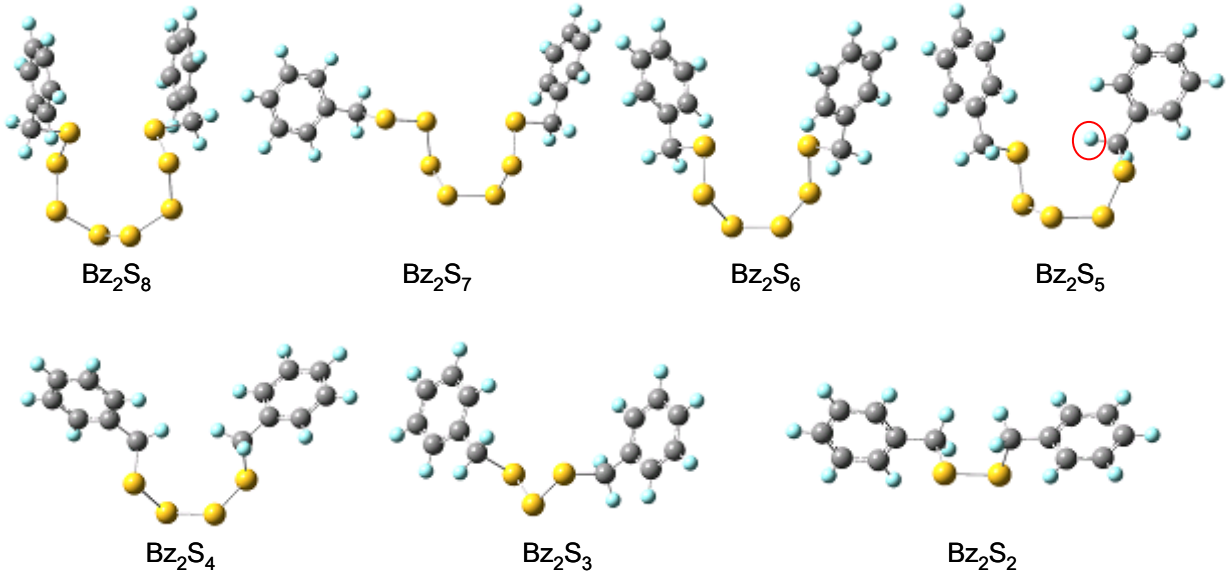

Fig. S3 Benzylized polysulfide models for calculation of ^{1}H NMR chemical shifts. (yellow, S; gray, C; and light blue, H) The methylene H in Bz_2S_5 circled in red is located close to the fifth S atom, resulting in a hydrogen-bond-like interaction.

D. UV-Vis spectra at measuring points during cell charge.

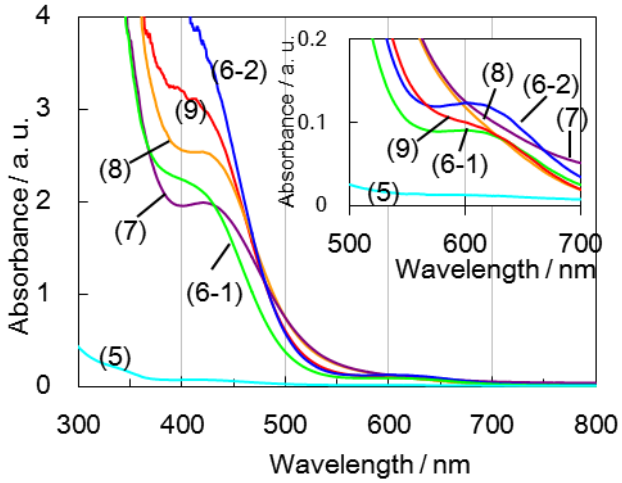

Fig. S4 Variations in UV-Vis spectra of electrolyte solutions over the charging process. Measuring points are shown in Fig. 1 of the text.

E. Models for the calculations of UV-Vis spectra.

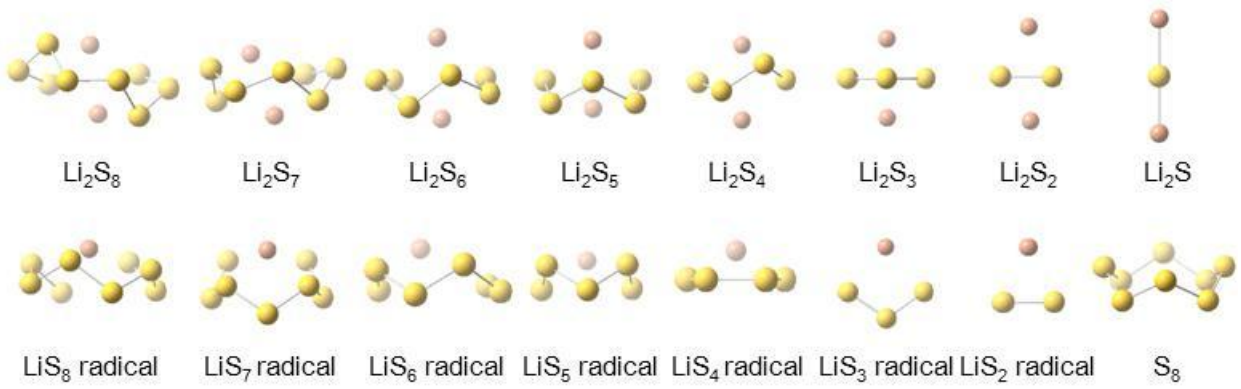

Fig. S5 Lithium-polysulfide, lithium-polysulfide radical and sulfur models for the calculations of UV-Vis spectra (yellow, S; and red, Li).

F. HOMO and LUMO levels of lithium polysulfide species.

Table S1. HOMO and LUMO levels, and the HOMO-LUMO gap (ΔHOMO-LUMO) of Li_2S_x, LiS_x radicals and S_8.

Closed-shell species

	Li_2S	Li_2S_2	Li_2S_3	Li_2S_4	Li_2S_5	Li_2S_6	Li_2S_7	Li_2S_8	S_8
LUMO / eV	−0.25	−0.69	−1.13	−1.40	−2.16	−1.90	−2.80	−2.69	−2.75
HOMO / eV	−4.77	−4.66	−4.91	−5.47	−5.78	−5.68	−6.24	−6.02	−7.40
ΔHOMO-LUMO / eV	4.52	3.97	3.78	4.07	3.63	3.78	3.43	3.34	4.65

Radical species

	LiS_2·	LiS_3·	LiS_4·	LiS_5·	LiS_6·	LiS_7·	LiS_8·
β -LUMO / eV	−3.28	−3.52	−3.65	−4.07	−2.26	−4.06	−3.85
β -HOMO / eV	−5.27	−6.32	−5.78	−5.82	−5.70	−6.01	−6.33
ΔHOMO-LUMO / eV	1.99	2.80	2.13	1.75	3.44	1.95	2.48

G. Color change as a result of conversion from Li_2S_x to Bz_2S_x

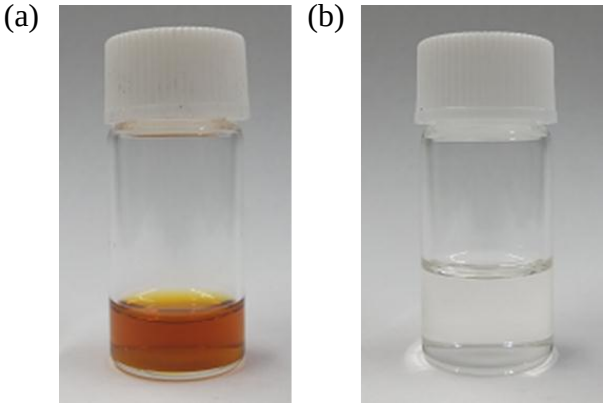

Fig. S6 (a) Li_2S_x (x = 3 to 8) solution and (b) Bz_2S_x solution. One ml of Li_2S_x solution becomes transparent within one minute of the addition of 1 ml of benzyl chloride, indicating immediate conversion of Li_2S_x to Bz_2S_x. The red color of the Li_2S_x solution well correlates with UV-Vis spectra in Fig. 4 of the text.

H. Conversion behavior of Li_2S_x (x= 3 to 8) and instability of long Bz_2S_x (x= 6 to 8)

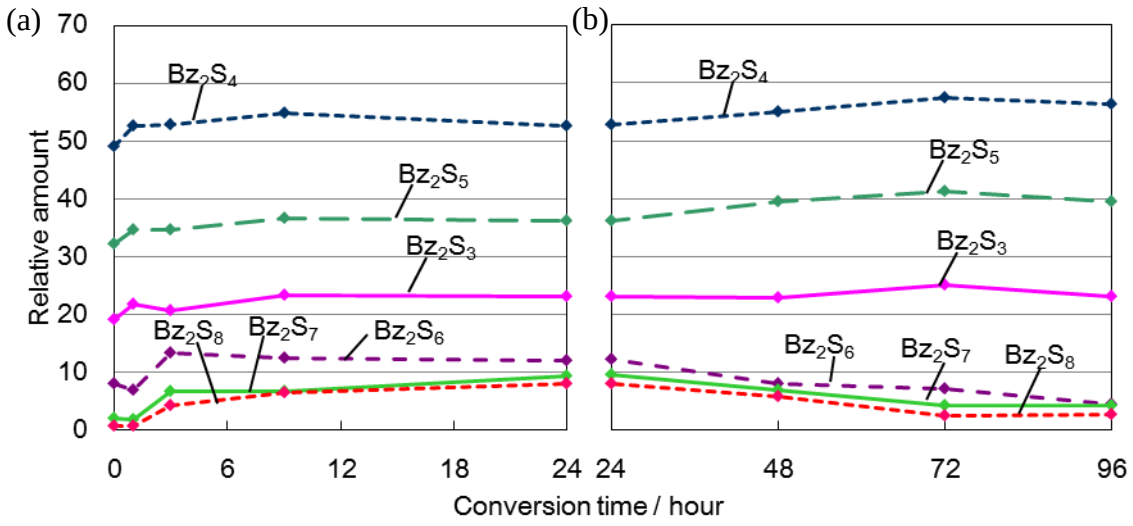

Fig. S7 Relative amounts of Bz_2S_x from Li_2S_x (x=3 to 8) against conversion time. The benzyl chloride was added at zero hour. Li_2S_x mixture was prepared by reaction of S_8 and Li_2S (S_8:Li_2S = 7:8 molar ratio) in DME and filtration. Relative amounts were estimated from LC peak area using the calculated relative absorbance at 254 nm. (a) The conversion of Li_2S_x (x=3 to 8) is almost complete within three hours. (b) The longer Li_2S_i (i = 6 to 8) are split to shorter Li_2S_j (j = 3 to 5) after 24 hours (one day).

I. Conversion behavior of Li_2S.

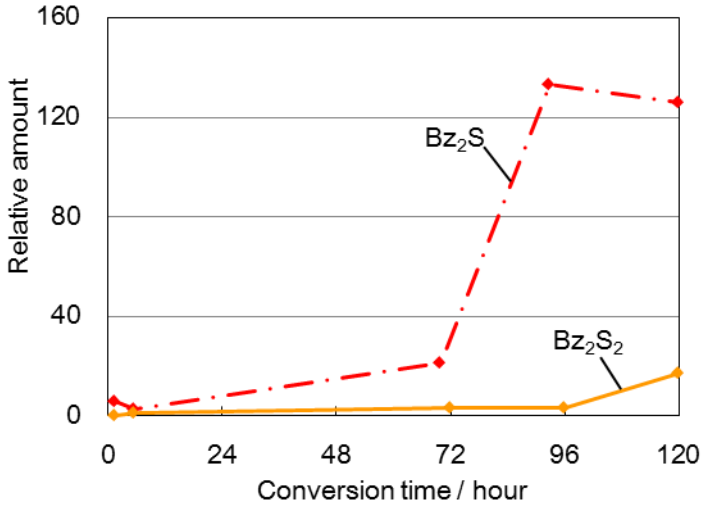

Fig. S8 Relative amounts of Bz_2S and Bz_2S_2 converted from Li_2S against conversion time. The benzyl chloride was added at zero hour and the solvent was DME. Relative amounts were estimated from LC peak area, using calibration curves. The Bz_2S maximum is around 96 hours (four days). After the Bz_2S maximum, Bz_2S_2 appears, indicating Li_2S coalesces to Li_2S_2.