

Supplementary Information for

Title: Screening of F-containing electrolyte additives and clarifying their decomposition routes for stable Li metal anodes

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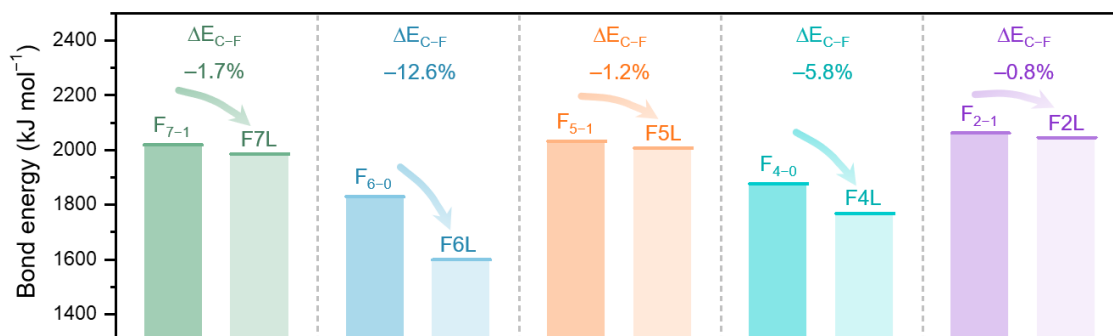
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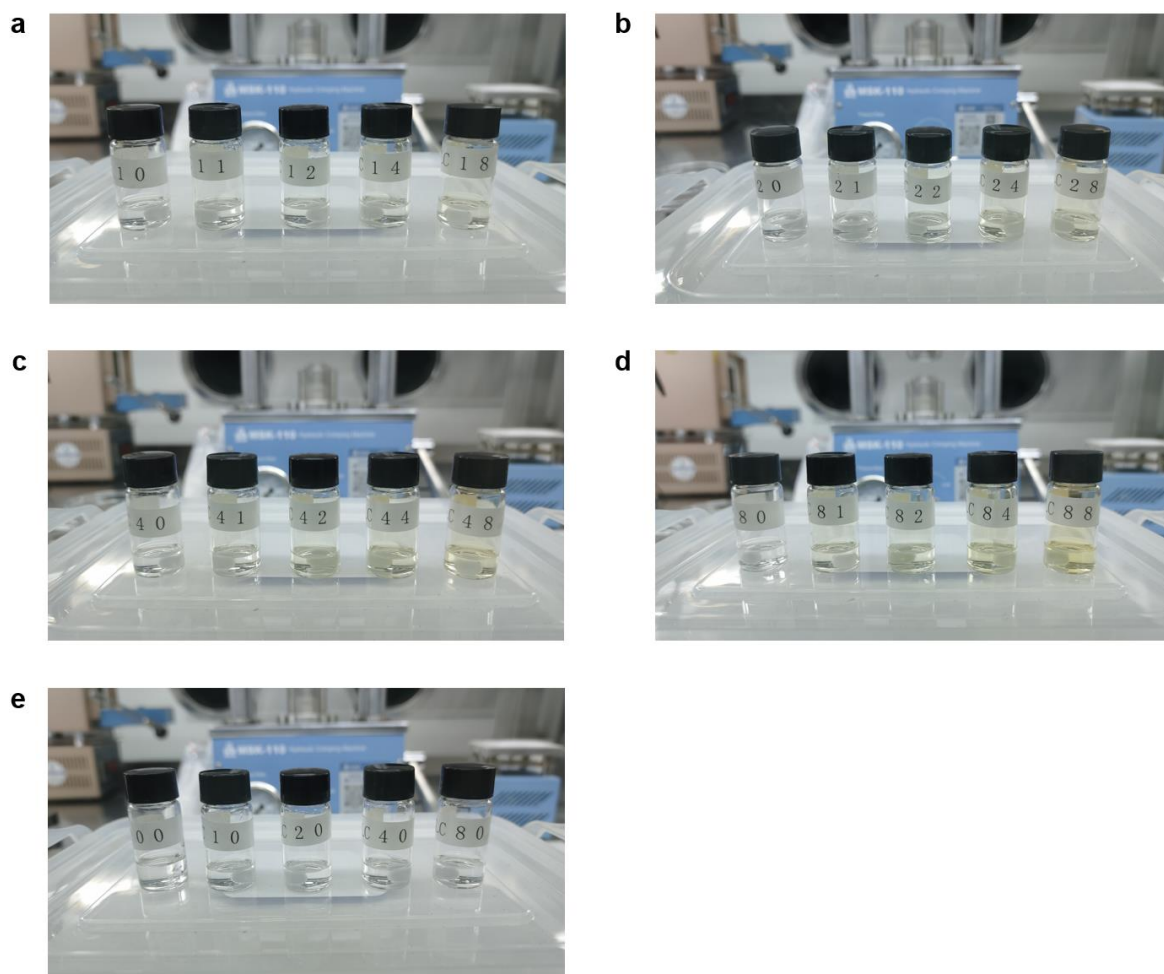
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Supplementary Figures



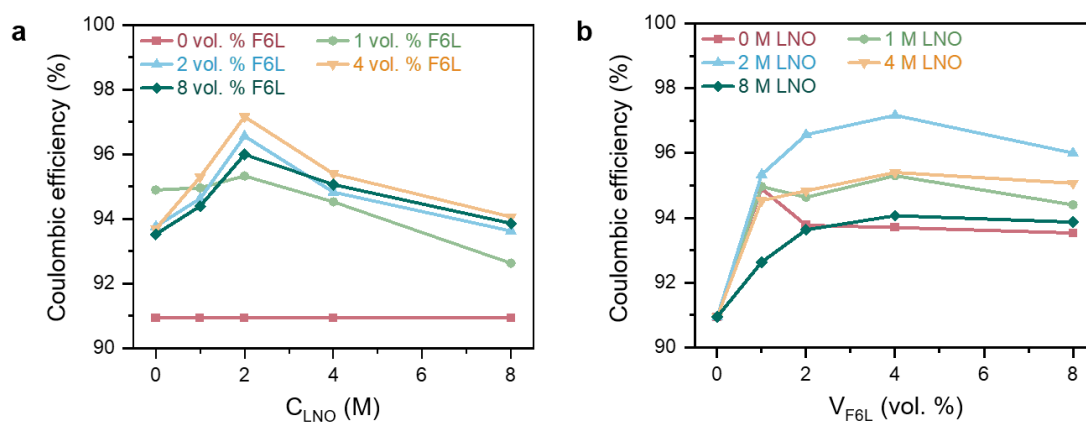
Supplementary Fig. 1. The average C–F bond energy in the F₇₋₁/F₆₋₀/F₅₋₁/F₄₋₀/F₂₋₁ (without LNO) and F_{7L}/F_{6L}/F_{5L}/F_{4L}/F_{2L} (with LNO).

Note of Supplementary Fig. 1: To investigate the synergistic interaction between fluorinated anhydrides and LNO and unveil how the decomposition of the fluorinated anhydrides occurs without and with LNO, first-principles calculation based on DFT was employed. The impact of LNO on fluorinated anhydrides under static conditions was analyzed. As displayed in **Supplementary Fig. 1**, the average bond energy of C–F in circular fluorinated anhydrides (F₆₋₀ and F₄₋₀) decreases more when the LNO molecule approaches them than in the linear ones, indicating a stronger interaction between circular fluorinated anhydrides and LNO. What's more, this is especially true for the much weaker C–F bond energy of F₆₋₀ (1598.6 kJ mol⁻¹) compared to other fluorinated anhydride molecules, which strongly supports the fact that F₆₋₀ is more prone to decomposition under LNO catalysis.

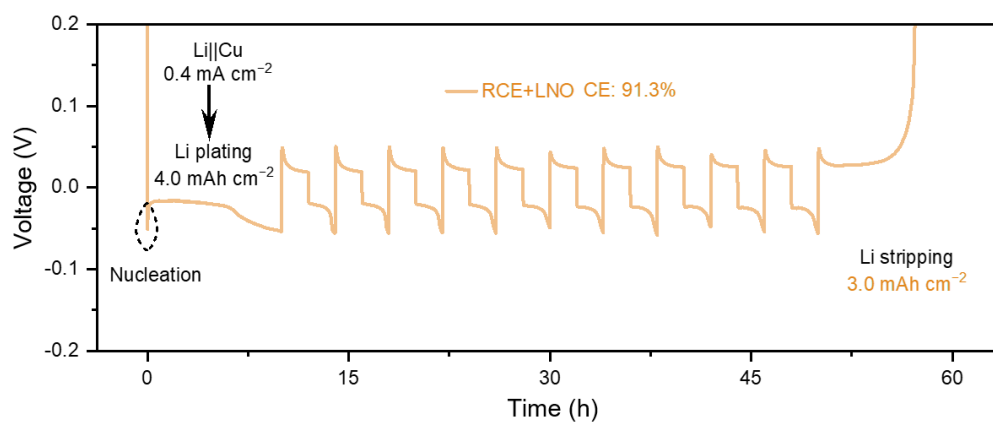


Supplementary Fig. 2. Digital photos of twenty-one different samples with combinations of varying amounts of F₆₋₀ and LNO in RCE. Electrolyte codes in **a**, **b**, **c**, **d**, and **e** can be corresponded in **Supplementary Table 1**.

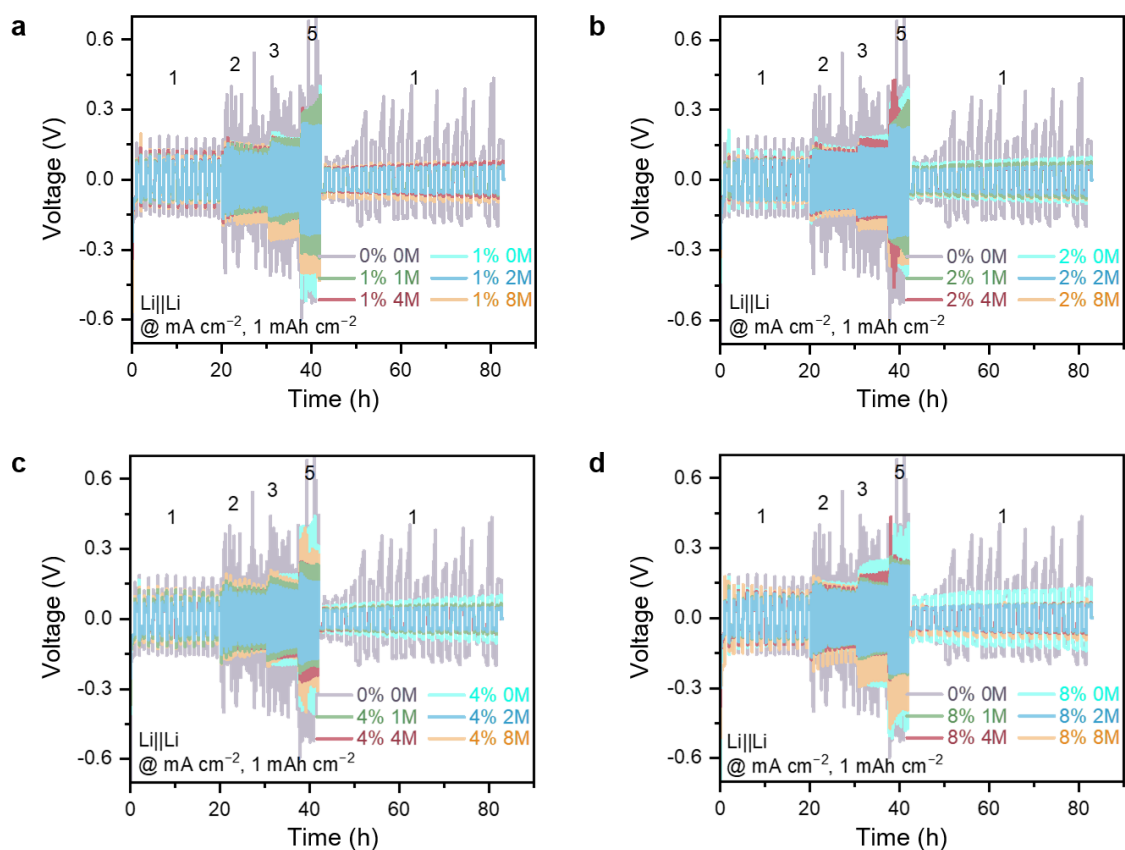
Note of Supplementary Fig. 2: As seen in **Supplementary Fig. 2a, 2b, 2c, and 2d**, when F₆₋₀ and LNO are gradually added to RCE, the color of the electrolytes deepens progressively. This phenomenon arises from the strong coordination interaction between the double C=O bonds in F₆₋₀ and LNO. A similar observation was found by Yang *et al.*¹. In contrast, when only F₆₋₀ is added in RCE, the electrolyte remains colorless and transparent (**Supplementary Fig. 2e**).



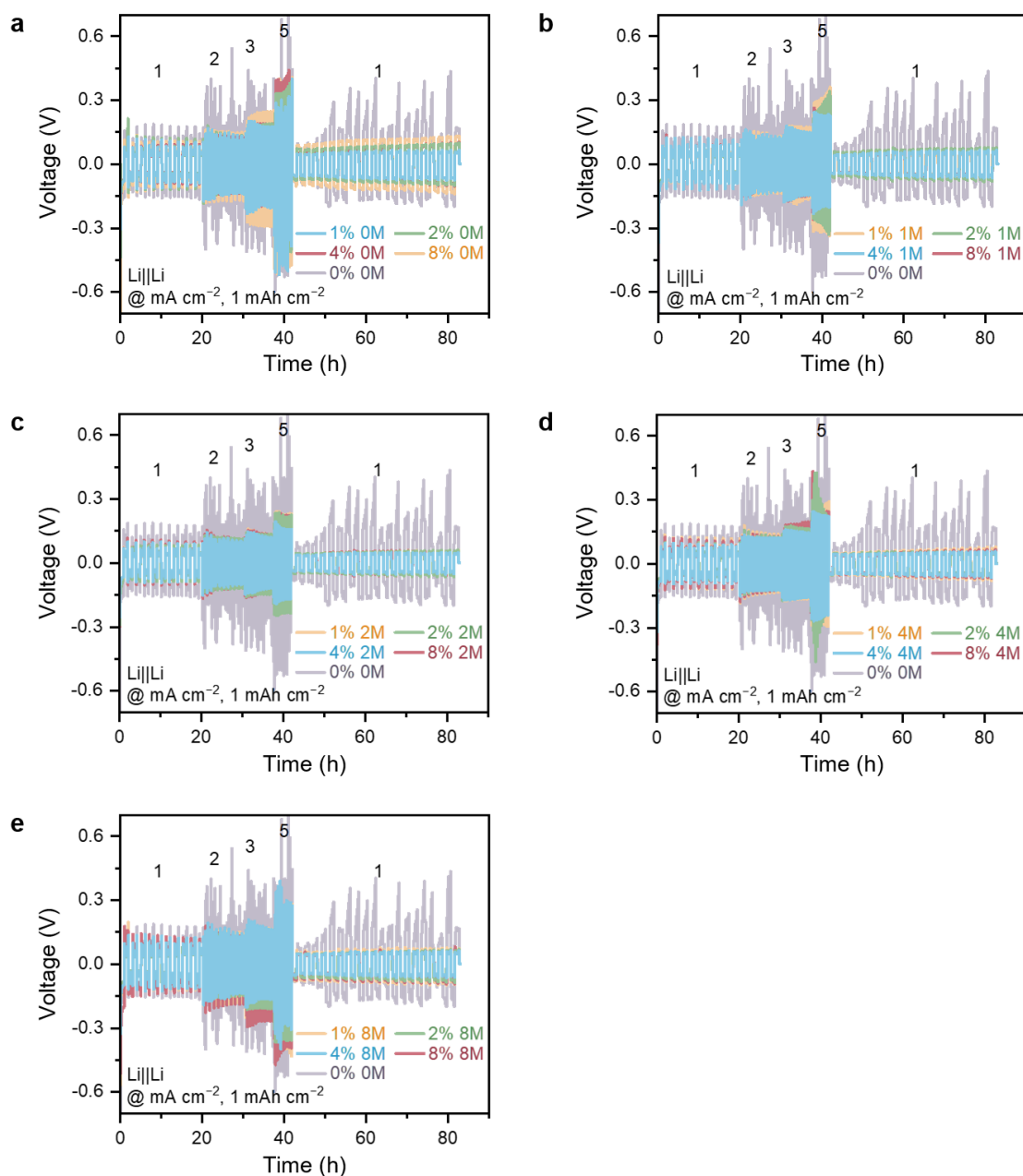
Supplementary Fig. 3. CEs recorded from the half-cells using the RCE with different amounts of additions of F6L possessing various ratios of F₆₋₀ and LNO at 0.4 mA cm^{-2} with 0.8 mAh cm^{-2} . Control variate for **a** the addition of F6L in RCE and **b** the concentration of LNO in F₆₋₀. Electrolyte codes in **a** and **b** can be corresponded in **Supplementary Table 1**.



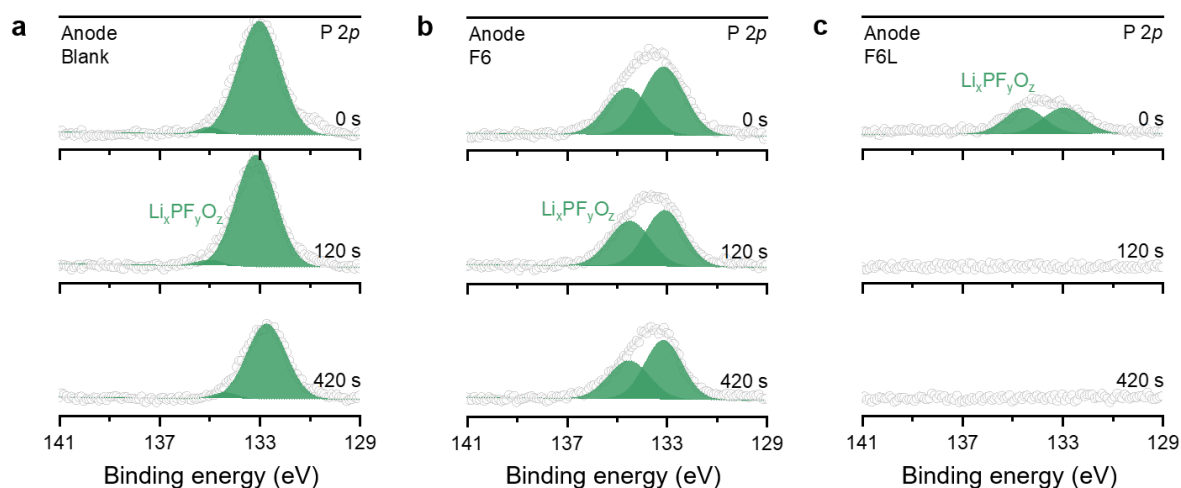
Supplementary Fig. 4. Voltage profiles of the half-cell using RCE+LNO.



Supplementary Fig. 5. The rate performance of Li symmetric cells using the RCE with different amounts of F6L possessing various ratios of F₆₋₀ and LNO at 1, 2, 3, 5, and 1 mA cm⁻² with 1 mAh cm⁻². Control variate for the addition of F6L in RCE. Electrolyte codes in **a**, **b**, **c**, and **d** can be corresponded in **Supplementary Table 1**.

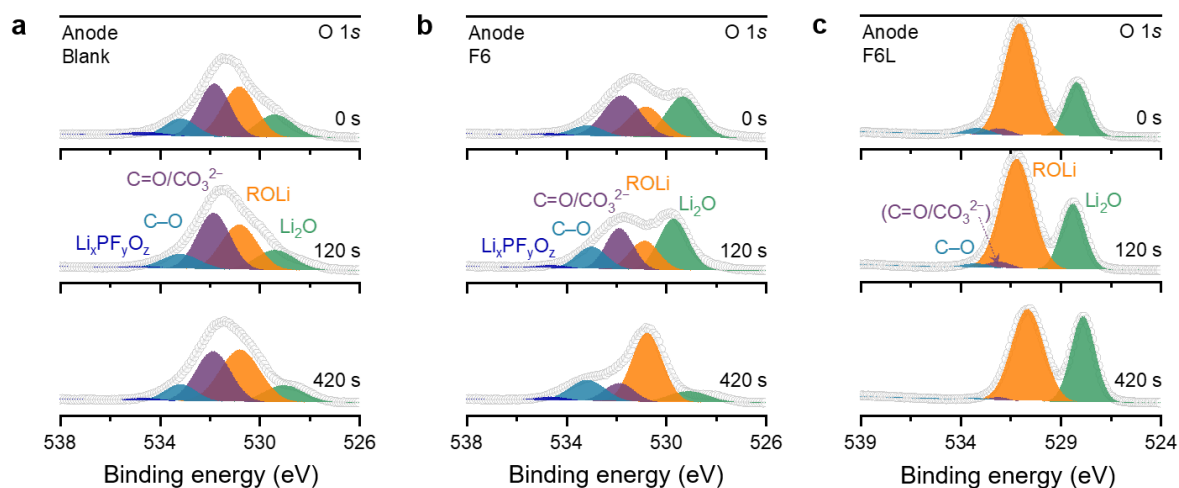


Supplementary Fig. 6. The rate performance of Li symmetric cells using the RCE with different amounts of F6L possessing various ratios of F₆₋₀ and LNO at 1, 2, 3, 5, and 1 mA cm⁻² with 1 mAh cm⁻². Control variate for the concentration of LNO in F₆₋₀. Electrolyte codes in **a**, **b**, **c**, **d**, and **e** can be corresponded in **Supplementary Table 1**.



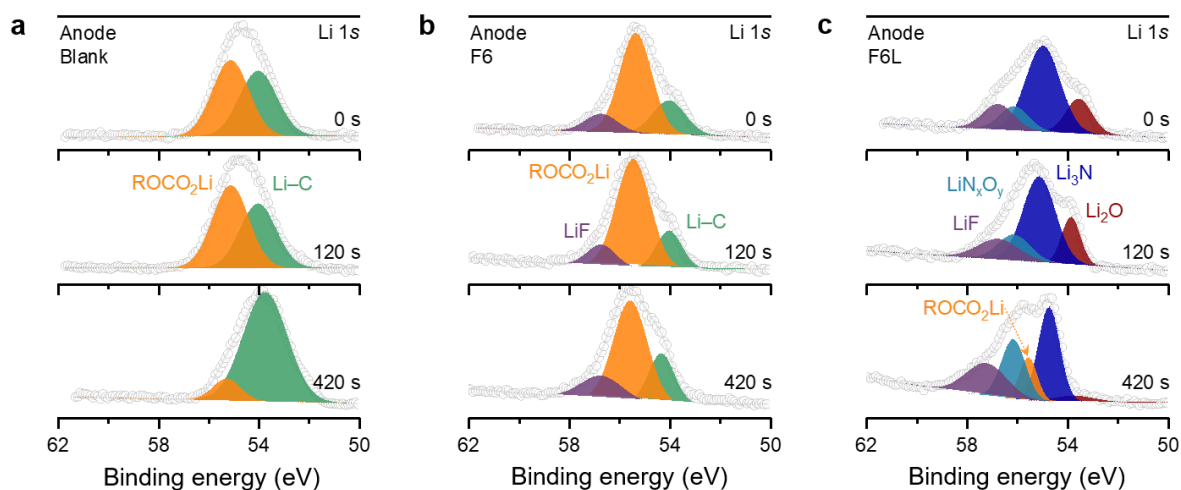
Supplementary Fig. 7. In-depth P 2p XPS spectra of Li metal anodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L.

Note of Supplementary Fig. 7: In the P 2p XPS spectra of Blank, the $\text{Li}_x\text{PF}_y\text{O}_z$ can be identified by the peaks at 133 and 135 eV. These substances originate from the decomposition of LiPF_6 in RCE and serve as the inorganic components of the SEI. Adding F6 could only mildly hampers the reduction of LiPF_6 with still heavy $\text{Li}_x\text{PF}_y\text{O}_z$ peak. By contrast, due to the LiF layer formed by the preferential decomposition of F6L, the reduction of LiPF_6 is hindered by the significantly reduced intensity of the $\text{Li}_x\text{PF}_y\text{O}_z$ peak. The results of the XPS spectra on the chemical states of SEI and the corresponding binding energy are listed in **Supplementary Table 2**.



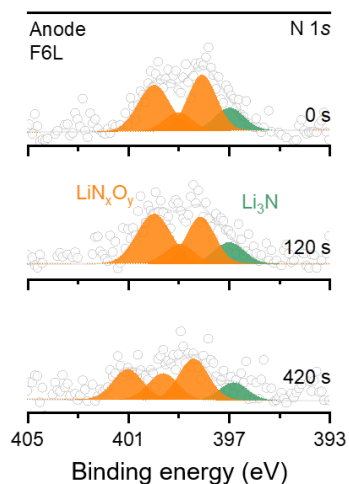
Supplementary Fig. 8. In-depth O 1s XPS spectra of Li metal anodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L.

Note of Supplementary Fig. 8: In the O 1s XPS spectra of Blank and F6, the $\text{Li}_x\text{PF}_y\text{O}_z$ can be identified by the peak at 534.5 eV. These substances originate from the decomposition of LiPF_6 in RCE and serve as the inorganic components of the SEI. By contrast, due to the LiF layer formed by the preferential decomposition of F6L, the reduction of LiPF_6 is hindered without the $\text{Li}_x\text{PF}_y\text{O}_z$ peak detected. The results of the XPS spectra on the chemical states of SEI and the corresponding binding energy are listed in **Supplementary Table 2**.



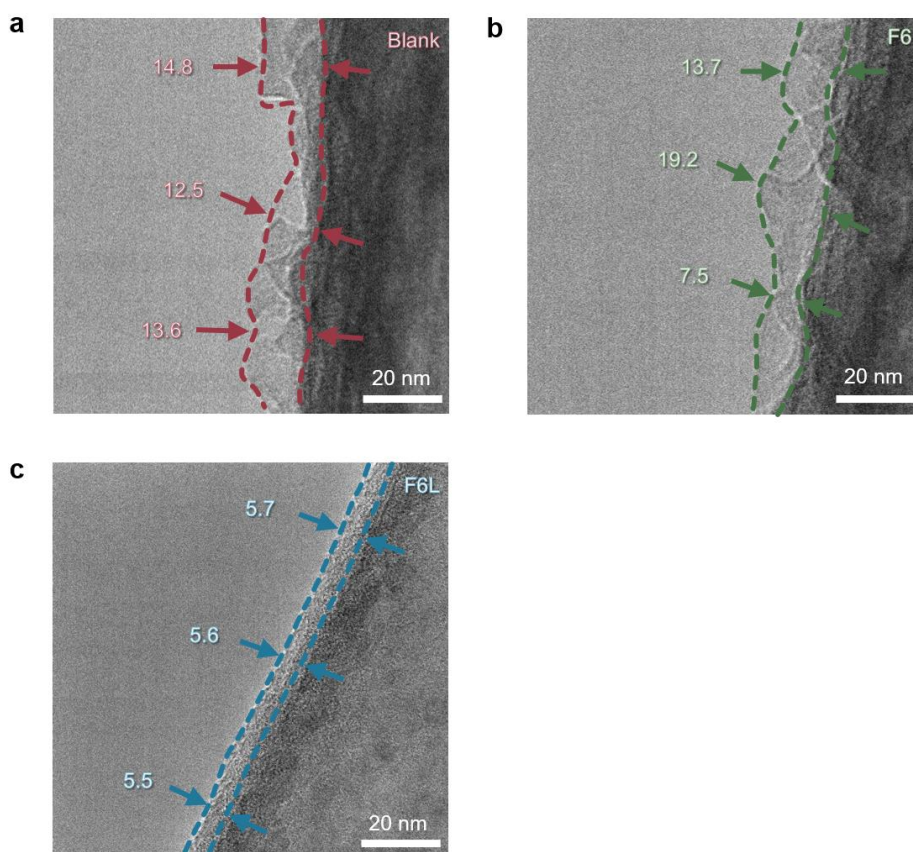
Supplementary Fig. 9. In-depth Li 1s XPS spectra of Li metal anodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L.

Note of Supplementary Fig. 9: In the Li 1s XPS spectra of F6L, the LNO-derived Li_3N can be identified by the peak at 55 eV at different thicknesses, emphasizing the role of F_{6-0} in inducing the decomposition of NO_3^- anion. The results of the XPS spectra on the chemical states of SEI and the corresponding binding energy are listed in **Supplementary Table 2**.



Supplementary Fig. 10. In-depth N 1s XPS spectra of the Li metal anode after 20 cycles in F6L.

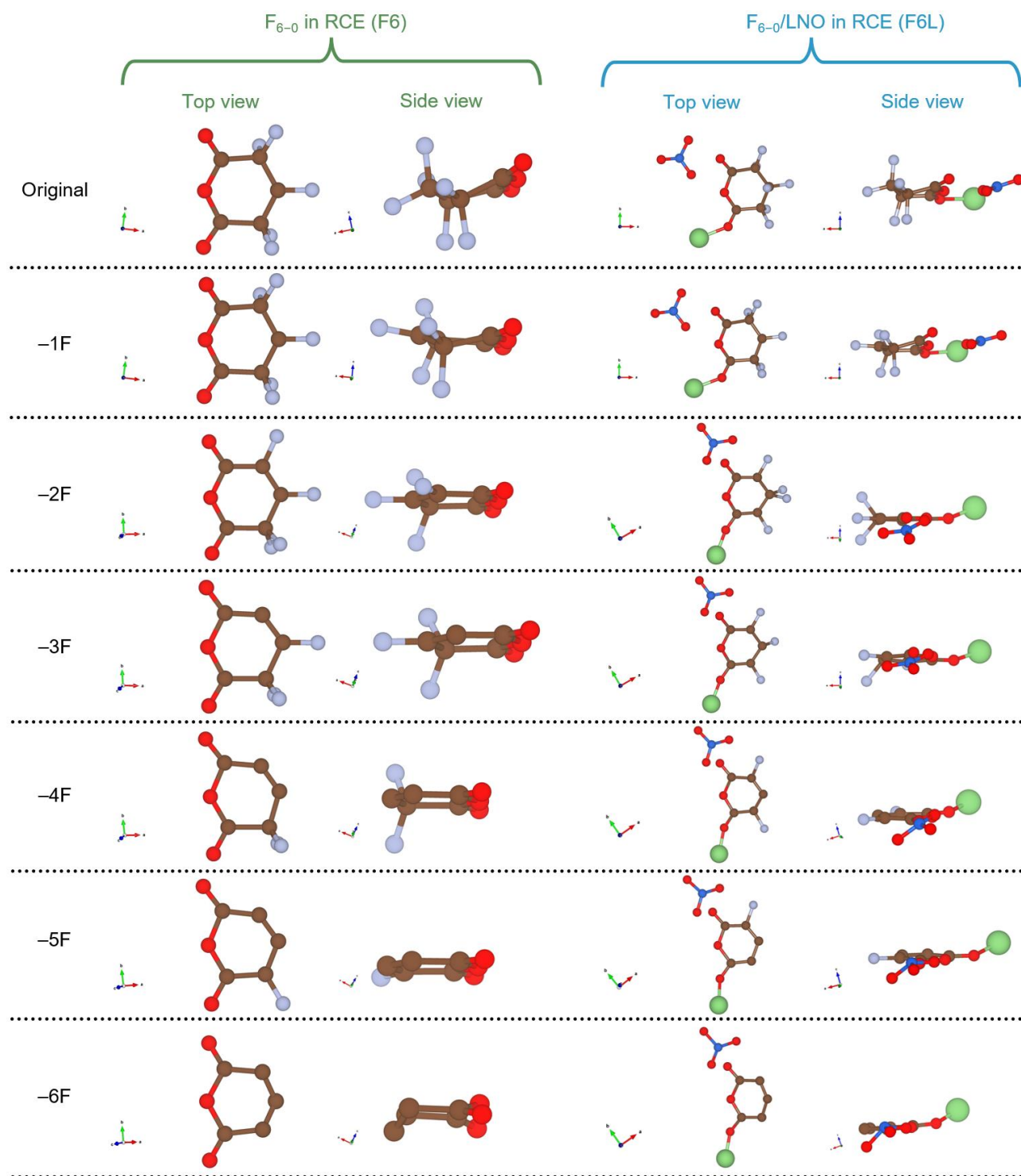
Note of Supplementary Fig. 10: In the N 1s XPS spectra of F6L, the LNO-derived Li_3N can be identified by the peak at 397 eV at different thicknesses, emphasizing the role of F_{6-0} in inducing the decomposition of NO_3^- anion. The results of the XPS spectra on the chemical states of SEI and the corresponding binding energy are listed in **Supplementary Table 2**.



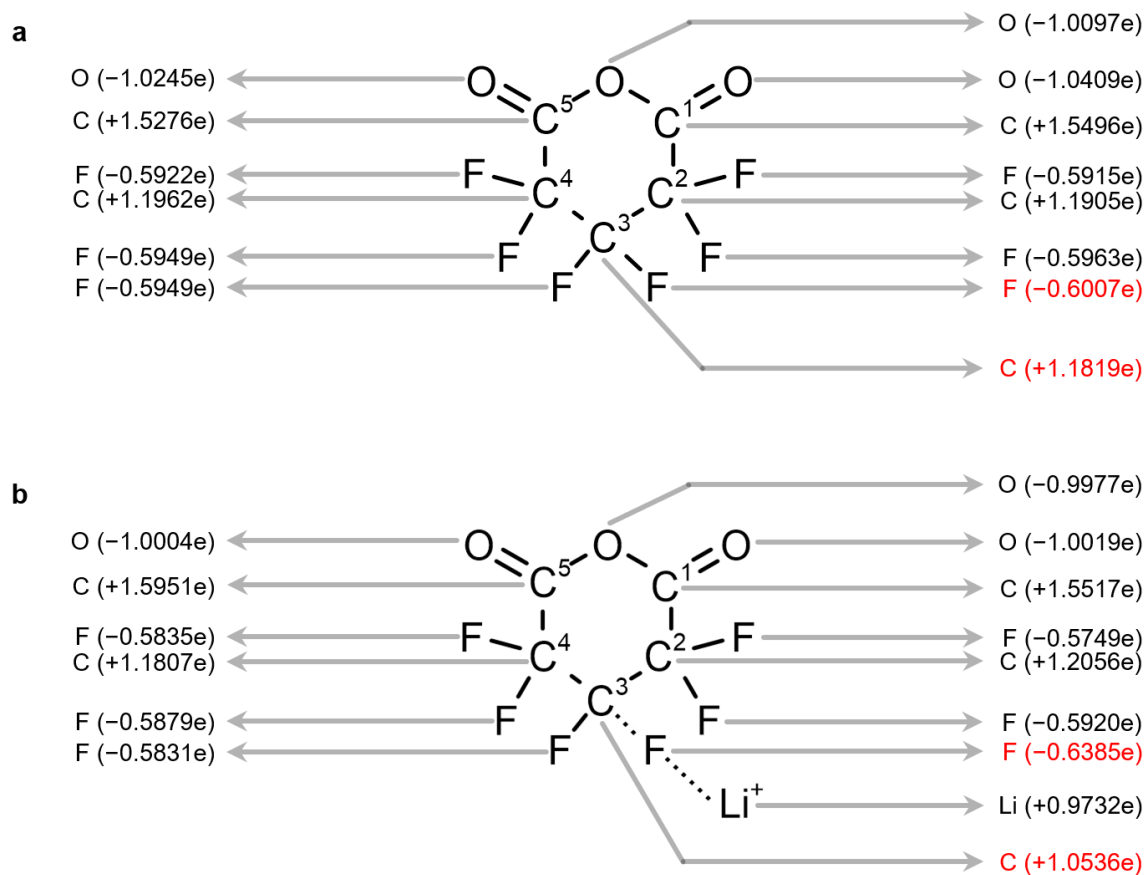
Supplementary Fig. 11. Cryo-TEM images of SEIs formed in **a** Blank, **b** F6, and **c** F6L after 50 cycles at $0.5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$.

Note of Supplementary Fig. 11: As shown in **Fig. 3h, 3i, and 3j**, the SEI thickness remained stable after 20 cycles at 0.5 mA cm^{-2} , but there was a substantial variation in the uniformity of SEI distribution. The CE of Li symmetric cells using Blank and F6 electrolytes are very low among the tested electrolytes. To further evaluate the advantages of F6L electrolyte in stabilizing the Li metal anode interface, we carried out the cryo-TEM to monitor the evolution process of the SEI. As cycles progress, it becomes increasingly evident that the SEIs formed in Blank and F6 exhibit similar characteristics, being both thick and uneven (**Supplementary Fig. 11a and 11b**). In contrast, the presence of LNO in RCE enhances the conversion kinetics of F_{6-0} to LiF, leading to the formation of a homogeneous and compact SEI structure (**Supplementary Fig. 11c**). As shown in **Fig. 3h and Supplementary Fig. 11a**, the SEI in the Blank should be mainly from EC. However, this SEI is not stable, as the cryo-TEM observed a dramatical increase of the SEI thickness from ~ 6.5 to ~ 13.6 nm in 50 cycles, which subsequently caused the increase of interface impedance and overpotential (**Fig. 5h and 5i**). When using F_{6-0} as an additive, a much smoother voltage curve of the Li||Li cell was obtained (**Fig. 5h and 5i**), probably due to a contribution of F_{6-0} to SEI. However, the polarization voltage became larger after long cycling, which was consistent with the increased thickness of SEI from ~ 6.4

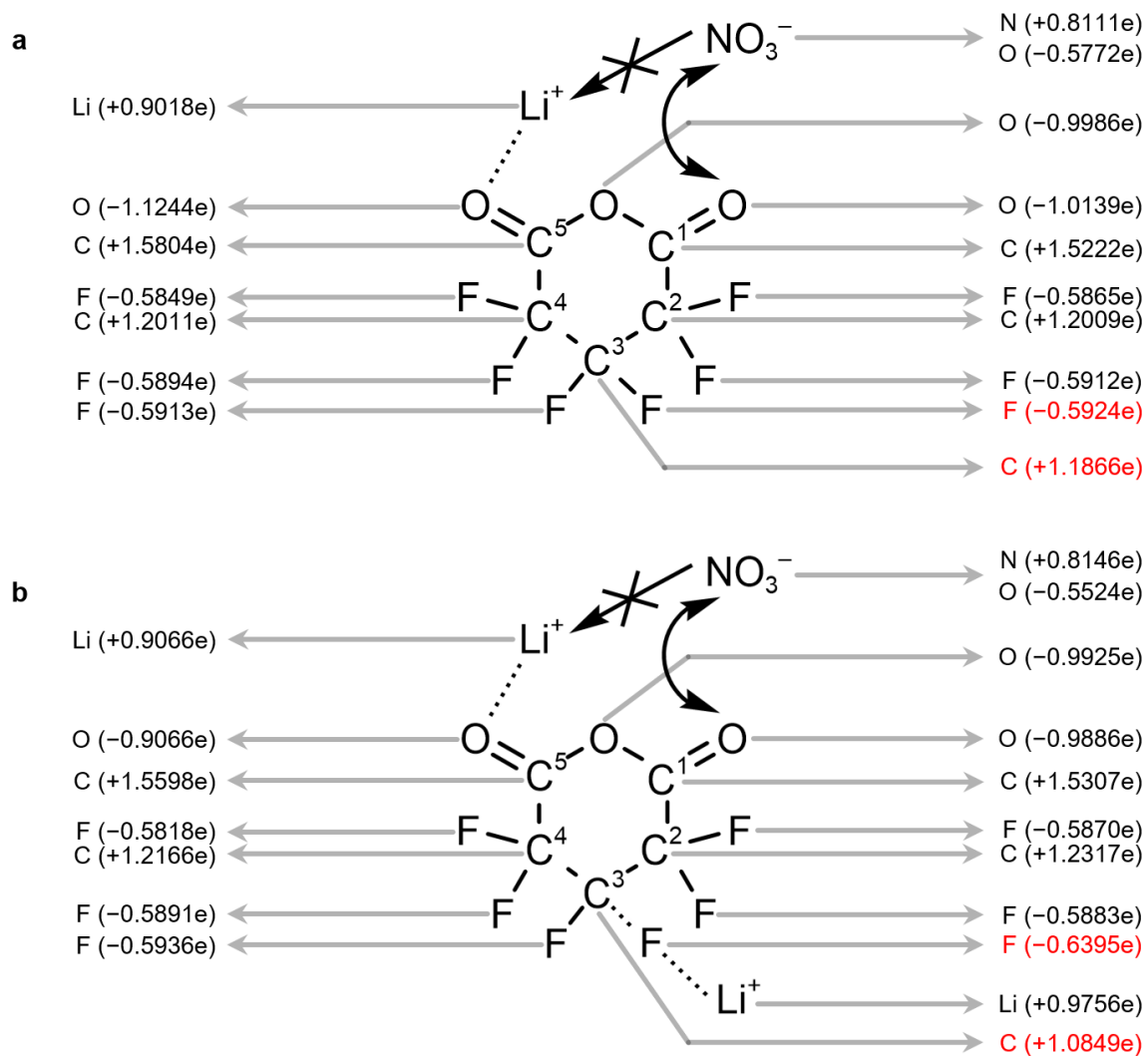
to ~13.7 nm (**Fig. 3i and Supplementary Fig. 11b**). In sharp contrast, the cell using F6L electrolyte showed the smallest polarization in long cycling even at a large current density of 5 mA cm⁻² (**Fig. 2f**), implying the formation of a robust and highly Li⁺-conductive SEI. Indeed, from cryo-TEM observation, this SEI is very thin (~5.5 nm) and remained stable during cycles (**Fig. 3j and Supplementary Fig. 11c**).



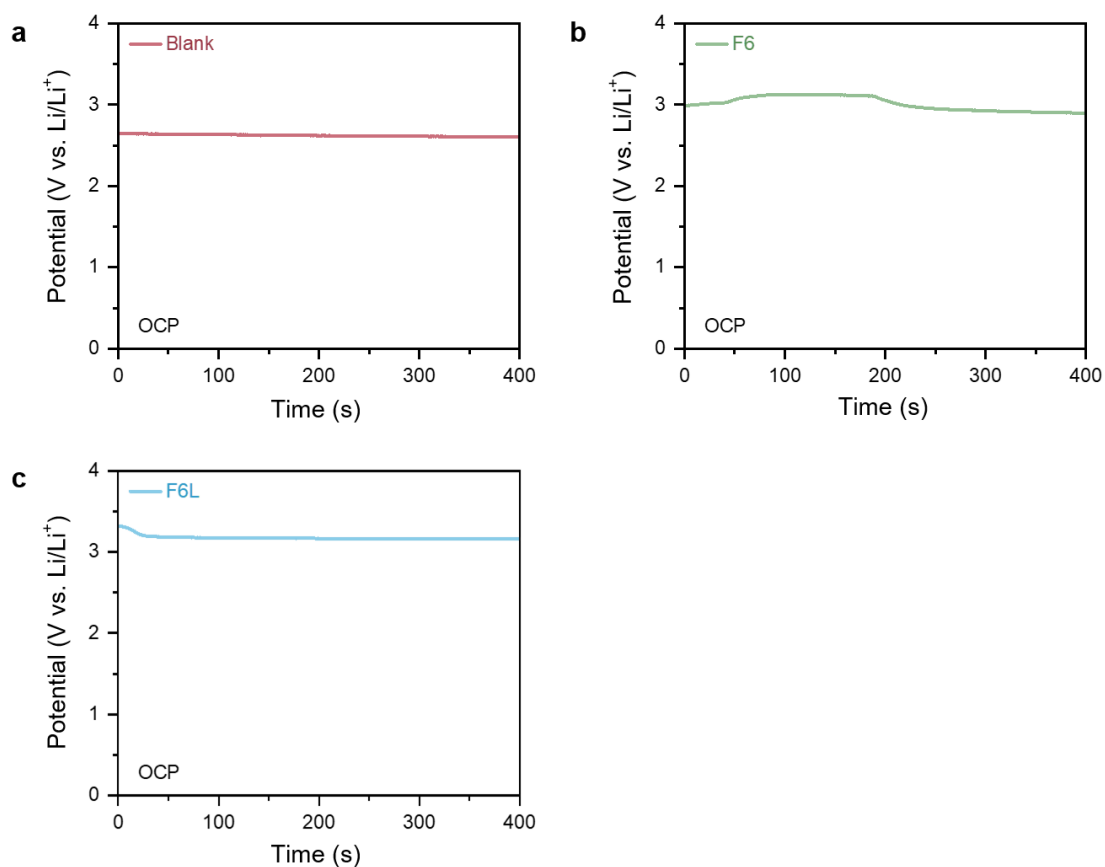
Supplementary Fig. 12. Geometrical structures of molecules involved showing the evolution of the F_{6-0} in RCE (F6) and F_{6-0}/LNO in RCE (F6L) with all six F atoms decomposed step-by-step. The green, brown, blue, red, and light blue balls represent Li, C, N, O, and F atoms, respectively.



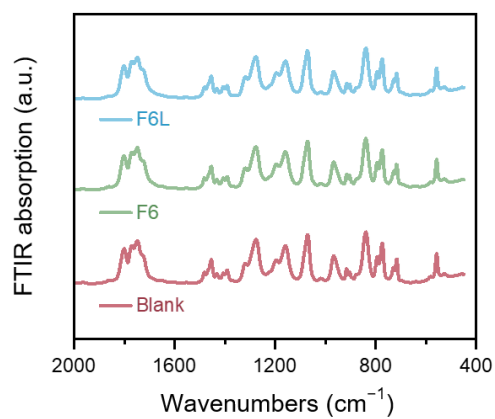
Supplementary Fig. 13. Bader charge of **a** F₆₋₀ and **b** TS-1 in F6.



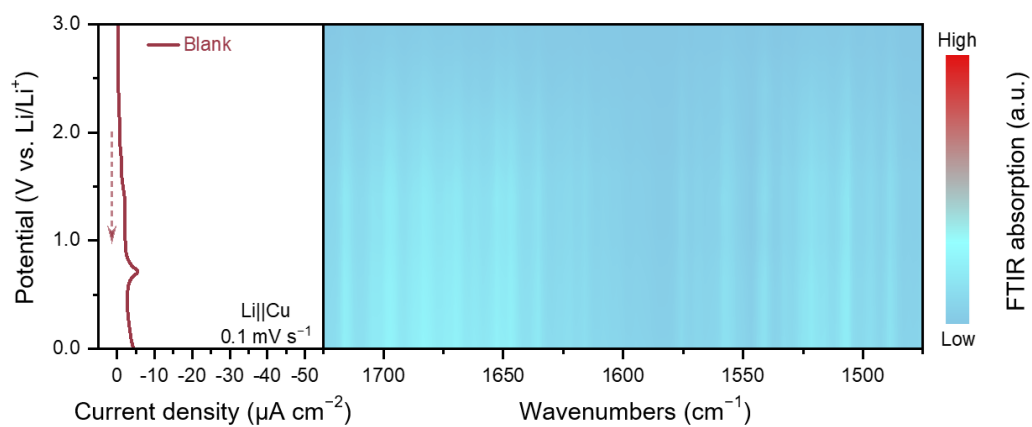
Supplementary Fig. 14. Bader charge of **a** F₆₋₀ with LNO and **b** TS-1 in F6L.



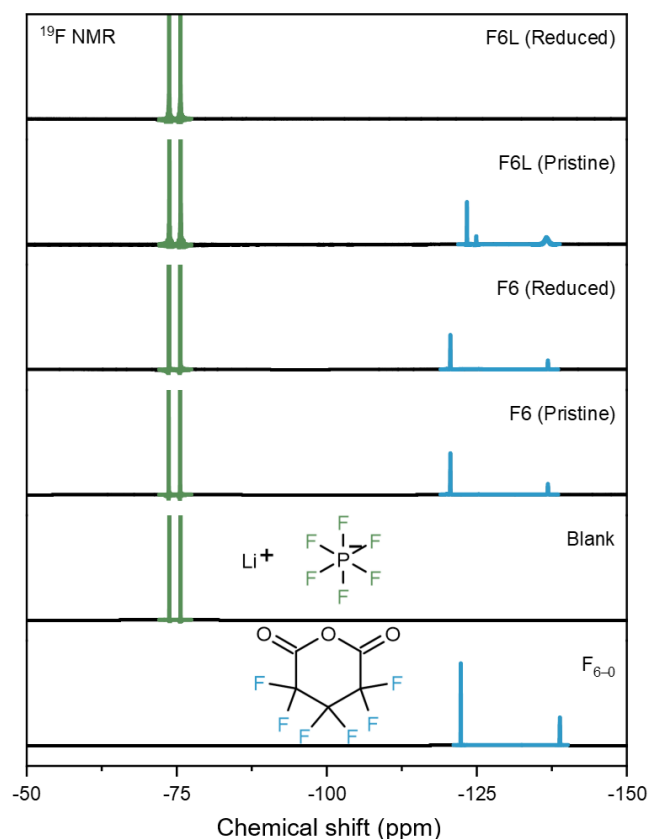
Supplementary Fig. 15. Open circuit potential profiles of the simulating Li||Cu half-cells with **a** Blank, **b** F6, and **c** F6L.



Supplementary Fig. 16. FTIR spectra of Li||Cu half-cells with Blank, F6, and F6L under open circuit potential.

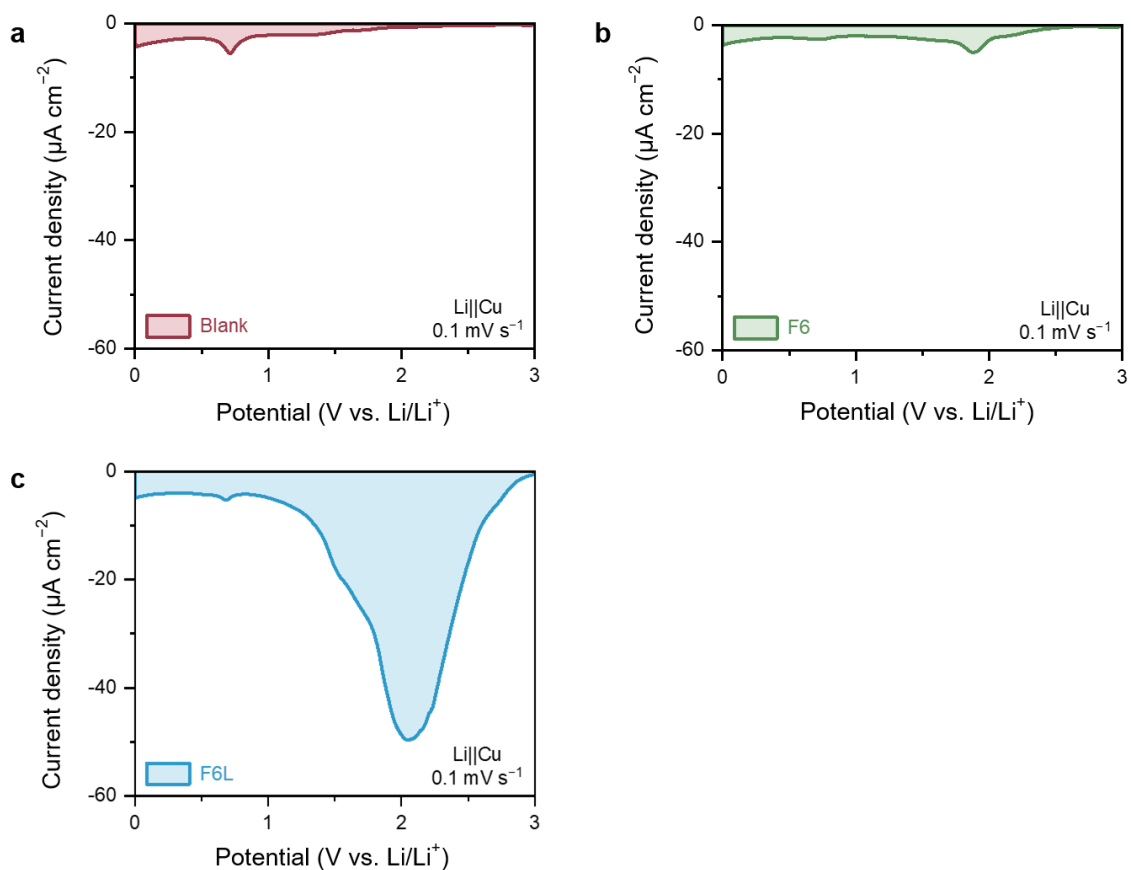


Supplementary Fig. 17. Electrochemical *in-situ* FTIR spectra of Li||Cu half-cells using Blank at 0.1 mV s⁻¹.



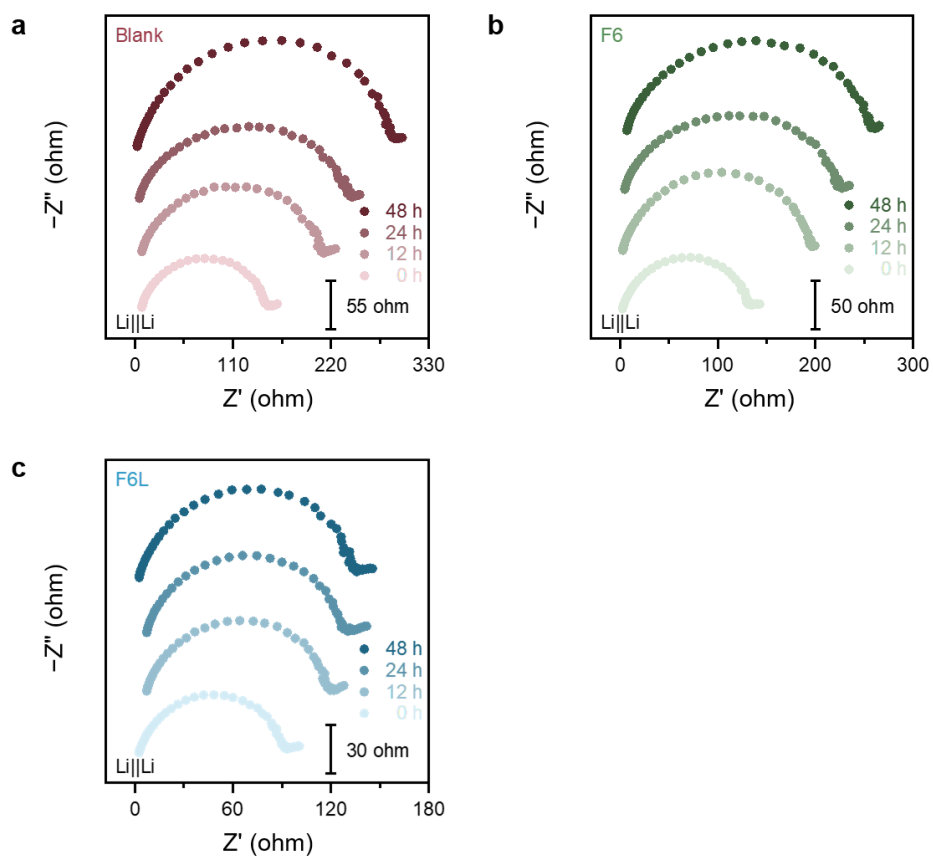
Supplementary Fig. 18. ^{19}F NMR spectra for F_{6-0} , Blank, F6 (Pristine), F6 (Reduced), F6L (Pristine), and F6L (Reduced).

Note of Supplementary Fig. 18: The ^{19}F NMR spectrum of F_{6-0} shows two chemical shifts at -122.3 and -138.8 ppm, while that of Blank is -73.7 and -75.6 ppm. The ^{19}F NMR spectra of F_{6-0} in F6 exhibit resonances at -120.6 and -136.9 ppm, observed without significant changes from the pristine to the reduced state in $\text{Li}||\text{Cu}$ cells. By contrast, due to the improved decomposition of the F6L, resonances at -123.4 , -124.9 , and -136.8 ppm disappear after being reduced in $\text{Li}||\text{Cu}$ cells.

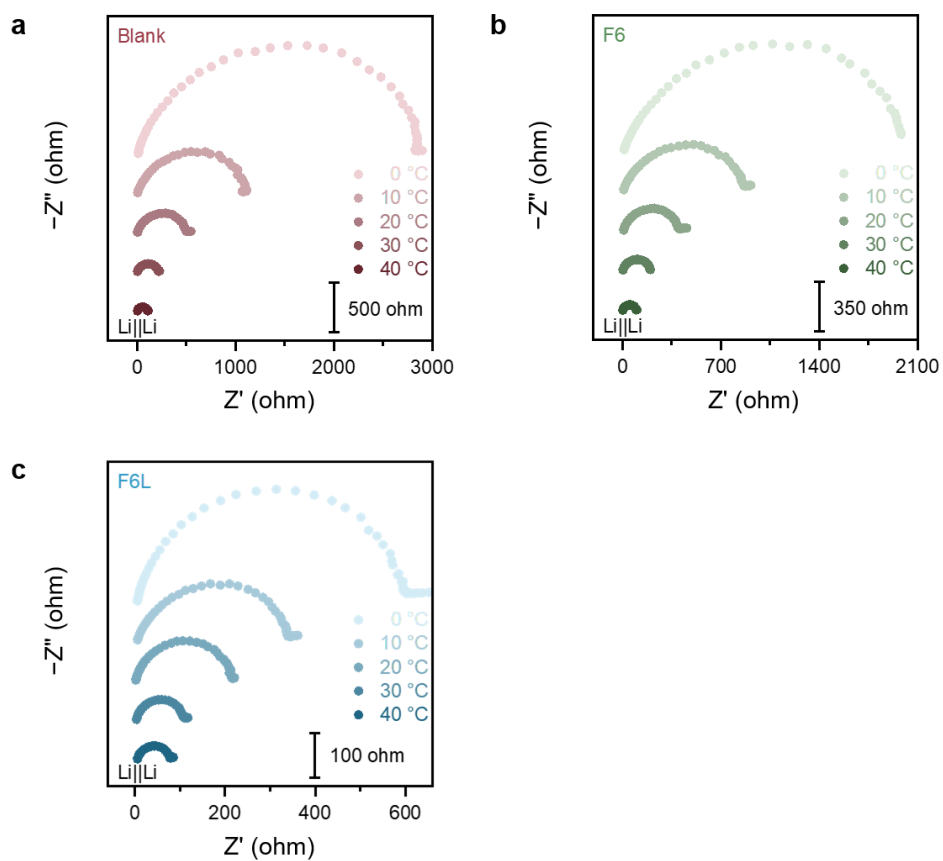


Supplementary Fig. 19. The integral of the electrochemical reduction curves associated with electrochemical *in-situ* FTIR spectra of Li||Cu half-cells using **a** Blank, **b** F6, and **c** F6L at 0.1 mV s⁻¹.

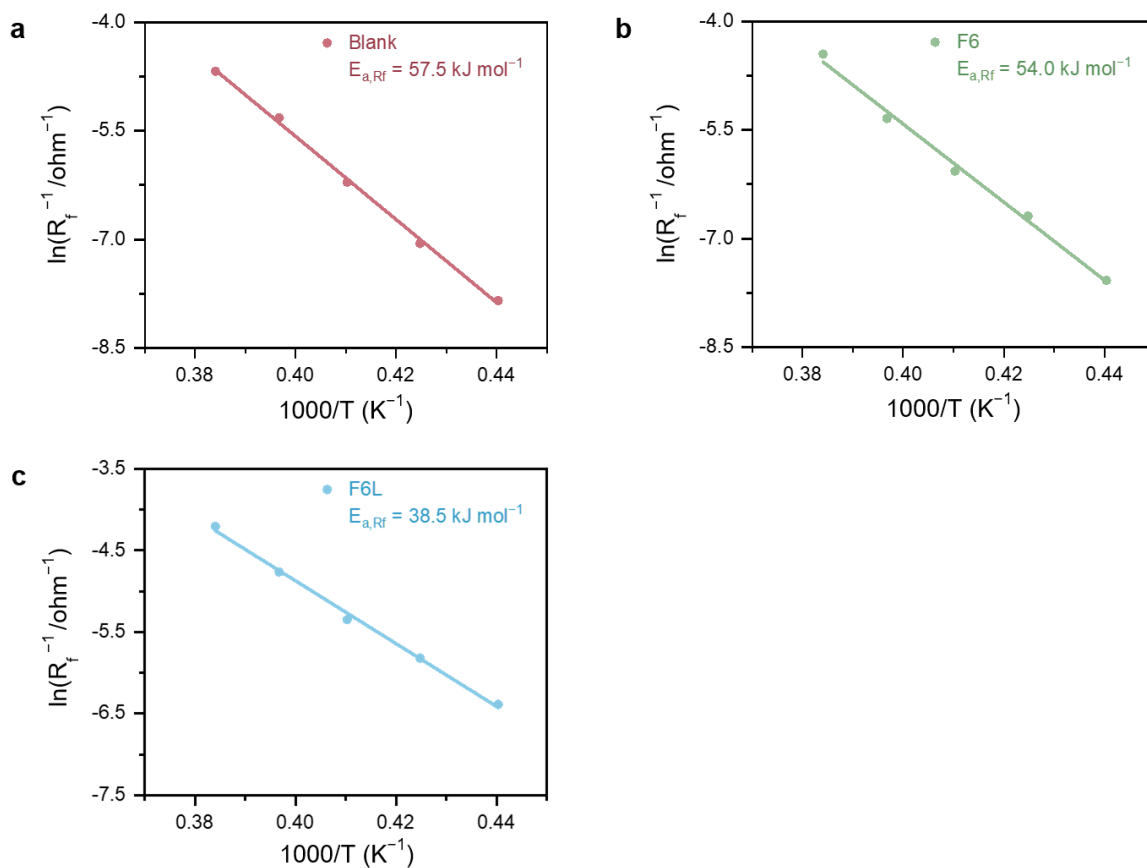
Note of Supplementary Fig. 19: The computational method to examine the reduction ratio of F₆₋₀ can be found in the **Methods** section of the main text.



Supplementary Fig. 20. Nyquist plots of Li symmetric cells with **a** Blank, **b** F6, and **c** F6L during different resting times at room temperature.



Supplementary Fig. 21. Nyquist plots of the cycled Li symmetric cells with **a** Blank, **b** F6, and **c** F6L at various temperatures ranging from 0 to 40 °C.

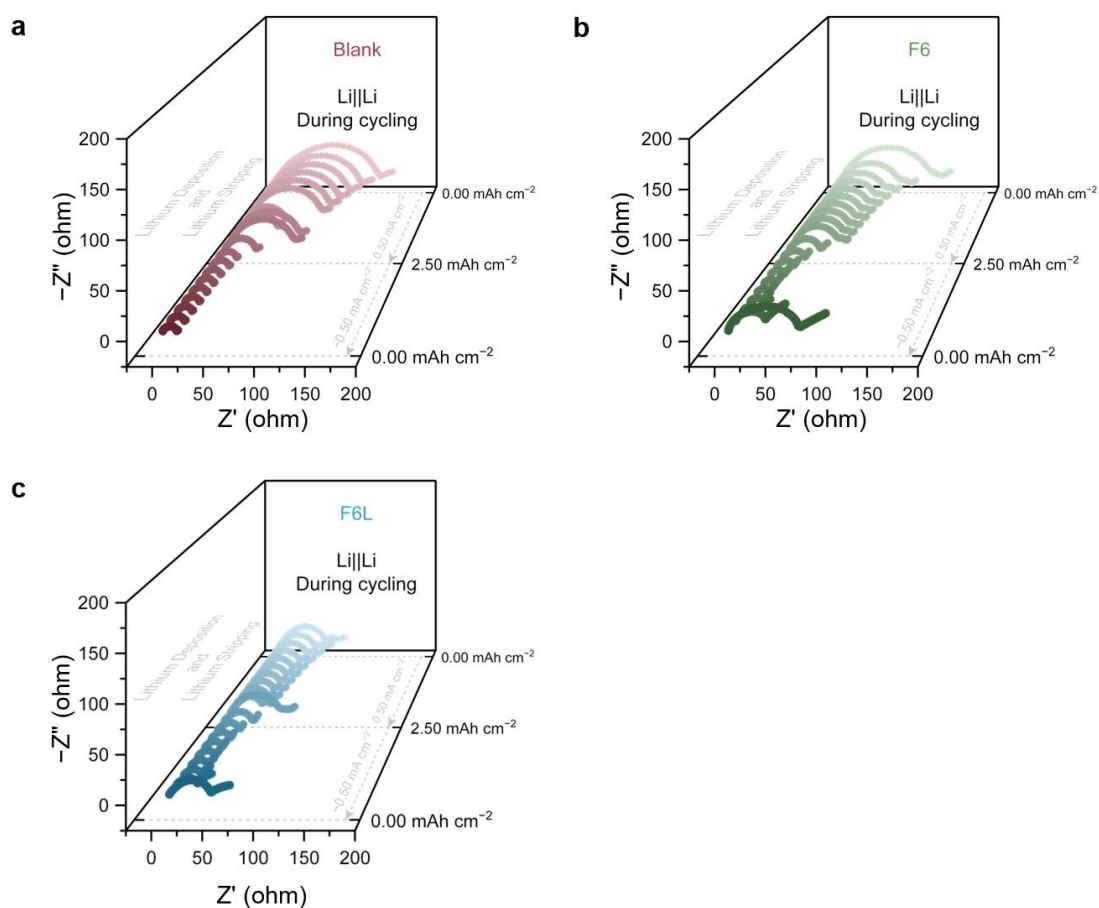


Supplementary Fig. 22. The E_a values calculated from the temperature-dependent EIS curves of Li symmetric cells with **a** Blank, **b** F6, and **c** F6L.

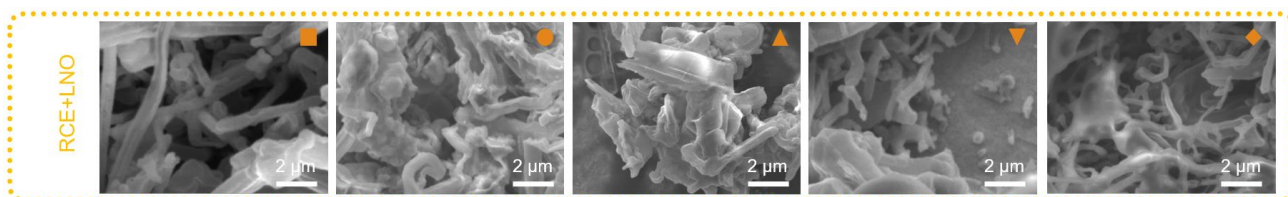
Note of Supplementary Fig. 22: The E_a values can be calculated based on the following Arrhenius equation,

$$R^{-1} = Ae^{-\frac{E_a}{RT}} \quad (1)$$

Where R is the molar gas constant, T is the thermodynamic temperature, and A is the pre-exponential factor.

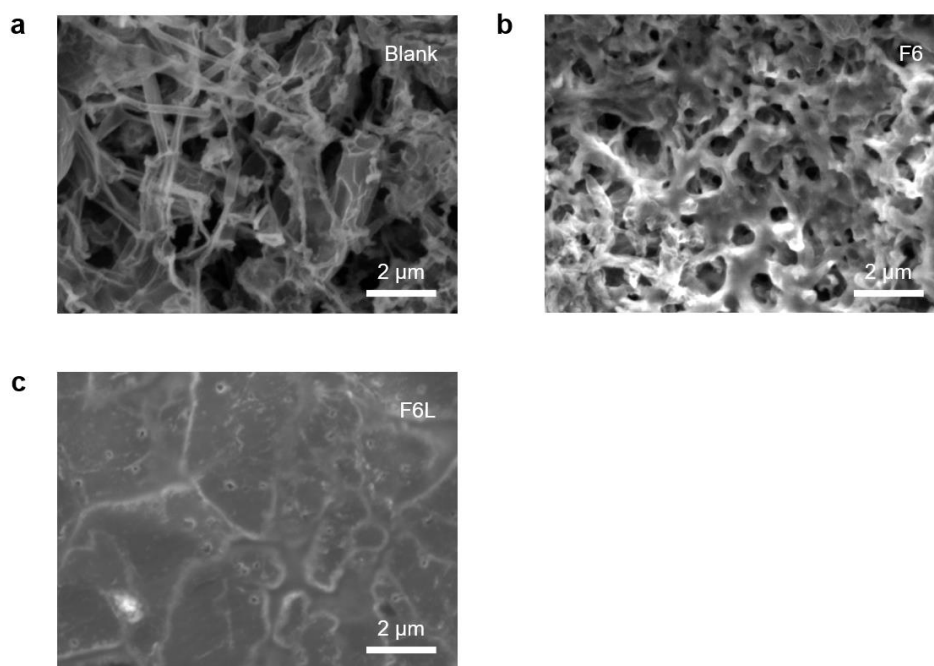


Supplementary Fig. 23. Nyquist plots of Li symmetric cells with **a** Blank, **b** F6, and **c** F6L during Li plating or stripping at 0.5 mA cm^{-2} with 0.25 mAh cm^{-2} at room temperature.



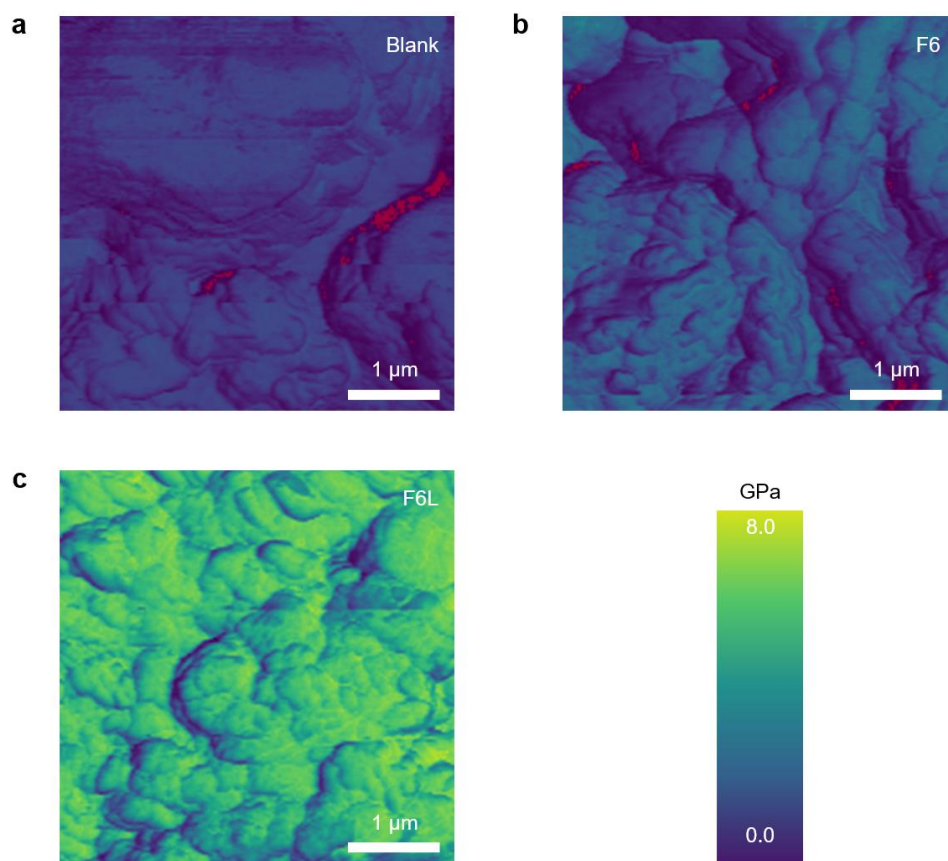
Supplementary Fig. 24. SEM images of the Li metal cycling in RCE+LNO at 0.5 mA cm^{-2} .

Note of Supplementary Fig. 24: The SEM images of Li plating show a rodlike morphology, which gradually grows into a dendritic structure as the deposition capacity increases. When the plated Li is stripped again, a large amount of dead Li remains on the surface of the Cu foil, corroborating the low reversibility revealed by the CE test result (**Supplementary Fig. 4**).



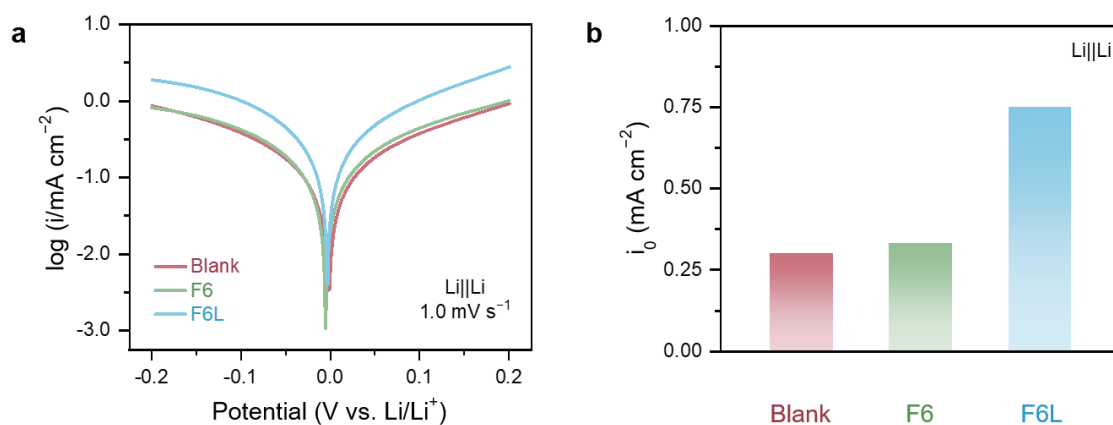
Supplementary Fig. 25. SEM images of Li metal anodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L at $0.5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$.

Note of Supplementary Fig. 25: The Li dissolution process was uneven under the unstable SEI when Li was stripped in Blank and F6, resulting in the fracture of dendrite and dead Li formation. Therefore, the remaining dead Li exacerbates the disorder of Li nucleation and further stimulates the dendrite growth after 20 cycles at $0.5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. By contrast, due to the fast Li-ion transport and high Young's modulus of LiF-rich SEI, the Li morphology in F6L remains relatively smooth without dendrite and dead Li formation after 20 cycles.



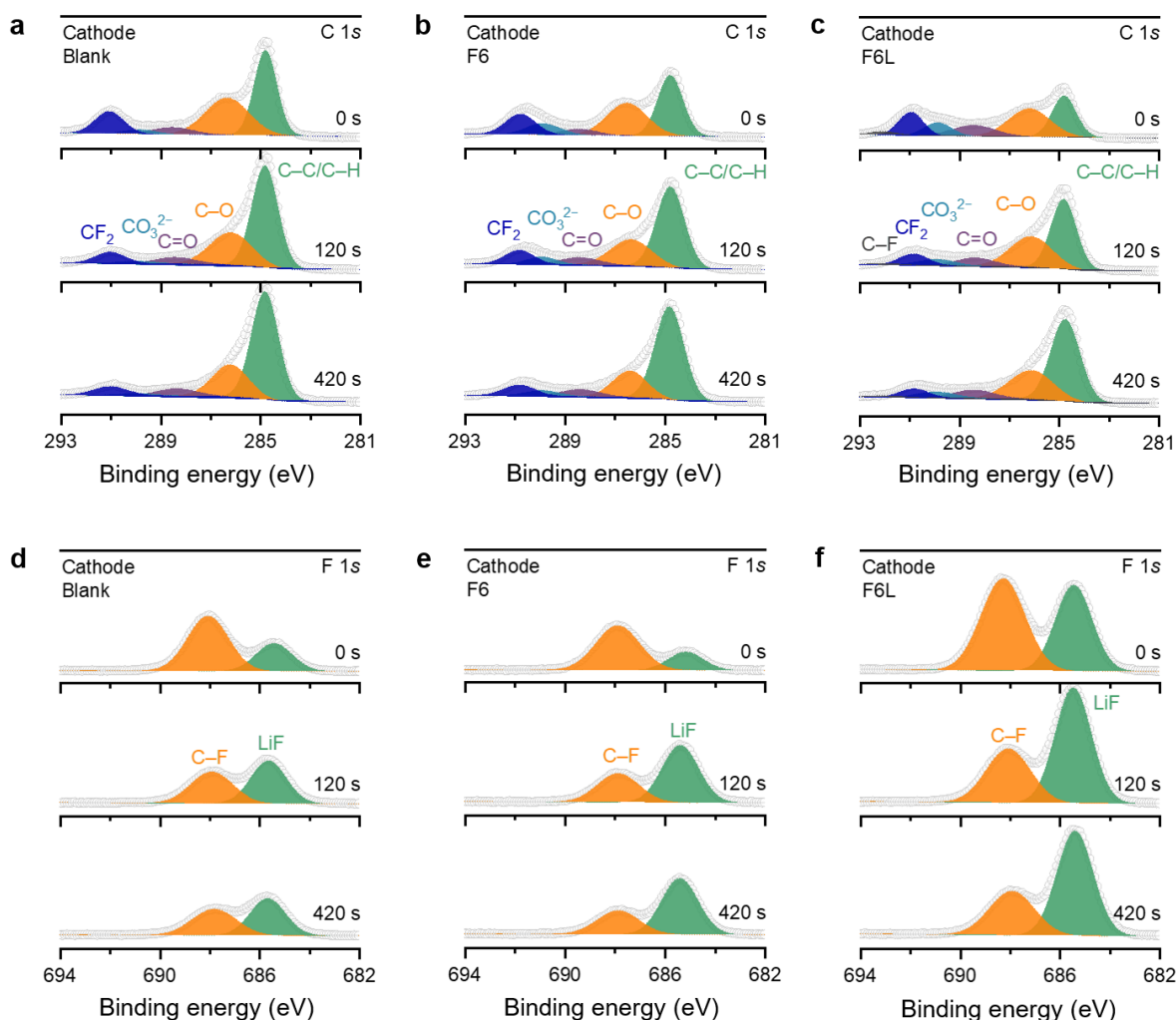
Supplementary Fig. 26. Young's modulus of the **a** Blank, **b** F6, and **c** F6L induced-SEI.

Note of Supplementary Fig. 26: A 200 μm-thick Cu foil was polished before being used as a substrate for SEI growth in different electrolytes. The half-cell using the Cu substrate was initially discharged to 0.001 V (vs. Li/Li⁺) at 0.1 mA cm⁻². Subsequently, the cell was disassembled, and the Cu substrate was taken out carefully. Before AFM testing, the Cu substrate underwent three rinses with DMC and was dried under a vacuum to eliminate residual Li salts and free solvent. The average Young's modulus for Blank, F6, and F6L is 0.73, 1.16, and 6.52 GPa, respectively.



Supplementary Fig. 27. **a** Tafel plots of Li symmetric cells with Blank, F6, and F6L at 1.0 mV s^{-1} , and **b** the corresponding exchange current density.

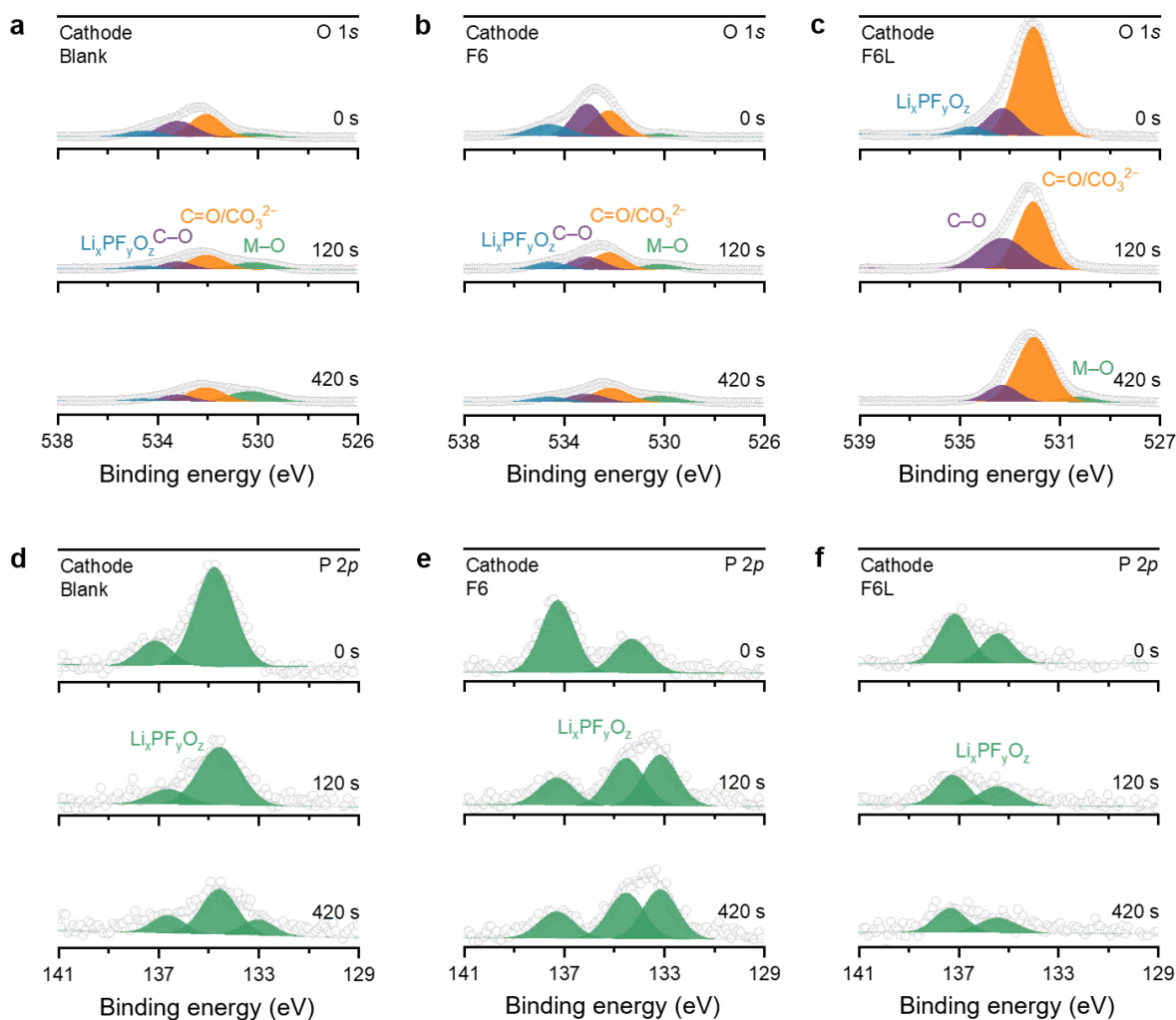
Note of Supplementary Fig. 27: The results of the Tafel plots confirm that the exchange current density of Li symmetric cells using F6L (0.75 mA cm^{-2}) is evidently higher than that using Blank (0.33 mA cm^{-2}) and F6 (0.30 mA cm^{-2}), which significantly disperses the local current density and promotes uniform Li nucleation/deposition to suppress the dendrite growth in F6L.



Supplementary Fig. 28. In-depth C 1s XPS spectra of MCN811 cathodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L. In-depth F 1s XPS spectra of MCN811 cathodes after 20 cycles in **d** Blank, **e** F6, and **f** F6L.

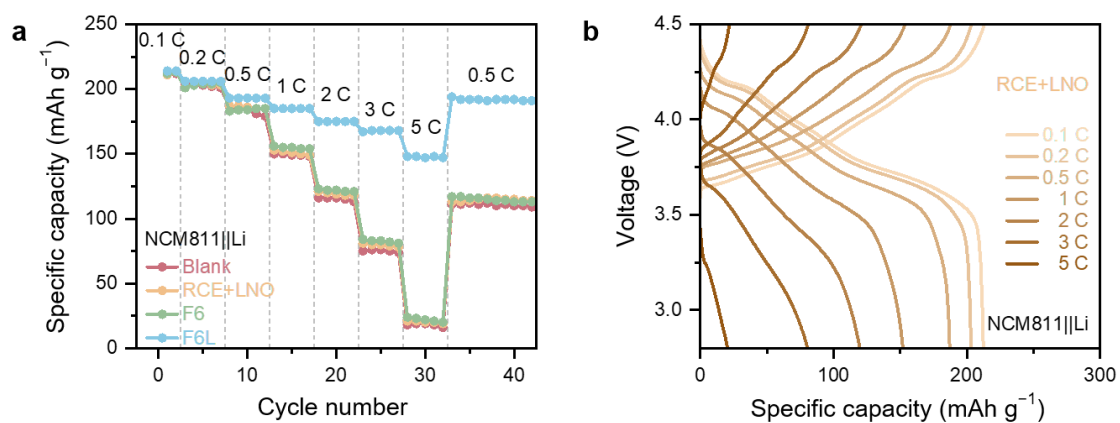
Note of Supplementary Fig. 28: In the C 1s XPS spectra of Blank (**Supplementary Fig. 28a**), the feature at 291 eV is caused by the F–C–F groups of PVDF². Adding F6 does not bring significant change in the types of peaks (**Supplementary Fig. 28b**). As to the F6L sample, its C 1s XPS spectra reveal that a C–F peak at 292 eV emerged (**Supplementary Fig. 28c**), indicating the F–C–F bond of F₆₋₀ breaking and the higher decomposition rate of the F6L as compared to the F6. In the F 1s XPS spectra of Blank, the LiF can be identified by the peak at ~685.5 eV (**Supplementary Fig. 28d**). These substances originate from the decomposition of LiPF₆ in RCE and serve as the inorganic components of the CEI. Adding F6 could somewhat increase the LiF content in the CEI (**Supplementary Fig. 28e**), but the oxidation of F6 is still low as confirmed by the undetected C–F peak in **Supplementary Fig. 28b**. By contrast, with a higher HOMO energy level (**Figure 4b**), the decomposition of the F6L is improved and the resulting LiF peak becomes abundant in the F 1s XPS spectra at different thicknesses

(Supplementary Fig. 28f). The results of the XPS spectra on the chemical states of CEI and the corresponding binding energy are listed in **Supplementary Table 3**.

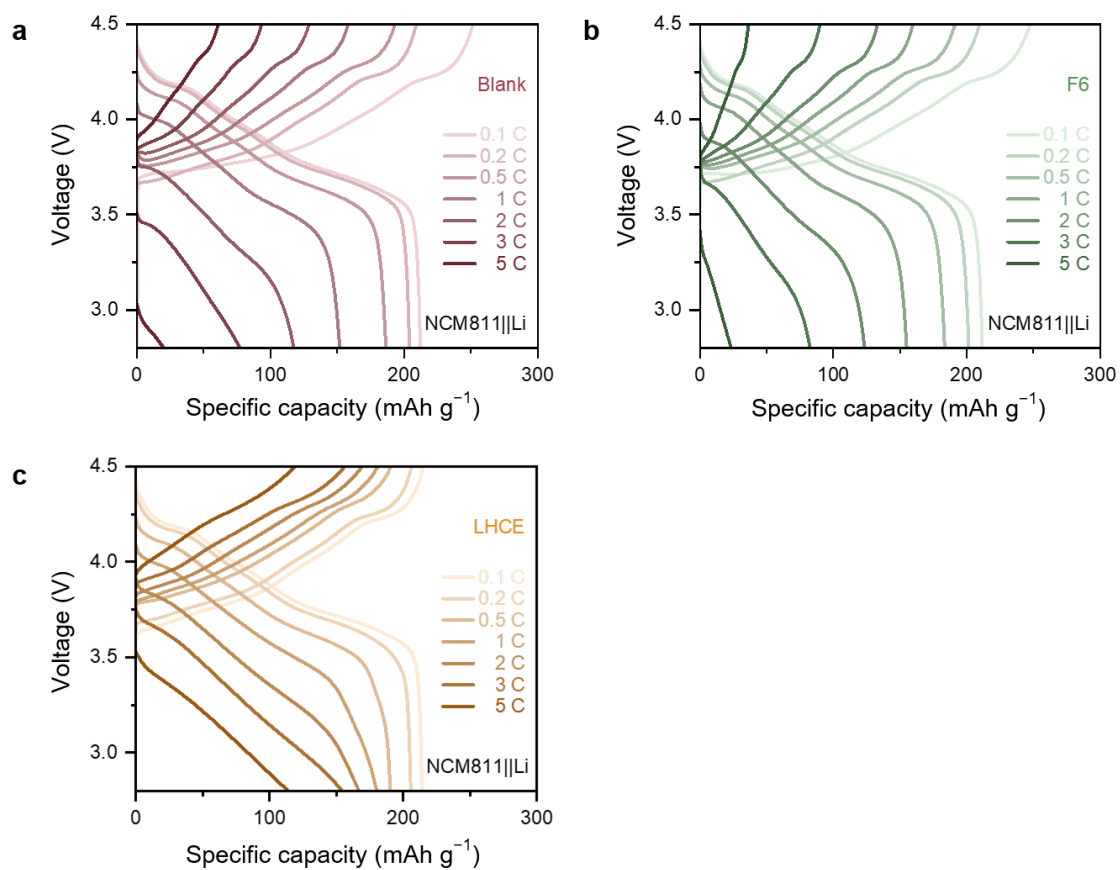


Supplementary Fig. 29. In-depth O 1s XPS spectra of MCN811 cathodes after 20 cycles in **a** Blank, **b** F6, and **c** F6L. In-depth P 2p XPS spectra of MCN811 cathodes after 20 cycles in **d** Blank, **e** F6, and **f** F6L.

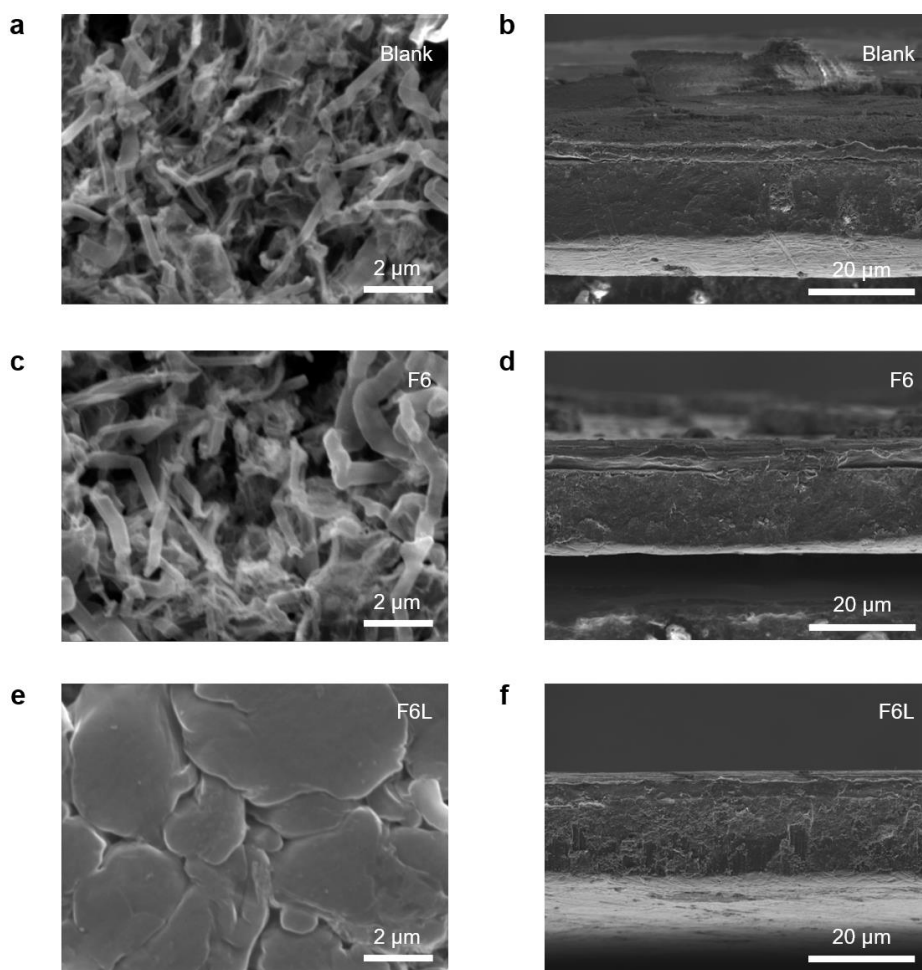
Note of Supplementary Fig. 29: In the O 1s XPS spectra of Blank and F6, the $\text{Li}_x\text{PF}_y\text{O}_z$ can be identified by the peak at 534.5 eV (**Supplementary Fig. 29a and 29b**). These substances originate from the decomposition of LiPF_6 in RCE and serve as the inorganic components of the CEI. By contrast, due to the LiF layer formed by preferential oxidation of F6L, the decomposition of LiPF_6 is hindered (**Figure S29c**), which is in line with our observation in the P 2p XPS spectra (**Supplementary Fig. 29d, 29e, and 29f**). The results of the XPS spectra on the chemical states of CEI and the corresponding binding energy are listed in **Supplementary Table 3**.



Supplementary Fig. 30. a The rate performance of NCM811||Li full-cells with Blank, RCE+LNO, F6, and F6L under the voltage window of 2.8~4.5 V. **b** Voltage profiles of the NCM811||Li full-cell with RCE+LNO at various rates.

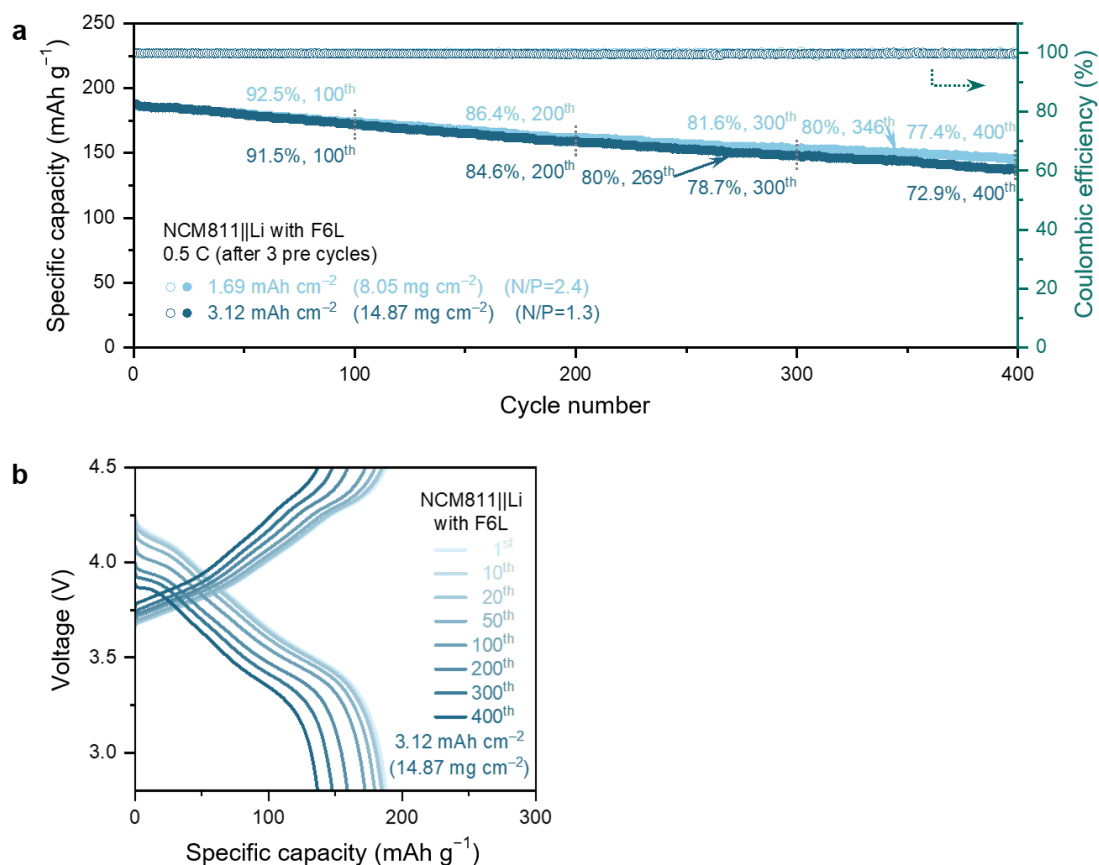


Supplementary Fig. 31. Voltage profiles of NCM811||Li full-cells with **a** Blank, **b** F6, and **c** LHCE at various rates.

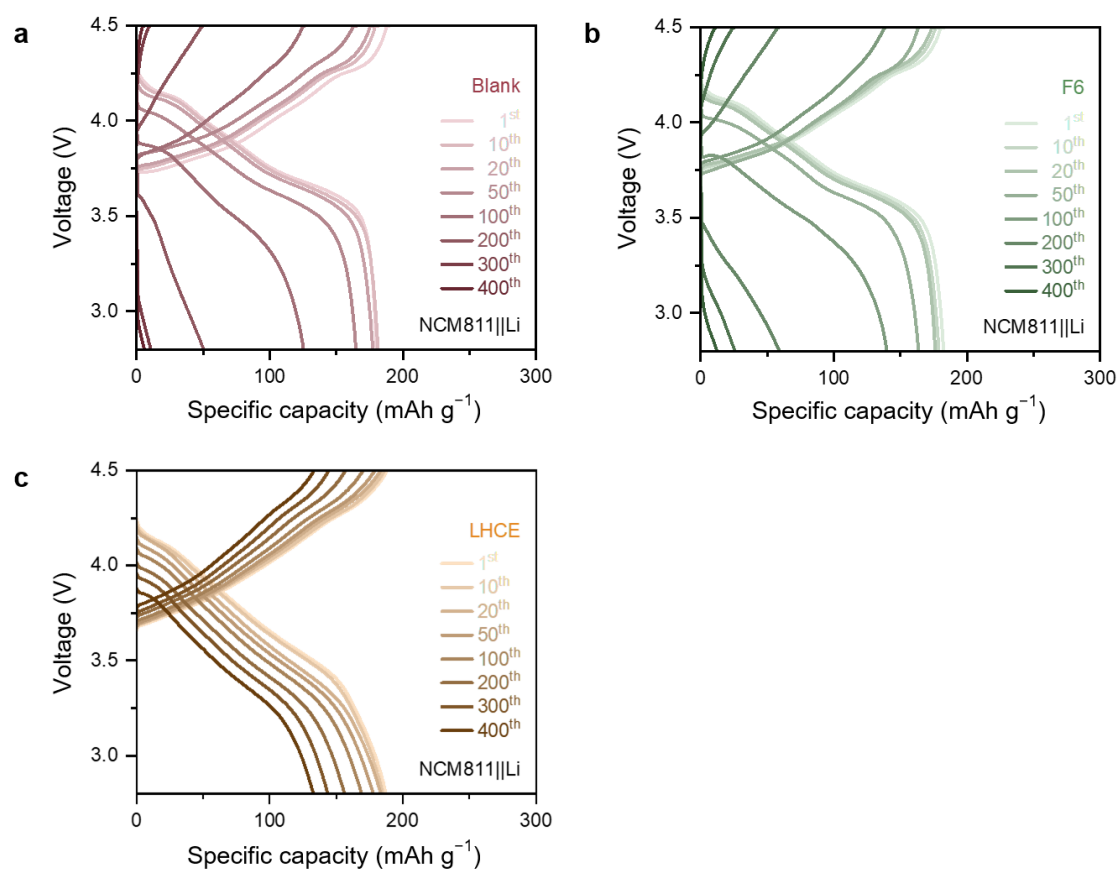


Supplementary Fig. 32. Top-view SEM images of the deposited Li metal from NCM811||Li full-cell after rate performance testing with **a** Blank, **c** F6, and **e** F6L. Cross-sectional SEM images of the corresponding deposited Li with **b** Blank, **d** F6, and **f** F6L.

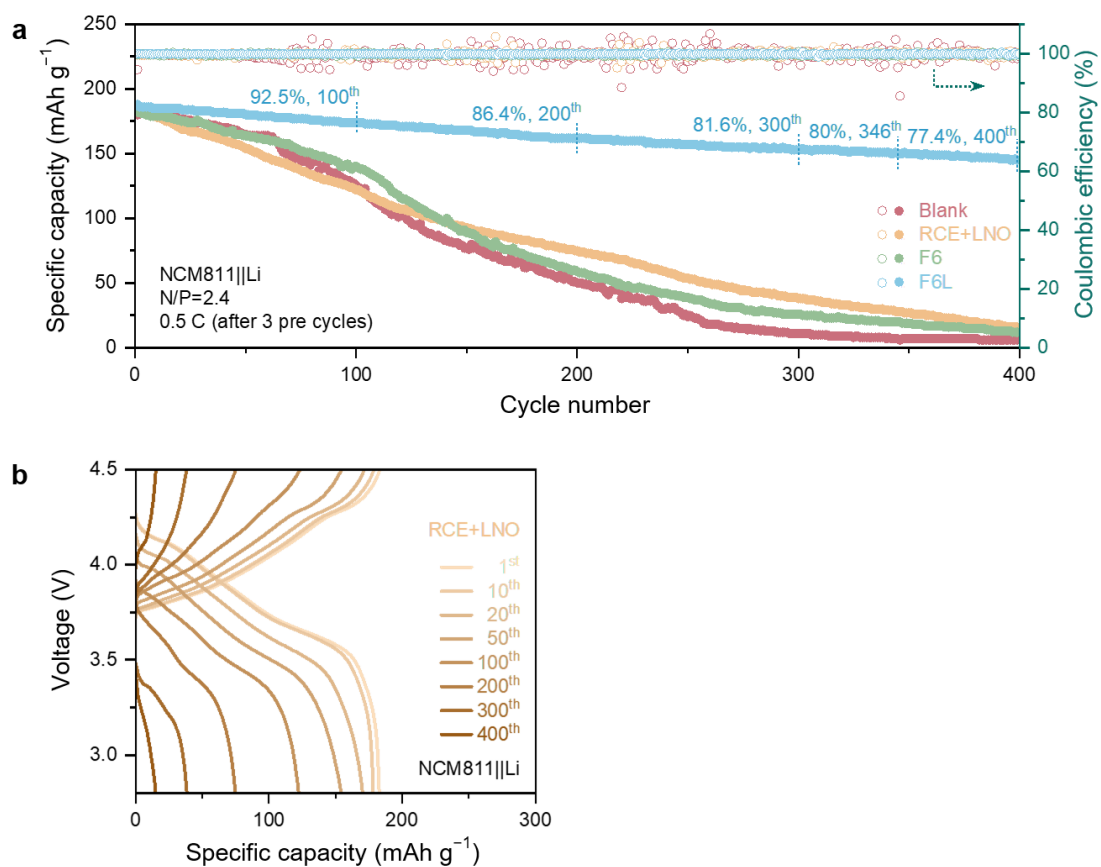
Note of Supplementary Fig. 32: Due to the formation of the local current density caused by the sluggish Li-ion transport and uneven distribution of the SEI, the abundant growth of dendrites was detected (**Supplementary Fig. 32a and 32c**). The corresponding Li metal is loose and uneven (**Supplementary Fig. 32b and 32d**). By contrast, owing to the fast Li-ion transport and high Young's modulus of LiF-rich SEI, the Li morphology in F6L remains relatively smooth without dendrite and dead Li formation during the rate performance testing (**Supplementary Fig. 32e**). The corresponding Li deposits are also densely-packed (**Supplementary Fig. 32f**).



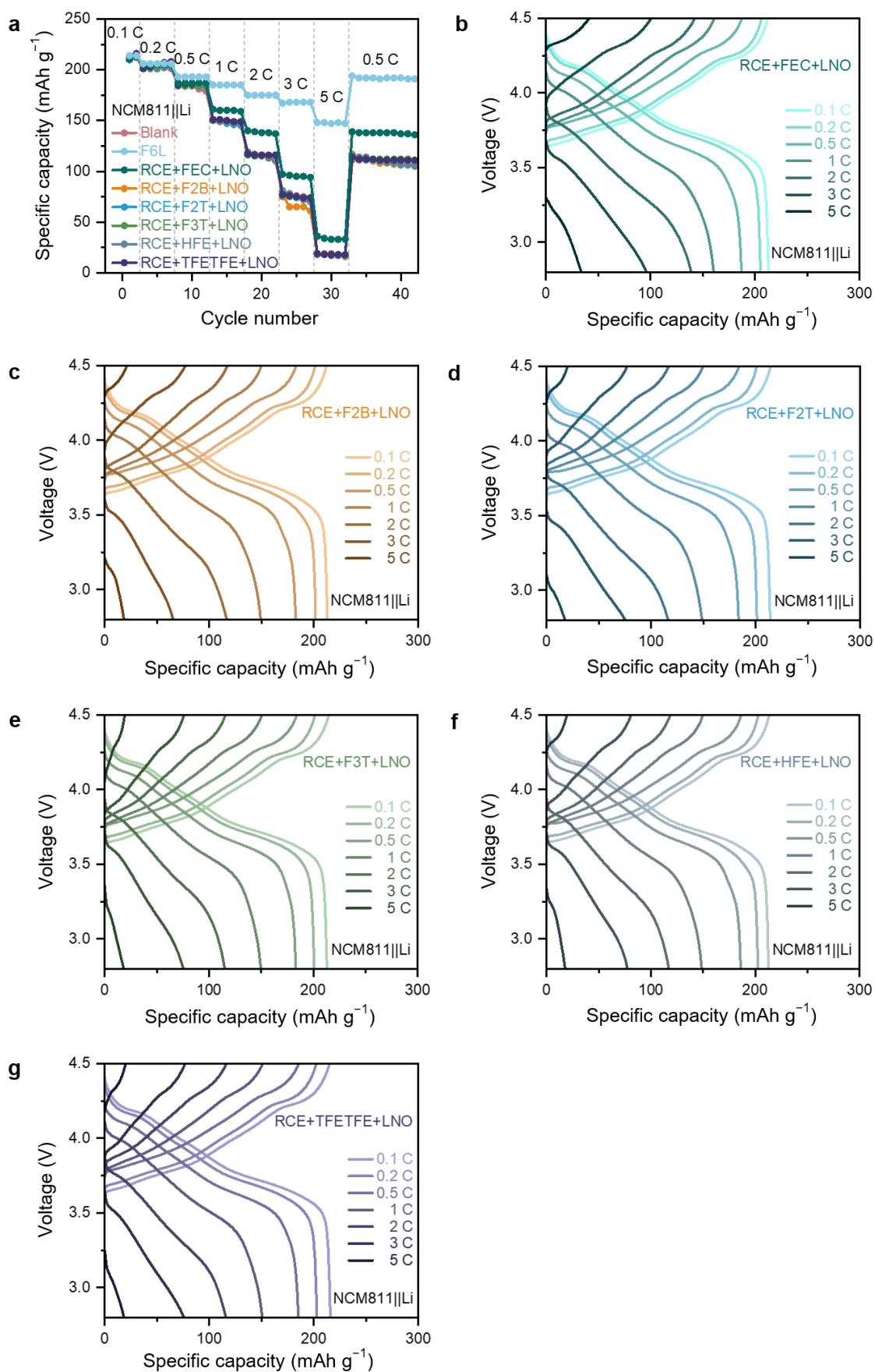
Supplementary Fig. 33. a The long-term cycling performance of NCM811||Li full-cells with different cathode loading using F6L at 0.5 C under the voltage window of 2.8~4.5 V. **b** Voltage profiles of the high-mass-loading NCM811||Li full-cell using F6L at different cycles.



Supplementary Fig. 34. Voltage profiles of NCM811||Li full-cells with **a** Blank, **b** F6, and **c** LHCE at different cycles.

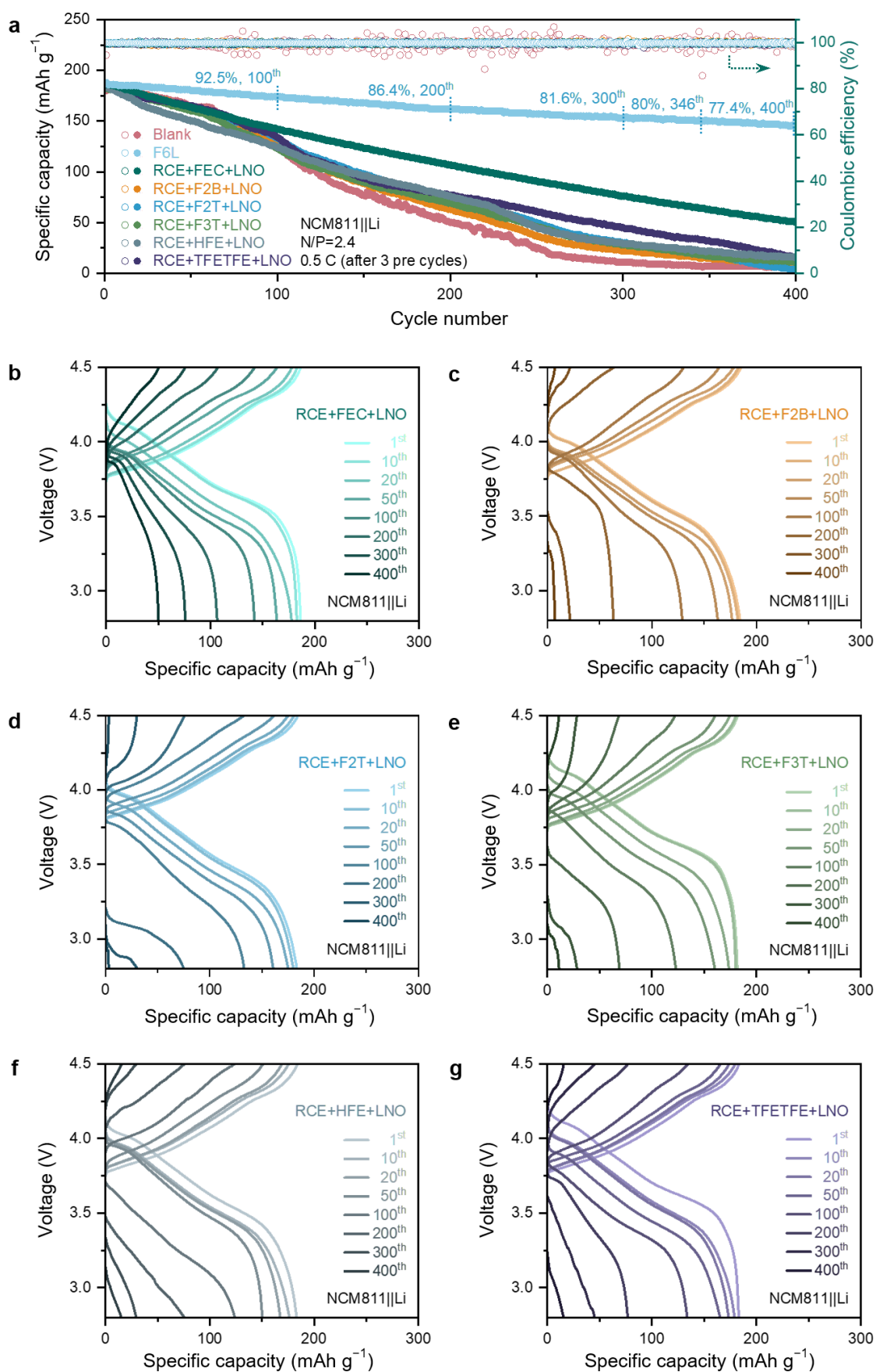


Supplementary Fig. 35. a The long-term cycling performance of NCM811||Li full-cells with Blank, RCE+LNO, F6, and F6L at 0.5 C under the voltage window of 2.8~4.5 V. **b** Voltage profiles of the NCM811||Li full-cell with RCE+LNO at different cycles.



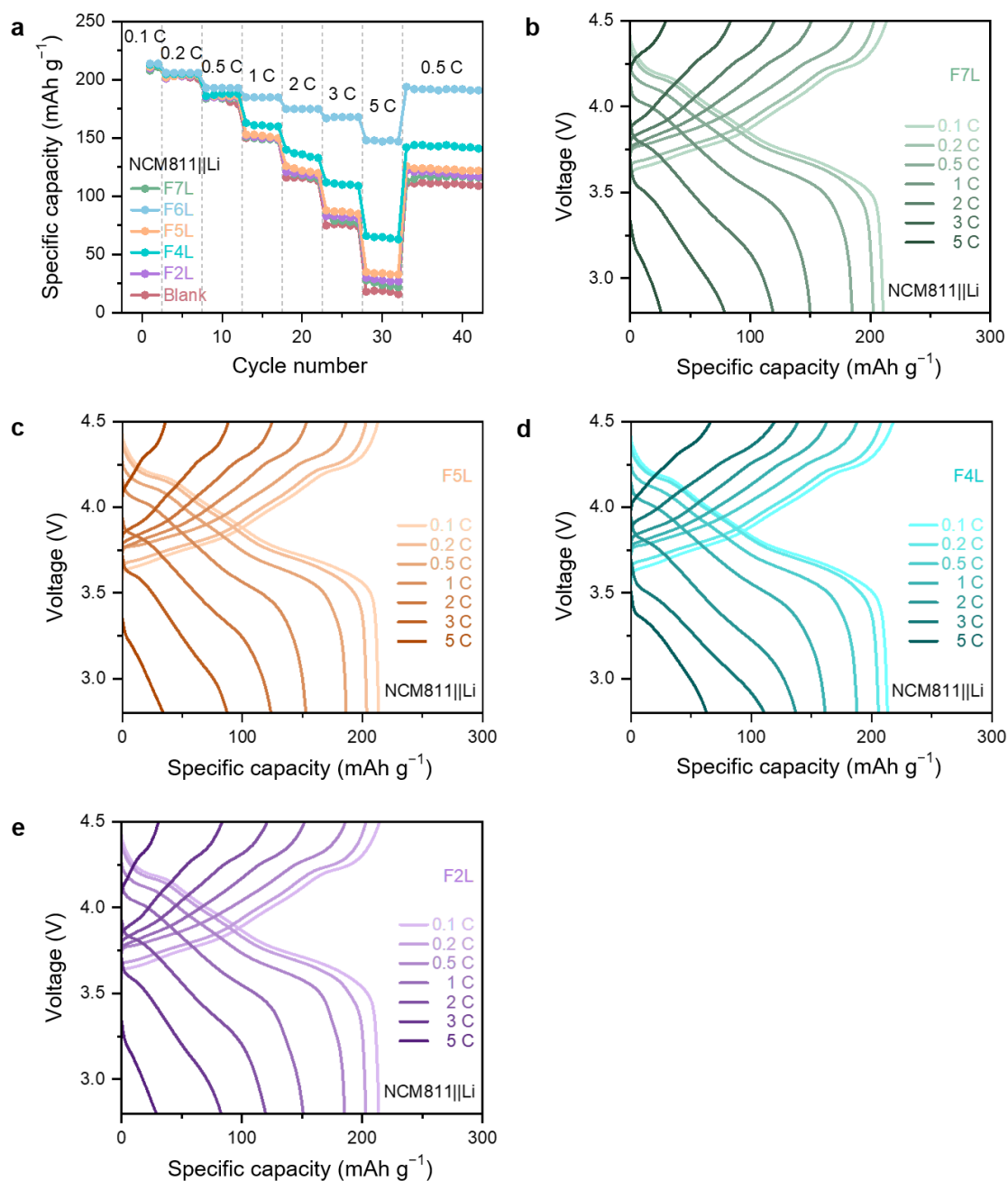
Supplementary Fig. 36. a The rate performance of NCM811||Li full-cells with RCE+FEC+LNO, RCE+F2B+LNO, RCE+F2T+LNO, RCE+F3T+LNO, RCE+HFE+LNO, RCE+TFETFE+LNO, F6L,

and Blank under the voltage window of 2.8~4.5 V. Voltage profiles of NCM811||Li full-cells with **b** RCE+FEC+LNO, **c** RCE+F2B+LNO, **d** RCE+F2T+LNO, **e** RCE+F3T+LNO, **f** RCE+HFE+LNO, and **g** RCE+TFETFE+LNO at various rates.

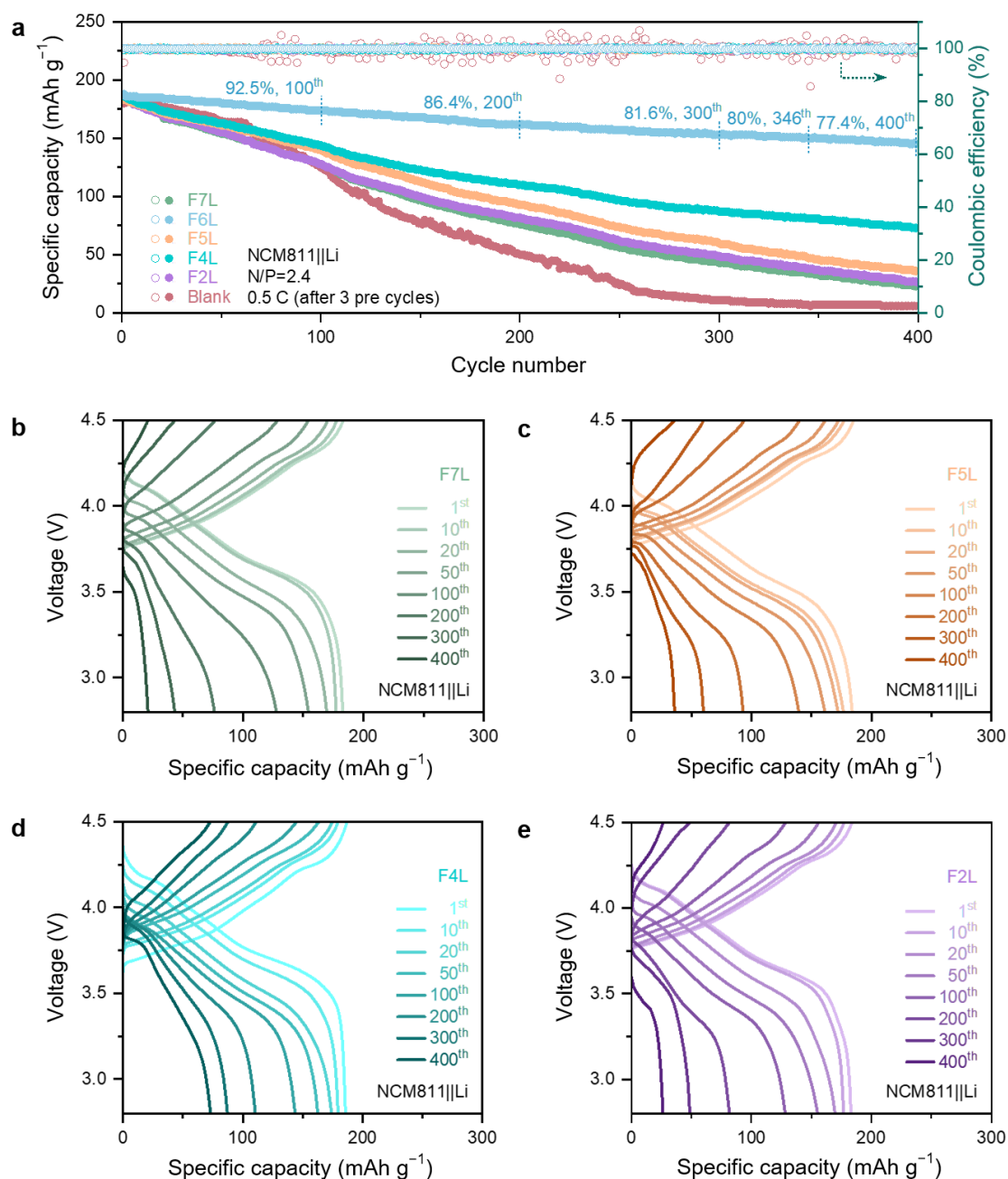


Supplementary Fig. 37. a The Long-term cycling performance of NCM811||Li full-cells with RCE+FEC+LNO, RCE+F2B+LNO, RCE+F2T+LNO, RCE+F3T+LNO, RCE+HFE+LNO,

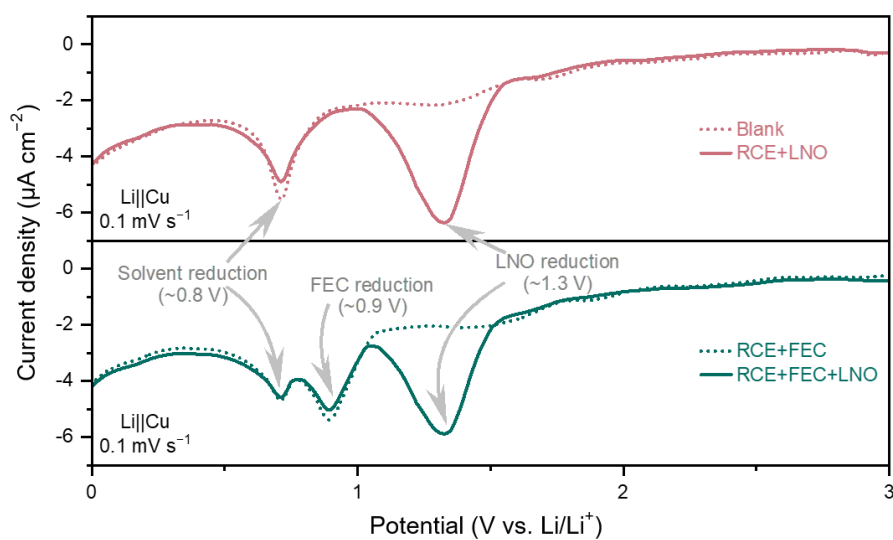
RCE+TFETFE+LNO, F6L, and Blank at 0.5 C under the voltage window of 2.8~4.5 V. Voltage profiles of NCM811||Li full-cells with **b** RCE+FEC+LNO, **c** RCE+F2B+LNO, **d** RCE+F2T+LNO, **e** RCE+F3T+LNO, **f** RCE+HFE+LNO, and **g** RCE+TFETFE+LNO at different cycles.



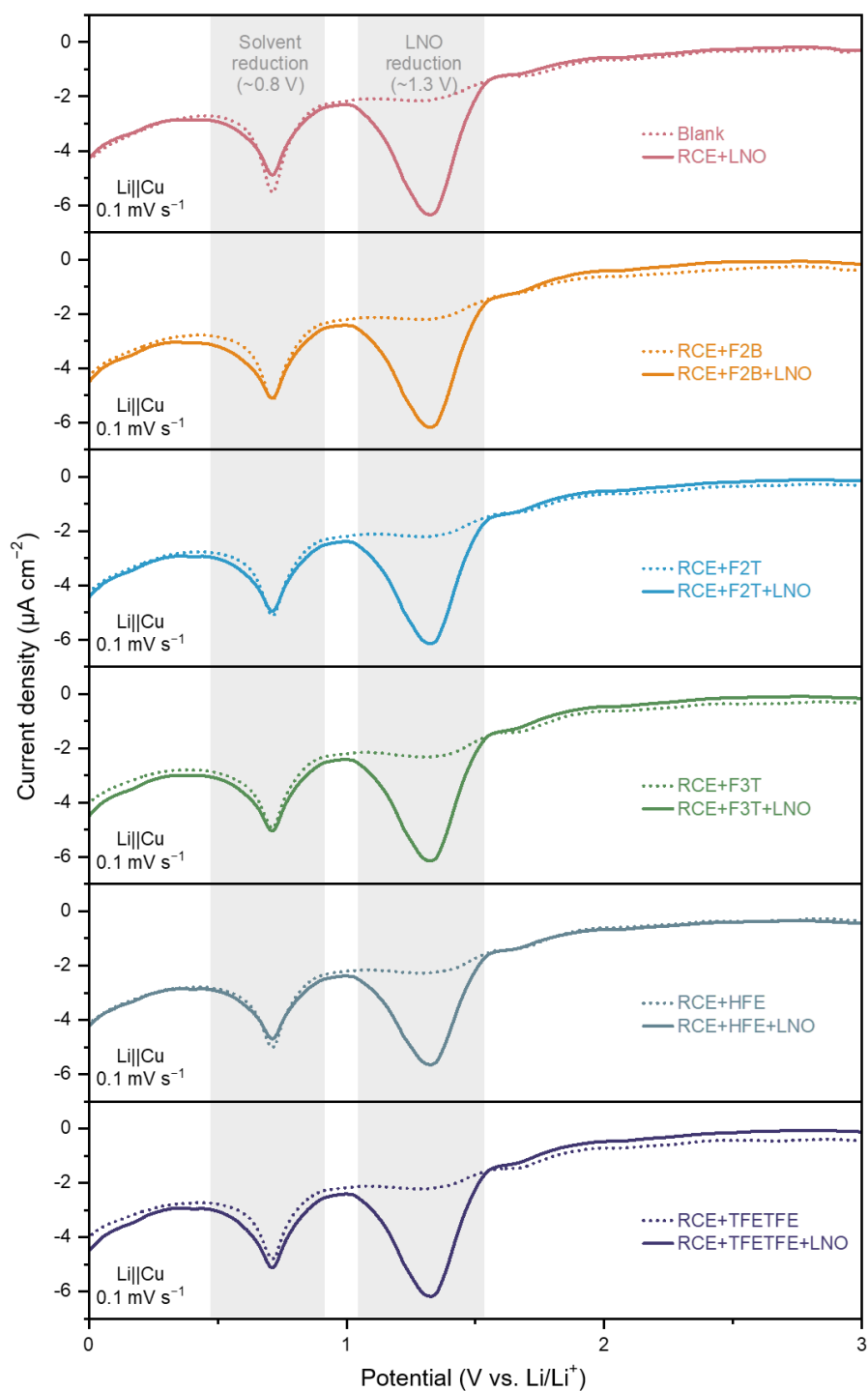
Supplementary Fig. 38. **a** The rate performance of NCM811||Li full-cells with F7L, F6L, F5L, F4L, F2L, and Blank under the voltage window of 2.8~4.5 V. Voltage profiles of NCM811||Li full-cells with **b** F7L, **c** F5L, **d** F4L, and **e** F2L at various rates.



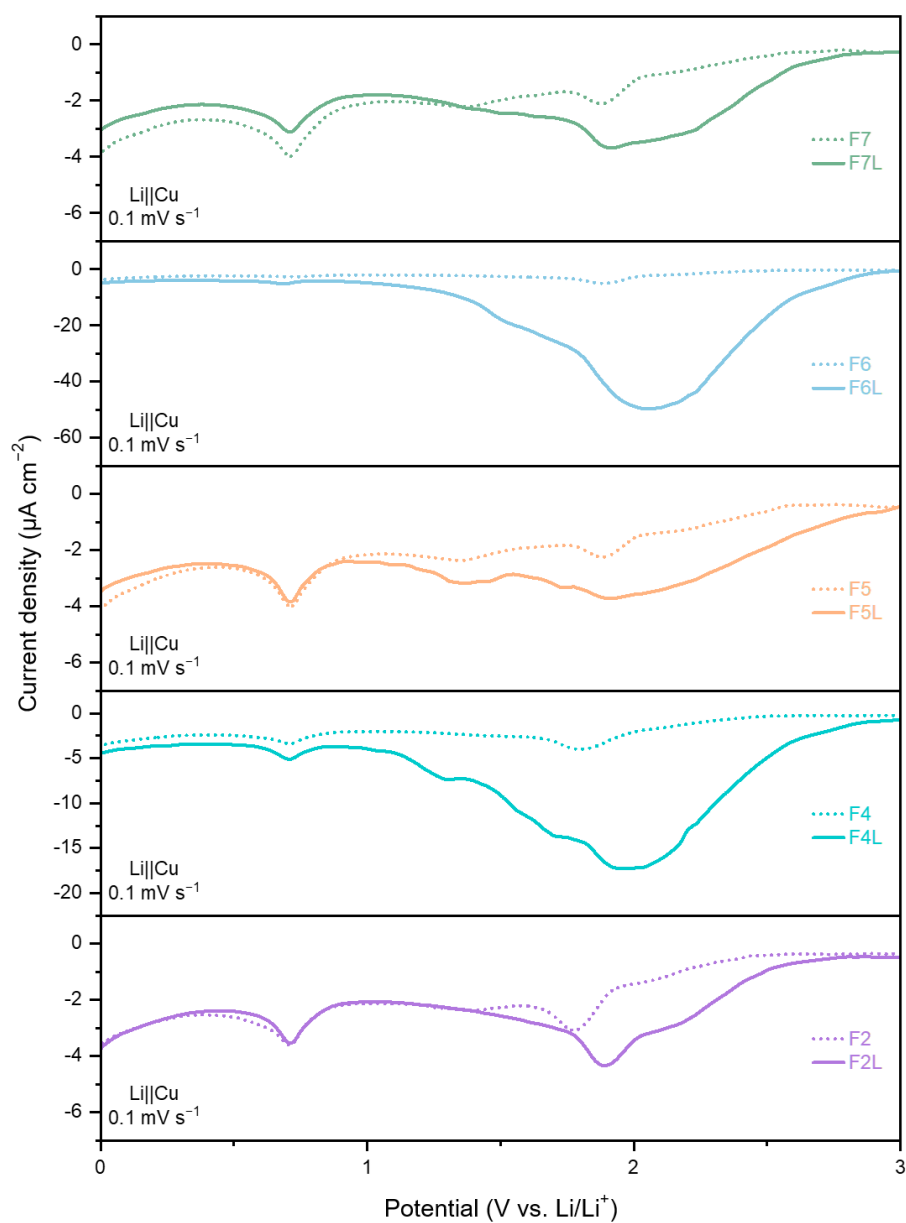
Supplementary Fig. 39. **a** The long-term cycling performance of NCM811||Li full-cells with F7L, F6L, F5L, F4L, F2L, and Blank at 0.5 C under the voltage window of 2.8–4.5 V. Voltage profiles of NCM811||Li full-cells with **b** F7L, **c** F5L, **d** F4L, and **e** F2L at different cycles.



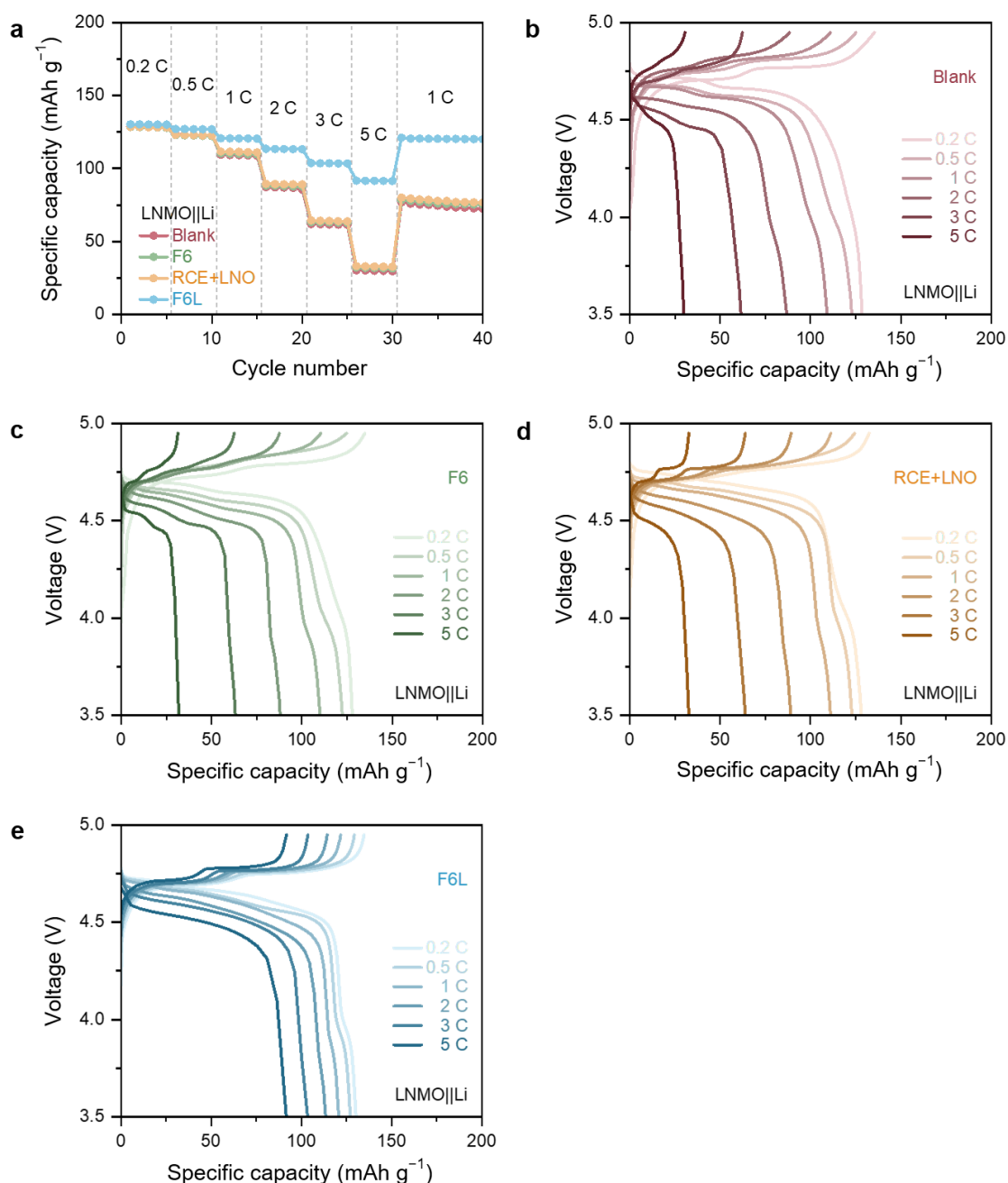
Supplementary Fig. 40. Electrochemical reduction curves of Li||Cu half-cells using Blank/RCE+LNO and RCE+FEC/RCE+FEC+LNO at 0.1 mV s^{-1} .



Supplementary Fig. 41. Electrochemical reduction curves of Li||Cu half-cells using Blank/RCE+LNO, RCE+F2B/RCE+F2B+LNO, RCE+F2T/RCE+F2T+LNO, RCE+F3T/RCE+F3T+LNO, RCE+HFE/RCE+HFE+LNO, and RCE+TFETFE/RCE+TFETFE+LNO at 0.1 mV s⁻¹.

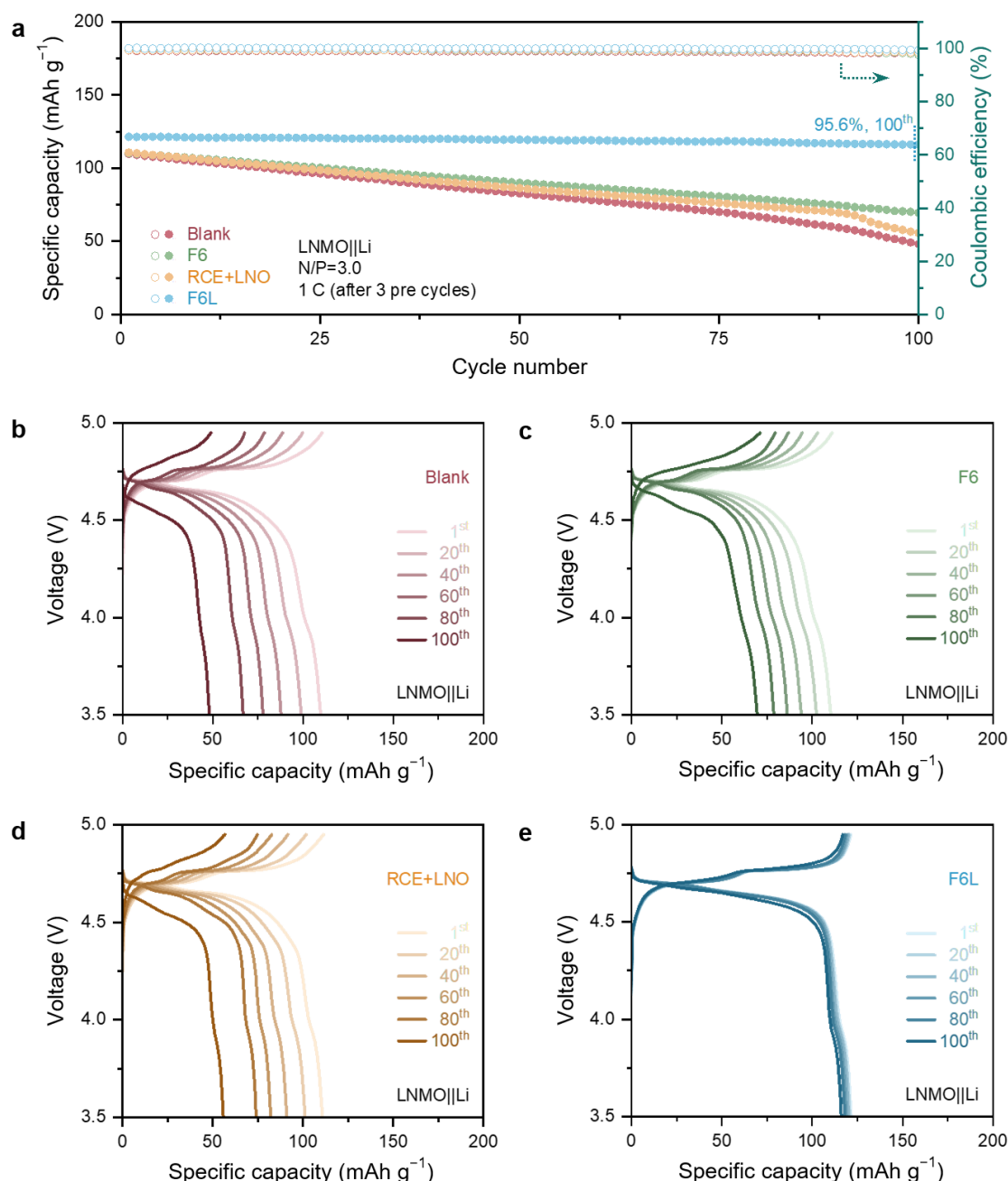


Supplementary Fig. 42. Electrochemical reduction curves of Li||Cu half-cells using F7/F6/F5/F4/F2 (without LNO) and F7L/F6L/F5L/F4L/F2L (with LNO) at 0.1 mV s^{-1} .



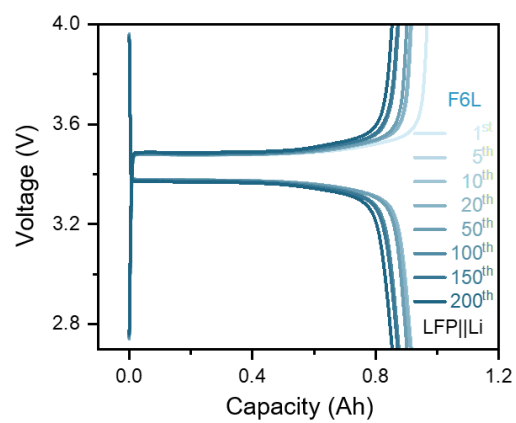
Supplementary Fig. 43. **a** The rate performance of the LNMO||Li full-cells with Blank, F6, RCE+LNO, and F6L under the voltage window of 3.5~4.95 V. Voltage profiles of the LNMO||Li full-cells with **b** Blank, **c** F6, **d** RCE+LNO, and **e** F6L at various rates.

Note of Supplementary Fig. 43: The F6L full-cell (N/P = 3.0) with low polarization and high voltage stability delivered the highest state of charge (SOC) over the tests (**Supplementary Fig. 43e**), especially after 1 C. The Blank, F6, and RCE+LNO cells exhibited the same attenuation trend in capacity after 1 C (**Supplementary Fig. 43b, 43c, and 43d**). When the rate returned to 1 C, the F6L cell can retain a reversible capacity of 120 mAh g⁻¹, indicating the high interface stability of the Li metal anode and the high voltage stability of the LNMO cathode in F6L.

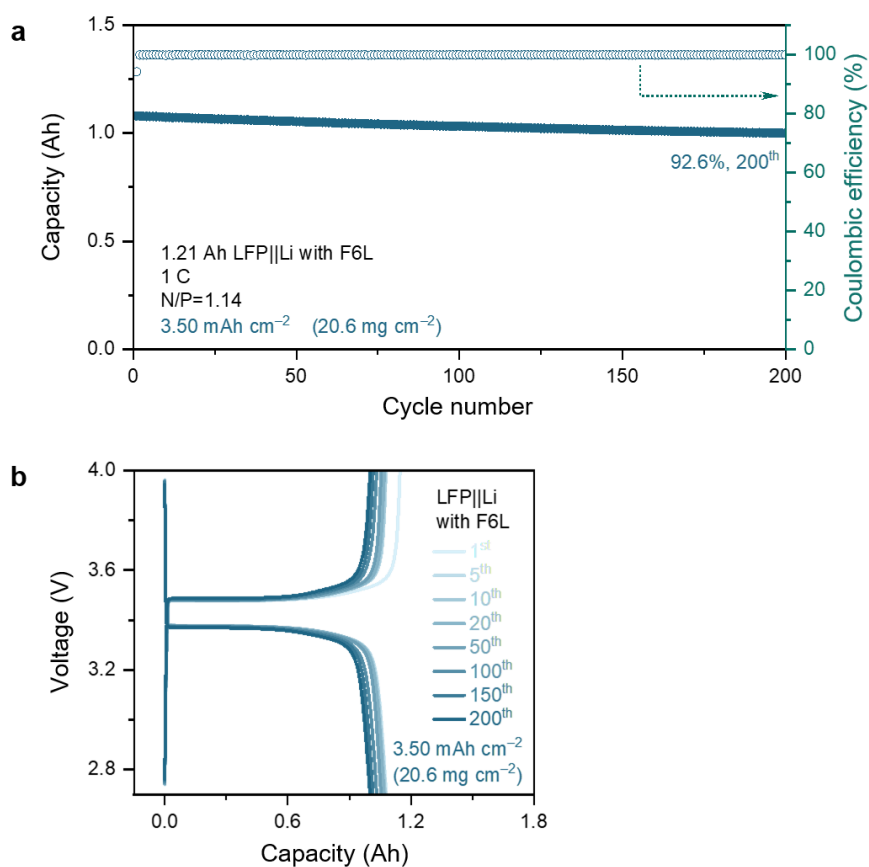


Supplementary Fig. 44. a The long-term cycling performance of the LNMO||Li full-cells with Blank, F6, RCE+LNO, and F6L at 1 C under the voltage window of 3.5~4.95 V. Voltage profiles of the LNMO||Li full-cells with b Blank, c F6, d RCE+LNO, and e F6L at different cycles.

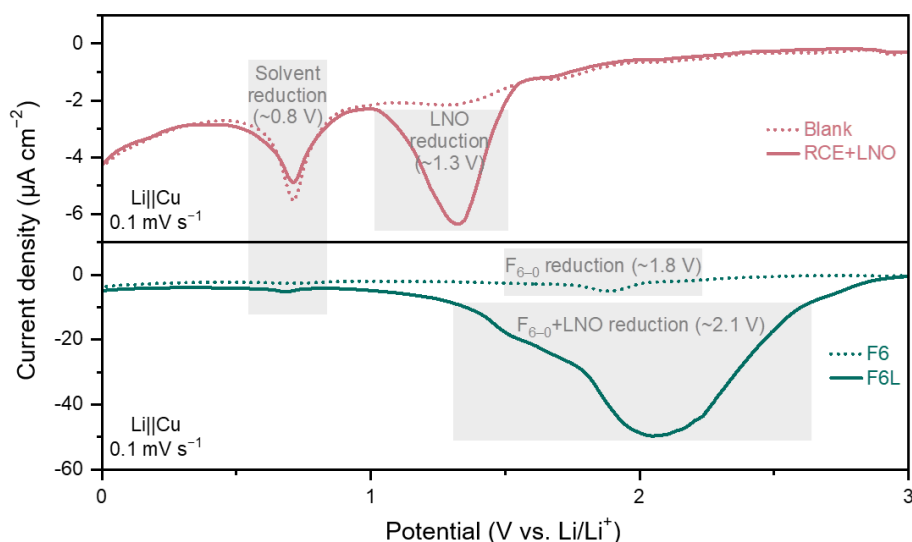
Note of Supplementary Fig. 44: At 1 C, the LNMO||Li full-cells (N/P = 3.0) using F6L cycled stably up to over 100 cycles, exhibiting a 121 mAh g^{-1} reversible capacity, lower polarization, higher voltage stability, and 95.6% retention over cycles (**Supplementary Fig. 44e**). Not surprisingly, the full-cells with Blank, F6, and RCE+LNO experienced an obvious capacity drop over cycles, corresponding to serious anode degradation and sustained electrolyte decomposition due to weak high-voltage stability (**Supplementary Fig. 44b, 44c, and 44d**).



Supplementary Fig. 45. Voltage profiles of the homemade 1.0-Ah LFP||Li pouch cell at 1 C.

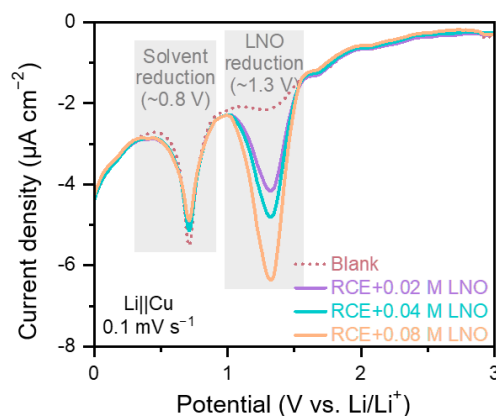


Supplementary Fig. 46. a The cycling performance of the homemade 1.21-Ah LFP||Li pouch cell at 1 C. **b** Voltage profiles of the homemade 1.21-Ah LFP||Li pouch cell at 1 C.



Supplementary Fig. 47. Electrochemical reduction curves of Li||Cu half-cells using Blank/RCE+LNO and F6/F6L at 0.1 mV s^{-1} .

Note of Supplementary Fig. 47: The charge balance calculations are based on the electrochemical reduction curves. By comparing the electrochemical reduction processes observed in the LSV tests, we can identify reduction potential peaks for the solvent in RCE, LNO in RCE+LNO, and F_{6-0} in F6 at approximately 0.8 V, 1.3 V, and 1.8 V, respectively (**Supplementary Fig. 47**). It is evident that the reduction of F_{6-0} in F6 takes precedence over that of LNO in RCE+LNO. When F_{6-0} and LNO coexist as F6L within RCE, a significant reduction peak emerges. This phenomenon can be attributed to an inductive effect between LNO and F_{6-0} , which lowers the C–F bond energy within F_{6-0} , accelerates the detachment of F elements, and greatly enhances the F_{6-0} reduction ratio. Simultaneously, this inductive effect also improves the reduction process of LNO. Consequently, the calculated F_{6-0} reduction ratio (91%) in F6L, based on the molar ratio of F_{6-0} to LNO, is a conservative approach, ensuring that the actual reduction ratio of F_{6-0} in F6L is at least 91%.



Supplementary Fig. 48. Electrochemical reduction curves of Li||Cu half-cells using Blank, RCE+0.02 M LNO, RCE+0.04 M LNO, and RCE+0.08 M LNO at 0.1 mV s⁻¹.

Note of Supplementary Fig. 48: The differential method allows for quantitative differentiation of contributions of reduction currents from various additives. Since it is not possible to quantitatively distinguish the contributions of different components to the reduction current through a single LSV curve, we conducted multiple sets of LSV tests with different additives (**Supplementary Fig. 47**). As discussed in section 4.3 on the computational method for determining the reduction ratio of F₆₋₀, by integrating the LSV curves of RCE+LNO, F6, and F6L and subtracting the integrated LSV curve of Blank, we can determine the reduction current contributions corresponding to LNO in RCE+LNO and F₆₋₀ in both F6 and F6L. Through charge balance calculations, we can obtain the reduction ratios of these additives. To standardize our criteria for calculating the reduction rate, we use the total amount of charge corresponding to the complete detachment of F from F₆₋₀ as a denominator to measure the actual reduction ratio of F₆₋₀ in electrolytes. For LNO, considering that nitrogen may exist in forms between LNO and Li₃N during the reduction process, we have standardized our criteria by using the charge associated with reducing LNO to its final state Li₃N as a reference equivalent. To further validate the feasibility of using this differential method for quantitatively calculating the additive's reduction ratio, three additional sets of LSV tests were conducted: RCE with 0.02 M LNO; RCE with 0.04 M LNO; and RCE with 0.08 M LNO (**Supplementary Fig. 48**). At same voltage scan rate, as concentration increases from 0.02 M to 0.08 M in RCE solution containing LNO additive, the intensity of the peak corresponding to the reduction of LNO progressively increases. By integrating these three curves and subtracting the integration of Blank, we can obtain the reduction ratios at different concentrations of LNO in RCE, which are 21.6% for 0.02 M LNO, 12.4% for 0.04 M LNO, and 8.7% for 0.08 M LNO. The reduction ratio of additives can be quantitatively calculated using the differential method, making it a feasible approach. However, due to the limited solubility of LNO in RCE (not exceeding 0.1 M), higher concentration gradients were not employed.

Supplementary Tables

Supplementary Table 1. RCE with different F6L additions.

Code	Composition
0% 0M (0 0)	RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v)
1% 0M (1 0)	1 vol. % F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 1 vol. % F ₆₋₀
1% 1M (1 1)	1 vol. % F6L containing 1 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 1 vol. % F ₆₋₀ + 0.01 M LNO
1% 2M (1 2)	1 vol. % F6L containing 2 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 1 vol. % F ₆₋₀ + 0.02 M LNO
1% 4M (1 4)	1 vol. % F6L containing 4 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 1 vol. % F ₆₋₀ + 0.04 M LNO
1% 8M (1 8)	1 vol. % F6L containing 8 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 1 vol. % F ₆₋₀ + 0.08 M LNO
2% 0M (2 0)	2 vol. % F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 2 vol. % F ₆₋₀
2% 1M (2 1)	2 vol. % F6L containing 1 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 2 vol. % F ₆₋₀ + 0.02 M LNO
2% 2M (2 2)	2 vol. % F6L containing 2 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 2 vol. % F ₆₋₀ + 0.04 M LNO
2% 4M (2 4)	2 vol. % F6L containing 4 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 2 vol. % F ₆₋₀ + 0.08 M LNO
2% 8M (2 8)	2 vol. % F6L containing 8 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 2 vol. % F ₆₋₀ + 0.16 M LNO
4% 0M (4 0)	4 vol. % F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 4 vol. % F ₆₋₀
4% 1M (4 1)	4 vol. % F6L containing 1 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 4 vol. % F ₆₋₀ + 0.04 M LNO
4% 2M (4 2)	4 vol. % F6L containing 2 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 4 vol. % F ₆₋₀ + 0.08 M LNO
4% 4M (4 4)	4 vol. % F6L containing 4 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 4 vol. % F ₆₋₀ + 0.16 M LNO
4% 8M (4 8)	4 vol. % F6L containing 8 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 4 vol. % F ₆₋₀ + 0.32 M LNO
8% 0M (8 0)	8 vol. % F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 8 vol. % F ₆₋₀
8% 1M (8 1)	8 vol. % F6L containing 1 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 8 vol. % F ₆₋₀ + 0.08 M LNO
8% 2M (8 2)	8 vol. % F6L containing 2 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 8 vol. % F ₆₋₀ + 0.16 M LNO
8% 4M (8 4)	8 vol. % F6L containing 4 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 8 vol. % F ₆₋₀ + 0.32 M LNO
8% 8M (8 8)	8 vol. % F6L containing 8 M LNO in F ₆₋₀ added into RCE <i>i.e.</i> 1.0 M LiPF ₆ in EC/DMC (1:1, v/v) + 8 vol. % F ₆₋₀ + 0.64 M LNO

Note of Supplementary Table 1: For example, the “4 vol. % F6L containing 2 M LNO in F₆₋₀ added into RCE” indicates that the 2 M LNO is relative to F₆₋₀. This labeling method is primarily for the

convenience of electrolyte preparation and screening of the optimal ratio. Therefore, the corresponding F6L solution (4 vol. % F6L + 96 vol. % RCE) for this sample is 1.0 M LiPF_6 in EC/DMC (1: 1, v/v) + 4 vol. % F_{6-0} + 0.08 M LNO, where the 0.08 M is derived from multiplying 2 M by 4 vol. %. Furthermore, taking into account the volume change, we will add an appropriate amount of LiPF_6 to maintain a concentration of 1.0 M in the final electrolyte solution.

Supplementary Table 2. Results of the XPS spectra on the chemical states of SEI and the corresponding binding energy.

Chemical states		Binding energy								
		RCE			F6-0			F6L		
		0 s	120 s	420 s	0 s	120 s	420 s	0 s	120 s	420 s
C 1s	Li-C	283.0	283.0	283.0	283.4	283.2	283.0	283.4	283.4	283.1
	C-C/C-H	284.8	284.8	284.8	284.7	284.8	284.8	284.8	284.7	284.7
	C-O	286.4	286.4	286.4	286.4	286.4	286.4	286.4	286.4	286.5
	C=O	288.3	288.4	288.3	288.4	288.4	288.4	288.4	288.4	288.7
	CO ₃ ²⁻	289.9	290.0	289.9	289.8	289.9	289.9	290.2	290.1	289.9
	CF ₂	--	--	--	291.1	291.1	--	--	--	--
	C-F	--	--	--	--	--	292.0	291.8	292.0	292.0
F 1s	LiF	684.6	684.9	685.1	684.4	685.1	684.9	685.2	685.1	685.1
	Li _x PF _y O _z	686.5	686.6	687.2	686.3	686.6	686.6	686.6	--	--
	C-F	--	--	--	688.2	688.2	688.2	688.2	687.8	687.8
N 1s	Li ₃ N	--	--	--	--	--	--	397.0	397.0	396.8
		--	--	--	--	--	--	398.1	398.1	398.4
	LiN _x O _y	--	--	--	--	--	--	399.0	399.0	399.6
		--	--	--	--	--	--	400.0	400.0	401.0
Li 1s	Li ₂ O	--	--	--	--	--	--	53.5	53.8	53.7
	Li-C	54.0	54.0	53.7	54.0	54.0	54.3	--	--	--
	Li ₃ N	--	--	--	--	--	--	55.0	55.1	54.7
	ROCO ₂ Li	55.1	55.1	55.3	55.3	55.4	55.6	--	--	55.5
	LiN _x O _y	--	--	--	--	--	--	56.1	56.1	56.1
	LiF	--	--	--	56.7	56.7	56.7	56.7	56.7	57.2
O 1s	Li ₂ O	529.4	529.4	529.0	529.3	529.7	529.1	528.2	528.4	527.9
	ROLi	530.8	530.8	530.8	530.8	530.9	530.8	531.0	531.2	530.6
	C=O/CO ₃ ²⁻	531.8	531.8	531.9	531.8	531.9	531.9	532.1	532.1	532.1
	C-O	533.2	533.2	533.2	533.2	533.0	533.2	533.1	533.2	533.1
	Li _x PF _y O _z	534.5	534.5	534.5	534.5	534.5	534.5	--	--	--
P 2p	Li _x PF _y O _z	133.0	133.1	132.7	133.1	133.1	133.1	133.0	--	--
		135.0	135.0	134.4	134.6	134.5	134.5	134.5	--	--

Supplementary Table 3. Results of the XPS spectra on the chemical states of CEI and the corresponding binding energy.

Chemical states		Binding energy								
		RCE			F6-0			F6L		
		0 s	120 s	420 s	0 s	120 s	420 s	0 s	120 s	420 s
C 1s	C-C/C-H	284.8	284.8	284.8	284.8	284.8	284.8	284.8	284.8	284.7
	C-O	286.3	286.2	286.2	286.5	286.3	286.4	286.2	286.1	286.1
	C=O	288.5	288.4	288.3	288.4	288.4	288.4	288.4	288.4	288.4
	CO ₃ ²⁻	289.8	289.9	289.9	289.9	289.9	289.9	289.9	289.9	289.9
	CF ₂	291.1	291.0	291.0	290.8	290.8	290.8	290.9	290.8	290.8
	C-F	--	--	--	--	--	--	292.0	292.0	292.0
F 1s	LiF	685.4	685.6	685.7	685.2	685.4	685.4	685.4	685.5	685.4
	Li _x PF _y O _z	--	--	--	--	--	--	--	--	--
	C-F	688.1	687.9	687.8	687.9	687.9	687.9	688.3	688.1	687.9
O 1s	M-O	530.3	530.2	530.3	530.2	530.2	530.2	530.3	530.3	530.3
	C=O/CO ₃ ²⁻	532.1	532.0	532.1	532.2	532.2	532.1	532.1	532.0	532.0
	C-O	533.2	533.2	533.2	533.1	533.1	533.1	533.3	533.3	533.3
	Li _x PF _y O _z	534.5	534.5	534.5	534.6	534.6	534.6	534.5	--	--
P 2p		--	--	133.0	--	133.2	133.1	--	--	--
	Li _x PF _y O _z	134.7	134.6	134.6	134.3	134.3	134.5	135.4	135.4	135.4
		137.1	136.6	136.6	137.2	137.3	137.3	137.1	137.2	137.3

Supplementary Table 4. Ion conductivity of the electrolyte using Blank, F6, F6L, and LHCE.

Electrolyte	Ion conductivity (mS cm ⁻¹)
Blank	12.2
F6	12.4
F6L	12.9
LHCE	2.44 ^{Ref. 3}

Supplementary Table 5. Related work focusing on the electrolyte additives in the LMB's field.

Ref.	Electrolyte	Electrode	Operating mode	Performance
Zhao⁴	0.06 M Al(OTf) ₃ + 0.5 M LNO + 0.2 M LiDFOB + 0.2 M LiBOB + 0.6 M LiFSI + 0.05 M LiPF ₆ + 0.03 M LiBF ₄ in EC/DMC (2: 1 by vol.) with 1 vol. % FEC, 2 vol. % VC, and 3 vol. % TFEC	NCM811 Li-50μm	0.2 C (1.0 C = 4 mAh cm ⁻²)	92.5% retention after 200 cycles
Zhao⁵	2 wt. % LiBOB + 1 M LiPF ₆ in EC/EMC (4: 6 by wt.)	NMC76 Li-450μm	C/3 (1.0 C = 200 mAh g ⁻¹)	96.8% retention after 200 cycles
Li⁶	1 wt. % BFA + 1 M LiPF ₆ in EC/DMC (1: 1 by vol.)	NCM622 Li	0.5 mA cm ⁻²	78.5% retention after 200 cycles
Wen⁷	1.0×10 ⁻⁵ M I ₂ + 1 M LiPF ₆ in EC/DMC (1: 1 by vol.) with 1 vol. % FEC, and 5 vol. % G4 (4 M LNO in G4)	NCM523 Li-400μm	0.5 C (1.0 C = 200 mAh g ⁻¹)	93.3% retention after 100 cycles
Su⁸	20 wt. % FEC + 1.2 M LiPF ₆ in EC/EMC (3: 7 by wt.)	NCM811 Li	0.33 C	≈76.9% retention after 240 cycles
Ma⁹	2% TTFEB + 1 M LiPF ₆ in EC/DMC (1: 2 by vol.)	LFP Li	1.0 C (1.0 C = 170 mAh g ⁻¹)	≈92.1% retention after 500 cycles
Piao¹⁰	1 M LiPF ₆ in EC/DMC (1: 2 by vol.) with 5 wt. % FEC and 5 wt. % SL/LNO (9: 1 by wt.)	NCA Li-50μm	0.5 C (1.0 C = 1.65 mAh cm ⁻²)	90.8% retention after 150 cycles
Zhang¹¹	1 M LiPF ₆ in EC/DEC (1: 1 by vol.) with 5 vol. % FEC	NCM523 Li	1.0 C (1.0 C = 180 mAh g ⁻¹)	65.0% retention after 100 cycles
Zhou¹²	0.1 M LiFSI + 0.1 M LiBF ₄ + 1 M LiPF ₆ in EC/DMC/DEC (1: 1: 1 by vol.) with 2 wt. % VC and 10 wt. % FEC	LMR Li-100μm	1.0 C (1.0 C=300 mAh g ⁻¹)	76.6% retention after 400 cycles
Liu¹³	0.8 M LiPF ₆ in FEC/DMC (1: 4 by vol.) with 5 wt. % (4 M LNO in DMSO)	NCM811 Li-50μm	0.5 C (1.0 C=2.5 mAh cm ⁻²)	75.0% retention after 200 cycles
This work	4 vol% F ₆₋₀ + 0.08 M LNO + 1 M LiPF ₆ in EC/DMC (1: 1 by vol.)	NCM811 Li-20μm	0.5 C (1.0 C=210 mAh g ⁻¹)	77.4% retention after 400 cycles

Note of Supplementary Table 5: The abbreviations appearing in the table, their meanings are as follows: Al(OTf)₃ (aluminum triflate), LNO (lithium nitrate), LiDFOB (lithium difluoro(oxalato)borate), LiBOB (lithium bis(oxalato)borate), LiFSI (lithium bis(fluorosulfonyl)amide), LiPF₆ (lithium hexafluorophosphate), LiBF₄ (lithium tetrafluoroborate), BFA (bisfluoroacetamide), I₂ (iodine), TTFEB (tris(2, 2, 2-trifluoroethyl) borate), SL (sulfolane), F₆₋₀ (hexafluoroglutaric anhydride), EC (ethylene carbonate), DMC (dimethyl carbonate), FEC (fluoroethylene carbonate), VC (vinylene carbonate), TFEC (bis(2,2,2-trifluoroethyl) carbonate), EMC (ethyl methyl carbonate), G4 (tetraglyme), DEC (diethyl carbonate), DMC (dimethyl carbonate), DMSO (dimethyl sulfoxide), NCM811 (LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂), NMC76 (LiNi_{0.76}Mn_{0.14}Co_{0.10}O₂), NCM622 (LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂), NCM523 (LiNi_{0.5}Co_{0.2}Mn_{0.3}), LFP (LiFePO₄), NCA (LiNi_{0.80}Co_{0.15}Al_{0.05}O₂), LMR (lithium–manganese-rich).

Supplementary Table 6. The reduction ratios of fluorinated anhydrides in RCE without and with LNO.

Fluorinated anhydrides	Reduction ratios	
	Without LNO	With LNO
F ₇₋₁	2.5% (F7)	9.0% (F7L)
F ₆₋₀	3.1% (F6)	91.0% (F6L)
F ₅₋₁	2.1% (F5)	6.8% (F5L)
F ₄₋₀	2.6% (F4)	41.5% (F4L)
F ₂₋₁	1.8% (F2)	5.3% (F2L)

Note of Supplementary Table 6: Referencing the “4.3 Computational method of the reduction ratio of F₆₋₀” in the main text, the 10 curves in **Supplementary Fig. 41** were integrated and the corresponding reduction ratios were calculated.

Supplementary Table 7. Related LMB work focusing on the LHCE and HCE.

Ref.	Electrolyte		Electrode	Operating mode	Performance
	Formulation	Cost (USD \$ L ⁻¹)			
Zhang¹⁴	1.1 M LiFSI in DME/PFPN (28: 72 by vol.)	56334	LFP Li-50μm	1.0 C (1.0 C = 170 mAh g ⁻¹)	89.5% retention after 1000 cycles
Liu¹⁵	1.5 M LiFSI in DME/PFPN (1: 2 by vol.)	52145	NCM811 Li-25μm	0.5 C (1.0 C = 3.8 mAh cm ⁻²)	86.5% retention after 200 cycles
Yu¹⁶	1.2 M LiTFSI + 0.15 M LiDFOB in EC/EMC/BTFE (4: 23: 73 by vol.)	24687	NMC333 Li-250μm	0.263 C (1.0 C = 3.8 mAh cm ⁻²)	84.0% retention after 100 cycles
Wang¹⁷	4 M LiTFSI + 0.5 M LiDFOB in FEC/DMC (3: 7 by vol.)	10026.8	NCM Li-25μm	1.0 C (1.0 C = 170 mAh g ⁻¹)	86.2% retention after 200 cycles
Lin¹⁸	1.6 M LiTFSI + 0.4 M LiDFOB in TMS/EA/HFE (15: 35: 50 by vol.) with 10 wt. % FEC	6160.6	NCM523 Li-1000μm	1.0 C (1.0 C = 200 mAh g ⁻¹)	89.0% retention after 200 cycles
Huangzhang¹⁹	1.2 M LiFSI in DME/FEC/OFE (12: 12: 76, by vol.)	3892.7	NCM811 Li	0.5 C (1.0 C = 3.1 mAh cm ⁻²)	91.4% retention after 140 cycles
Jia²⁰	0.1 M LNO + 1 M LiDFOB in TMP/D ₂ (24: 76 by vol.)	3247.3	NCM87 Li-50μm	0.5 C (1.0 C = 210 mAh g ⁻¹)	84.0% retention after 100 cycles
Li²¹	2.3 M LiFSI in DME/TTE (35: 65 by vol.)	2880.1	NCM523 Li-50μm	0.4 C (1.0 C = 3 mAh cm ⁻²)	95.7% retention after 100 cycles
Lin²²	1.65 M LiFSI in DME/HFE (3: 5 by vol.)	2733.2	NCM523 Li-1000μm	0.5 C (1.0 C = 160 mAh g ⁻¹)	83.0% retention after 250 cycles
Dai²³	3 M LiPF ₆ in DMC/FEC/HFPM (6: 1: 3 by vol.)	2095.9	LNMO Li	0.5 C (1.0 C = 147 mAh g ⁻¹)	≈94.0% retention after 400 cycles
This work	4 vol. % F ₆ -0 + 0.08 M LNO + 1 M LiPF ₆ in EC/DMC (1: 1 by vol.)	389.8	NCM811 Li-20μm	0.5 C (1.0 C = 210 mAh g ⁻¹)	77.4% retention after 400 cycles

Note of Supplementary Table 7: The abbreviations appearing in the table, their meanings are as follows: LiFSI (lithium bis(fluorosulfonyl)amide), LiDFOB (lithium difluoro(oxalato)borate), LiTFSI (lithium bis(trifluoromethanesulfonyl)imide), LNO (lithium nitrate), LiPF₆ (lithium hexafluorophosphate), DME (1,2-dimethoxyethane), PFPN (ethoxy(pentafluoro)cyclotriphosphazene), EC (ethylene carbonate), EMC (ethyl methyl carbonate), BTFE (bis(2,2,2-trifluoroethyl)), FEC (fluoroethylene carbonate), DMC (dimethyl carbonate), TMS (sulfolane), EA (ethyl acetate), HFE (1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether), OFE (1H,1H,5H-octafluoropentyl-1,1,2,2-tetrafluoroethyl ether), TMP (trimethyl phosphate), D₂ (1,1,2,2-tetrafluoroethyl-2,2,3,3-

tetrafluoropropylether), TTE (1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether), HFPM (1,1,1,3,3,3-hexafluoroisopropyl methyl ether), LFP (LiFePO_4), NCM811 ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$), NMC333 ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$), NCM ($\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$), NCM523 ($\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$), NCM87 ($\text{LiNi}_{0.87}\text{Co}_{0.08}\text{Mn}_{0.05}\text{O}_2$), LNMO ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$).

Supplementary Table 8. LFP||Li pouch cell parameters.

1.0-Ah pouch cell	Specifications	Parameters
Cathode	Cathode material	LFP
	Mass loading (mg cm^{-2})	17.0
	Active material (wt %)	91.5
	Compact density (g mL^{-1})	2.0
	Thickness (μm)	85
	Voltage window (V)	2.7~4
Anode	Anode material	Li-20 μm
Cell	Dimension ($\text{cm} \times \text{cm}$)	5.4×5.6
	Nominal capacity (Ah)	1.0
	Electrolyte injection (g Ah^{-1})	3
	N/P ratio	1.4

Note of Supplementary Table 8: Specific energy density calculation method: The total weight of LFP||Li pouch cell is 19.4 g, and the average output voltage is 3.34 V (**Supplementary Fig. 45**). Thus, the calculated specific energy density of 4.0 V-level LFP||Li pouch cell is 172 Wh kg^{-1} ($= 1.0 \text{ Ah} \times 3.34 \text{ V} / 0.0194 \text{ kg}$). Specific power density calculation method: Given that the output time at 1 C is 0.91 h (**Fig. 6g**), the calculated specific power density of 4.0 V-level LFP||Li pouch cell is 189 W kg^{-1} ($= 172 \text{ Wh kg}^{-1} / 0.91 \text{ h}$).

Supplementary Table 9. NCM811||Li and LNMO||Li full cells parameters.

Full cells	Specifications	Parameters
Cathode: NCM811 (8.05 mg cm ⁻²)	Mass loading (mg cm ⁻²)	8.52
	Active material (wt %)	94.5
	Compact density (g mL ⁻¹)	3.35
	Thickness (μm)	25.4
	Diameter (mm)	12
	Area (cm ²)	1.13
	Voltage window (V)	2.8~4.5
	1 C (mAh g ⁻¹)	210
Cathode: NCM811 (14.87 mg cm ⁻²)	Mass loading (mg cm ⁻²)	15.74
	Active material (wt %)	94.5
	Compact density (g mL ⁻¹)	3.35
	Thickness (μm)	47.0
	Diameter (mm)	12
	Area (cm ²)	1.13
	Voltage window (V)	2.8~4.5
	1 C (mAh g ⁻¹)	210
Cathode: LNMO (9.03 mg cm ⁻²)	Mass loading (mg cm ⁻²)	10.03
	Active material (wt %)	90.0
	Compact density (g mL ⁻¹)	3.21
	Thickness (μm)	31.2
	Diameter (mm)	12
	Area (cm ²)	1.13
	Voltage window (V)	3.5~4.95
	1 C (mAh g ⁻¹)	147
Anode: Li metal	Thickness (μm)	20
Separator: Celgard 2325	Porosity	0.39

Note of Supplementary Table 9: The pre-activation procedure for the full cell testing was carried out at 0.1 C (1 C = 210 mAh g⁻¹ for NCM811 under the voltage window of 2.8~4.5 V and 147 mAh g⁻¹ for LNMO under the voltage window of 3.5~4.95 V). The metal electrode (Li metal anode) was purchased from China Energy Lithium Co., Limited.

Supplementary Table 10. Compositions of the modelling systems of F6 and F6L.

Composition	System of F6	System of F6L
EC	750	750
DMC	600	600
LiPF ₆	100	100
F ₆₋₀	24	24
LNO	--	6
Total No. of atoms	15836	15866
Simulation system size	(5.6433 nm) ³	(5.6436 nm) ³

Note of Supplementary Table 10: Ionic models and computational methods can be found in the **Methods** section of the main text.

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