

Supporting Information:

In-situ Raman Spectroscopy of Sulfur Speciation in Lithium-Sulfur Batteries

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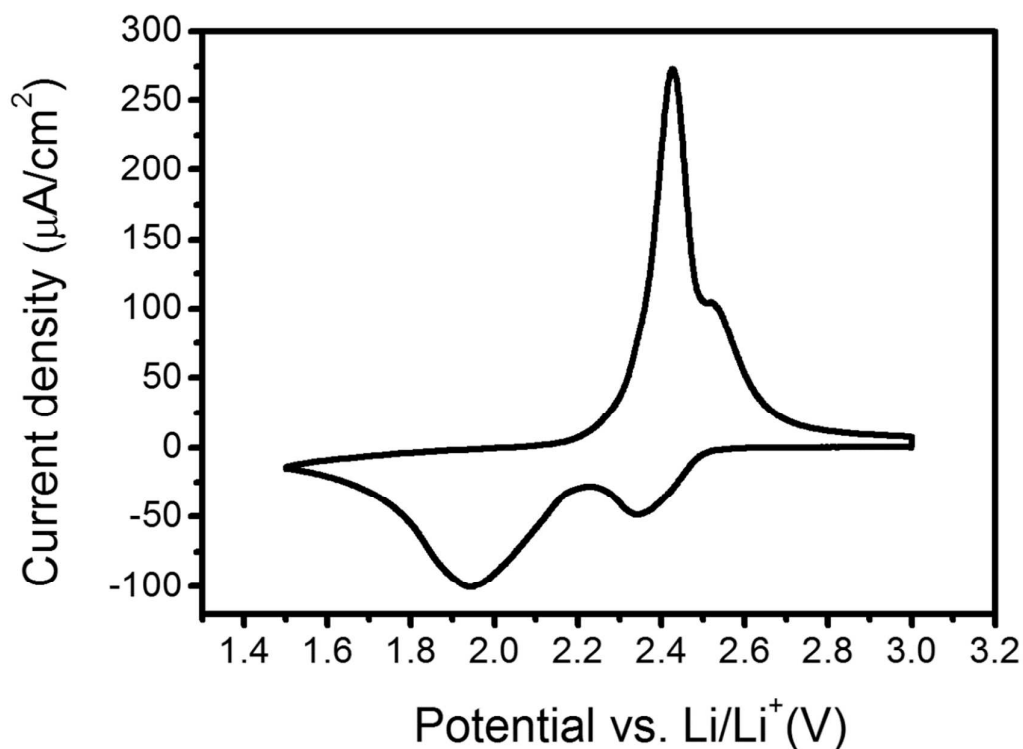


Figure S1. Cyclic voltammetry of the as-prepared sulfur-carbon cathode at a scan rate of 20 $\mu\text{V}/\text{s}$ in a coin cell.

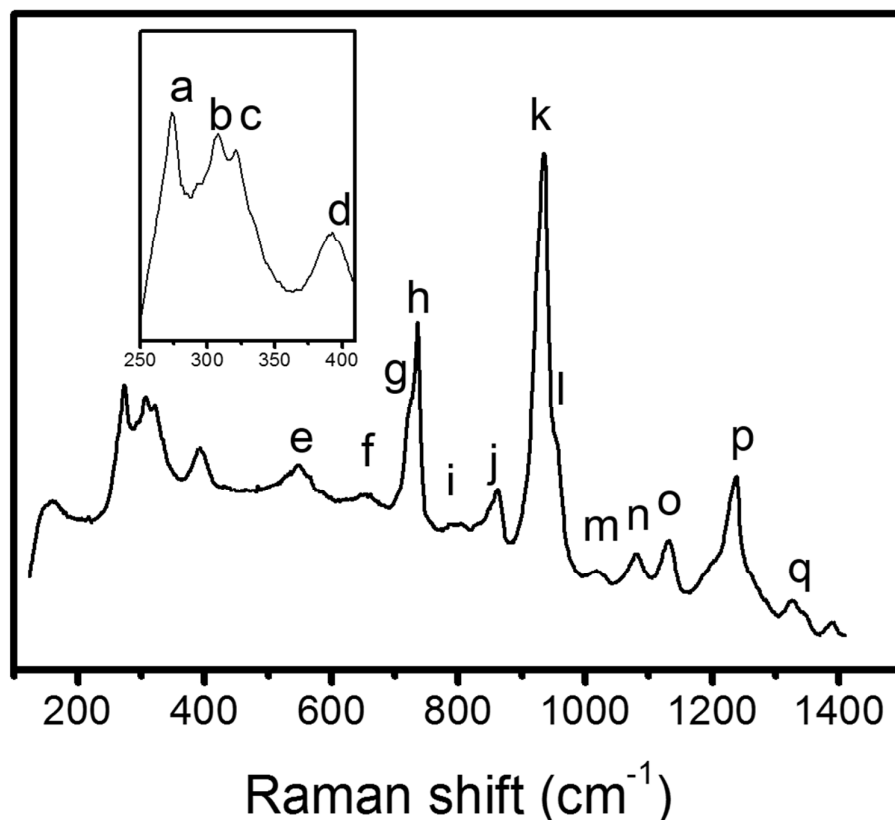


Figure S2. In-situ Raman spectra of the sulfur-carbon cathode shown at 3.2 V in 1M LiTFSI with TEGDME/DIOX (1:1, by vol).

Peak label	Peak position (cm ⁻¹)	Assignment (cm ⁻¹)
a	273	CF ₃ (rocking mode from TFSI ⁻)
b	307	SO ₂ (rocking mode from TFSI ⁻)
c	321	SO ₂ (rocking mode from TFSI ⁻)
d	392	SO ₂ (wagging mode from TFSI ⁻)
e	522-573 (broad peak)	O-C-C (bending mode from TEGDME) CF ₃ (bending mode from TFSI ⁻)
f	644-661 (broad peak)	SNS (bending mode from TFSI ⁻) Ring deformation from 1,3-Dioxolane
g	722	C-O-C (bending mode from 1,3-Dioxolane)
h	735	CF ₃ (bending mode from TFSI ⁻)
i	782-810 (broad peak)	C-S (stretching mode from TFSI ⁻)
j	863	CH ₂ (rocking mode from TEGDME)
k	934	C-O + C-C (stretching mode from 1,3-Dioxolane)
l	955	C-O (stretching mode from 1,3-Dioxolane)
m	1023	C-O stretching from TEGDME
n	1080	C-O stretching and CH ₂ rocking mode from 1,3-Dioxolane
o	1132	SO ₂ (stretching mode from TFSI ⁻)
p	1237	CH ₂ (twisting mode from 1,3-Dioxolane)
q	1325	CH ₂ (wagging mode from 1,3-Dioxolane)

Table S1. Vibrational frequencies and assignments for TFSI⁻, TEGDME and DIOX as shown in Figure S2.¹⁻⁴

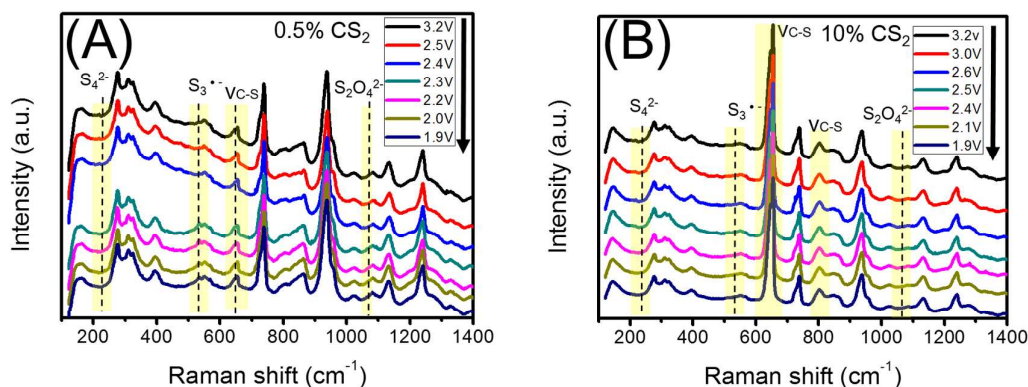


Figure S3. In-situ Raman spectra of sulfur-carbon cathode obtained during discharge with (A) 0.5% CS₂ additive and (B) 10% CS₂ additive (by vol.) at 3.2 V.^{5,6}

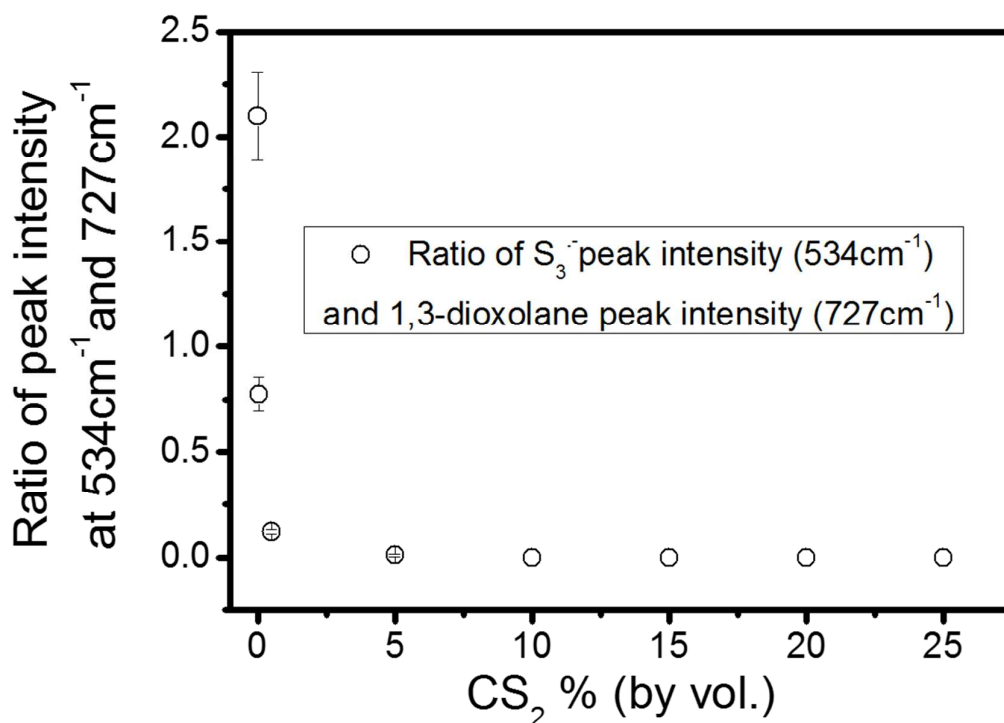


Figure S4. The ratio of maximum peak intensity for S₃²⁻ (534 cm⁻¹) and C-O-C bending mode of 1,3-dioxolane (727 cm⁻¹) were plotted as a function of different amounts of CS₂.

Figure S4 shows the peak intensity ratio of the S₃²⁻ peak at 534 cm⁻¹ and the C-O-C bending mode of 1,3-dioxolane at 727 cm⁻¹ as a function of different amounts of added CS₂. The intensity of the 1,3-dioxolane peak at 727 cm⁻¹ is constant and can

be used as an internal standard. This result shows the formation of S_3^{2-} in the second anodic peak is suppressed with CS_2 addition. The ratio quickly drops with addition of as little as 0.05% CS_2 and S_3^{2-} formation was not observed with 10% or more CS_2 .

References:

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