

Supplementary information

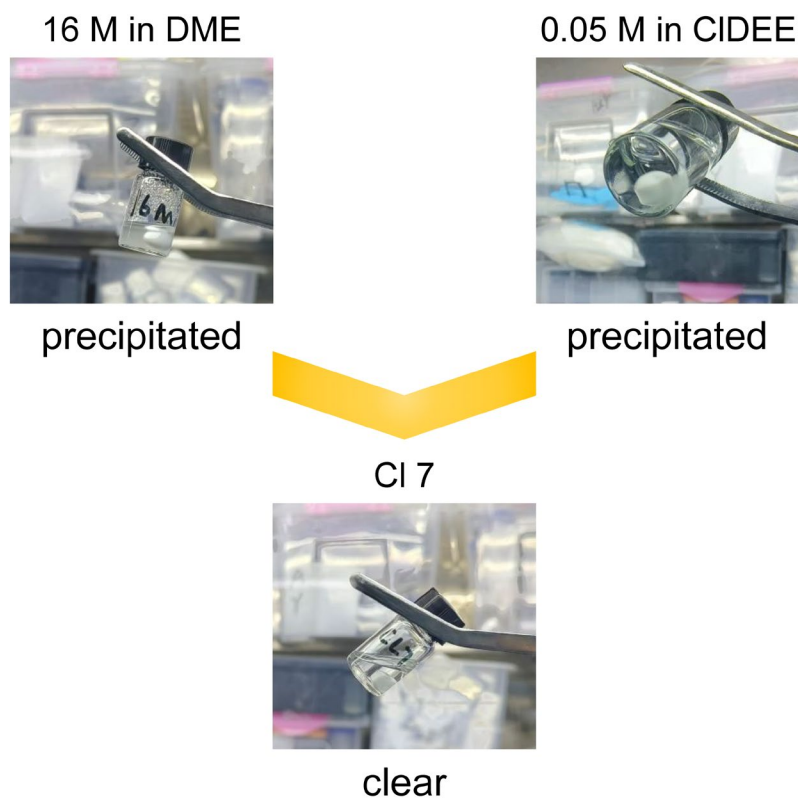
Advancing lithium metal electrode beyond 99.9% coulombic efficiency via super-saturated electrolyte with compressed solvation structure

Wujie Yang^{1,2}, Aoyuan Chen^{1,2}, Ping He^{1,2*}, Haoshen Zhou^{1,2*}

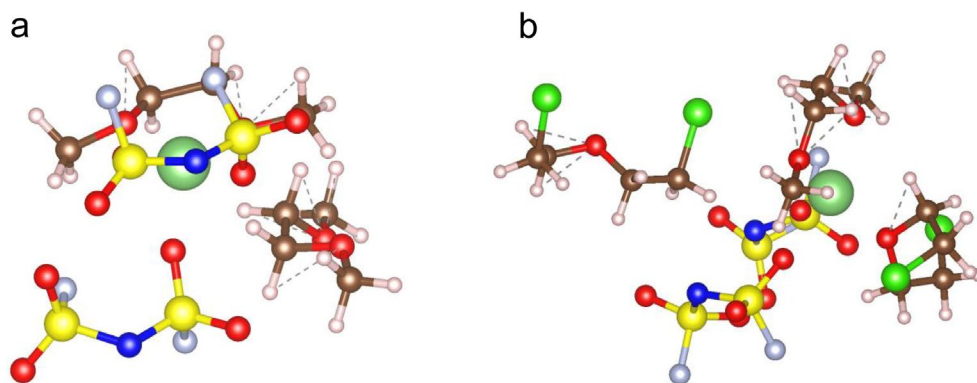
¹Center of Energy Storage Materials & Technology, College of Engineering and Applied Sciences, Jiangsu Key Laboratory of Artificial Functional Materials, Nanjing University, Nanjing, 210093, P. R. China

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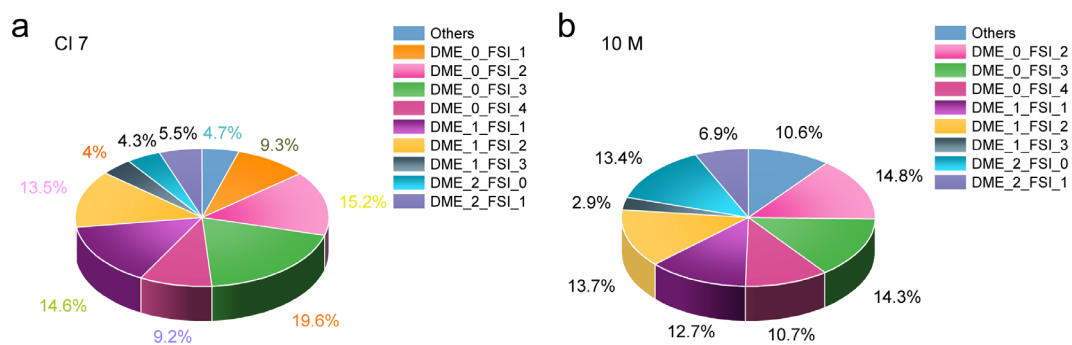
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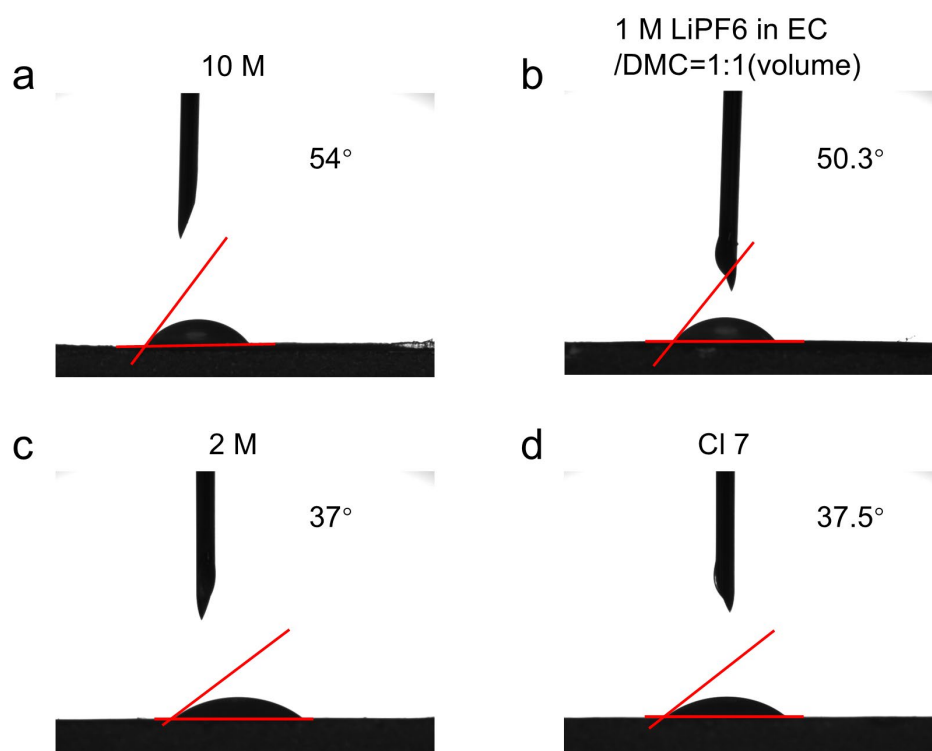
Supplementary Fig. 1. Photographs of the electrolytes. It can be observed that when 16 M LiFSI is added to DME or 0.05 M LiFSI is added to CIDEe, a noticeable turbidity and precipitate occur. Yet, with a 1:7 volume ratio of DME to CIDEe, the 2 M LiFSI dissolves entirely, which is equivalent to attaining 16 M LiFSI in the DME solvent phase, highlighting the crucial role of CIDEe in the realization of ultra-high local concentration.



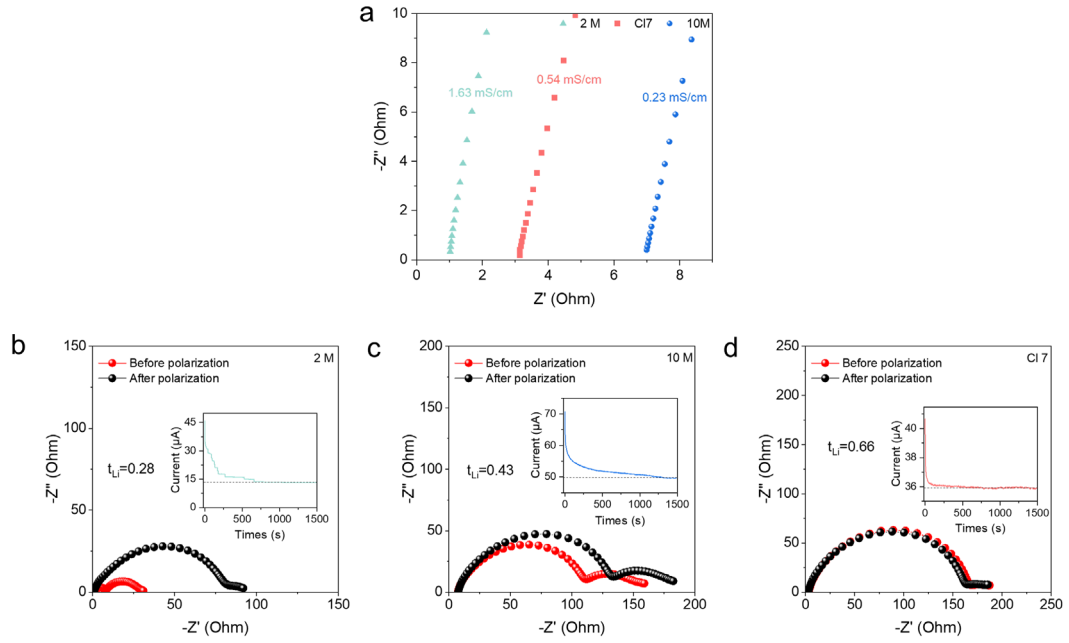
Supplementary Fig. 2. Local structures of MD simulation. Typical Li^+ solvation structures in (a) 10 M electrolyte and (b) Cl 7 electrolyte. Colorings of atoms are O: red, Li: dark green, C: brown, H: pink, Cl: bright green, S: yellow, N: blue.



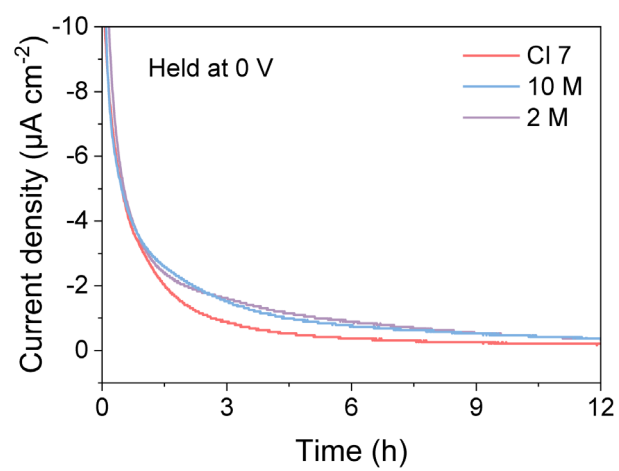
Supplementary Fig. 3. Statistical evaluation of solvation clusters with various DME –FSI– ratio. (a) Cl 7 electrolyte and (b) 10 M electrolyte.



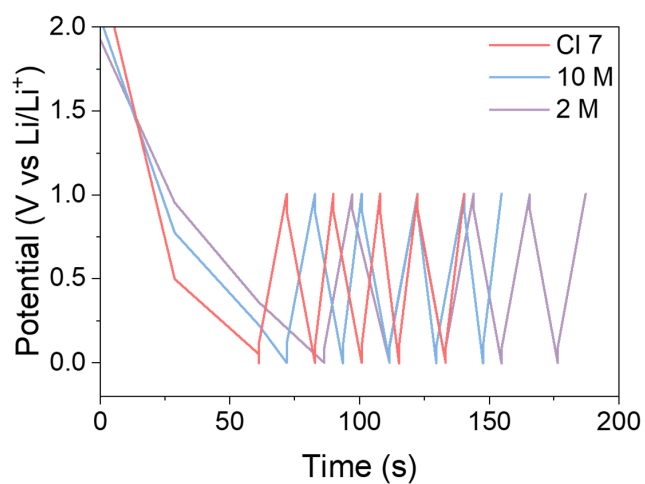
Supplementary Fig. 4. Contact angles of (a) 10 M electrolyte, (b) traditional carbonate-based electrolyte, (c) 2 M electrolyte and (d) Cl 7 electrolyte with PE separator.



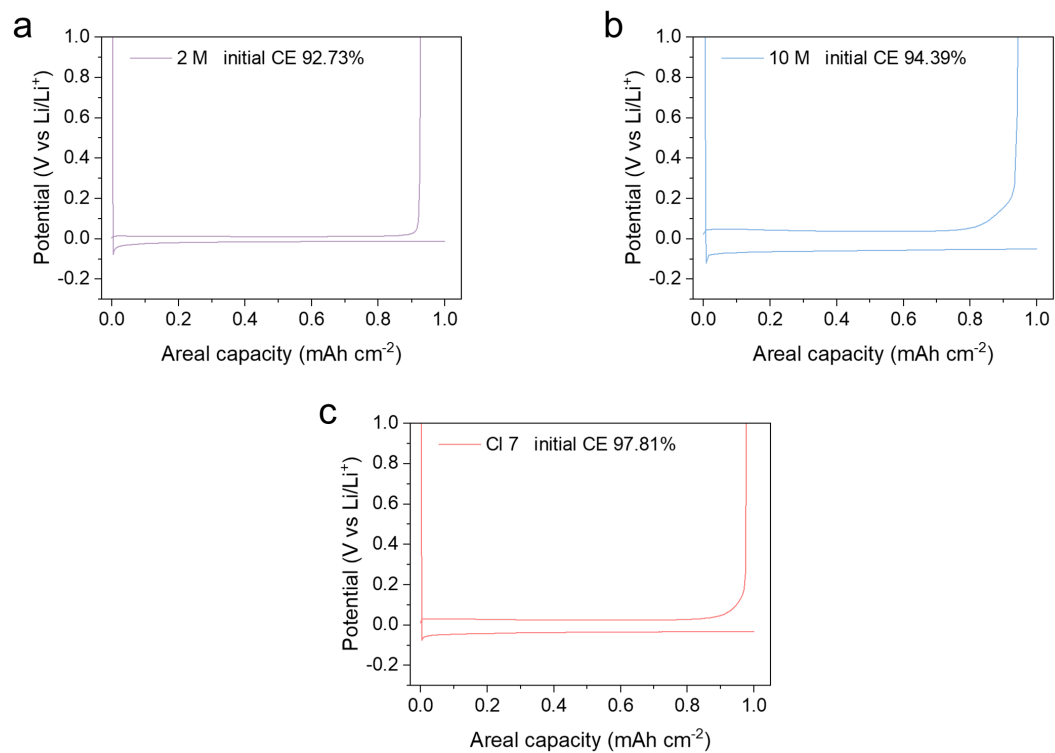
Supplementary Fig. 5. (a) The Nyquist plots of various electrolytes. Impedance spectra of the cell in the initial state and the steady state with (b) 2 M electrolyte, (c) 10 M electrolyte and (d) Cl 7 electrolyte. Inset shows the polarization curves. All electrochemical tests are conducted at 30°C.



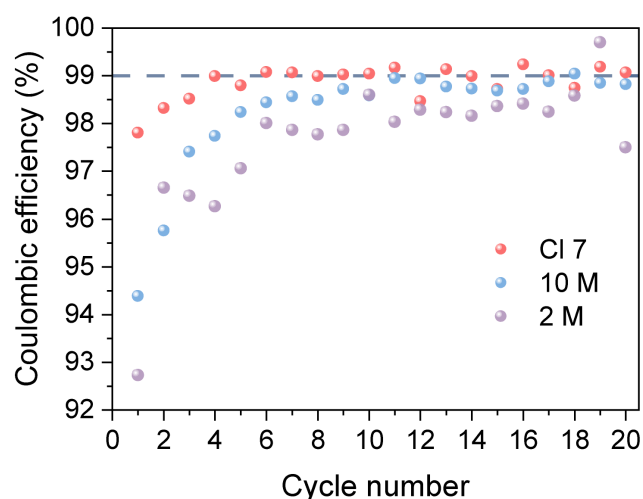
Supplementary Fig. 6. Corrosion current during a constant voltage process at 0 V in the Li||Cu cells. Electrochemical tests are conducted at 30°C.



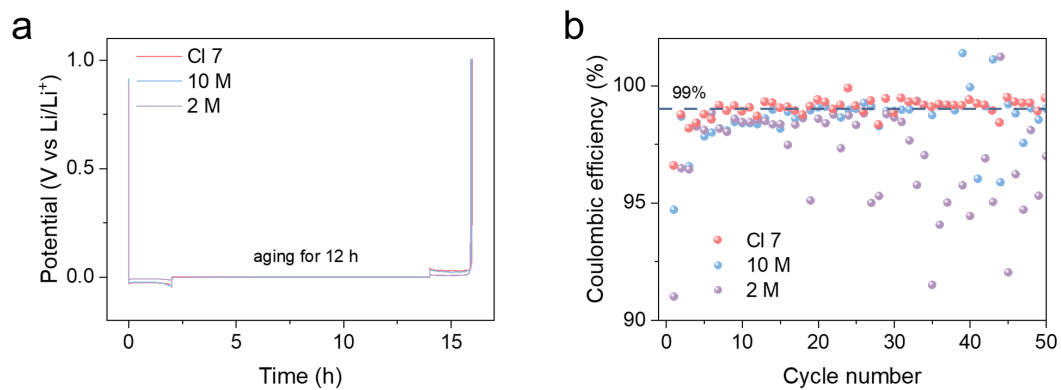
Supplementary Fig. 7. Galvanostatic tests of the Li||Cu cells between 0-1 V at a current density of 0.2 mA cm⁻². All electrochemical tests are conducted at 30°C.



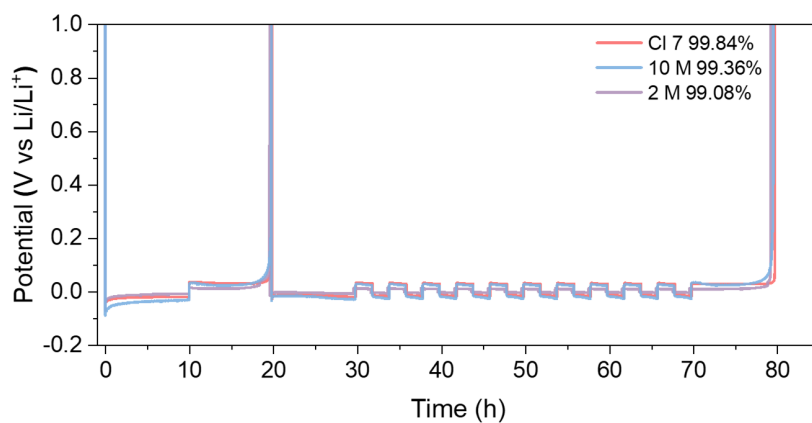
Supplementary Fig. 8. Initial CE in different electrolytes. Initial voltage profiles of Li||Cu cells at 0.5 mA cm⁻² and 1 mAh cm⁻² with (a) 2 M, (b) 10 M and (c) Cl 7 electrolyte. All electrochemical tests are conducted at 30°C.



Supplementary Fig. 9. Initial 20 cycles of the activation process in Li||Cu half cells. All electrochemical tests are conducted at 30°C. The Cl 7 electrolyte not only achieves an initial CE of 97.81%, but also enables the CE to reach over 99% within just six cycles, which powerfully demonstrates the critical role of the deep decomposition of tightly packed anionic clusters in the compressed solvation structure for the rapid and sufficient passivation of LMN, thus improving the reversibility of Li plating/stripping.

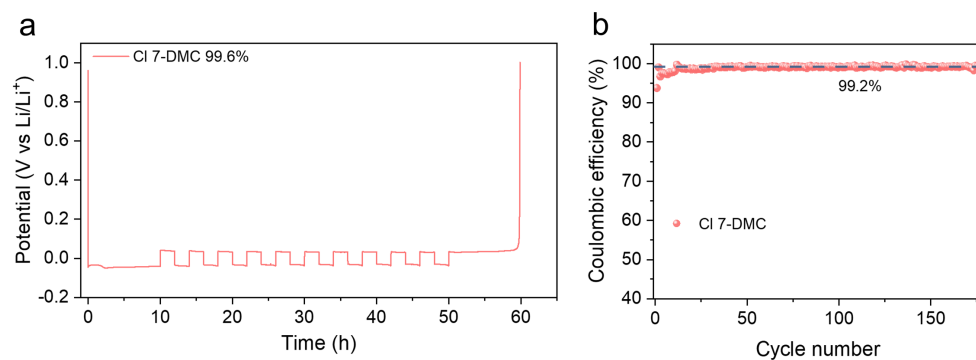


Supplementary Fig. 10. LMN CE under full plating/stripping conditions at 0.5 mA cm⁻² and 1 mAh cm⁻², with a 12-hour aging period after Li deposition. (a) Typical voltage-time curves of Li||Cu cells with a 12-hour aging period after Li deposition. (b) CE evolution of Li||Cu cells with a 12-hour aging period after Li deposition. All electrochemical tests are conducted at 30°C.

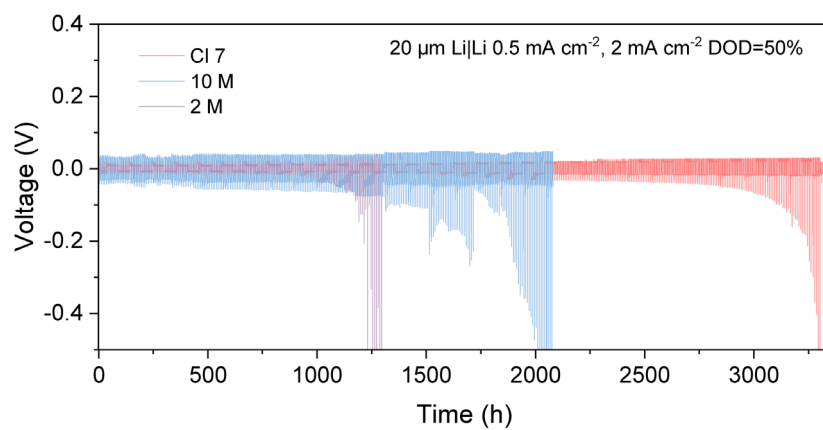


Supplementary Fig. 11. Common Aurbach's measurement of LMN CE.

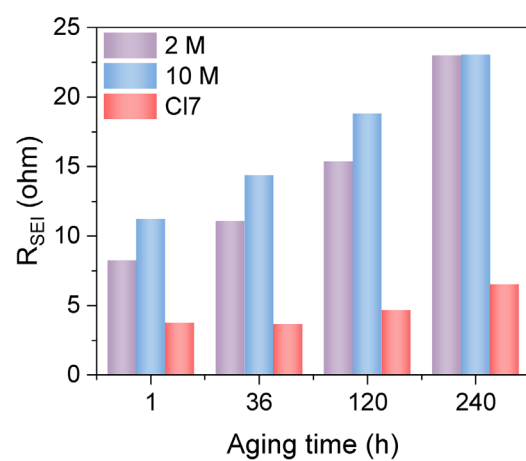
To verify the advancement of our CI 7 electrolyte, we adopted the general Aurbach protocol with a formation capacity of 5 mAh cm^{-2} to test the average CE. Our CI 7 electrolyte still demonstrated a superior CE of 99.84%. All electrochemical tests are conducted at 30°C .



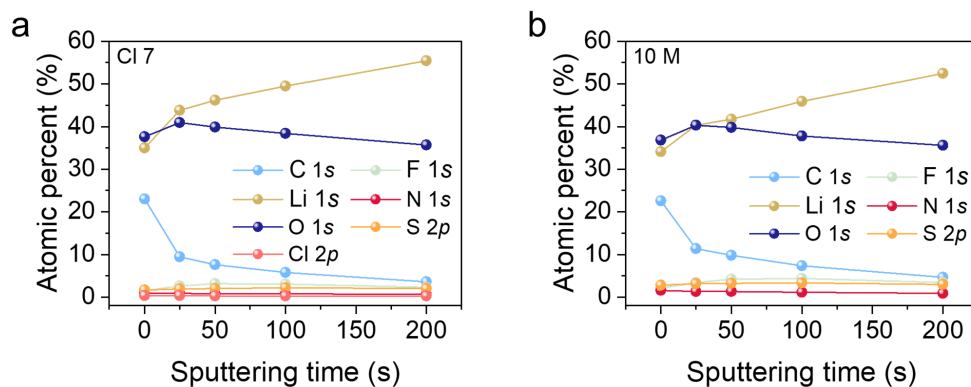
Supplementary Fig. 12. LMN stability in compressed solvation structure composed of DMC solvent. (a) Modified Aurbach's measurement of LMN CE. **(b)** LMN CE under full plating/stripping conditions at 0.5 mA cm^{-2} and 1 mAh cm^{-2} . All electrochemical tests are conducted at 30°C .



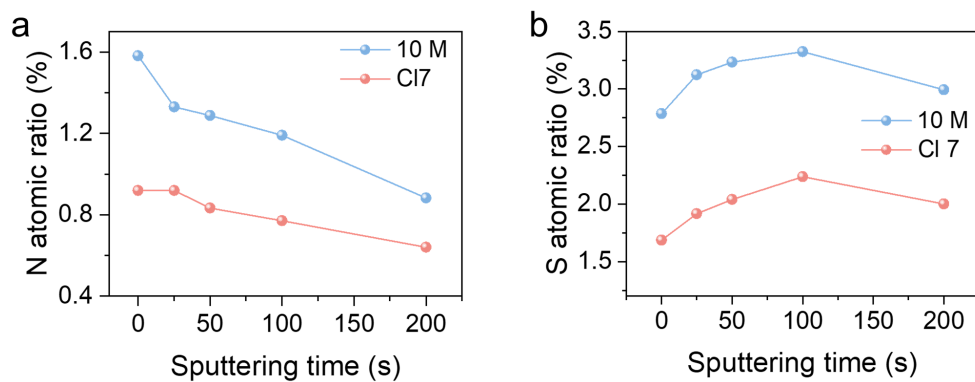
Supplementary Fig. 13. Cycling performance of lean-Li Li||Li symmetric cells at 0.5 mA cm⁻² and 2 mA cm⁻² (DOD=50%). All electrochemical tests are conducted at 30°C.



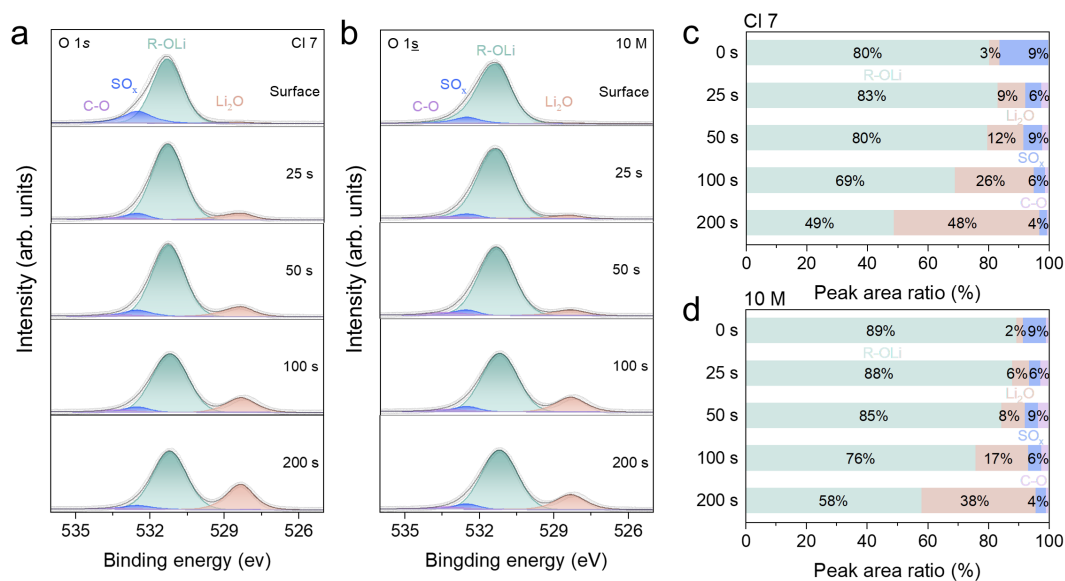
Supplementary Fig. 14. Evolution of R_{SEI} in Li||Li cell with different electrolytes. All electrochemical tests are conducted at 30°C.



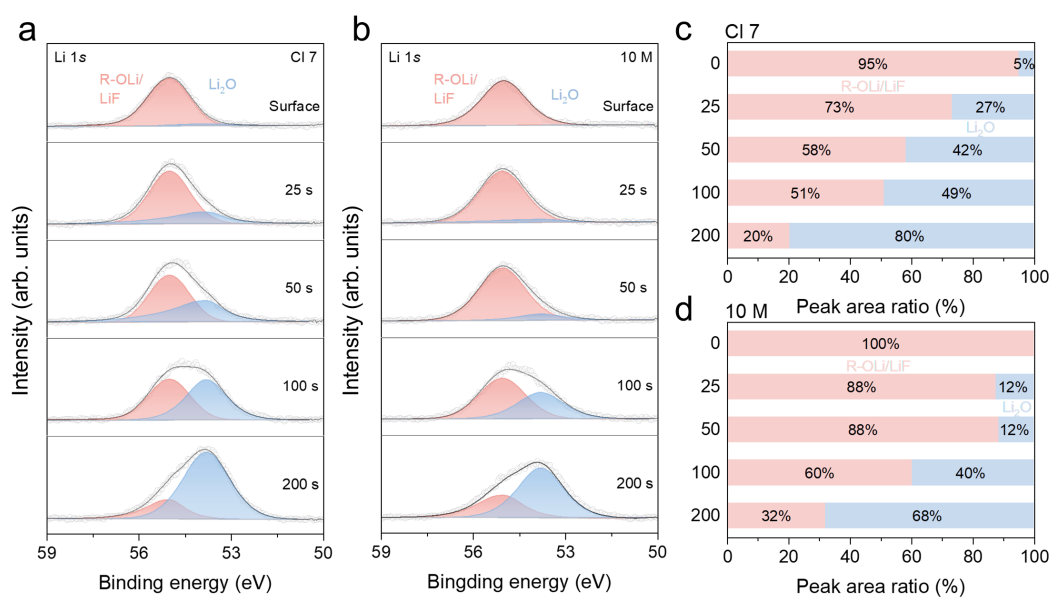
Supplementary Fig. 15. The atomic contents at different depths of SEI derived from (a) CI 7 electrolyte and (b) 10 M electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm^{-2} Li at 0.5 mA cm^{-2} on Cu after cycling at 0.5 mA cm^{-2} and 2 mAh cm^{-2} for 10 cycles.



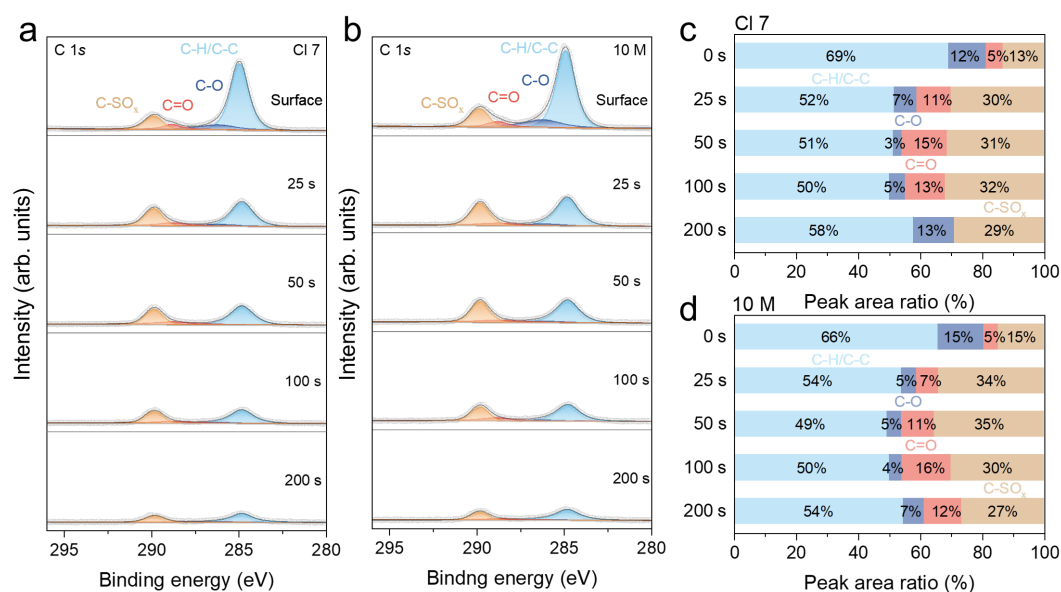
Supplementary Fig. 16. (a) N and (b) S atomic ratio at different depths of SEI. The LMN used for XPS tests was obtained by deposited 3 mAh cm^{-2} Li at 0.5 mA cm^{-2} on Cu after cycling at 0.5 mA cm^{-2} and 2 mAh cm^{-2} for 10 cycles.



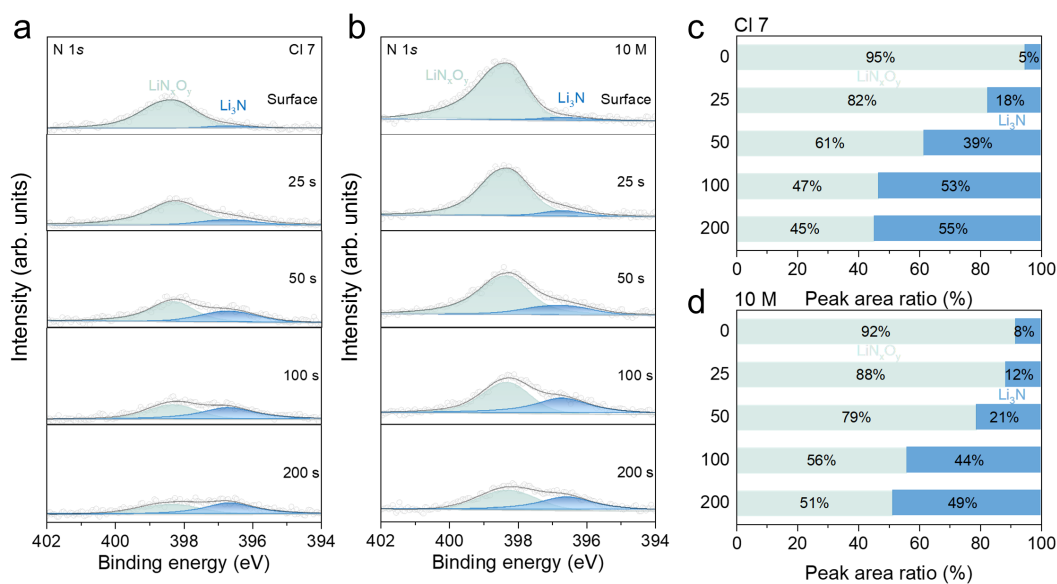
Supplementary Fig. 17. O 1s XPS depth profiles. XPS analysis of O 1s spectra in (a) CI 7 electrolyte and (b) 10 M electrolyte. Detail peak area ratio of different O-containing species in (c) CI 7 electrolyte and (d) 10 M electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm⁻² Li at 0.5 mA cm⁻² on Cu after cycling at 0.5 mA cm⁻² and 2 mAh cm⁻² for 10 cycles.



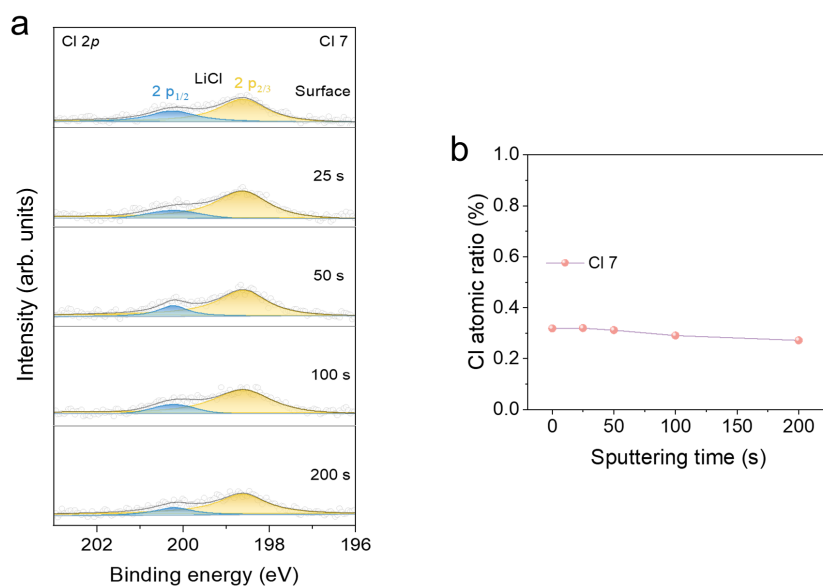
Supplementary Fig. 18. Li 1s XPS depth profiles. XPS analysis of Li 1s spectra in (a) Cl 7 electrolyte and (b) 10 M electrolyte. Detail peak area ratio of different Li-containing species in (c) Cl 7 electrolyte and (d) 10 M electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm⁻² Li at 0.5 mA cm⁻² on Cu after cycling at 0.5 mA cm⁻² and 2 mAh cm⁻² for 10 cycles.



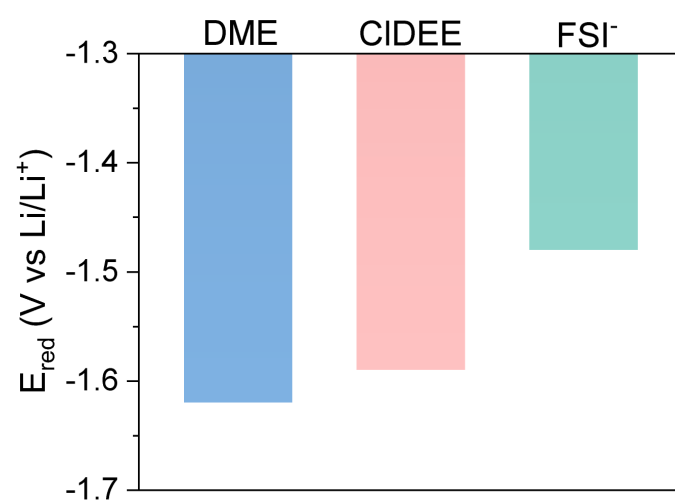
Supplementary Fig. 19. C 1s XPS depth profiles. XPS analysis of C 1s spectra in (a) CI 7 electrolyte and (b) 10 M electrolyte. Detail peak area ratio of different C-containing species in (c) CI 7 electrolyte and (d) 10 M electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm⁻² Li at 0.5 mA cm⁻² on Cu after cycling at 0.5 mA cm⁻² and 2 mAh cm⁻² for 10 cycles.



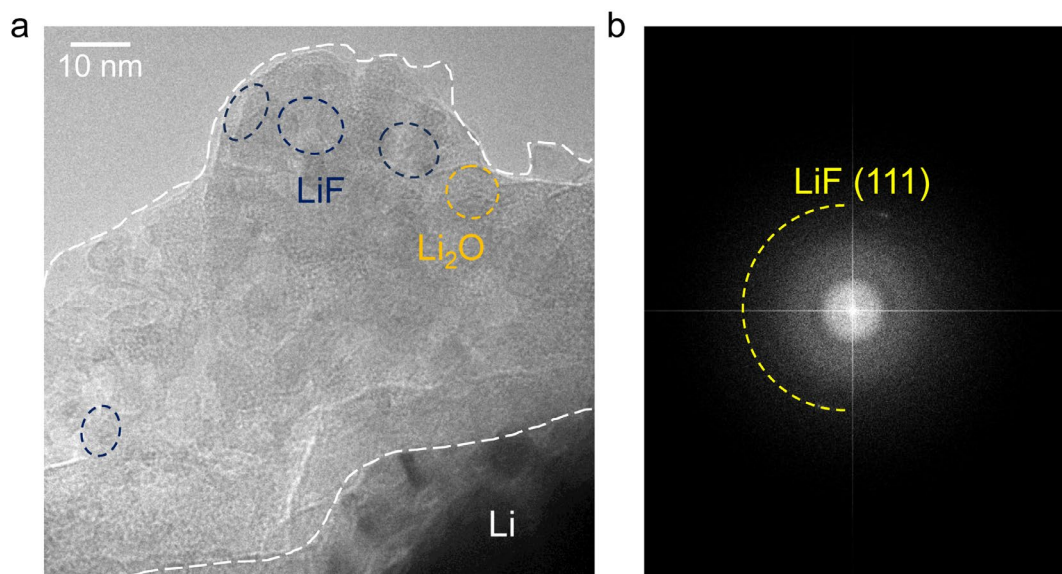
Supplementary Fig. 20. N 1s XPS depth profiles. XPS analysis of N 1s spectra in (a) CI 7 electrolyte and (b) 10 M electrolyte. Detail peak area ratio of different N-containing species in (c) CI 7 electrolyte and (d) 10 M electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm^{-2} Li at 0.5 mA cm^{-2} on Cu after cycling at 0.5 mA cm^{-2} and 2 mAh cm^{-2} for 10 cycles.



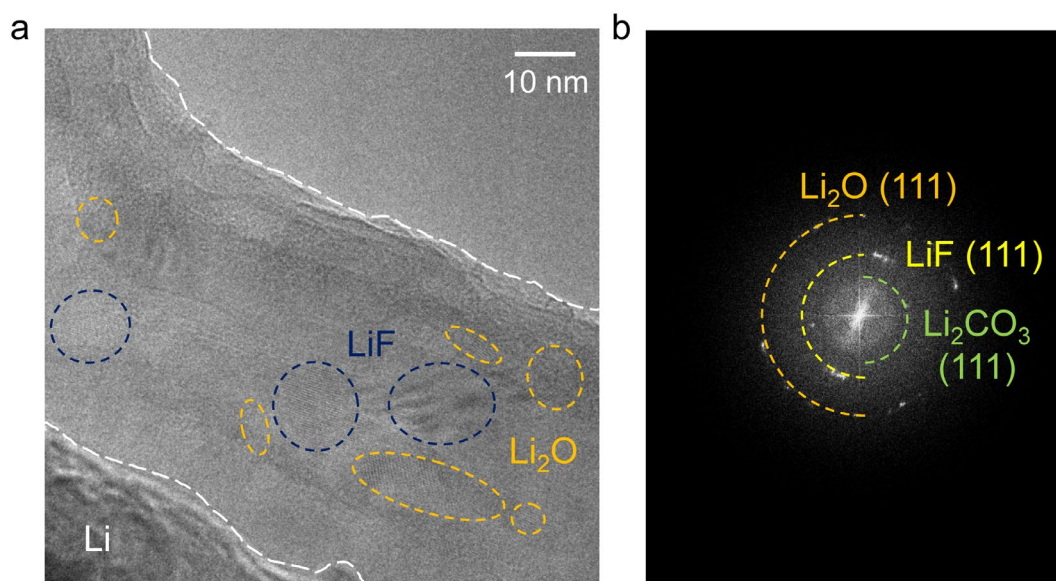
Supplementary Fig. 21. Cl 2p XPS depth profiles. (a) XPS analysis of Cl 2p spectra in Cl 7 electrolyte and (b) Cl atomic ratio at different depths of SEI in Cl 7 electrolyte. The LMN used for XPS tests was obtained by deposited 3 mAh cm⁻² Li at 0.5 mA cm⁻² on Cu after cycling at 0.5 mA cm⁻² and 2 mAh cm⁻² for 10 cycles.



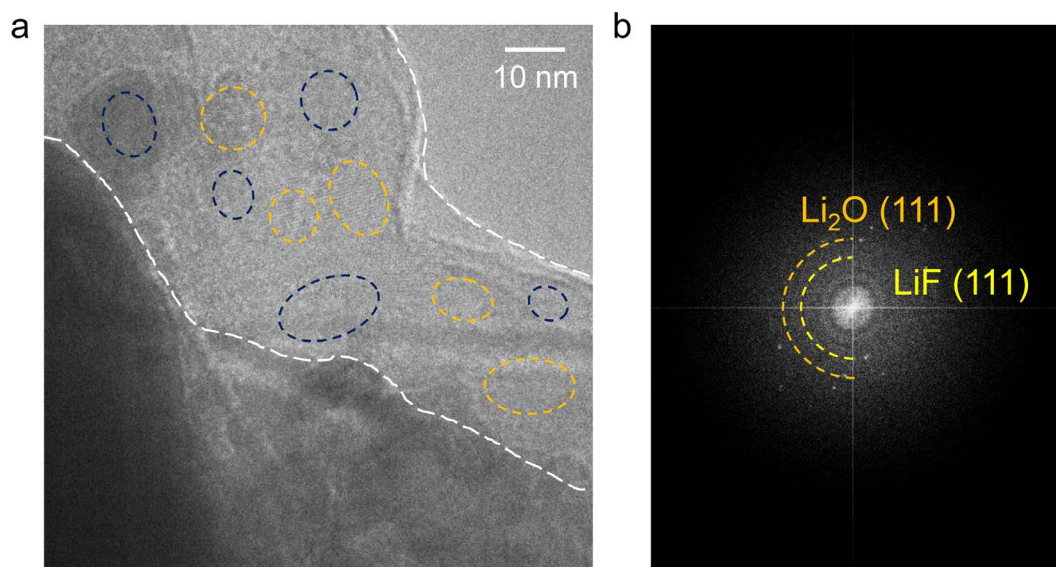
Supplementary Fig. 22. Calculated reduction potential (E_{red}) of DME, CIDE and FSI^- based on density functional theory.



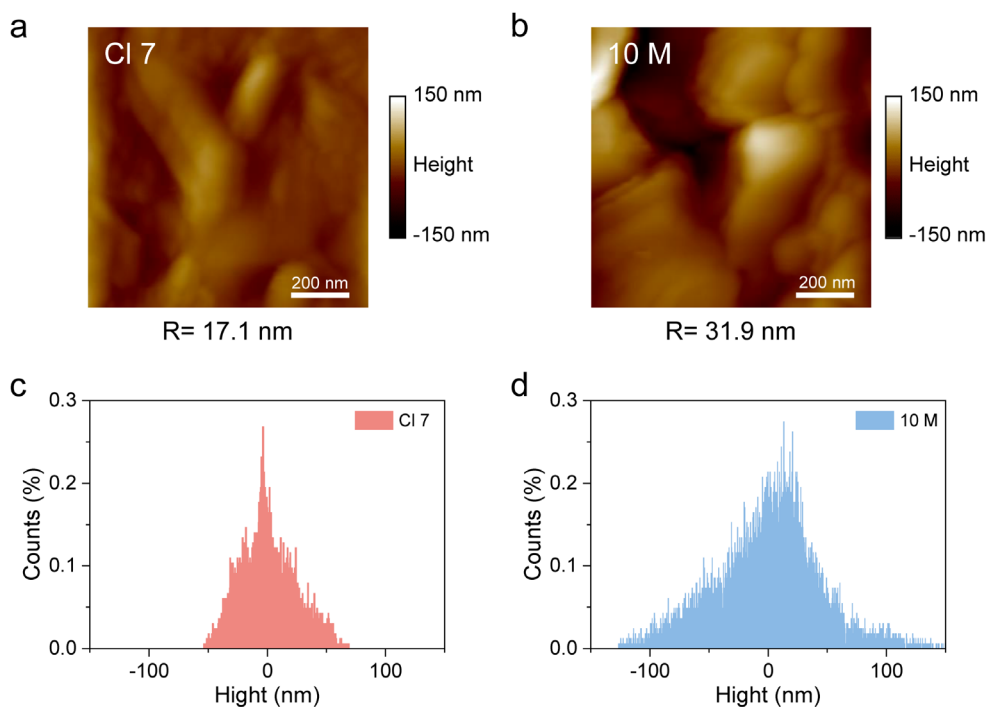
Supplementary Fig. 23. Cryo-TEM characterization of SEI formed in 2 M electrolyte. (a) Cryo-TEM image of SEI layer formed in 2 M electrolyte and (b) corresponding fast Fourier transform (FFT) image. For cryo-TEM characterization, Li was deposited onto a lacey carbon grid in Li||Cu coin cells at 0.5 mA cm^{-2} for 20 min.



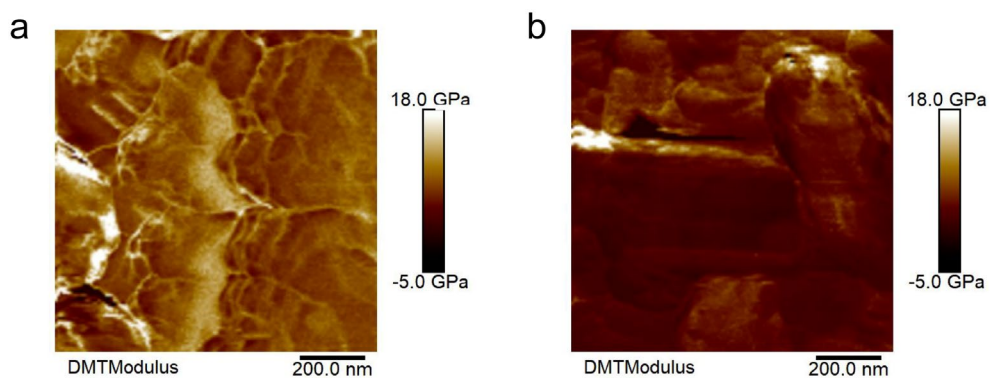
Supplementary Fig. 24. Cryo-TEM characterization of SEI formed in 10 M electrolyte. (a) Cryo-TEM image of SEI layer formed in 10 M electrolyte and (b) corresponding fast Fourier transform (FFT) image. For cryo-TEM characterization, Li was deposited onto a lacey carbon grid in Li||Cu coin cells at 0.5 mA cm^{-2} for 20 min.



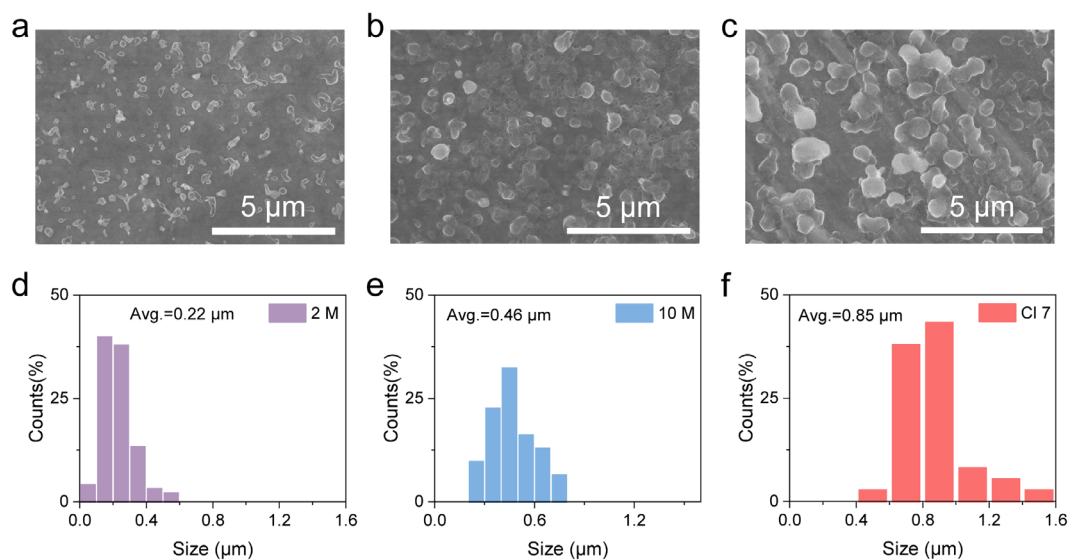
Supplementary Fig. 25. Cryo-TEM characterization of SEI formed in CI 7 electrolyte. (a) Cryo-TEM image of SEI layer formed in CI 7 electrolyte and (b) corresponding fast Fourier transform (FFT) image. For cryo-TEM characterization, Li was deposited onto a lacey carbon grid in Li||Cu coin cells at 0.5 mA cm^{-2} for 20 min.



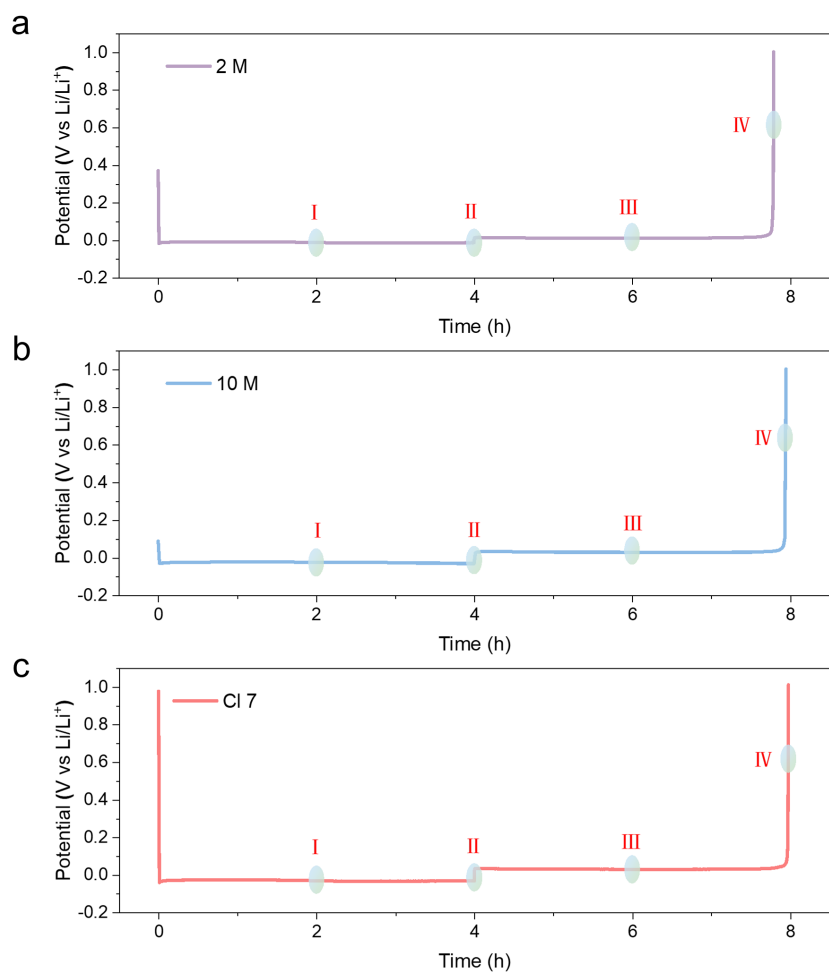
Supplementary Fig. 26. Height distribution of SEI. 2D morphology diagram of SEI in (a) Cl 7 electrolyte and (b) 10 M electrolyte. Statistics of height distribution of SEI in (c) Cl 7 electrolyte and (d) 10 M electrolyte. The LMN used for AFM tests was obtained by deposited 3 mAh cm^{-2} Li at 0.5 mA cm^{-2} on Cu after cycling at 0.5 mA cm^{-2} and 2 mAh cm^{-2} for 10 cycles.



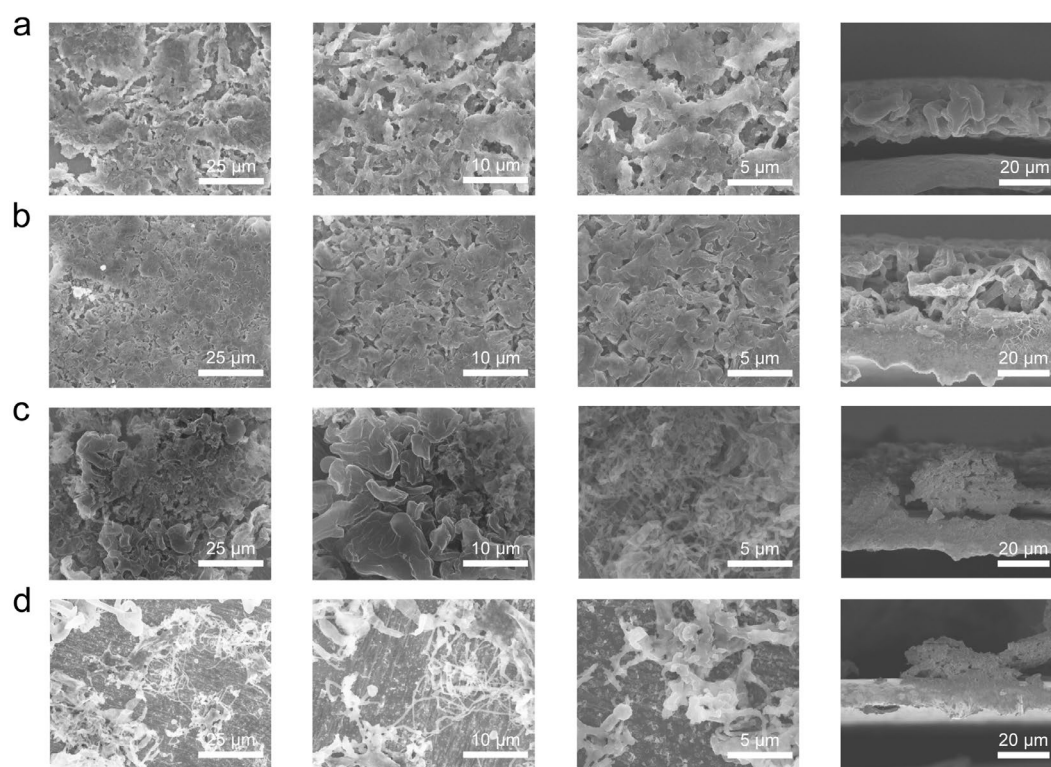
Supplementary Fig. 27. Spatial distribution of DMT modulus in (a) Cl 7 electrolyte and (b) 10 M electrolyte. The LMN used for AFM tests was obtained by deposited 3 mAh cm⁻² Li at 0.5 mA cm⁻² on Cu after cycling at 0.5 mA cm⁻² and 2 mAh cm⁻² for 10 cycles.



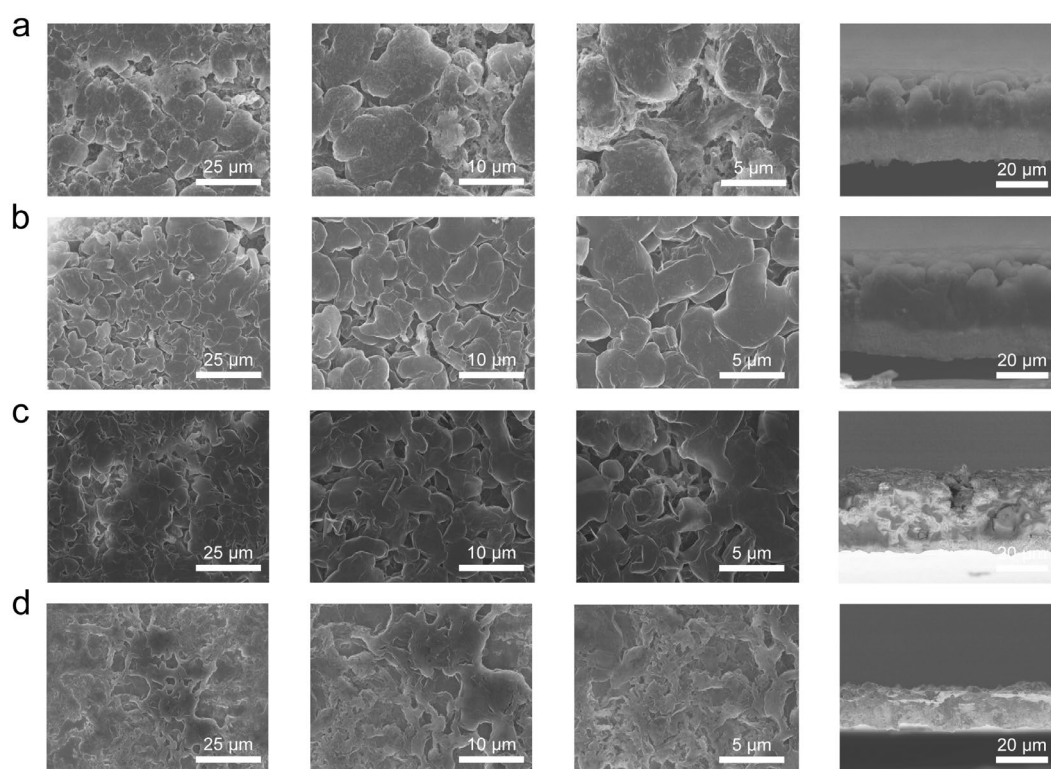
Supplementary Fig. 28. The nucleation behavior of Li. SEM images of deposited Li on Cu at 0.1 mA cm^{-2} current density for 0.1 mAh cm^{-2} in (a) 2 M, (b) 10 M and (c) Cl 7 electrolyte and the corresponding size distribution (d) 2 M (e) 10 M and (f) Cl 7 electrolyte.



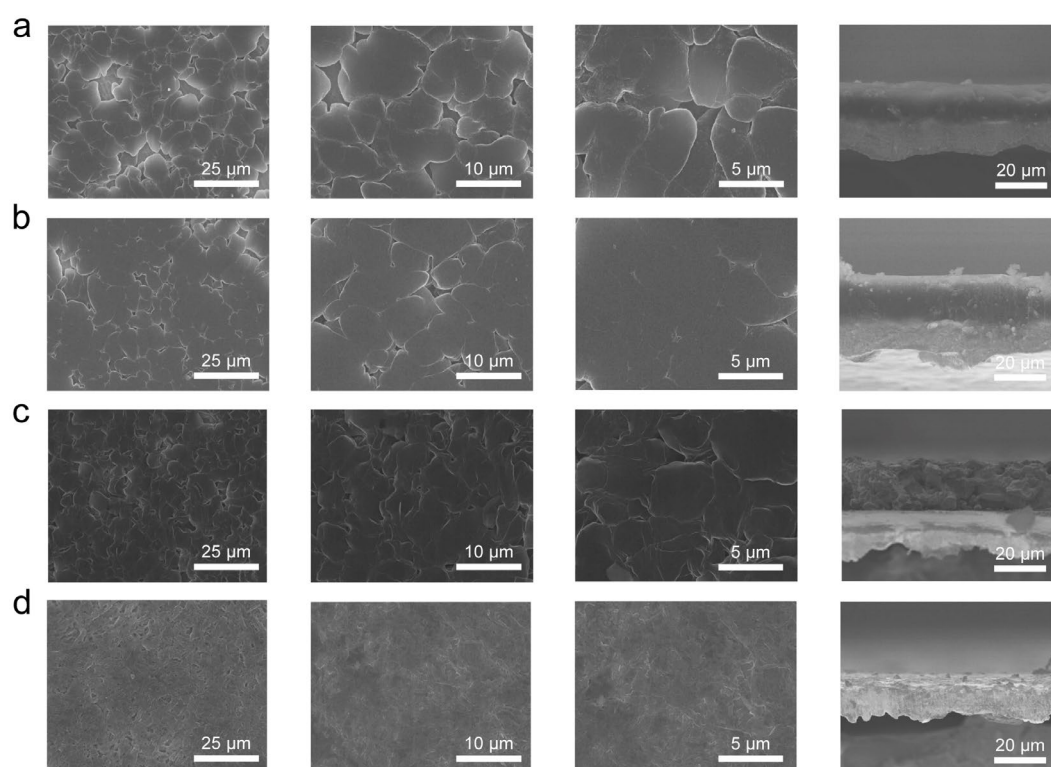
Supplementary Fig. 29. Voltage profiles for analyzing evolution of Li plating and stripping. Galvanostatic discharge/charge voltage profiles at 0.5 mA cm⁻² of Li || Cu cells in (a) 2 M electrolyte, (b) 10 M electrolyte and (c) Cl 7 electrolyte.



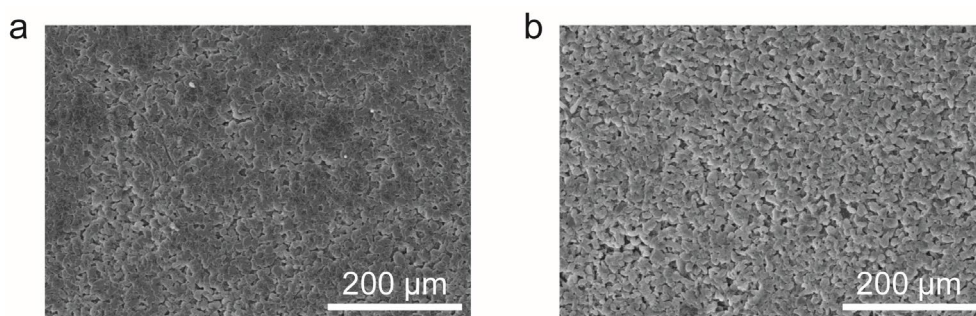
Supplementary Fig. 30. Li deposition morphology evolution at various stages in 2 M electrolyte. SEM images in 2 M electrolyte at (a) stage I , (b) stage II , (c) stageIII, and (d) stageIV.



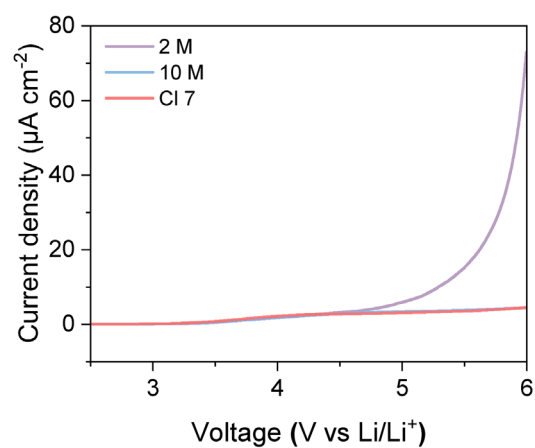
Supplementary Fig. 31. Li deposition morphology evolution at various stages in 10 M electrolyte. SEM images in 10 M electrolyte at (a) stage I , (b) stage II , (c) stage III, and (d) stage IV.



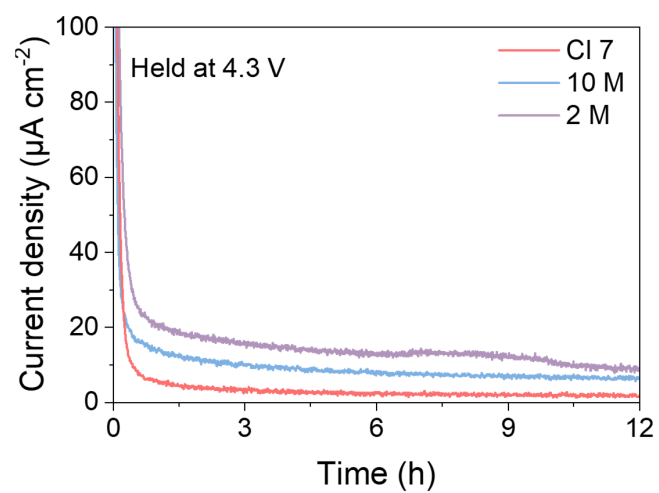
Supplementary Fig. 32. Li deposition morphology evolution at various stages in Cl 7 electrolyte. SEM images in Cl 7 electrolyte at (a) stage I , (b) stage II , (c) stage III, and (d) stage IV.



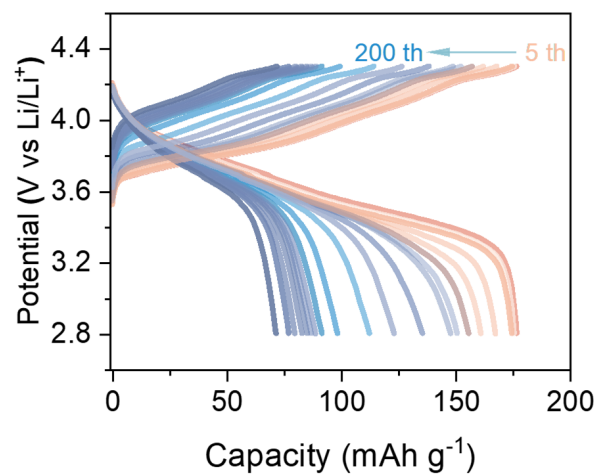
Supplementary Fig. 33. SEM images of Li at higher deposition level and wider field views. Li deposition with areal capacity of 3.0 mAh cm^{-2} at 0.5 mA cm^{-2} in (a) Cl 7 electrolyte and (b) 10 M electrolyte.



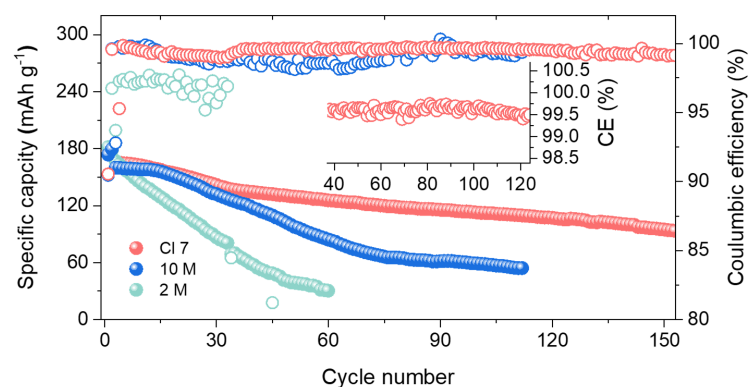
Supplementary Fig. 34. LSV curves of Li||Al cells with different electrolytes at a scanning rate of 0.5 mV s^{-1} . All electrochemical tests are conducted at 30°C .



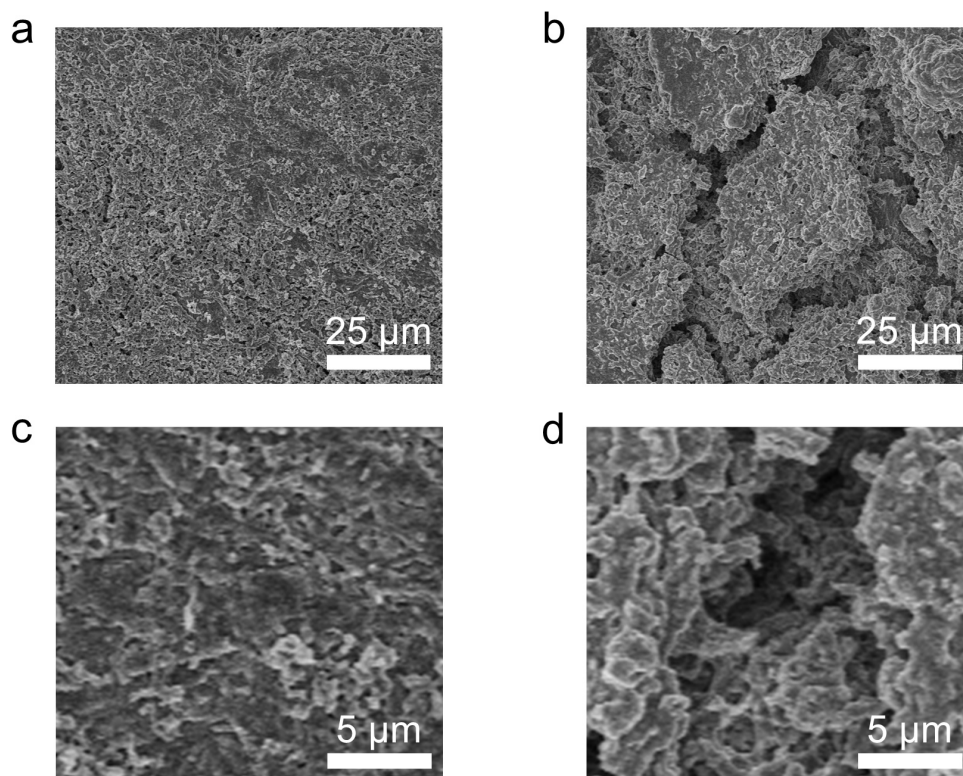
Supplementary Fig. 35. Floating test of different electrolytes under 4.3 V in Li||NCM811 cells. All electrochemical tests are conducted at 30°C.



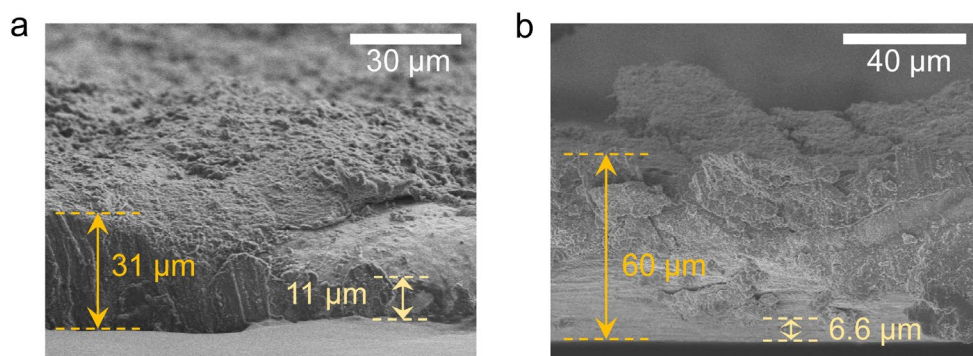
Supplementary Fig. 36. Evolution of voltage profiles in Li||NCM811 full cell (N/P ratio=1.05) with 10 M electrolyte.



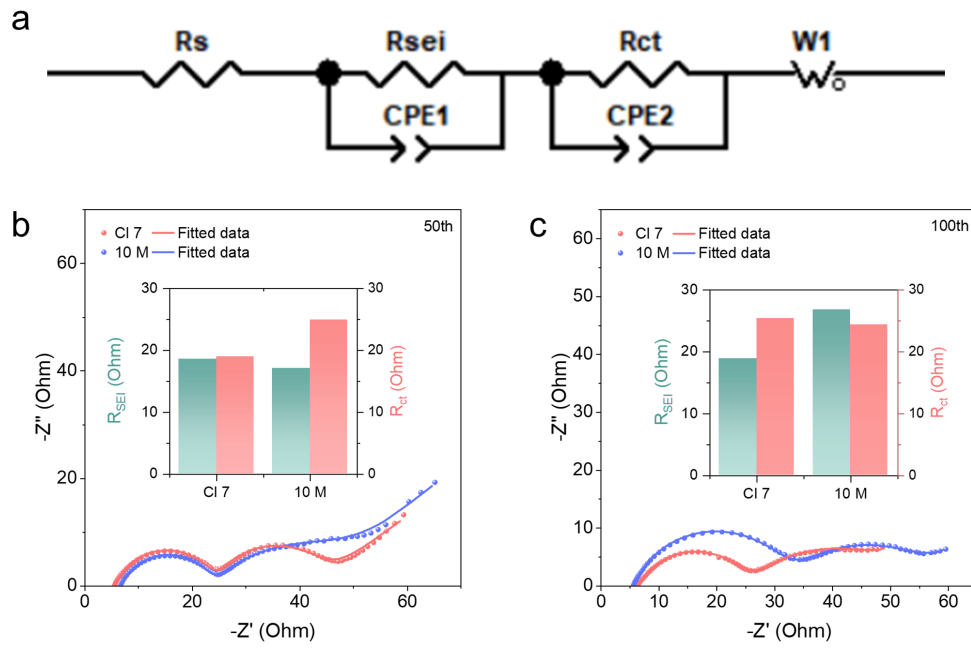
Supplementary Fig. 37. Cycling performance of the initially anode-free Cu||NCM811 coin cells during 2.8-4.2 V, with positive electrodes loading of 3.8 mAh cm^{-2} , at 0.2 C charge/0.5 C discharge, $1 \text{ C}=200 \text{ mA g}^{-1}$. The inset shows the magnified CE within Cl 7 electrolyte from 40 to 120 cycles. All electrochemical tests are conducted at 30°C .



Supplementary Fig. 38. Top-view SEM images of LMN in Li||NCM811 full cell (N/P ratio=0.89) after 100 cycles in the discharged state. (a,c) Cl 7 electrolyte and (b,d) 10 M electrolyte.



Supplementary Fig. 39. Cross-sectional-view SEM images of LMN in Li||NCM811 full cell (N/P ratio=0.89) after 100 cycles in the discharged state. (a) Cl 7 electrolyte and (b) 10 M electrolyte.



Supplementary Fig. 40. Evolution of impedance in Li||NCM811 full cell (N/P ratio=0.89). (a) Equivalent circuit diagram for EIS analysis. Nyquist plots at (b) 50th and (c) 100th cycles.

Supplementary Note 1

Analysis of ion transport properties

As shown in Supplementary Fig. 5. The tight ion aggregation in CI 7 electrolyte results in a lower conductivity (0.54 mS cm^{-1}) compared to conventional low-concentration electrolyte (2 M electrolyte, 1.63 mS cm^{-1}). However, due to its low viscosity and excellent wettability, the conductivity is notably higher than that of traditional high-concentration electrolyte (10 M electrolyte, 0.23 mS cm^{-1}). Additionally, the CI 7 electrolyte exhibits the highest Li^+ transference number (0.66), which compensates for its relatively low conductivity and ensures sufficient ion transport for efficient battery operation.

Supplementary Note 2

The passivation capability to LMN

We tested the $\text{Li}||\text{Cu}$ cells between 0-1 V at a current density of 0.2 mA cm^{-2} to monitor voltage changes, without plating Li (Supplementary Fig. 7.). It can be observed that during the initial discharge to 0 V (equivalent to the first SEI formation process), the CI 7 electrolyte requires the shortest time, indicating its most rapid passivation capability and superior reduction resistance. In subsequent cycles, the CI 7 electrolyte also exhibits the lowest cycling charge, suggesting fewer side reactions and better stability of the electrolyte.

Supplementary Note 3

Feasibility of compressing solvation structure strategy in carbonate electrolyte

To verify the versatility of the strategy involving compressed solvation structures, we conducted additional tests on a DMC-based electrolyte known to be incompatible with LMN (Supplementary Fig. 12). CI 7-DMC consists of 1.8 M LiFSI dissolved in a mixture of DMC and CIDEe with a volume ratio of 1:7. By modified Aurbach's method, the average CE in CI 7-DMC can achieve 99.6%. Even under full plating/stripping conditions at a current density of 0.5 mA cm^{-2} and a capacity of 1 mAh cm^{-2} , a CE of 99.2% can still be realized.

Supplementary Note 4

Electrochemical processes for monitoring lithium deposition/stripping behavior

We conducted SEM observations of Li morphology at various stages (Supplementary Fig. 29): upon reaching 1 mAh cm^{-2} deposition (stage I), upon reaching 2 mAh cm^{-2} deposition (stage II), after plating 2 mAh cm^{-2} and then stripping 1 mAh cm^{-2} (stage III), and after full stripping following 2 mAh cm^{-2} deposition (stage IV), to trace the morphological evolution of Li during the plating and stripping process.

Supplementary Note 5

The tolerance of electrolytes to NCM811

To assess the antioxidant performance of the electrolytes in realistic full cells, we have conducted the floating tests in $\text{Li}||\text{NCM811}$ cells (Supplementary Fig. 35). The results

demonstrate that, even when considering the catalytic activity of the cathode, the Cl 7 electrolyte exhibits exceptional oxidation resistance, as evidenced by the lowest oxidation current.