Supplementary material

Lithium interphase enhancement for applications in lithium-sulfur batteries

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Imaging

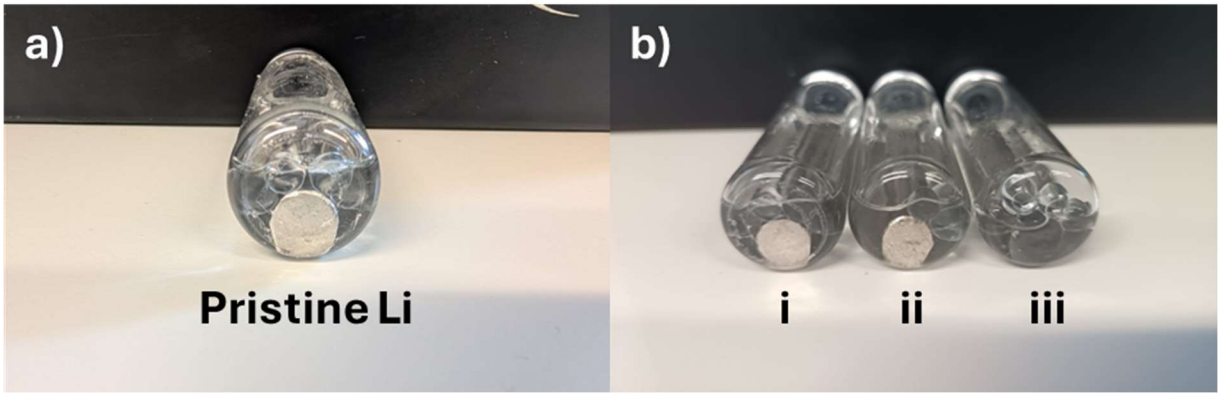

Figure S1. Pictures of (a) pristine Li, (b) i. Li left 2.5 h in DOL: DME, ii. Li left 2.5 h DOL: DME with Ar bubbling, iii. T-Li.

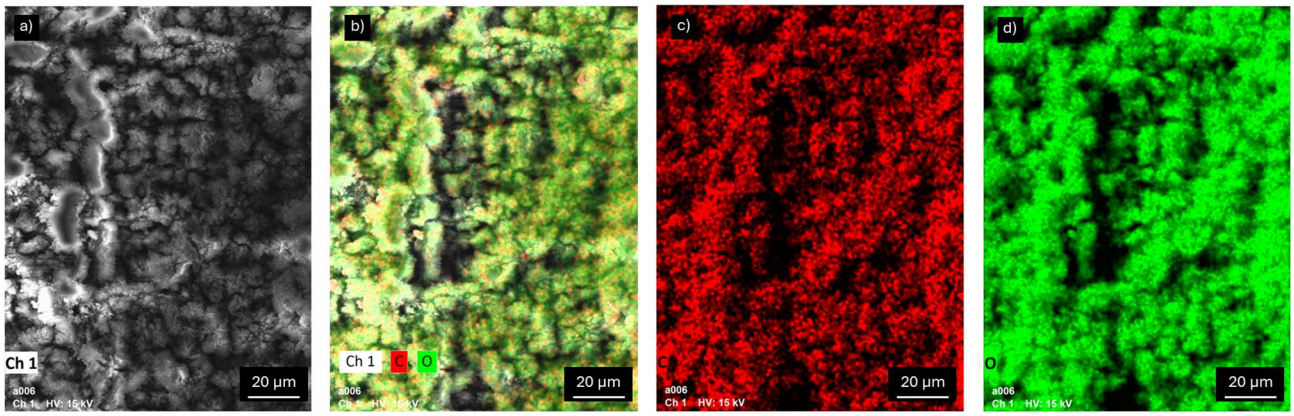

Figure S2. EDS images of T-Li sample.

X-ray photoelectron spectroscopy

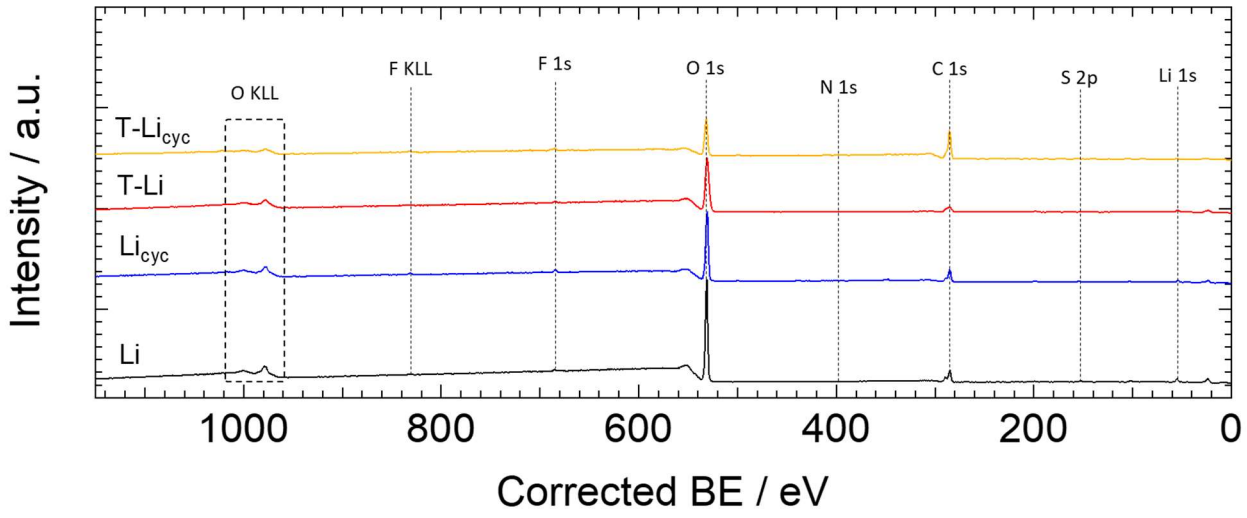

Figure S3. Survey XPS spectra and qualitative analysis of the surface elemental composition of the different samples.

Table S1. Surface elemental composition obtained from XPS studies.

Sample	**C / at.%**	**O / at.%**	**Li / at.%**	**F / at.%**	**N / at.%**	**S / at.%**	**others / at.%**
Li	15.81	40.91	40.42	1.33	-	-	1.53
Li_{cyc}	19.04	41.85	34.36	1.96	0.26	0.26	2.27
T-Li	13.65	39.05	45.83	0.86	-	-	0.61
T-Li_{cyc}	46.06	28.62	20.58	2.15	0.42	0.14	2.03

Table S2. Surface carbon relative composition obtained from XPS studies.

Sample	**C-H / at.%**	**C-O/C-F / at.%**	**CO_3^{2-} / at.%**
Li	70.50	4.07	25.43
Li_{cyc}	65.37	13.94	20.69
T-Li	67.76	13.04	19.20
T-Li_{cyc}	71.72	12.45	15.83

Table S3. Surface oxygen relative composition obtained from XPS studies.

Sample	Li_2O / at.%	LiOH / at.%	CO_3^{2-} / at.%	ads / at.%
Li	-	73.69	23.71	2.60
Li_{cyc}	-	72.85	20.10	7.05
T-Li	12.29	65.24	21.19	1.28
T-Li_{cyc}	-	52.53	39.30	8.16

Table S4. Surface lithium relative composition obtained from XPS studies.

Sample	$LiOH/Li_2O$ / at.%	Li_2CO_3 / at.%
Li	76.39	23.61
Li_{cyc}	81.22	18.78
T-Li	100.00	-
T-Li_{cyc}	69.73	30.27

The ^{1}H NMR spectrum recorded after dissolving the powder collected from the T-Li surface in DMSO-d_6 is reported in Figure S4. The resulting spectrum reflects the soluble organic species formed on the lithium surface. A sharp singlet at ca. 8.5 ppm indicates the presence of aldehydic species, consistent with oxidative cleavage of the dioxolane ring. The intense, overlapping resonances between 3.1 and 3.7 ppm, partially covered by the residual water signal, are characteristic of protons α to oxygen atoms (–CH_2–O–) and correspond to a mixture of DOL-derived fragments formed by polymerization. Minor features around 2.3–2.6 ppm suggest methylene groups adjacent to carbonyl functional groups (–CH_2–CHO), while weaker aliphatic signals near 1.0–1.5 ppm can be attributed to trace dimethoxyethane (DME) or other low-molecular-weight by-products. Overall, the spectrum indicates that DOL underwent ring opening in the treatment conditions and subsequent oxidation, yielding a complex mixture of aldehydes, glycols, and ethers.

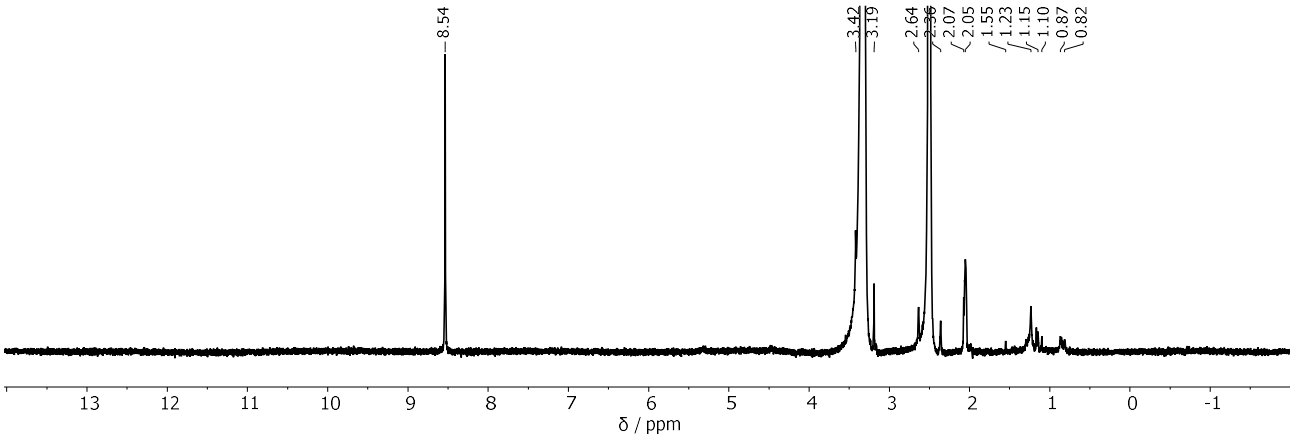

Figure S4. ^{1}H NMR in DMSO-d_6 of T-Li interphase obtained scratching the electrode after the treatment.

Symmetric cell performance

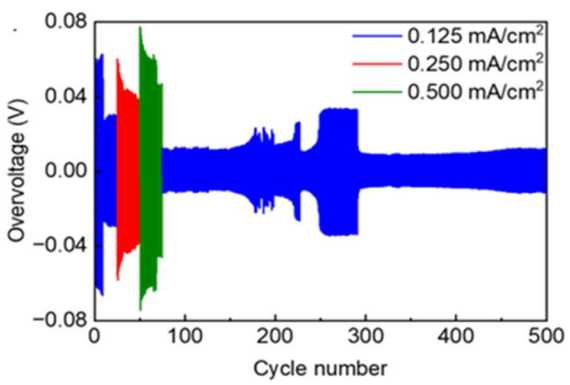

Figure S5. Voltage profiles in 1M LiTFSI DOL:DME with $LiNO_3$ 0.45 M of Li//Li symmetric cell at different current density (0.5 h stripping/0.5 h plating).

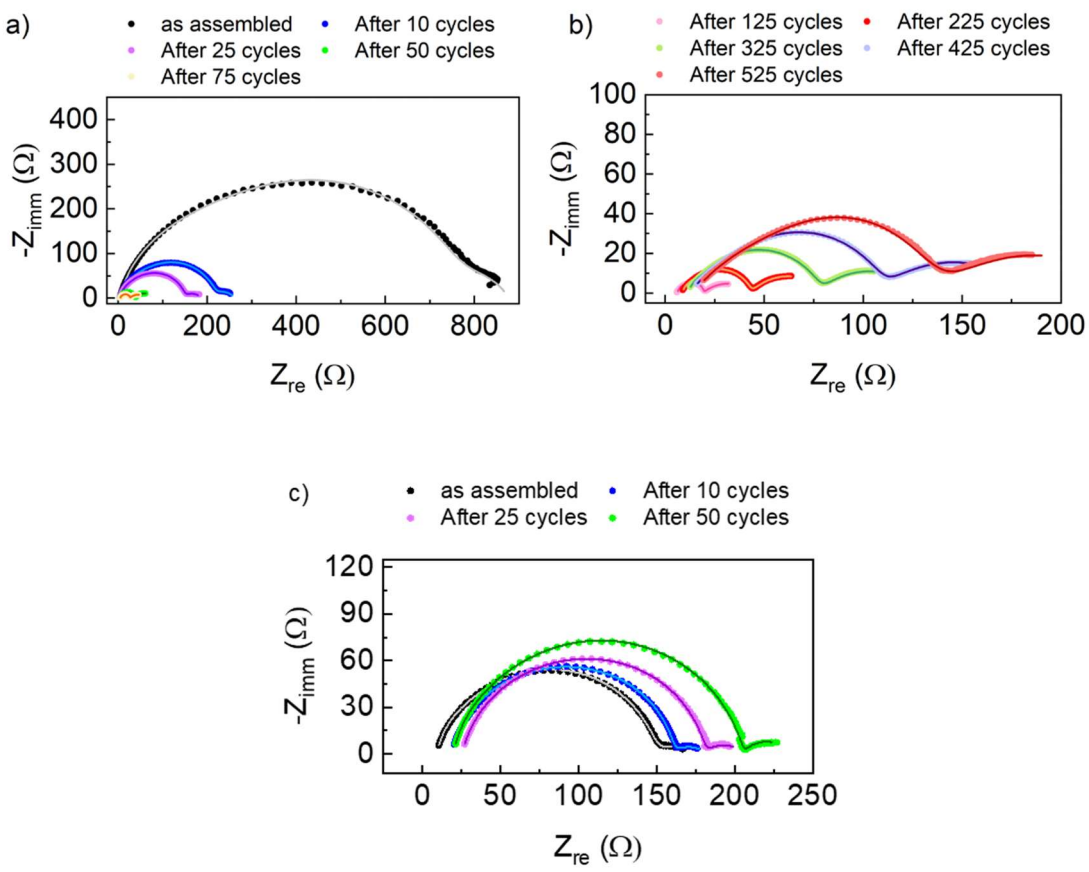

Figure S6. Impedance spectra and fitted curves for (a,b) T-Li//T-Li symmetric cells and (c) Li//Li cells at fresh state and after 10, 25, 50, 75, 125, 225, 325, 425, 525 cycles at 30°C. The solid lines are the data fittings.

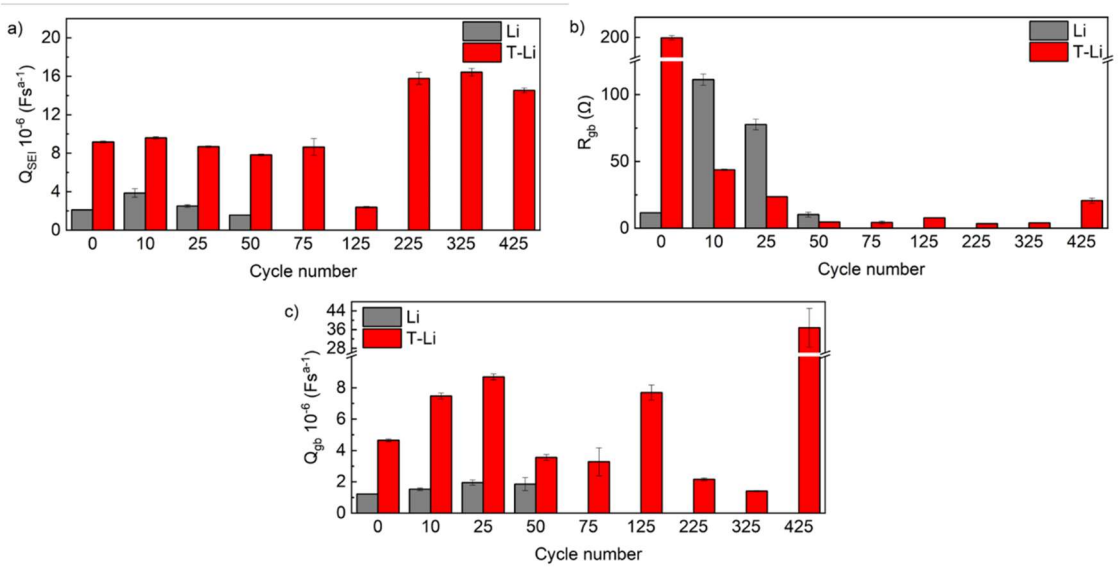

Figure S7. Evolution of Q_{SEI}, R_{gb} and Q_{gb} over cycling for symmetric Li//Li and T-Li//T-Li cells.

Table S5. Results from the fitting of the EIS recorded for the T-Li//T-Li cell at 30°C.

Equivalent component	**R_{el}** **Ω**	**R_{SEI}** **Ω**	**Q_{SEI}** **(10^{-6})** **$F \cdot s^{a-1}$**	**a_{SEI}**	**R_{gb}** **Ω**	**Q_{gb}** **(10^{-6})** **$F \cdot s^{a-1}$**	**a_{gb}**	**R_{ct}** **Ω**	**Q_{dl}** **(10^{-2})** **$F \cdot s^{a-1}$**	**a_{dl}**
As assembled	4.1 ± 0.1	555 ± 3	9.2 ± 0.1	0.859 ±0.001	200 ±3	4.65 ±0.09	0.870 ± 0.002	117 ± 5	0.18 ± 0.02	0.696 ±0.002
10 cycles	4.5 ± 0.1	169 ± 3	9.6 ± 0.1	0.879 ± 0.001	43.8 ± 0.5	7.5 ± 0.2	0.899 ± 0.003	44.9 ± 0.9	0.60 ± 0.03	0.624 ± 0.001
25 cycles	4.5 ± 0.1	120.9 ± 0.4	8.69 ± 0.08	0.883 ± 0.001	23.6 ± 0.3	8.7 ± 0.2	0.915 ± 0.002	44.9 ± 0.9	1.07 ± 0.04	0.578 ± 0.001
50 cycles	5.0 ± 0.1	27.7 ± 0.1	7.83 ± 0.08	0.905 ± 0.001	4.67 ± 0.06	3.6 ± 0.2	1 ± 10^{-6}	46.6 ± 0.6	2.53 ± 0.02	0.539 ± 0.002
75 cycles	5.2 ± 0.1	17 ± 1	8.7 ± 0.9	0.92 ± 0.02	4 ± 1	3.3 ± 0.9	1 ± 10^{-6}	35.2 ± 0.8	2.75 ± 0.05	0.514 ± 0.006
125 cycles	6.32 ± 0.08	4.9 ± 0.2	2.39 ± 0.08	1 ± 10^{-6}	7.8 ± 0.3	7.7 ± 0.5	1 ± 10^{-6}	25.9 ± 0.7	4.77 ± 0.07	0.447 ± 0.007

225 cycles	8.78 ± 0.09	31.0 ± 0.4	15.8 ± 0.6	0.814 ± 0.007	3.4 ± 0.3	2.16 ± 0.09	1 ± 10^{-6}	37.8 ± 0.6	2.97 ± 0.01	0.534 ± 0.006
325 cycles	11.67 ± 0.07	62.2 ± 0.4	16.4 ± 0.4	0.763 ± 0.003	4.1 ± 0.2	1.41 ± 0.04	1 ± 10^{-6}	50 ± 2	1.92 ± 0.05	0.52 ± 0.01
425 cycles	12.9	76 ± 2	14.5 ± 0.2	0.791 ± 0.004	21 ± 2	37 ± 8	0.65 ± 0.02	71 ± 2	1.12 ± 0.01	0.519 ± 0.007
525 cycles	16.3	107 ± 2	15.0 ± 0.4	0.750 ± 0.002	15 ± 2	5 ± 2	0.80 ± 0.03	86 ± 4	1.03 ± 0.03	0.510 ± 0.008

Table S6. Results from the fitting of the EIS recorded for the Li//Li cell at 30°C.

Equivalent component	**R_{el} Ω**	**R_{SEI} Ω**	**Q_{SEI} (10^{-6}) F · s^{a-1}**	**a_{SEI}**	**R_{gb} Ω**	**Q_{gb} (10^{-6}) F · s^{a-1}**	**a_{gb}**	**R_{ct} Ω**	**Q_{dl} (10^{-2}) F · s^{a-1}**	**a_{dl}**
As assembled	9.22 ± 0.06	127.7 ± 0.2	2.109 ± 0.004	0.866 ± 0.001	11.6 ± 0.1	1.22 ± 0.02	1 ± 10^{-6}	22.8 ± 0.2	0.138 ± 0.002	0.479 ± 0.002
10 cycles	18.5 ± 0.2	31 ± 4	3.9 ± 0.4	0.993 ± 0.006	111 ± 4	1.53 ± 0.08	0.861 ± 0.005	21.3 ± 0.4	0.188 ± 0.007	0.495 ± 0.002
25 cycles	25.3 ± 0.2	77 ± 4	2.5 ± 0.1	0.914 ± 0.005	77 ± 4	2.0 ± 0.2	0.860 ± 0.007	26.7 ± 0.7	2.2 ± 0.09	0.491 ± 0.003
50 cycles	19.7 ± 0.2	175 ± 2	1.57 ± 0.04	0.863 ± 0.004	10 ± 2	1.9 ± 0.4	0.990 ± 0.009	30 ± 3	3.11 ± 0.02	0.618 ± 0.002