Electronic supplementary information (ESI) for

Aligned artificial solid electrolyte interphase layers as versatile interfacial stabilizer on lithium metal anodes

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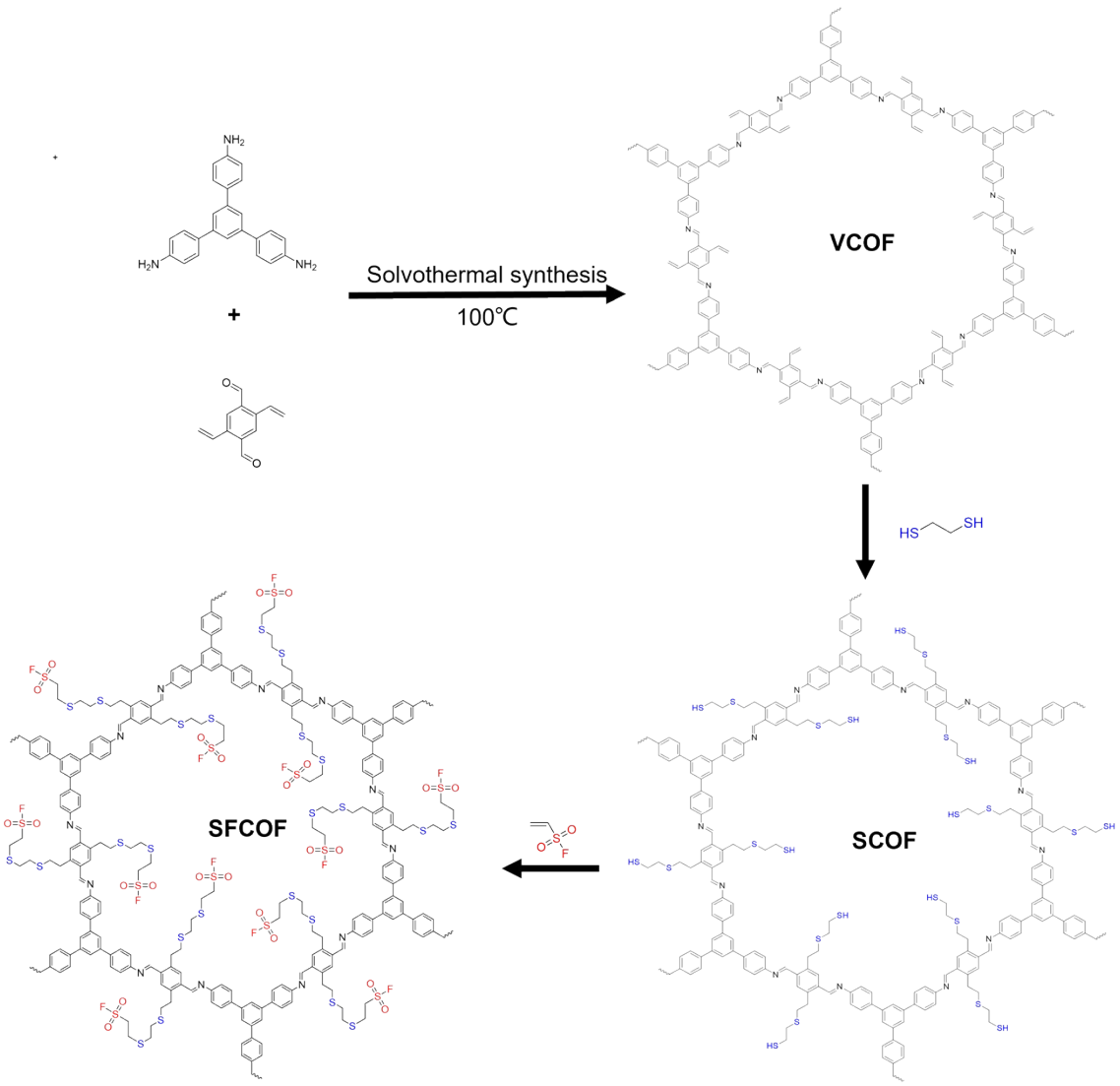

Scheme S1. The synthesis route to VCOF, SCOF, and SFCOF.

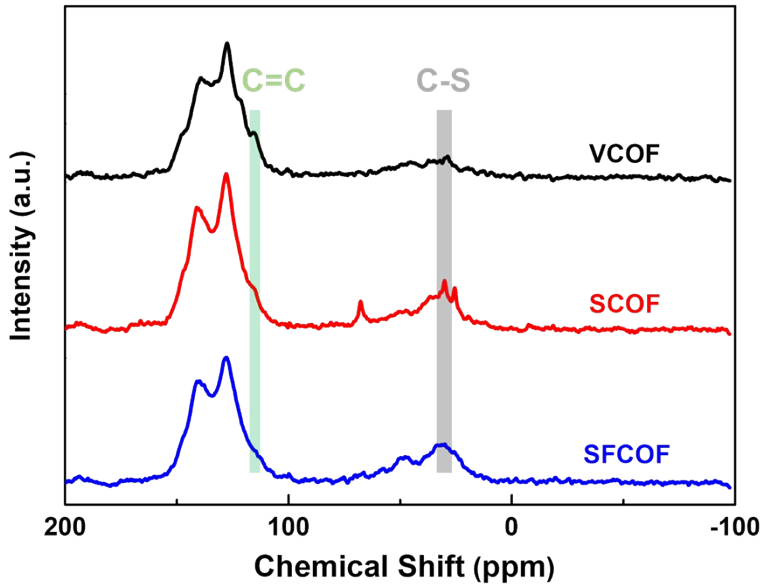

Fig. S1 The solid-state ^{13}C NMR spectra of VCOF, SCOF, and SFCOF.

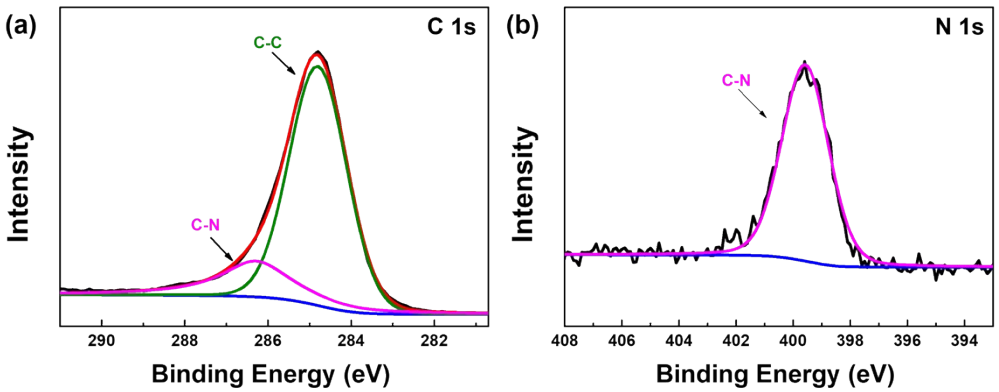

Fig. S2 (a) The C 1s and (b) N 1s spectra of VCOF.

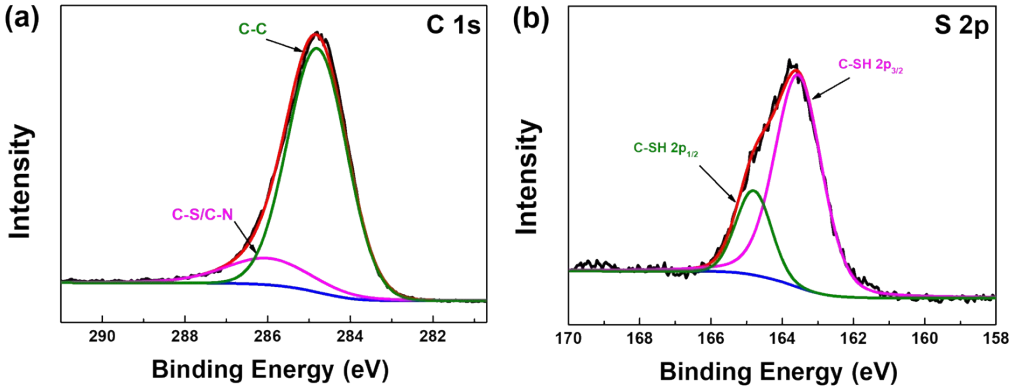

Fig. S3 (a) The C 1s and (b) S 2p spectra of SCOF.

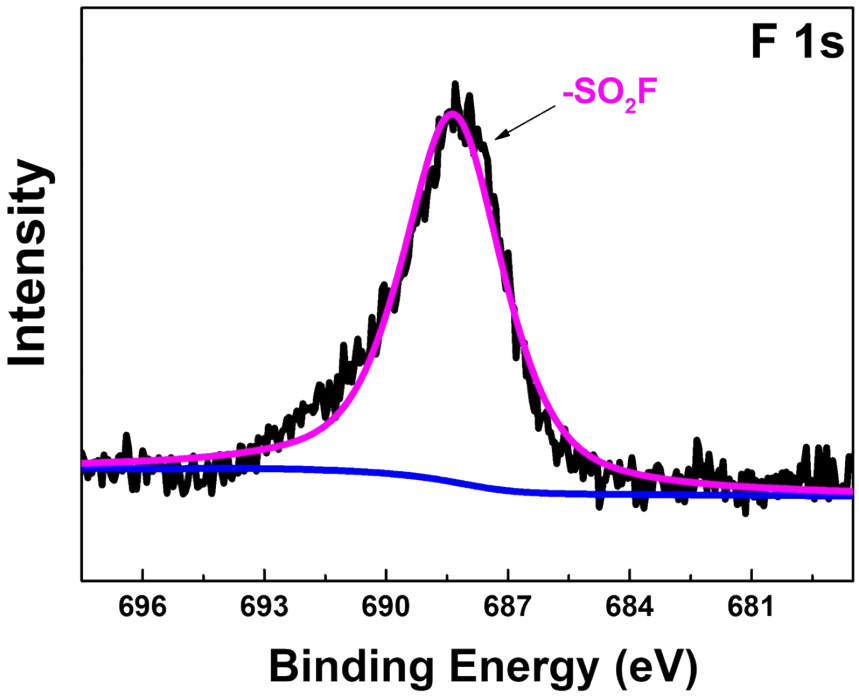

Fig. S4 The F 1s spectra of SFCOF.

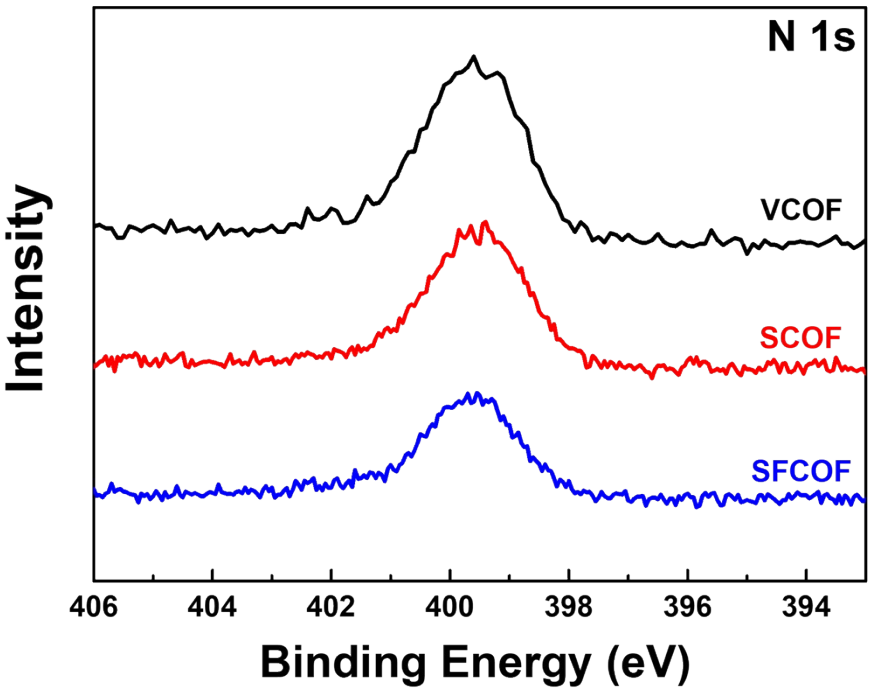

Fig. S5 The comparison of N 1s spectra of VCOF, SCOF and SFCOF.

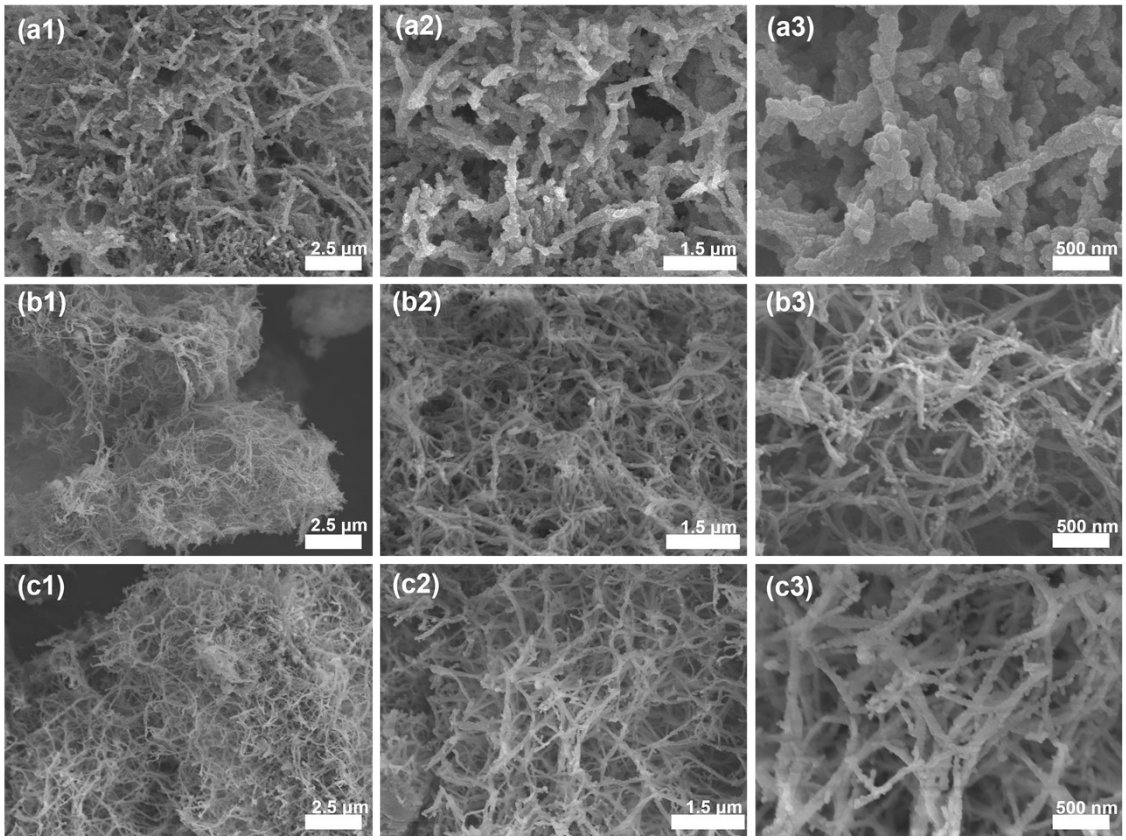

Fig. S6 The scanning electron microscopy (SEM) images of (a) VCOF, (b) SCOF, and (c) SFCOF.

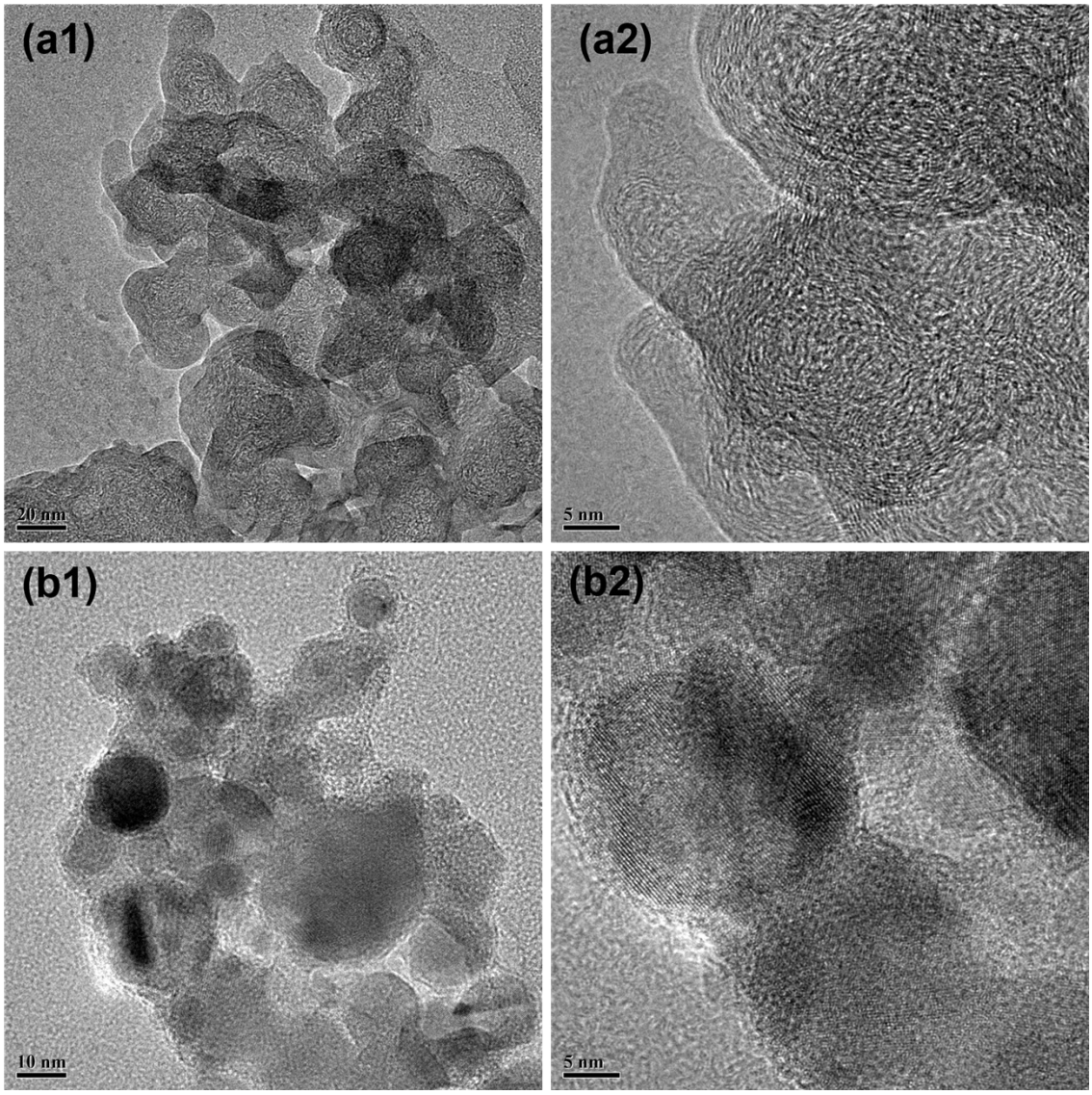

Fig. S7 The transmission electron microscopy (TEM) images of (a) VCOF and (b) SCOF.

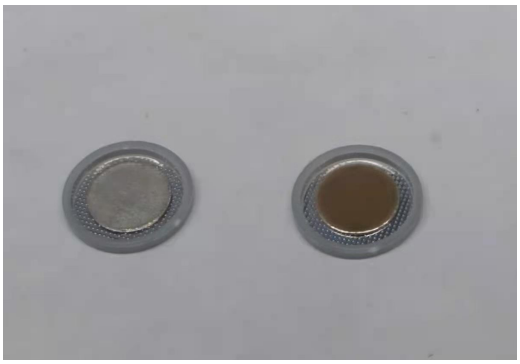

Fig. S8 The digital picture of SFCOF@Li (right) and Li sheets (left).

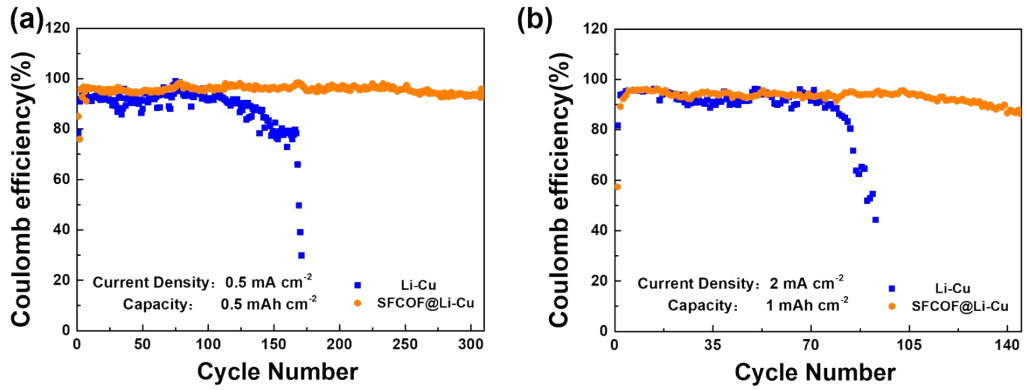

Fig. S9 Comparison of the Coulomb efficiency (CE) of the Li–Cu batteries at a current density of (a) 0.5 and (b) 2 mA cm^{-2}.

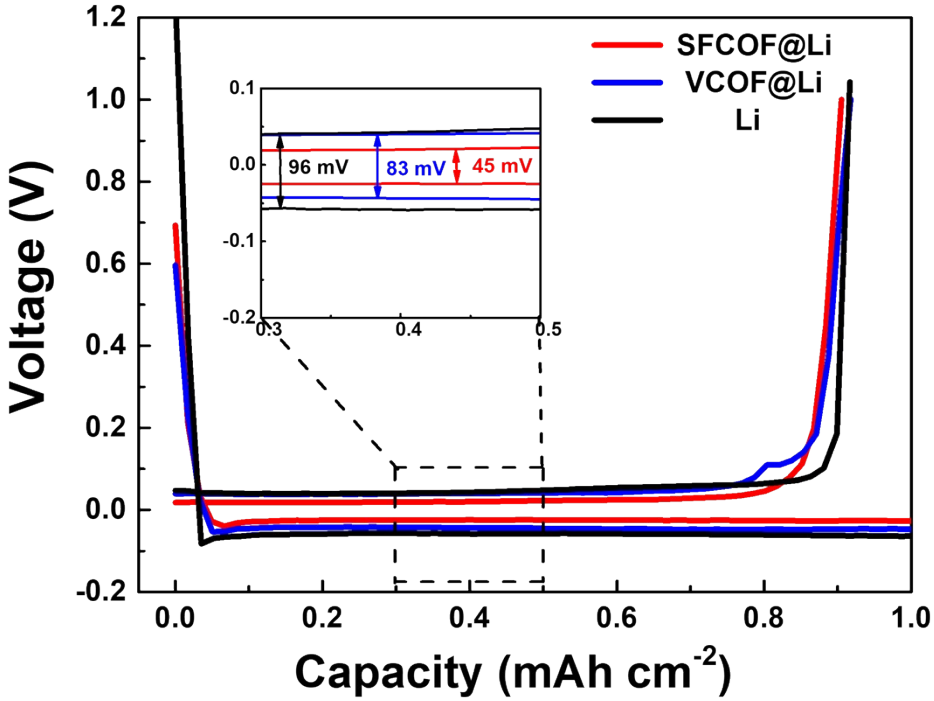

Fig. S10 The voltage–capacity curves of Li–Cu batteries based on Li, VCOF@Li, and SFCOF@Li electrodes at third cycle.

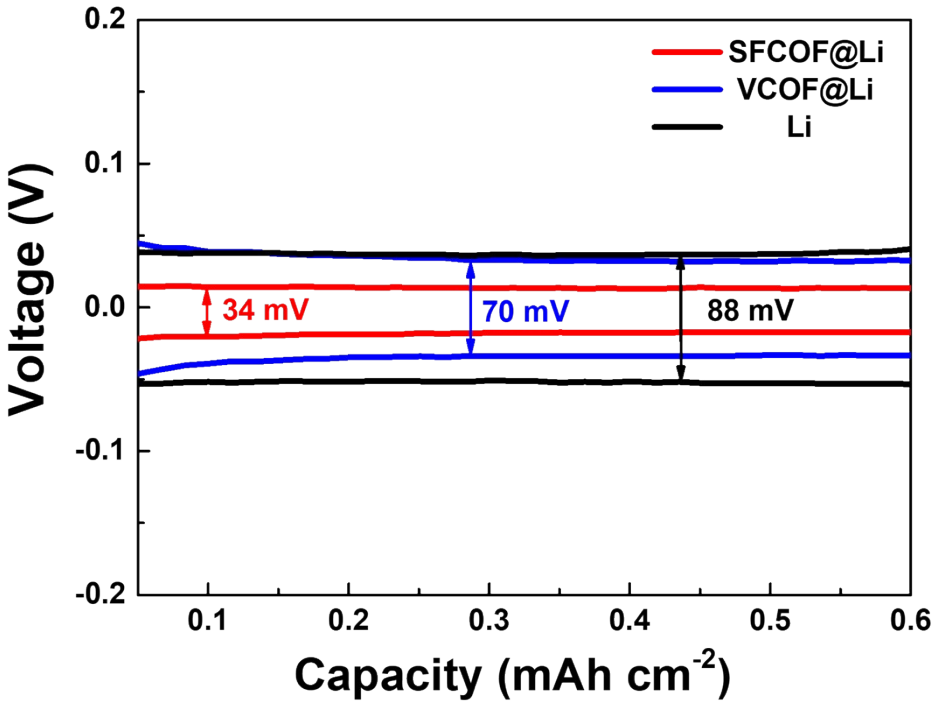

Fig. S11 The voltage–capacity curves of Li–Cu batteries based on Li, VCOF@Li, and SFCOF@Li electrodes at the 70th cycle.

Table S1 The comparison of the Li–Cu batteries for different modifications in LiTFSI electrolyte system.

Current density ($mA\ cm^{-2}$)	Capacity ($mAh\ cm^{-2}$)	Cycles	CE (%)	Modification	Reference
0.5	0.5	80	96	COF-1	S1
0.5	0.5	140	97	S-COF	S2
0.5	0.5	150	96	COF-TPB-BD$(OH)_2$	S3
0.5	0.5	240	95	DqTp	S4
0.5	**0.5**	**308**	**96**	**SFCOF**	**This work**
1	1	80	90	COF-TpTG	S5
1	1	100	98	Porous carbon cloth	S6
1	1	100	98	EB-COF	S7
1	1	120	97	3D porous Cu	S8
1	1	140	98	COF-COOH	S9
1	**1**	**150**	**98**	**SFCOF**	**This work**
1	**1**	**200**	**90**	**SFCOF**	**This work**

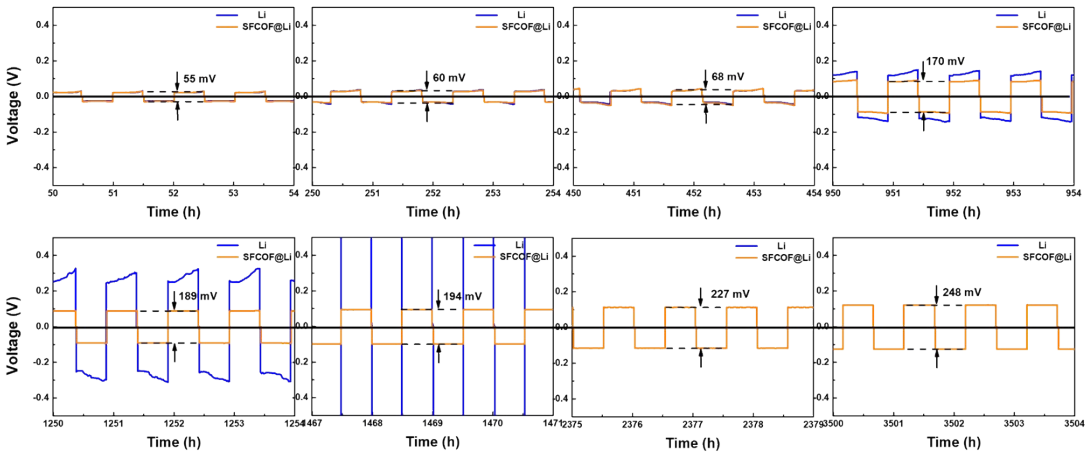

Fig. S12 The enlarged voltage curves of symmetric batteries with Li and SFCOF@Li electrodes under current density of 2 mA cm^{-2}.

Table S2 The comparison of the symmetric Li cells for different modifications with fixed capacity of 1 mAh cm^{-2} and current density of 2 mA cm^{-2} in LiTFSI electrolyte system.

Cycling time (h)	Modification	References
200	$COF_{TAPB\text{-}PDA}$ film	S10
250	$Li_{4.4}Sn$/hollow graphene spheres	S11
400	Cuboid LiF host	S12
500	CNTs modifying carbon cloth film	S6
560	3D copper-based magnetic current collector	S13
620	N-doped carbon rod array	S14
1200	Nitrogen-doped graphitic carbon foams	S15
1250	Nitrogen-doped carbon microcavities	S16
2000	COF-TpPa	S17
2600	Polyacrylamide-modified separators	S18
3550	**Aligned artificial SEI layer**	**This work**

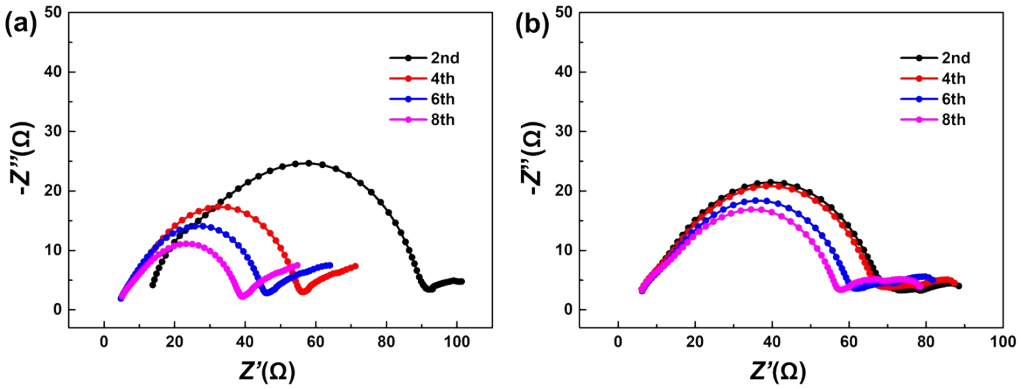

Fig. S13 The electrochemical impedance spectroscopy (EIS) plots of symmetric batteries with (a) and without (b) SFCOF protection after cycling tests.

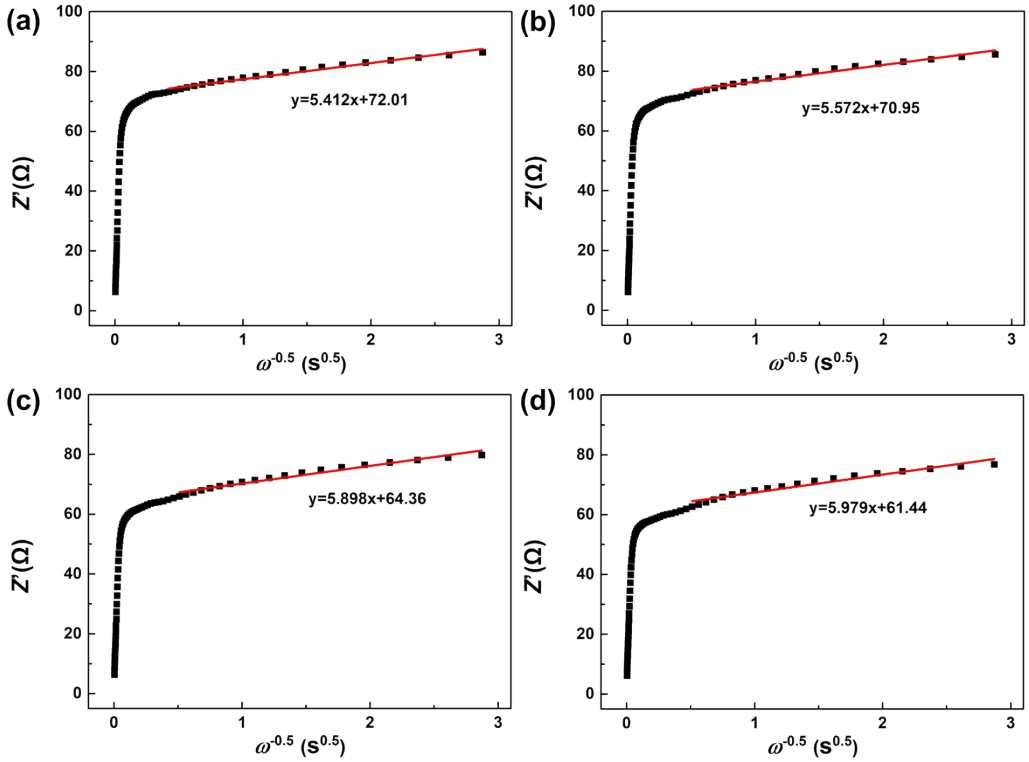

Fig. S14 The relationship and fitted lines of *Z*' and frequency (ω) in Li|Li symmetric batteries after (a) 2, (b) 4, (c) 6, and (d) 8 cycles. The slopes of the fitted lines represent the Warburg coefficient *W*.

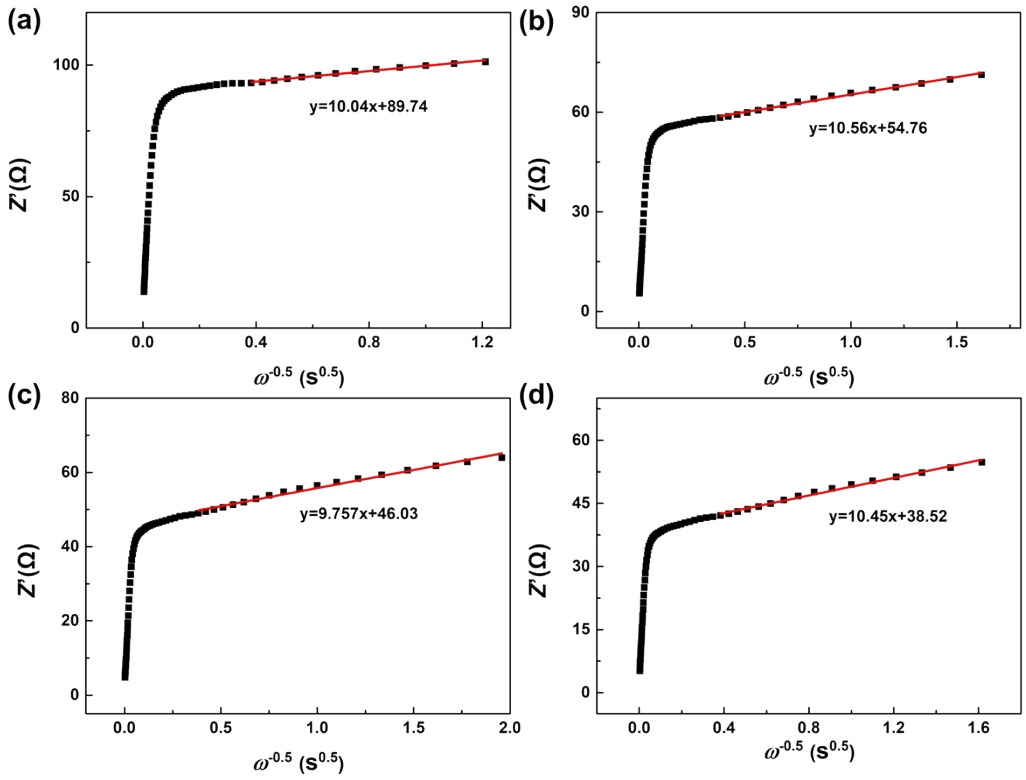

Fig. S15 The relationship and fitted lines of *Z*' and frequency (ω) in SFCOF@Li|SFCOF@Li symmetric batteries after (a) 2, (b) 4, (c) 6, and (d) 8 cycles. The slopes of the fitted lines represent the Warburg coefficient *W*.

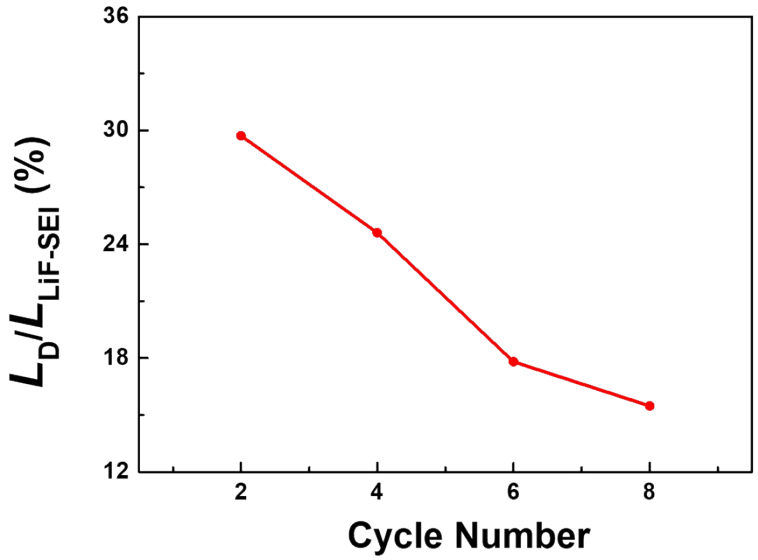

Fig. S16 The ratio of Debye length (L_D) over the thickness LiF-dominated SEI layer ($L_{LiF\text{-}SEI}$) in SFCOF@Li|SFCOF@Li batteries after 2, 4, 6, and 8 cycles.

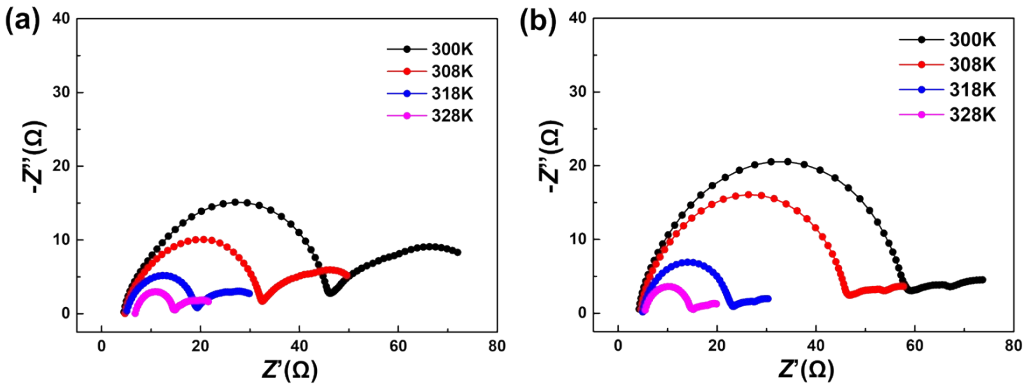

Fig. S17 The EIS plots of symmetric batteries with (a) and without (b) SFCOF protection in the range of 300 to 328 K.

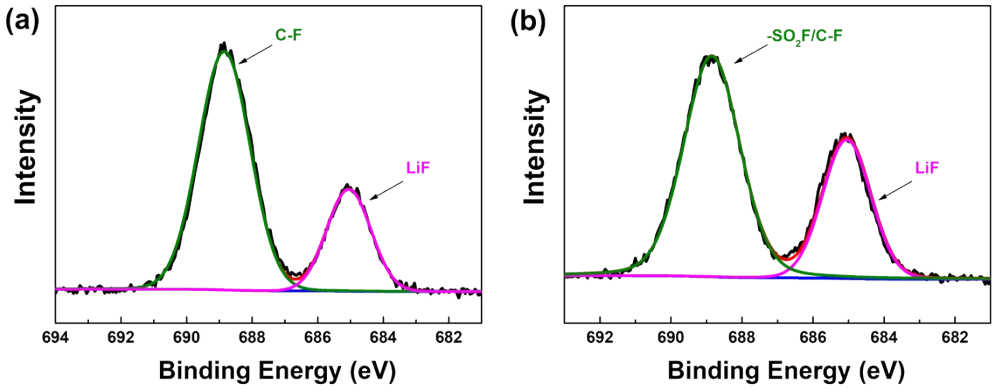

Fig. S18 The F 1s spectra of SEI layers in (a) Li–Cu and (b) SFCOF@Li–Cu batteries after 150 cycles in LiTFSI-based electrolyte.

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