

Electronic Supplementary Information (ESI)

Degradation mechanisms of lithium sulfide (Li₂S) composite cathode in carbonate electrolyte and improvement by increasing electrolyte concentration

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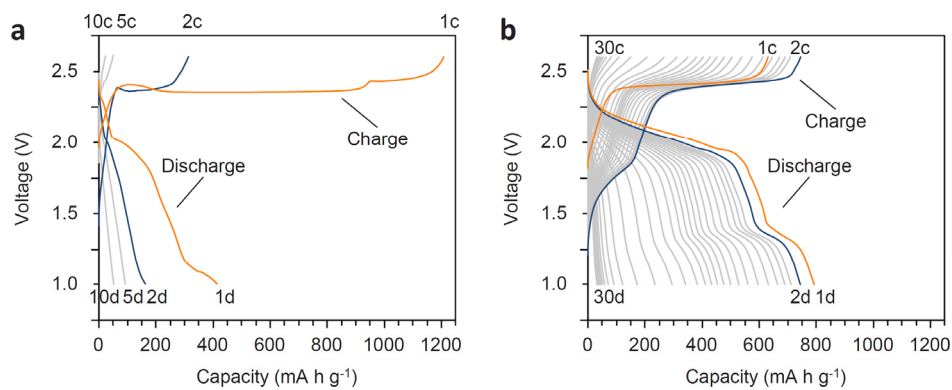


Fig. S1 Voltage profiles of Li₈FeS₅ (Li₂S/FeS = 4/1, mol/mol) composite sulfide//Li cell. The cell uses (a) 1.0 M LiTFSI + 0.1 M LiNO₃/DOL-DME (DOL/DME = 1/1, v/v) or (b) 1.0 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) (the same as Fig. 1a) electrolyte. 1c/1d, 2c/2d, 5c/5d, 10c/10d, and 30c/30d denote the first, second, fifth, tenth, and thirtieth charges/discharges, respectively.

Table S1 ICP-MS analysis of Fe and S concentrations in 1.0 M LiPF₆/EC–DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from cycled Li₈FeS₅/Li cells.

	Fe ($\mu\text{g/g}$)	S ($\mu\text{g/g}$)
1st Discharge		59
5th Discharge		88
10th Discharge		300
15th Discharge		430
30th Discharge	< 0.5	770
50th Discharge		1900

Although the cell had little discharge capacity left (less than 4% of the initial discharge capacity) after 30 cycles (not shown in Fig. 1a), the amount of sulfur continued to increase.

Table S2 Possible molecular composition and structure of compounds corresponding to LC-MS chromatogram peaks detected in 1.0 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from cycled Li₈FeS₅/Li cells.

Structural formula	n	Com- pound ^a	T _R ^b (min)	Peak No. ^c	Accurate mass		Ion ^d	Formula
					Measured	Calculated		
Carbonate oligomers								
	1	1₁	5.42	(2)	284.0979	284.0982	[M+NH ₄] ⁺	C ₉ H ₁₄ O ₉
	2	1₂	6.02	(5)	372.1143	372.1142	[M+NH ₄] ⁺	C ₁₂ H ₁₈ O ₁₂
	3	1₃	6.43	(6)	460.1298	460.1302	[M+NH ₄] ⁺	C ₁₅ H ₂₂ O ₁₅
	4	1₄	6.73		548.1467	548.1463	[M+NH ₄] ⁺	C ₁₈ H ₂₆ O ₁₈
	1	2₁	4.73		223.0811	223.0818	[M+H] ⁺	C ₈ H ₁₄ O ₇
	2	2₂	4.99	(1)	284.1341	284.1345	[M+NH ₄] ⁺	C ₁₀ H ₁₈ O ₈
	3	2₃	5.14		328.1606	328.1608	[M+NH ₄] ⁺	C ₁₂ H ₂₂ O ₉
	1	3₁	5.58	(3)	328.1242	328.1244	[M+NH ₄] ⁺	C ₁₁ H ₁₈ O ₁₀
	2	3₂	5.70	(4)	372.1504	372.1506	[M+NH ₄] ⁺	C ₁₃ H ₂₂ O ₁₁
	3	3₃	5.75		416.1769	416.1768	[M+NH ₄] ⁺	C ₁₅ H ₂₆ O ₁₂
	1	4₁	6.12		399.1131	399.1139	[M+H] ⁺	C ₁₄ H ₂₂ O ₁₃
Sulfur-containing carbonate oligomers								
	2	5₂	6.95	(9)	316.0881	316.0889	[M+NH ₄] ⁺	C ₁₀ H ₁₈ O ₆ S ₂
	3	5₃	7.67	(11)	376.0921	376.0922	[M+NH ₄] ⁺	C ₁₂ H ₂₂ O ₆ S ₃
	4	5₄	8.24	(13)	436.0963	436.0956	[M+NH ₄] ⁺	C ₁₄ H ₂₆ O ₆ S ₄
	5	5₅	8.70	(14)	496.0990	496.0990	[M+NH ₄] ⁺	C ₁₆ H ₃₀ O ₆ S ₅
	6	5₆	8.70	(15)	556.1020	556.1023	[M+NH ₄] ⁺	C ₁₈ H ₃₄ O ₆ S ₆
	7	5₇	9.35		616.1049	616.1057	[M+NH ₄] ⁺	C ₂₀ H ₃₈ O ₆ S ₇
		1	6₁	6.46	(7)	344.1012	344.1015	[M+NH ₄] ⁺
2		6₂	7.23	(10)	404.1049	404.1049	[M+NH ₄] ⁺	C ₁₃ H ₂₂ O ₉ S ₂
3		6₃	7.83	(12)	464.1087	464.1083	[M+NH ₄] ⁺	C ₁₅ H ₂₆ O ₉ S ₃
4		6₄	8.31		524.1116	524.1116	[M+NH ₄] ⁺	C ₁₇ H ₃₀ O ₉ S ₄
5		6₅	8.75		584.1157	584.1150	[M+NH ₄] ⁺	C ₁₉ H ₃₄ O ₉ S ₅
	1	7₁	6.82	(8)	432.1176	432.1176	[M+NH ₄] ⁺	C ₁₄ H ₂₂ O ₁₂ S
	2	7₂	7.44		492.1209	492.1209	[M+NH ₄] ⁺	C ₁₆ H ₂₆ O ₁₂ S ₂
	3	7₃	7.96		552.1249	552.1243	[M+NH ₄] ⁺	C ₁₈ H ₃₀ O ₁₂ S ₃
	2	8₂	7.55		376.9468	376.9460	[M+Ag] ⁺	C ₉ H ₁₈ O ₃ S ₃
	3	8₃	8.20		436.9509	436.9503	[M+Ag] ⁺	C ₁₁ H ₂₂ O ₃ S ₄
	4	8₄	8.77		408.0823	408.0829	[M+NH ₄] ⁺	C ₁₃ H ₂₆ O ₃ S ₅
	5	8₅	9.18		468.0855	468.0863	[M+NH ₄] ⁺	C ₁₅ H ₃₀ O ₃ S ₆
		9	6.06		300.1110	300.1117	[M+NH ₄] ⁺	C ₁₀ H ₁₈ O ₇ S
		10	6.54		388.1271	388.1277	[M+NH ₄] ⁺	C ₁₃ H ₂₂ O ₁₀ S

^a The subscript is the number (n) of repeating units (enclosed in parentheses in the structural formula) in the structure. ^b TR is the retention time. ^c Peaks (1)–(15) also appear in Fig. 2, which shows the relative intensities of the peaks at each cycle. ^d Ion denotes the molecular-weight related ion.

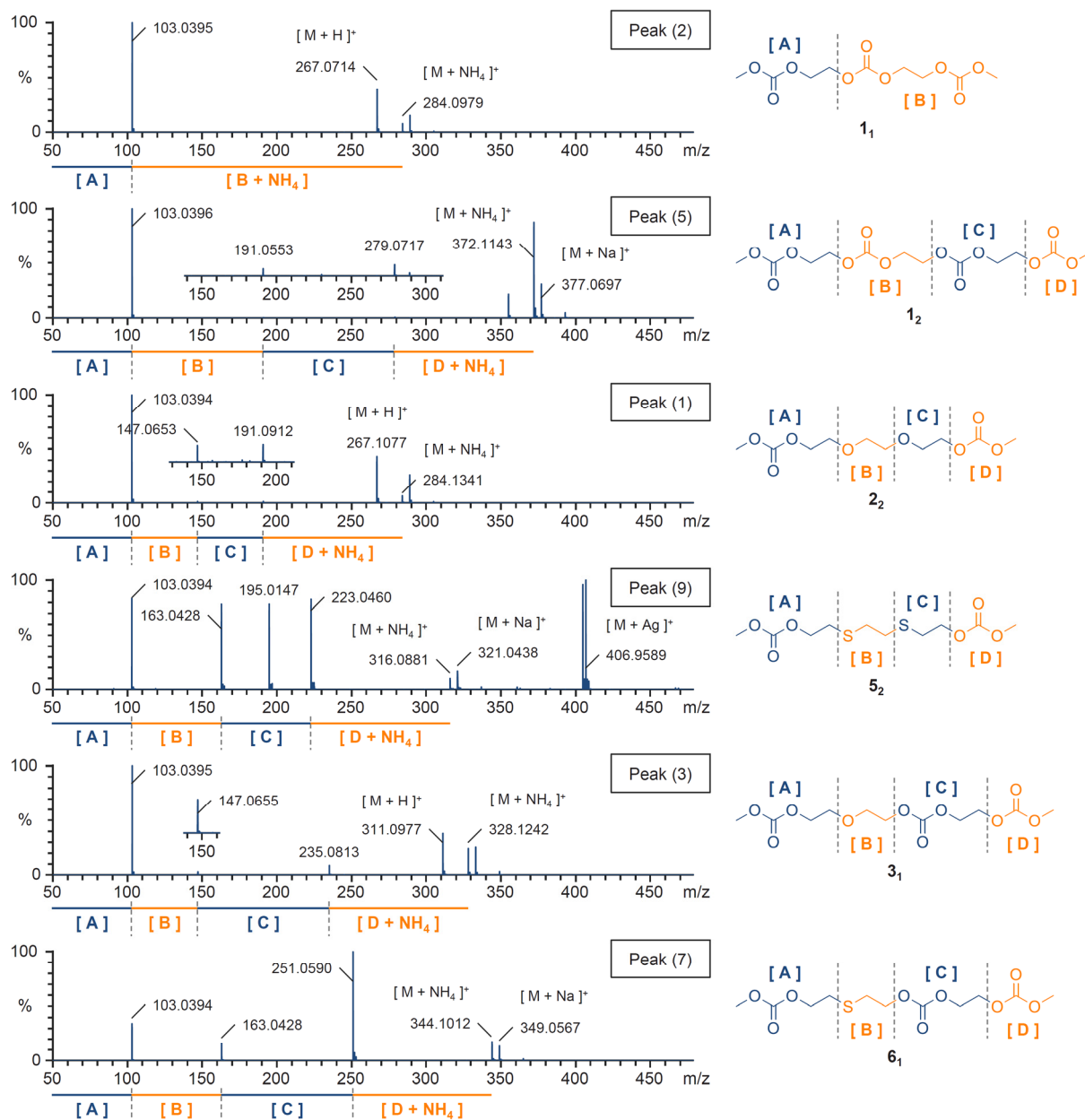
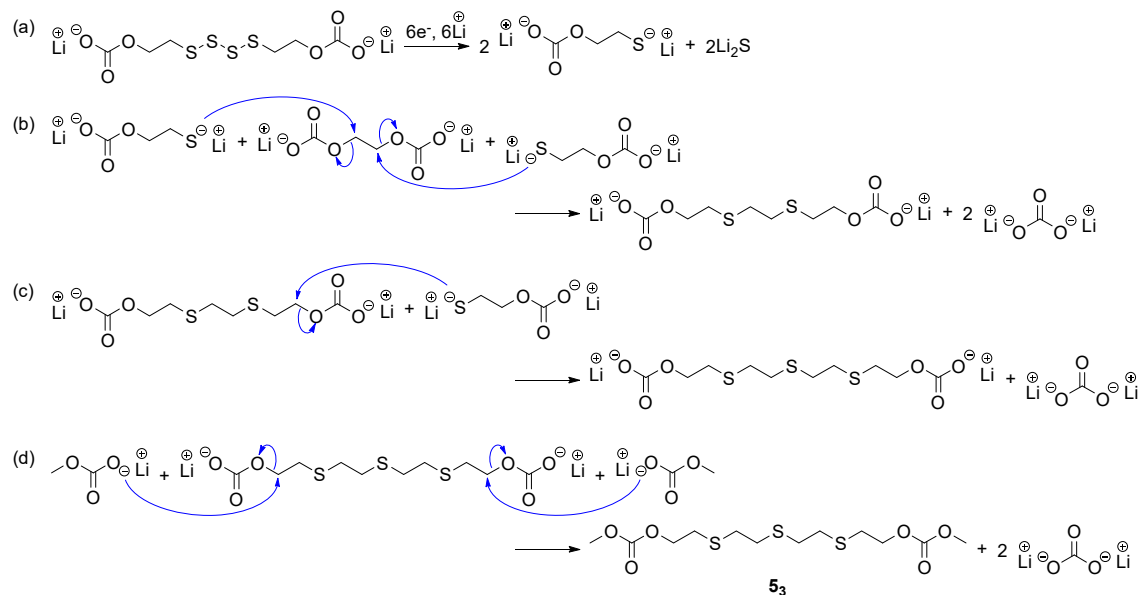
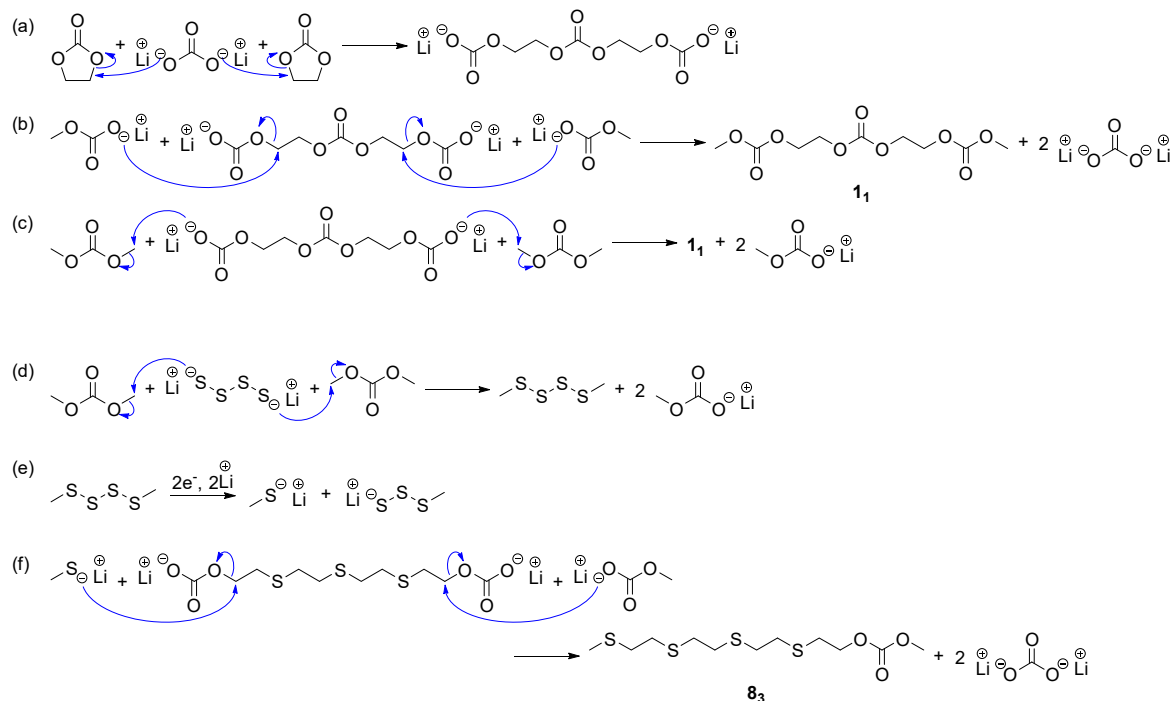


Fig. S2 LC-MS spectra of chromatographic peaks (1), (2), (3), (5), (7), and (9) (Fig. 2) and corresponding proposed molecular structure. Possible molecular structures are determined by analyzing the m/z differences between two mass peaks ([A], [B], [C], [B+NH₄], [D+NH₄], etc.).



Scheme S1 Possible reactions leading to formation of sulfur-containing carbonate oligomer **5₃**.

- (a) Reductive scission of the R-S_n-R product generated by Scheme 3(a) to produce lithium thioalkoxide (RSLi) on the cathode during discharge.
- (b) Nucleophilic substitution of the product from Scheme 1(b) with RSLi resulting from Scheme S1(a).
- (c) Continuous nucleophilic substitution with RSLi from Scheme S1(a).
- (d) Subsequent nucleophilic substitution with lithium methyl carbonate (CH₃OCO₂Li), produced by reductive degradation of DMC (Scheme 1(e)), to form sulfur-containing carbonate oligomer **5₃**.



Scheme S2 Possible reactions leading to formation of carbonate oligomer **1** and sulfur-containing carbonate oligomer **8**. DMC participates in (c) and (d) while EC in (a) as electrophiles.

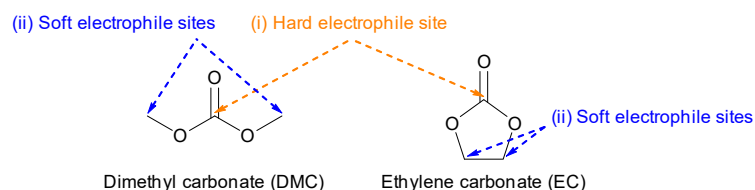
Possible carbonate degradation reactions where DMC as well as EC participates as an electrophile

Possible reactions to form carbonate oligomer **1.** As described in the main article, EC is an electrophile and can be attacked by the CO_3^{2-} anion (Scheme 2(a) or S2(a)). The product can then undergo nucleophilic substitution with $\text{CH}_3\text{-OC(=O)O}^-$, the reductive product of DMC (Scheme 1(e)), to give carbonate oligomer **1** (Scheme 2(b) or S2(b)). Meanwhile, DMC is also an electrophile and thought to react with the nucleophile arising from Scheme 2(a) or S2(a) to give **1** (Scheme S2(c)). Additionally, $\text{CH}_3\text{-OC(=O)O}^-$ generated through Scheme S2(c) can also give **1** through Scheme 2(b) or S2(b).

Possible reaction to form sulfur-containing carbonate oligomer **8.** Sulfur-containing carbonate oligomer **8** has a thiomethyl group ($\text{CH}_3\text{-S-}$) at the terminal, suggesting that DMC can act as an electrophile. Specifically, DMC can be attacked by the dissolved S_n^{2-} anions during charge (Scheme S2(d)). Subsequently, as shown in Scheme S2(e), reductive -S-S- bond cleavage of the organic polysulfide product during discharge can give thiomethoxide ($\text{CH}_3\text{-S}^-$). As shown in scheme S2(f), $\text{CH}_3\text{-S}^-$ is then believed to participate in the reaction of Scheme S1(d) instead of $\text{CH}_3\text{-OC(=O)O}^-$.

Which carbonates' electrophile site do nucleophiles react with? (Supplementary explanation for carbonate electrolyte degradation)

Organic carbonates (*e.g.*, DMC and EC) have two different electrophile sites: (i) a carbonyl carbon (C=O) and (ii) α -carbons of the carbonate group (CH₃- and -CH₂- for DMC and EC, respectively).^{1,2} The C=O double bond of the former is more strongly polarized than the C-O single bonds of the latter (CH₃-O- and -CH₂-O-) because the C=O has, in addition to the higher electronegativity of the oxygen atom, an alternative resonance structure, *i.e.*, C⁺-O⁻. The former, therefore, has a large partial positive charge and can be regarded as a hard electrophile site; meanwhile, the latter have partial positive charges due to the polarization of the C-O single bonds, considered to be soft electrophile sites.



Generally, hard nucleophiles tend to react with hard electrophiles and soft nucleophiles with soft electrophiles (HSAB concept). In addition, hard nucleophiles contain small, electronegative atoms (*e.g.*, O and N) with high localization of the negative charge (high charge density); soft nucleophiles, on the other hand, have large atoms (*e.g.*, S and P) and delocalization of the negative charge (low charge density). Therefore, the polysulfide and sulfide anions (S_n²⁻, R-S_n⁻, and R-S⁻) are good soft nucleophiles, and prefer to react with the soft electrophilic sites (Site (ii)) of the carbonates (Scheme 3(a), 3(e), and 3(h)). Additionally, the carbonate anions (CO₃²⁻ and R-OC(=O)O⁻) can also be considered soft nucleophiles and react with the soft electrophile sites (Site (ii)) because the negative charge is delocalized in the carbonate group (Scheme 1(b), 1(g), 2(a), 2(b), 2(e), 3(b), 3(c), and 3(f)).

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- 2 P. Tundo, L. Rossi and A. Loris, *J. Org. Chem.*, 2005, **70**, 2219–2224.

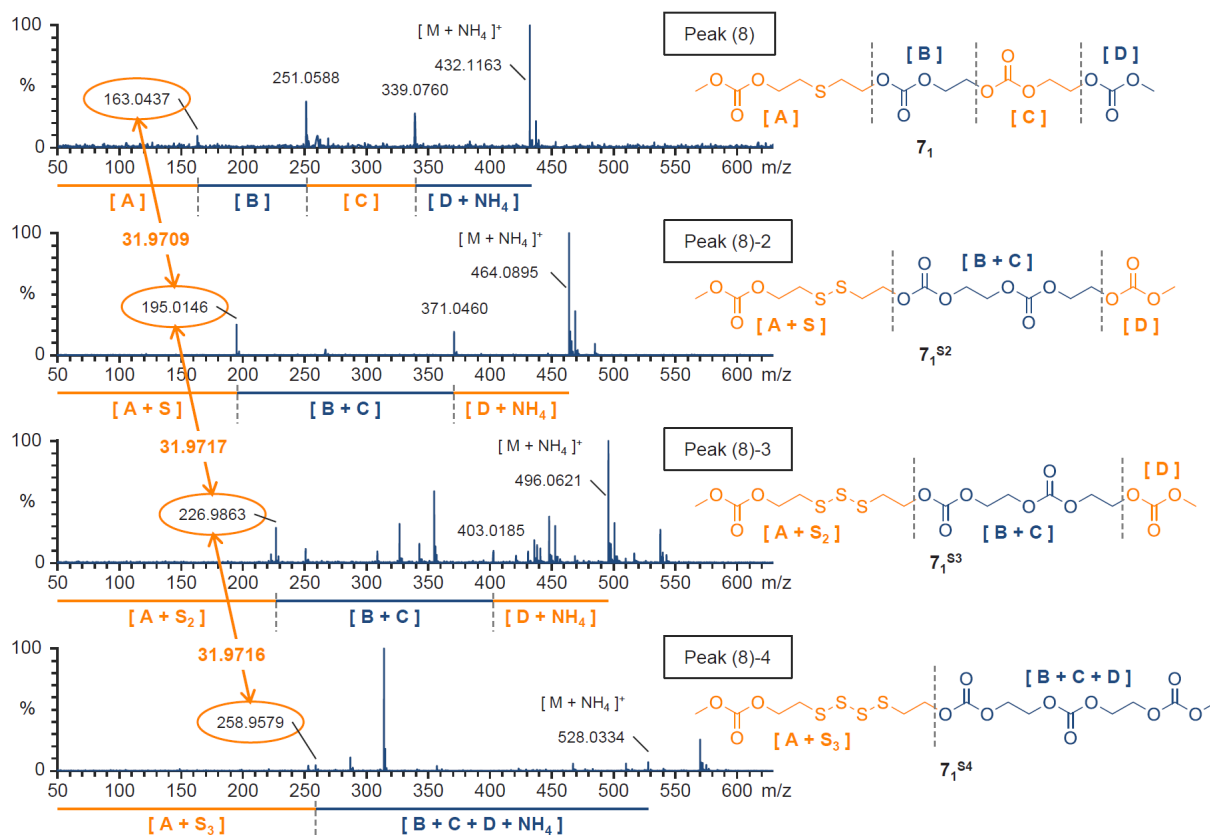


Fig. S3 LC-MS spectra of chromatographic peaks (8), (8)-2, (8)-3, and (8)-4 and corresponding proposed molecular structure. Only peak (8) is shown in Fig. 3. Chromatographic peaks (8)-2, (8)-3, and (8)-4 have retention times of 7.3, 7.6, and 8.1 min, respectively. Possible molecular structures are determined by analyzing the m/z differences between two mass peaks ([A], [B], [C], etc.). The circled m/z values for [A] increase from the top (m/z 163.0437) to the bottom (m/z 258.9579) at an interval that is nearly equal to the calculated exact mass of sulfur (^{32}S = 31.97207). This suggests that organic polysulfides 7_1^{S2} – 7_1^{S4} , in which sulfur atoms additionally link to the sulfur atom of 7_1 , are formed during the first charge, along with organic polysulfides 6_1^{S2} – 6_1^{S5} .

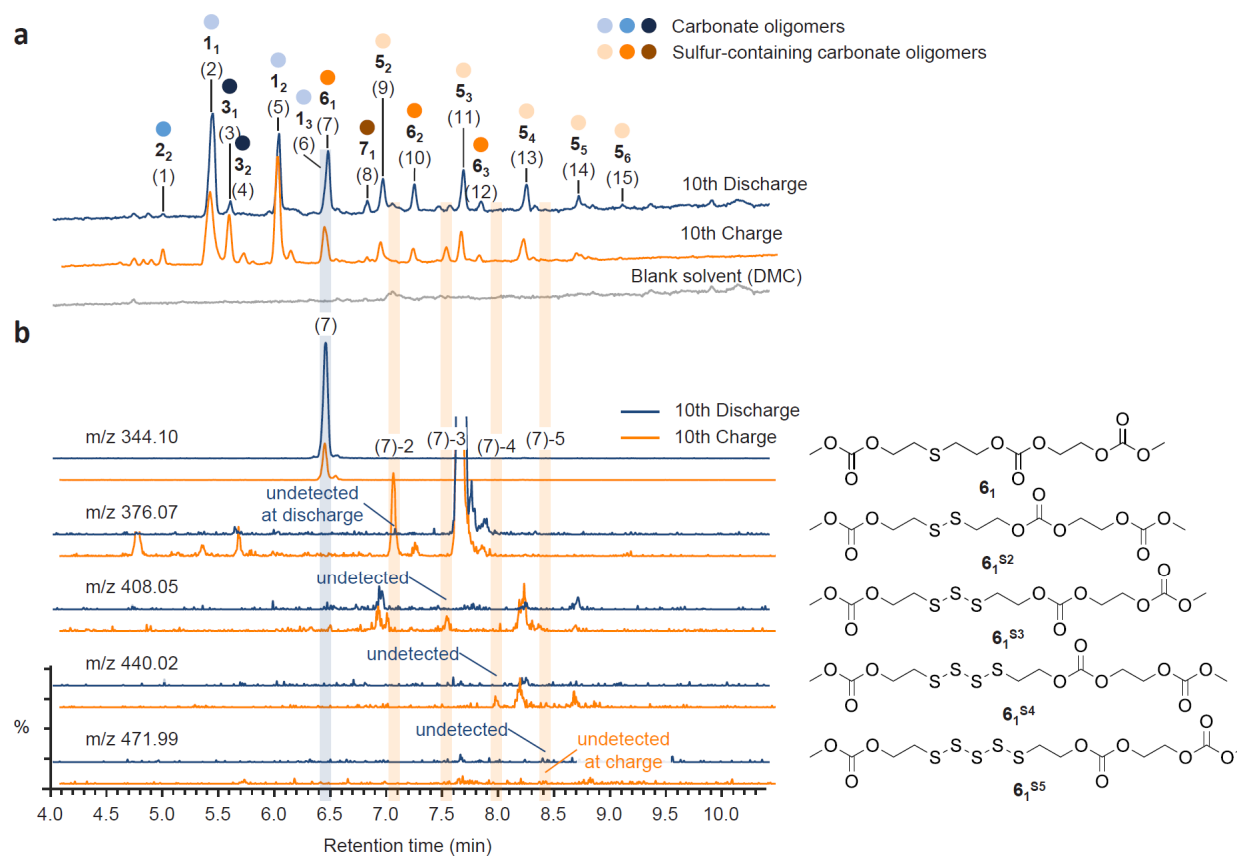


Fig. S4 LC-MS analysis of 1.0 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from Li₈FeS₅/Li cells stopped at the end of the 10th charge and end of the subsequent 10th discharge. (a) Total ion current chromatograms. The compound identified at each peak (represented by a numeral in parenthesis) by LC-MS analysis is denoted by a bold numeral, which is the same as that used in Fig. 2 and Table S2. (b) Mass chromatograms at m/z 344.10, 376.07, 408.05, 440.02, and 471.99, corresponding to the molecular-weight-related ions ([M+NH₄]⁺) of **6₁**, **6₁^{S2}**, **6₁^{S3}**, **6₁^{S4}**, and **6₁^{S5}**, respectively. The proposed molecular structures of these compounds are identified in Fig. 4. In the same way as in the first cycle (Fig. 3b), peaks (7)-2, (7)-3, and (7)-4, corresponding to organic polysulfides (R-S_n-R) **6₁^{S2}**, **6₁^{S3}**, and **6₁^{S4}**, respectively, appear at the end of the 10th charge but disappear at the end of the following 10th discharge. Peak (7), corresponding to organic sulfide (R-S-R) **6₁** appears instead. This suggests that oxidation of the Li₈FeS₅ cathode during charging, accompanied by sulfur oxidation (S²⁻/S⁰ or S²⁻/S₂²⁻), generates electrolyte-soluble lithium polysulfides (Li₂S_n), which react with the carbonate solvents to give R-S_n-R. Reductive -S-S- bond scission of the latter to yield R-S-R is believed to occur on the cathode during discharge.

Table S3 ICP-MS analysis of S concentrations in 3.5 M LiPF₆/EC–DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from cycled Li₈FeS₅/Li cells.

	S in the diluted electrolyte solution ^a (μg/g)	Dilution ratio ^b	S in the electrolyte solution ^c (μg/g)
1st Discharge	< 30	1:2.1	< 70
5th Discharge	< 30	1:2.4	< 70
10th Discharge	< 30	1:2.4	< 70
15th Discharge	< 30	1:2.3	< 70
30th Discharge	30	1:2.3	70

^a The 3.5 M electrolyte solutions were diluted with 1,2-dimethoxyethane (DME) to overcome their high viscosity, which would otherwise make fixed-volume sampling with a micropipette difficult, before any ICP-MS measurements. ^b The dilution ratio was calculated from the weight percent of DME included in the diluted electrolyte solution, which was measured using gas chromatography (GC). ^c The sulfur content in the cycled 3.5 M electrolyte solution was then found by calculating from the amount of sulfur in the diluted electrolyte solution and the dilution ratio.

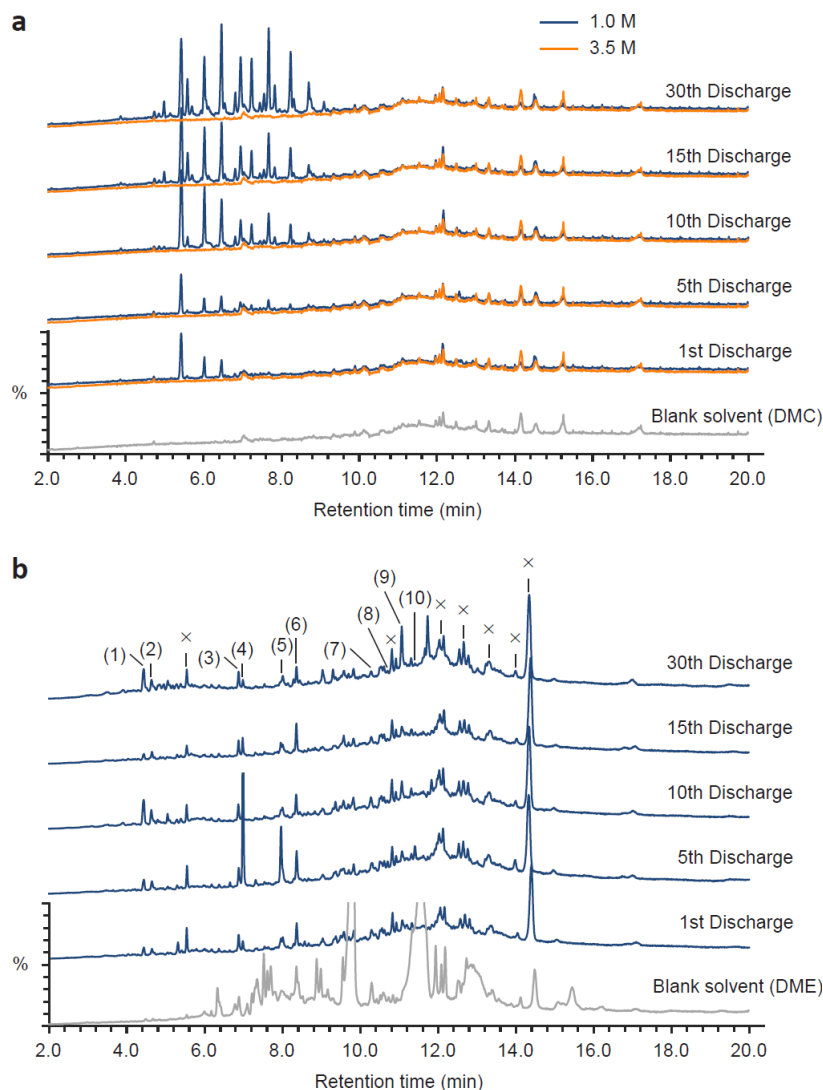


Fig. S5 LC-MS analysis of 3.5 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from Li₈FeS₅//Li cells stopped at the end of discharge after a specific number of cycles (1, 5, 10, 15, 30). (a) Comparison of total ion current (TIC) chromatograms of 1.0 and 3.5 M electrolyte solutions. The latter are superimposed on the baselines of the former for each cycle. The electrolyte solutions were diluted at a ratio of 1:100 for the LC-MS measurements, and 0.2 μ L of the diluted samples were injected into the LC-MS system. (b) TIC chromatograms of the 3.5 M electrolyte solutions. The electrolyte solutions were diluted at the respective dilution ratios shown in Table S3 (at 1:2.1–2.4), and 1 μ L of the diluted samples were injected into the system. The chromatographic peaks appear clearly by increasing the amount of components in the samples (*i.e.*, reducing the dilution ratio and/or increasing the amount of sample injected). However, the carbonate and sulfur-containing carbonate oligomers found in the 1.0 M electrolyte solutions are not detected, suggesting that the higher concentration can considerably suppress the dissolution of sulfur from the cathode and decomposition of the carbonate solvents (EC and DMC). Chromatographic peaks (1)–(10), assigned by MS analysis, are summarized in Table S4. Peaks marked with X are derived from the blank solvent.

Table S4 Possible molecular composition of compounds corresponding to LC-MS chromatogram peaks detected in 3.5 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) electrolyte solutions extracted from cycled Li₈FeS₅/Li cells.

Peak No.	T _R (min)	Accurate mass		Ion	Formula	Possible compound
		Measured	Calculated			
(1)	4.4	315.0478	315.0481	[M+H] ⁺	C ₉ H ₁₅ O ₁₀ P	phosphorus-containing carbonate compound
(2)	4.6	359.0733	359.0743	[M+H] ⁺	C ₁₁ H ₁₉ O ₁₁ P	phosphorus-containing carbonate compound
(3)	6.9	225.1494		[M+H] ⁺	unidentified	
(4)	7.0	352.2521	352.2522	[M+H] ⁺	C ₁₇ H ₃₇ NO ₄ S	sulfur-containing compound (A)
(5)	8.0	423.2420	423.2416	[M+H] ⁺	C ₂₀ H ₃₈ O ₇ S	sulfonate (SO ₃) with C ₈ alkyl group
(6)	8.4	325.2015		[M+H] ⁺	unidentified	
(7)	10.3	227.2024	227.2011	[M+H] ⁺	C ₁₄ H ₂₆ O ₂	aliphatic acid
		255.2341	255.2324	[M+H] ⁺	C ₁₆ H ₃₀ O ₂	aliphatic acid
(8)	10.7	534.4196	534.4192	[M+H] ⁺	C ₂₉ H ₅₉ NO ₅ S	A with C ₁₂ H ₂₂ O
(9)	11.1	283.2640	283.2637	[M+H] ⁺	C ₁₈ H ₃₄ O ₂	aliphatic acid
(10)	11.4	562.4514	562.4505	[M+H] ⁺	C ₃₁ H ₆₃ NO ₅ S	A with C ₁₄ H ₂₆ O

Table S5 Calculated mole ratio of salt (LiPF₆) and solvent (EC and DMC) in 1.0 and 3.5 M LiPF₆/EC–DMC (EC/DMC = 1/1, v/v) electrolyte solutions^a.

	Solution density ^b (g cm ⁻³)	LiPF ₆ ^c (mol)	LiPF ₆ (g)	Solvent (g)	EC ^d (g)	DMC ^d (g)	EC ^c (mol)	DMC ^c (mol)	Solvent/ LiPF ₆ (mol/mol)
1.0 M LiPF ₆ in EC:DMC (1:1 v/v)	1.30	1.0	151.9	1148.1	634.1	514.0	7.2	5.7	12.9
3.5 M LiPF ₆ in EC:DMC (1:1 v/v)	1.50	3.5	531.7	968.3	534.8	433.5	6.1	4.8	3.1

^a All weights and mole numbers of the salt (LiPF₆) and solvent (EC and DMC) are expressed per liter of electrolyte solution. ^b Densities were measured at 20 °C. ^c The molar masses (g mol⁻¹) of LiPF₆, EC, and DMC are 151.90, 88.06, and 90.08, respectively. ^d The densities of EC (1.32 g cm⁻³ at 40 °C) and DMC (1.07 g cm⁻³ at 20 °C) were used to calculate the respective weights.

Positive secondary ions

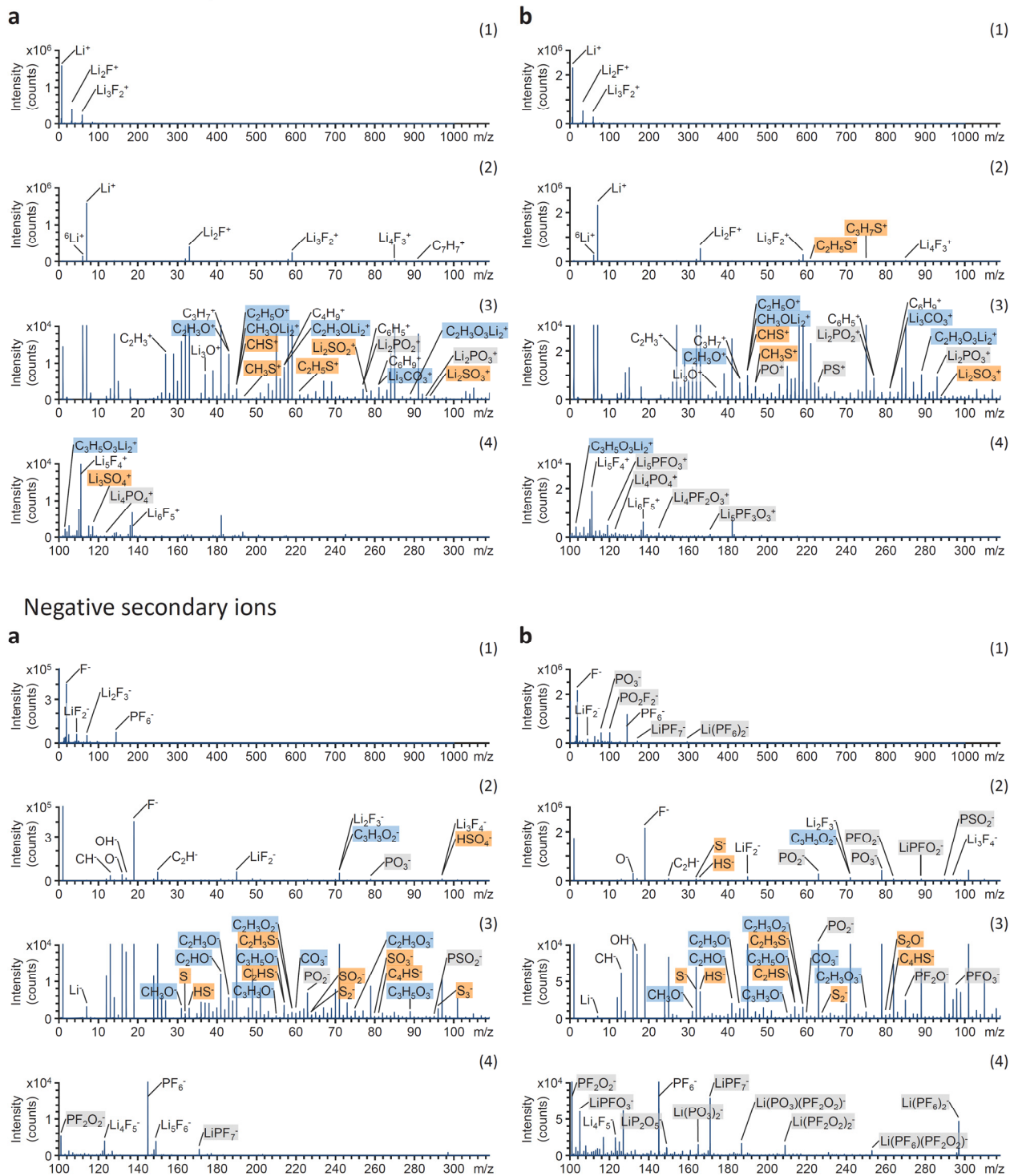


Fig. S6 TOF-SIMS spectra on Li₈FeS₅ cathode surface extracted from cycled Li₈FeS₅/Li cells. The cathodes were taken out of the cells using (a) 1.0 M or (b) 3.5 M LiPF₆/EC-DMC (EC/DMC = 1/1, v/v) electrolytes after 50 charge-discharge cycles (not shown in Fig. 1). TOF-SIMS spectra (2)–(4) are given by expanding the y-axis (ion intensity) scale of the respective spectra (1) with the expansion of the x-axis (m/z) scale.

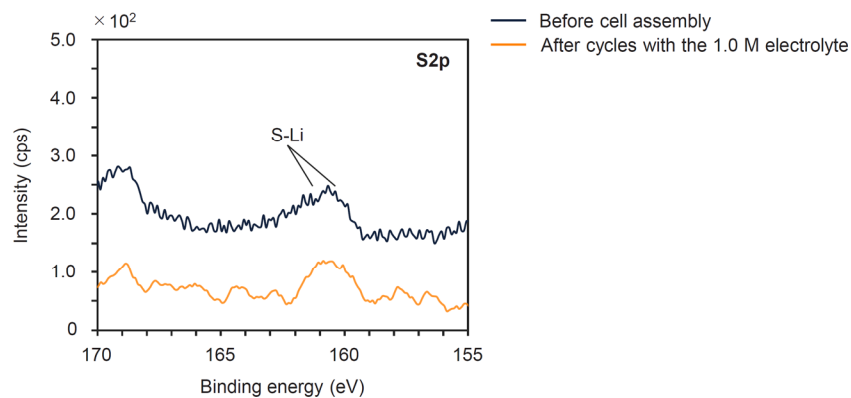


Fig. S7 XPS high-resolution spectra of S2p on the surface of Li_8FeS_5 composite cathodes. The cycled cathode (orange line), taken out of the $\text{Li}_8\text{FeS}_5/\text{Li}$ cell using 1.0 M $\text{LiPF}_6/\text{EC}-\text{DMC}$ (EC/DMC = 1/1, v/v) electrolyte after charge–discharge cycling (50 cycles), was compared with a fresh cathode (blue line) before cell assembly.