

Molecular design of methylated fluorinated-ether electrolytes for high-voltage lithium-metal batteries

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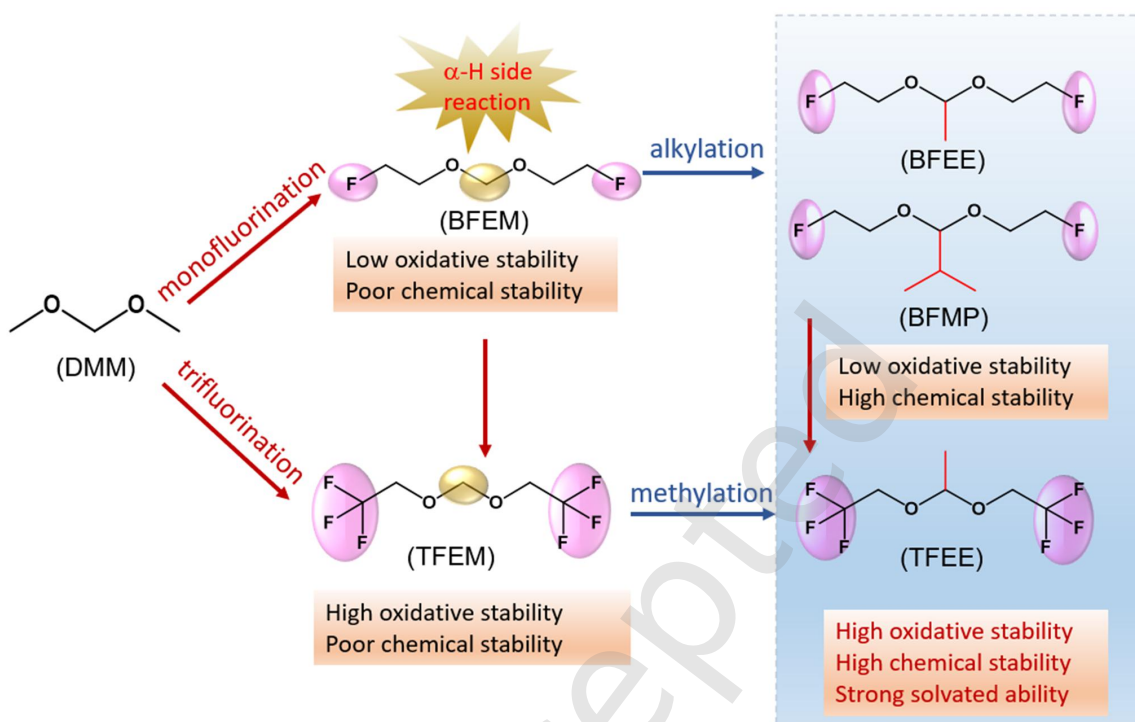
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Molecular engineering via methyl modification on acetal-structured fluorinated ethers effectively suppresses side reactions triggered by active oxygen species, improving the oxidative stability, ionic conductivity of ether-based electrolyte for high-voltage lithium metal batteries.

Molecular design of methylated fluorinated-ether electrolytes for high-voltage lithium-metal batteries

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ABSTRACT: Fluorinated-ethers are recognized as promising electrolyte solvents for high-voltage lithium metal batteries (HV-LMBs) due to its exceptional oxidation resistance and high reductive stability on anode. However, their oxidative and chemical stability are strongly influenced by the fluorination degree and α -hydrogen reactivity which easily be attacked by active oxygen species. Herein, a series of methyl-modified fluorinated-ethers on the acetal structure motif were designed and synthesized, and the fluorinated-ether featuring simultaneous trifluoromethyl and methyl substitution delivered outstanding electrochemical performances. With the designed fluorinated-ether of 1,1,1-trifluoro-2-(1-(2,2,2-trifluoroethoxy) ethoxy) ethane (TFEE), the electrolyte enabled highly reversible Li deposition/stripping, achieving an average Coulombic efficiency of 98.5% over 455 cycles. Li||LiNi_{0.8}Co_{0.1}Mn_{0.1} cells maintained 79.2% capacity retention after 410 cycles under 4.5 V, exceeding those containing non-methylated or monofluorinated ether analogs. Li||LiNi_{0.8}Co_{0.1}Mn_{0.1} pouch cell with 1 Ah theoretical capacity could stably cycle for 80 cycles with 79.6% capacity retention. This molecular design strategy provides new insights for developing advanced high-voltage electrolytes for next-generation LMBs.

KEYWORDS: fluorinated-ether electrolyte; Li metal anode; high-voltage electrolyte; high-nickel layered oxide cathodes; α -hydrogen substitution

1 Introduction

The growing demand for high-energy-density storage systems in electrical vehicles and smart grids has accelerated the development of lithium metal batteries (LMBs). Conventional Li-ion batteries using graphite anodes are fundamentally limited by their low theoretical specific capacity (372 mAh g⁻¹). In contrast, Li metal anodes are considered as the ultimate candidate due to their lowest reductive potential (-3.04 V vs. standard hydrogen electrode), low density (0.59 g cm⁻³) and high theoretical specific capacity (3860 mAh g⁻¹) [1-3]. When paired with the high-nickel layered oxide cathodes (e.g., LiNi_xCo_yMn_{1-x-y}O₂, Ni 60%), LMBs are projected to deliver energy densities exceeding 500 Wh kg⁻¹, meeting the essential requirements for next-generation energy storage systems [4-6]. Nevertheless, state-of-the-art electrolytes-particularly the commercial carbonate-based electrolytes, exhibit limited thermodynamic stability under high-voltage conditions, which usually leads to poor interfacial compatibility, low Coulombic efficiency, large polarization voltage and rapid capacity decay in LMBs [7-9]. Ether-based electrolytes are widely used in LMBs as their high reductive stability on the Li metal anode. However, conventional ether-based electrolytes such as 1,2-methoxyethyl ethane (DME) or diethyl ether (DEE) suffer from poor oxidative stability in

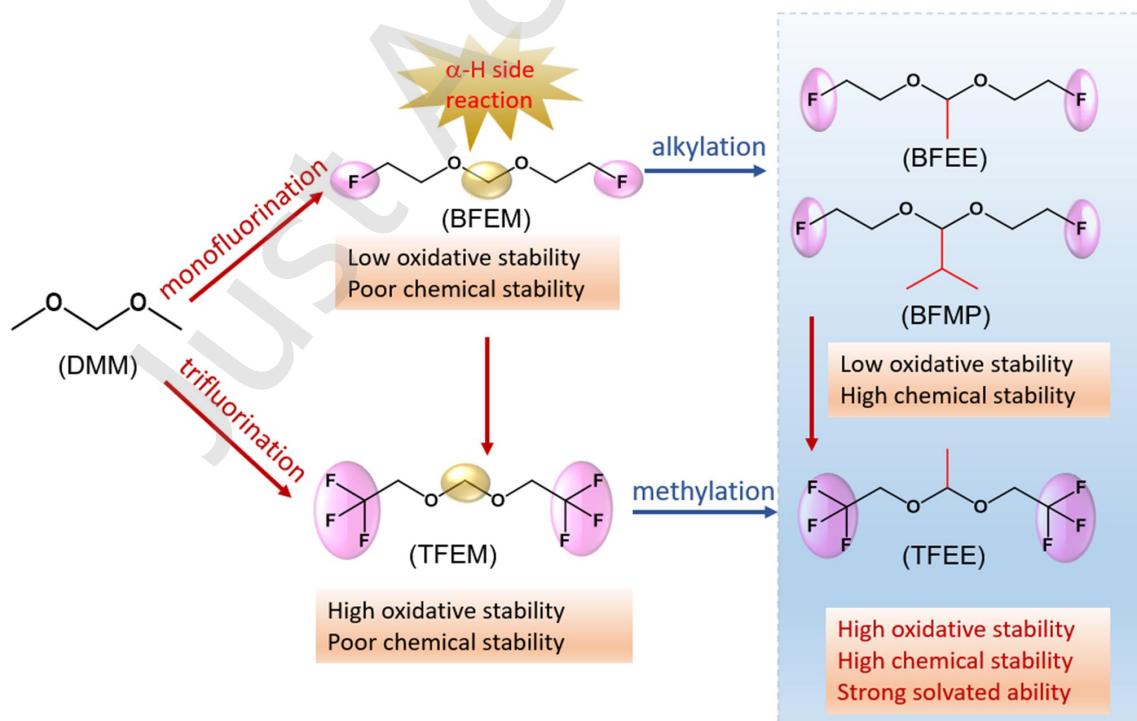
high-voltage LMBs [10-12]. In recent years, electrolyte engineering has emerged as an effective strategy to broaden the electrochemical stability window and stabilize electrode interfaces by regulating the anion-dominated solvation structure in ether-based electrolytes [13, 14]. Notable advances include the development of high-concentration electrolytes (HCEs) [15-17] and localized high-concentration electrolytes (LHCEs) [18-20]. These systems reduce the proportion of free solvent molecules and promote the formation of anion-rich solvation structures, thereby facilitating the formation of a robust electrode-electrolyte interphase and enhancing the operation voltage of ether-based electrolytes [21, 22]. Nevertheless, these approaches also introduce certain drawbacks, such as poor ion transport kinetics in HCEs and the high cost of diluents in LHCEs [23]. The limited oxidative stability of ether-based electrolytes primarily stems from the high electron cloud density on the oxygen atom [24]. Molecular structure modification such as fluorination of the solvent molecule, has been considered as an effective avenue to improve the reversibility of Li metal and enhance oxidation resistance at the cathode. Fluorination, can effectively lower the electron cloud density on oxygen atom and reduce the highest occupied molecular orbital (HOMO) energy level of ether molecules. For instance, Bao et al first introduced

-CF₂ groups into the ether backbone to enhance electrolyte oxidation stability. The designed 1,4-dimethoxybutane (FDMB) electrolyte with a single Li salt exhibited improved compatibility with the Li anode and better tolerance toward high-voltage [25]. However, the high fluorination degree in FDMB leads to low ionic conductivity and compromises the rate performance of the battery. To balance the ionic conductivity and high oxidative stability, numerous fluorinated ethers have been designed by precisely modulating the degree of fluorination and the position of ether bonds. For example, Zheng et al. designed an amphiphilic fluorinated-ether of 1,1,2,2-tetrafluoro-3-methoxypropane (TFMP), which incorporates -CF₂ groups adjacent to a single ether bond. This design enhances the oxidative stability while maintaining a moderate solvation capability toward Li⁺ [26]. Subsequently, Deng et al. synthesized 1,1,1-trifluoro-2-(2-methoxyethoxy) ethane solvent by introducing a strong electron-withdrawing -CF₃ group at one terminal of the DME backbone. Such solvent exhibits high oxidative resistance, strong Li⁺ solvation ability, and facilitates the formation of anion-dominated clusters in the electrolyte, enabling LMBs to achieve high energy density and fast-charging performance [27]. However, it should be noted that the high reactivity of the α -H in the -O-CH₂- backbone of fluorinated ethers can trigger irreversible side reactions with reactive oxygen species released from the cathode under high-voltage conditions. Such side reactions usually result in increased cell polarization, accumulation of side products, and rapid capacity fading [28]. Therefore, developing an ideal fluorinated ether that simultaneously meets the design criteria of high oxidation stability, high ionic conductivity, and robust chemical/electrochemical compatibility remains an ongoing

challenge.

In light of the superior oxidative stability, strong solvating ability, and structural robustness of fluorinated ethers, we herein propose a synergistic fluorination-alkylation strategy applied to an acetal-ether backbone. This approach yields the solvent molecule 1,1,1-trifluoro-2-(1-(2,2,2-trifluoroethoxy)ethoxy) ethane (TFEE), featuring two terminal -CF₃ groups on the acetal-ether chain and a methyl group replacing the α -H atom. The strong electron-withdrawing nature of the -CF₃ groups creates a lithiophobic environment, which not only enhances oxidative stability but also promotes the formation of an anion-enhanced solvation structure in the electrolyte. Meanwhile, methylation of the acetal ether effectively increases the electron cloud density on the oxygen atom, thereby improving Li⁺ solvation capacity while suppressing undesirable side reactions involving α -H at the cathode.

With this synergistic molecular design, the synthesized TFEE-based electrolyte (TFEE-N) exhibits higher oxidation tolerance (5.62 V), stronger solvating ability, and improved chemical stability compared to mono-fluorinated or non-methylated ether counterparts. In the Li||Cu cell, the TFEE-N electrolyte enables a high average Coulombic efficiency (CE) of 98.5% over 455 cycles of Li deposition/stripping. Moreover, Li||LiNi_{0.8}Co_{0.1}Mn_{0.1} (NCM811) cell using TFEE-N retains 72.4% of its capacity after 235 cycles at 4.6 V, significantly outperforming cells with control electrolytes. This work thus demonstrates the effectiveness of a combined highly fluorination and methylation strategy in simultaneously balancing ionic conductivity, oxidation stability, and chemical stability in fluorinated ether electrolytes[29].



Scheme 1 Chemical structure design and the associated properties of fluorinated-ethers

2. Experimental section

2.1 Materials

Lithium foil (450 μ m thickness) was purchased from China Energy Lithium Co., Ltd. Copper foil (12 μ m thickness) and aluminum foil (12 μ m thickness) were bought from Guangdong Canrd New Energy Technology Co., Ltd. LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811, Canrd Co., Ltd)

cathode was prepared by mixing NCM811 powder, Super P, and poly(vinylidene fluoride) (PVDF) at a mass ratio of 84:8:8 with N-methyl-2-pyrrolidone (NMP) as diluent. The resulting slurry was coated onto aluminum foil and dried at 120 °C in a vacuum oven for 12 h. The areal loading of the NCM811 cathode was in the range of 6–9 mg cm⁻². Similarly, the cathode of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM622) was fabricated in the same way. A Celgard 2325 separator (25 μm thickness) was used in all cells. The following chemicals were purchased from Sigma-Aldrich: lithium bis(fluorosulfonyl)imide (LiFSI), tetraethylene glycol dimethyl ether (G4), lithium nitrate (LiNO₃), paraformaldehyde, metaldehyde, and isobutyraldehyde. 2-Fluoroethanol (≥98%) and 2,2,2-trifluoroethanol (≥98%) were obtained from Shangfluoro Co., Ltd. All the Li salts were dried under 120 °C for 24 h in vacuum before use. The electrolytes of 1 M LiFSI+0.2M LiNO₃ in TFEE/G4 (V: V=7:3), 1 M LiFSI+0.2M LiNO₃ in BFEE/G4 (V: V=7:3), 1 M LiFSI+0.2M LiNO₃ in BFME/G4 (V: V=7:3), 1 M LiFSI+0.2M LiNO₃ in TFME/G4 (V: V=7:3) and 1 M LiFSI+0.2M LiNO₃ in G4 were prepared inside the glovebox. All coin cells (Li||Cu, Li||Li, Li||NCM622, and Li||NCM811) were assembled with 60 μL of electrolyte to ensure sufficient wetting of the separator and electrodes. Electrolyte preparation and cell assembly were carried out in an Ar-filled glovebox with O₂ and H₂O levels maintained below 0.1 ppm. The electrolyte-to-capacity ratio was controlled at 3 g Ah⁻¹ before sealing. The energy density of the pouch cell was calculated based on the actual capacity (1.1 Ah) and the total cell mass (17.2 g), which includes all the cell components.

Equation 1: Energy density (Wh kg⁻¹) = capacity (Ah) × mid-discharge voltage (V) / weight (kg) = 246

2.2 Materials synthesis

2.2.1 Synthesis of BFEM

A mixture of 2-fluoroethanol (35 g), paraformaldehyde (9.6 g), and 98% sulfuric acid (2 mL) was stirred in an oil bath at 60 °C for 6 h. Upon reaction completion, the mixture was poured into ice water. The organic phase was extracted twice with diethyl ether and dried over anhydrous magnesium sulfate. After solvent removal under reduced pressure, the product was collected as a colorless liquid by vacuum distillation at 60 °C (40 Torr). Yield: 80%. The obtained BFEM was further dried over 4 Å molecular sieves for one week prior to use.

2.2.2 Synthesis of BFEE

A mixture of 2-fluoroethanol (51.248 g), metaldehyde (17.621 g), and 98% sulfuric acid (2 mL) was stirred at low temperature for 10 minutes and then allowed to react at room temperature for 12 hours under continuous stirring. After completion, the reaction mixture was poured into ice water. The organic layer was extracted twice with diethyl ether and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum, and the product was obtained as a colorless liquid via vacuum distillation at 60 °C (40 Torr). Yield: 78%. The resulting BFEE was further dried over 4 Å molecular sieves for one week before use.

2.2.3 Synthesis of BFMP

A mixture of 2-fluoroethanol (64.06 g), isobutyraldehyde (39.66 g), and 98% sulfuric acid (2 mL) was stirred at low temperature for 10 minutes and subsequently at room temperature for 12 hours. After the reaction was complete, the mixture was poured into ice water. The organic phase was extracted twice with diethyl ether and dried over anhydrous magnesium sulfate. Following solvent evaporation under reduced pressure, the product was isolated as a colorless liquid by vacuum distillation at 60 °C (40 Torr). Yield: 82%. The obtained BFMP was further dried over 4 Å molecular sieves for one week prior to use.

2.2.4 Synthesis of TFEE

A mixture of 2,2,2-trifluoroethanol (80.032 g), metaldehyde (17.621 g), and 98% sulfuric acid (2 mL) was stirred at low temperature for 10 minutes and then at room temperature for 12 hours. Upon completion, the mixture was poured into ice water. The organic phase was extracted twice with diethyl ether and dried over anhydrous magnesium sulfate. After solvent removal under vacuum, the product was collected as a colorless liquid by vacuum distillation at 60 °C (40 Torr). Yield: 15%. The resulting TFEE was further dried over 4 Å molecular sieves for one week before use.

2.2.5 Synthesis of TFEM

A solution of paraformaldehyde (18 g) in 95% sulfuric acid (90 mL) was cooled in an ice bath. 2,2,2-Trifluoroethanol (108 g) was then added quickly under stirring. The mixture was stirred for 10 minutes in the ice bath and subsequently for 1 hour at room temperature. After the reaction was complete, the top phase was separated and poured into ice water. The mixture was extracted with diethyl ether (2 × 100 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the product was collected by vacuum distillation at 35 °C (40 Torr). Yield: 20%. The obtained TFEM was further dried over 4 Å molecular sieves for one week prior to use.

2.3 Electrochemical Measurements

All 2032-type coin cells were assembled in an argon-filled glovebox with both H₂O and O₂ levels maintained below 0.01 ppm. Cyclic voltammetry (CV) of Li||NCM811 cells was conducted on a CHI760E electrochemical workstation (CH Instruments, China) within a voltage window of 2.8–4.5 V at a scan rate of 0.1 mV s⁻¹. Linear sweep voltammetry (LSV) was performed using a CHI660E workstation with a glassy carbon working electrode and lithium metal as both counter and reference electrode, scanning at 0.2 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 0.1 Hz to 10⁵ Hz with an amplitude of 5 mV. Galvanostatic charge/discharge tests were performed using a NEWARE battery test system (CT-4008Q-5V6A-164/S1). The lithium ion transference number (*t*₊) was determined according to the Bruce–Vincent–Evans equation:

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where I_0 and I_{ss} are the initial and steady-state currents, ΔV is the applied DC polarization voltage (10 mV), and R_0 and R_{ss} represent the interfacial resistance before and after polarization, respectively. The corresponding polarization test was conducted by applying a 10 mV DC bias for 1 hour.

Ionic conductivity was measured using a conductivity meter (Shanghai Leici) equipped with a DJS-1C type conductivity electrode.

2.4 Materials Characterization

^1H , ^{13}C , and ^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer, with DMSO- d_6 as the internal standard. ^7Li NMR spectra were acquired using a Bruker AVANCE NEO-400 spectrometer, also referenced to DMSO- d_6 . Cycled cells were disassembled in an argon-filled glovebox. The retrieved electrodes were rinsed three times with dimethyl carbonate (DMC) and dried under an argon atmosphere at 50 °C for 3 hours. The surface morphologies of lithium deposited on the Cu current collector were characterized by scanning electron microscopy (SEM, Zeiss Supra55). The cycled cathodes were similarly washed with DMC and dried on a 45 °C hotplate inside the glovebox prior to analysis. The cathode-electrolyte interphase (CEI) layer on the cathode surface was examined by field-emission transmission electron microscopy (FE-TEM, Talos F200X G2). Cross-sectional images of NCM811 particles were prepared and observed using focused ion beam scanning electron microscopy (FIB-SEM, Helios G4 UC). The uniformity and mechanical properties of the CEI were assessed by atomic force microscopy (AFM, Bruker Dimension Icon). The surface elemental composition and chemical states of the cycled cathodes were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). Changes in the crystal structure of the NCM811 cathode after cycling were examined by X-ray diffraction (XRD, Rigaku D/MAX2500VL/PC) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Time-of-flight secondary ion mass spectrometry (TOF-SIMS, PHI nanoTOF II, ULVAC-PHI) with Ar cluster sputtering was employed to analyze the composition of the cathode-electrolyte interphase (CEI) film. Raman spectroscopy was performed on a LabRAM HR Evolution spectrometer using a 633 nm argon-ion laser source to examine the molecular structure of different electrolytes. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Ascend 600 MHz spectrometer. Cryogenic transmission electron microscopy (cryo-TEM) characterization was conducted on a JEOL JEM-F200 instrument equipped with a Gatan 698 cryo-transfer holder and a Gatan 1065 IS electron energy loss spectroscopy system. A cryo-transfer box was used to prevent exposure to ambient air during sample loading. The sample was maintained at -179 °C during both transfer and observation to minimize electron beam damage. All high-resolution TEM (HRTEM), high-angle annular dark-field (HAADF) imaging, and energy-dispersive X-ray spectroscopy (EDS) analyses of solid-electrolyte interphases (SEIs) were performed at 200 kV under low electron flux conditions. Cryo-TEM data were processed using Gatan Microscopy Suite software, with masks (smooth edge: 5 pixels) applied to the crystal signals identified in the fast Fourier transform (FFT)

patterns. Differential scanning calorimetry (DSC) measurements were carried out by sealing 45 mg of liquid sample in high-pressure crucibles and heating at a rate of 5 °C min $^{-1}$.

2.4 Theoretical Calculations

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of each molecule were computed using Gaussian 16. Geometries were optimized at the B3LYP/6-31+G(d) level of theory, and single-point energy calculations were performed with the larger 6-311++G(d,p) basis set. All calculations incorporated the polarizable continuum model (PCM) with ether solvent parameters and included Grimme's DFT-D3 dispersion correction. The binding energy (E_b) between Li^+ and solvent/anion species was calculated according to the following equation:

$$E_b = E_{(\text{Li}^+ - \frac{\text{sol}}{\text{anion}})} - E_{\text{Li}^+} - E_{\text{sol/anion}}$$

where $E_{(\text{Li}^+ - \frac{\text{sol}}{\text{anion}})}$ represents the total energy of the Li^+ - solvent (or anion) complex, $E_{(\text{Li}^+)}$ is the energy of an isolated Li^+ ion, and $E_{(\text{sol/anion})}$ denotes the energy of the free solvent or anion molecule.

Molecular dynamics simulations were performed using the GROMACS 2018 software package. The General Amber Force Field (GAFF) was employed for all solvent molecules and anions. Force field parameters were generated using Sobtop 1.0 (dev3.1, available at <http://sobereva.com/soft/Sobtop>), and RESP2 (0.5) charges computed with Multiwfn were assigned to all solvent molecules and anions. To account for charge transfer effects, atomic partial charges for Li^+ ions and anions were scaled by a factor of 0.8. All bulk electrolyte systems were constructed in cubic simulation boxes with an initial edge length of 7 nm.

The TFEE-N electrolyte system contains 120 Li^+ , 100 FSI^- , 20 NO_3^- , 370 TFEE and 160 G4;

The G4-N electrolyte system contains 120 Li^+ , 100 FSI^- , 20 NO_3^- and 430 G4;

The TFEE electrolyte system contains 20 Li^+ , 20 NO_3^- , 370 TFEE and 160 G4;

The BFEM electrolyte system contains 20 Li^+ , 20 NO_3^- , 780 BFEM.

3. Result and discussion

3.1 Design principle and structural characterizations of fluorinated ethers

Previous reports have confirmed that the oxidative stability of ether electrolytes is strongly influenced by the fluorination degree, with the $-\text{CF}_3$ group exhibiting superior oxidation resistance compared to $-\text{CH}_2\text{F}$ [30]. The dimethoxymethane backbone was selected owing to its acetal structure, which generally leads to weak coordination with Li^+ and facilitates the formation of anion-dominated solvation clusters in the electrolyte [31-33]. Guided by this rationale, we designed a molecule featuring symmetric trifluoromethyl groups at both terminals of the DMM skeleton, along with an alkyl group substituted at the ethylene position of the acetal moiety. The target molecule, TFEE, was synthesized via a one-step aldol condensation between trifluoroethanol and metaldehyde (Fig.

S1). Several other fluorinated-ethers including bis(2-fluoroethoxy) methane (BFEM), 1,1-bis(2-fluoroethoxy) ethane (BFEE), 1,1-bis(2-fluoroethoxy)-2-methylpropane (BFMP), bis(2,2,2-trifluoroethoxy) methane (TFEM) were also synthesized to systematically investigate the effects of fluorination degree and methylation substitution on interfacial stability and electrochemical performance, as displayed in **Scheme. 1**, the dimethoxymethane (DMM) backbone possesses oxygen atoms with high electron cloud density, rendering it susceptible to decomposition at voltages exceeding 4 V. Although monofluorination reduces this electron density due to the strong electronegativity of fluorine (BFEM), the resulting oxidative stability remains insufficient for operation above 4.5 V. This limitation primarily arises from the comparatively higher

electron cloud density on oxygen and high reactivity of the α -H sites, which are vulnerable to attack by reactive oxygen species. TFEM, synthesized via trifluoromethylation of DMM, exhibits significantly improved oxidation stability. However, its limited solvating ability results in poor lithium salt solubility and consequently low ionic conductivity[34]. Instead, TFEE demonstrates enhanced solvating power while also resisting attack at the α -H position after alkylation. All fluorinated ethers were readily synthesized in a single step, with the corresponding reaction conditions detailed in **Fig. S1**. The molecular structures of the solvents were confirmed by ^1H NMR, ^{13}C NMR, and ^{19}F NMR (**Fig. S2**), and further verified by high-resolution mass spectrometry (HRMS, **Fig. S3**).

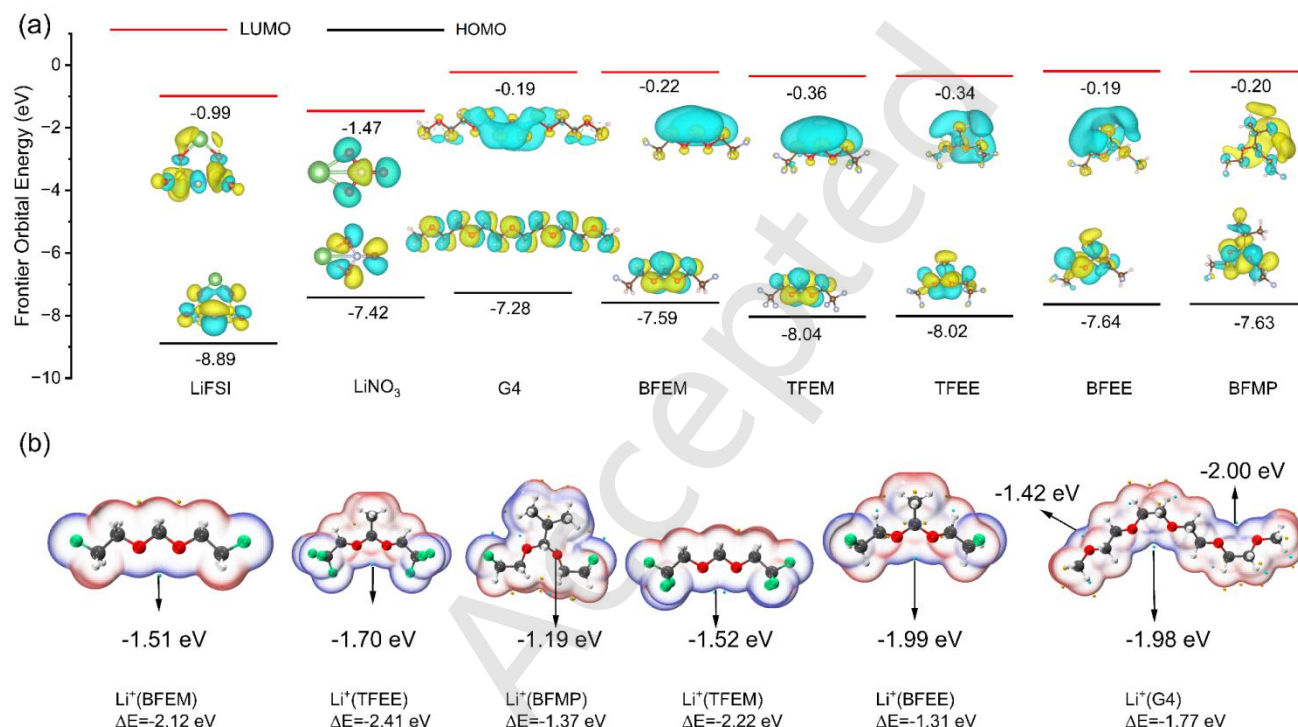


Figure 1 (a) Molecule orbital energies of the electrolyte species; (b) ESP distribution of fluorinated-ethers and the corresponding binding energies to Li⁺.

Density functional theory (DFT) calculations were carried out to assess the molecular orbital energy levels and electrostatic potential (ESP) distributions of the synthesized fluorinated ethers. As illustrated in **Fig. 1(a)**, the highest occupied molecular orbital (HOMO) energies of TFEM (−8.04 eV) and TFEE (−8.02 eV) are considerably lower than those of BFEM (−7.59 eV), BFEE (−7.64 eV) and BFMP (−7.63 eV) due to the strong electron-withdrawing nature of −CF₃ group. Methylation, on the one hand, exhibits minimal influence on the HOMO energy level, suggesting a negligible impact on intrinsic oxidation stability. However, it significantly modifies the ESP distribution. As shown in **Fig. 1(b)**, the ether-oxygen atom in TFEE exhibits a more negative electrostatic potential (ESP) value (−1.70 eV) compared to that in TFEM (−1.52 eV), suggesting that methyl substitution enhances the electron density on oxygen, thereby improving Li⁺ affinity. A similar trend is observed between BFEM and BFEE. Furthermore, the acetal structure in BFEM shows a higher ESP value than the −OCH₂CH₂O− moiety in tetraglyme (G4). This characteristic favors desolvation and promotes the formation of an anion-involved solvation structure with the acetal ether. Consistently,

the designed TFEE solvent demonstrates a stronger binding energy (−2.41 eV) with Li⁺ than TFEM (−2.22 eV), attributable to the increased electron density on oxygen, which reflects its enhanced solvation ability. Dissolution tests further reveal that TFEE can successfully dissolve 0.2 M LiFSI, yielding an ionic conductivity of 0.12 mS·cm^{−1}, whereas TFEM exhibits nearly no dissolution capability (**Fig. S4**). As expected, the monofluorinated ethers with higher affinity to Li⁺ demonstrated higher Li salt solubility compared to their trifluorinated counterparts. ^7Li NMR spectroscopy further revealed an upfield shift with strong shielding effect to Li⁺ in the TFEE-based electrolyte relative to monofluorinated ether systems (**Fig. 2(a)**), suggesting that the trifluoromethylated ether promotes a greater presence of FSI[−] anions in the primary solvation shell of Li⁺ with more anion-dominated solvation structures in electrolyte. Molecular dynamic (MD) calculation was conducted for the electrolytes. The radical diffusion function (RDF) results of 0.2M LiFSI/TFEE electrolyte revealed an anion-dominated solvation structure by forming a representative configuration of Li(FSI)_{2.54}(TFEE)_{1.32} due to the weak affinity of TFEE to Li⁺ (**Fig. S5**). In contrast, the strong solvated ability of BFEM/BFEE

resulted in the increased shielding effect around Li^+ and a lower chemical shift, forming a solvent-dominated structure typified by $\text{Li}(\text{FSI})_{0.32}(\text{BFEM})_{5.24}$, highlighting the distinct solvation environments and underscoring the key role of TFEE in regulating the solvation structure and interfacial components.

3.2 Physicochemical properties of fluorinated ethers

To compare the methylation effect on the electrochemical performances between TFEM and TFEE, the co-solvent of G4 was added to the fluorinated-ethers to enhance the solubility of Li salt in TFEM. The oxidation stability was firstly evaluated. Consistent to the DFT results, the TFEE/G4 (7:3 in volume ratio, abbreviated as TFEE)-based electrolyte showed a higher oxidation stability of 4.82 V than the monofluorinated-ethers of BFEM (4.61 V), BFEE (4.31 V) and BFMP (4.30 V) electrolyte (Fig. 2(b)). Such result revealed that the strong electron withdrawing effect of $-\text{CF}_3$ in TFEE /TFEM could greatly improve the oxidation tolerance, which was expected to be used

as high-voltage electrolytes. To investigate the reductive stability of fluorinated-ether on anode, the Li deposition/stripping reversibility in $\text{Li}||\text{Cu}$ cell was evaluated according to the Aurbach's method in Fig. 2(c). The $\text{Li}||\text{Cu}$ cell employing the TFEE-based electrolyte achieved a high average CE of 98.4%, superior to those with monofluorinated ethers. This enhancement is mainly attributed to the superior reductive stability of TFEE against Li metal and the formation of a robust, anion-derived solid-state electrolyte interface (SEI) at the interface. The long-term cycling results also revealed a higher Li deposition/stripping reversibility on anode with 98.4% average CE for 323 cycles in TFEM electrolyte (Fig. 2(d)). Specifically, the TFEE-based cell showed a longer cycle life than other fluorinated-ethers. For example, the BFEM and BFMP-based cells could only cycle for 141 and 51 cycles, respectively, much lower than that of TFEE. Then the Li deposition morphologies in different electrolytes were observed by scanning electron microscope (SEM) in Figs. S6–S7.

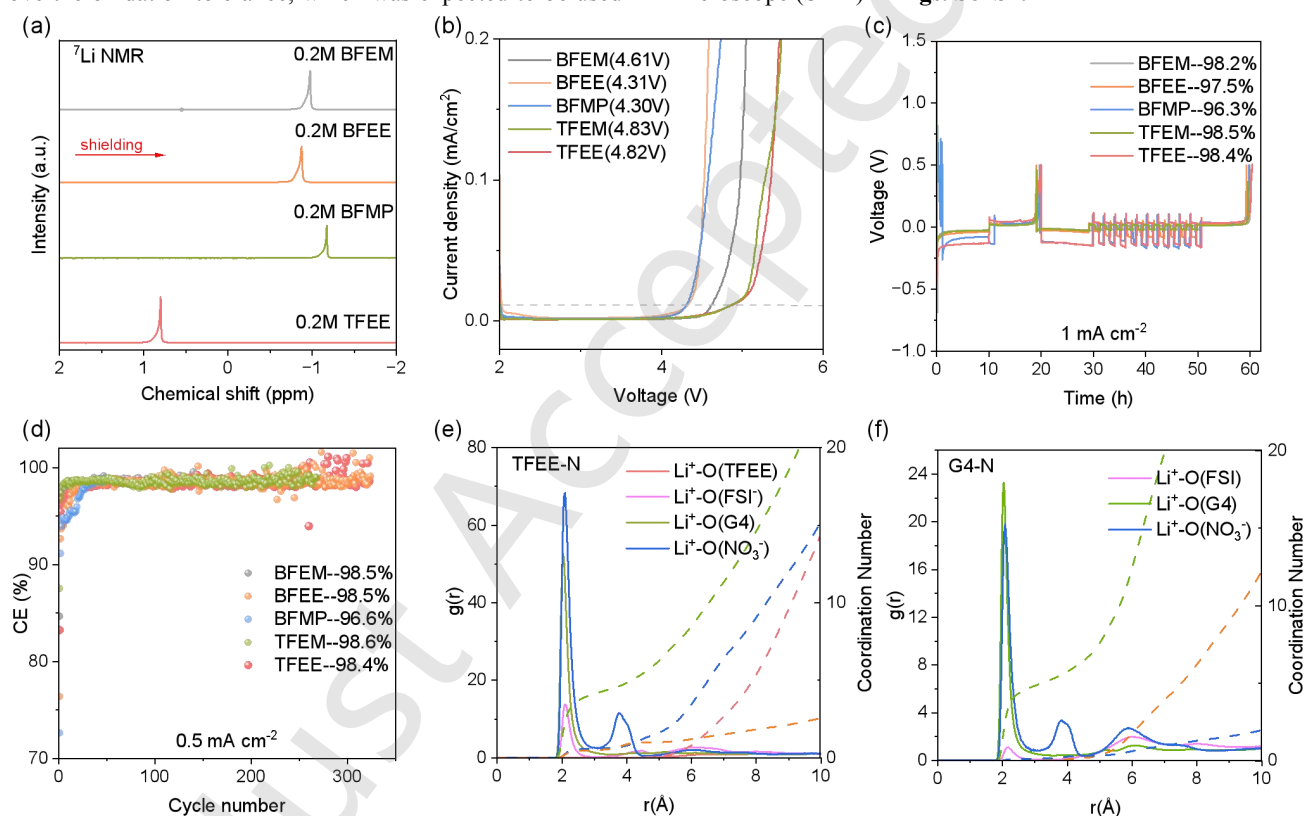


Figure 2 (a) ^7Li NMR spectra of the different electrolytes; (b) LSV results of the $\text{Li}||\text{SS}$ cells at a scan rate of 1 mV s^{-1} in the different electrolytes; (c) Average Coulombic efficiency of $\text{Li}||\text{Cu}$ cells with different electrolytes; (d) long-term cycling performances of $\text{Li}||\text{Cu}$ cells with different electrolytes at $0.5 \text{ mA}/\text{cm}^2$ current density; RDF curves and the corresponding coordination number of the Li^+ solvation structures in (e) TFEE-N and (f) G4-N electrolyte.

Obviously, Li deposited to a capacity of $3 \text{ mAh}/\text{cm}^2$ in the TFEE electrolyte kept a dense and smooth morphology with a uniform thickness of $20.4 \mu\text{m}$. Nevertheless, granular Li deposits with many porous structures and smaller particle sizes were found in other fluorinated-ether electrolytes, where the deposition thickness exceeded $21 \mu\text{m}$ in those electrolytes. Such porous morphology indicates an unstable interface and poor deposition reversibility, correlating well with cycling performance. It is worthy note that the TFEE-based cell exhibited a comparatively higher polarization voltage than the counterparts by comparing the deposition overpotential in $\text{Li}||\text{Cu}$ cells (Fig. 2(c)), this may be ascribed to the low ion conductivity in electrolyte and sluggish ion transfer rate across the interface.

Motivated by this situation, LiNO_3 was selected as electrolyte additive, because NO_3^- binds Li^+ strongly, preferentially enters the solvation sheath and is reduced to Li_3N . It is to be noted is that Li_3N delivers a high ionic conductivity of $\sim 6.6 \times 10^{-7} \text{ S cm}^{-1}$ and is conducive to the ion transfer across the interface[35]. Moreover, LiNO_3 has been proven effective in mitigating Al corrosion at the cathode [36]. Luckily, the electrolyte of $1\text{M LiFSI}+0.2\text{M LiNO}_3/\text{TFEE}/\text{G4}$ (7:3 in v: v) electrolyte (abbreviated as TFEE-N) exhibited a wider temperature adaptability range of -80 – 60°C by DSC analysis (Fig. S8). It also showed higher ionic conductivities than that of $1\text{M LiFSI}+0.2\text{M LiNO}_3/\text{G4}$ (abbreviated as G4-N) electrolyte at different temperatures owing to the decrease viscosity in TFEE-

N electrolyte (**Fig. S9**). Moreover, the TFEE-N electrolyte demonstrated higher reaction dynamic with a higher Li^+ transfer number of 0.72 and higher exchange current density of 1.91 mA cm^{-2} (**Figs. S10–S11**). Such results are mainly resulted from the improved ion conductivity and high interfacial stability with the reduction decomposition of LiNO_3 . On this basis, we found that the synergistic effect of LiNO_3 and TFEE solvent greatly enhanced the antioxidant stability which remained stable at 5.62 V of the electrolyte (**Fig. S12**).

The solvation structure with LiNO_3 additive was further analyzed by MD calculation. NO_3^- possesses a strong binding affinity toward Li^+ owing to its high charge density. For the electrolyte of G4-N with a strong coordination to Li^+ , RDF results revealed a strong $\text{Li}^+-\text{NO}_3^-$ peak appeared at $\sim 2 \text{ \AA}$, occupying the first solvation sheath. It revealed a solvent-dominated solvation configuration of $\text{Li}(\text{G4})_{4.84}(\text{NO}_3^-)_{0.15}(\text{FSI}^-)_{0.07}$ in G4-N electrolyte (**Fig. 2(f)**). By contrast, due to the weak solvating ability of TFEE, LiNO_3 barely dissolve in neat TFEE solvent. Even in TFEE-N electrolyte, RDF reveals a distinct representative solvation structure of $\text{Li}(\text{FSI}^-)_{0.59}(\text{NO}_3^-)_{0.49}(\text{G4})_{4.11}$ (**Fig. 2(e)**). The weakly solvating TFEE is excluded from the primary solvation sheath but promotes higher contents of NO_3^-

and FSI^- anions coordinated with Li^+ . Such structure would induce the preferentially reduction of anions and thus forming inorganics-dominated SEI film on anode. Then Raman analysis was further performed to verify the solvation structure (**Fig. S13**). According to the solvation effect of Li^+ , the stretching vibrations of S–N–S bond in FSI^- appeared at $700\text{--}750 \text{ cm}^{-1}$ frequency range, which is highly sensitive to the chemical environment. The coordination structure can be divided into solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs) and ion aggregates (AGGs). Obviously, the fraction of SSIPs and CIPs occupied 88.3% and 11.7% in the G4-N electrolyte, respectively (**Fig. S13(b)**), which is well established that high SSIPs content favors the decomposition of solvent molecules, leading to sluggish desolvation process and poor ion transfer across the interface. In contrast, the SSIP proportion decreased to 47.5% with a higher percentage of CIPs (48%) and AGGs (4.5%) in TFEE-N electrolyte (**Fig. S13(a)**), which is in accordance with the analysis from RDF results. More anions participation in the primary solvation structure favors the formation of inorganic-rich SEI with high ionic conductivity and robust mechanical strength.

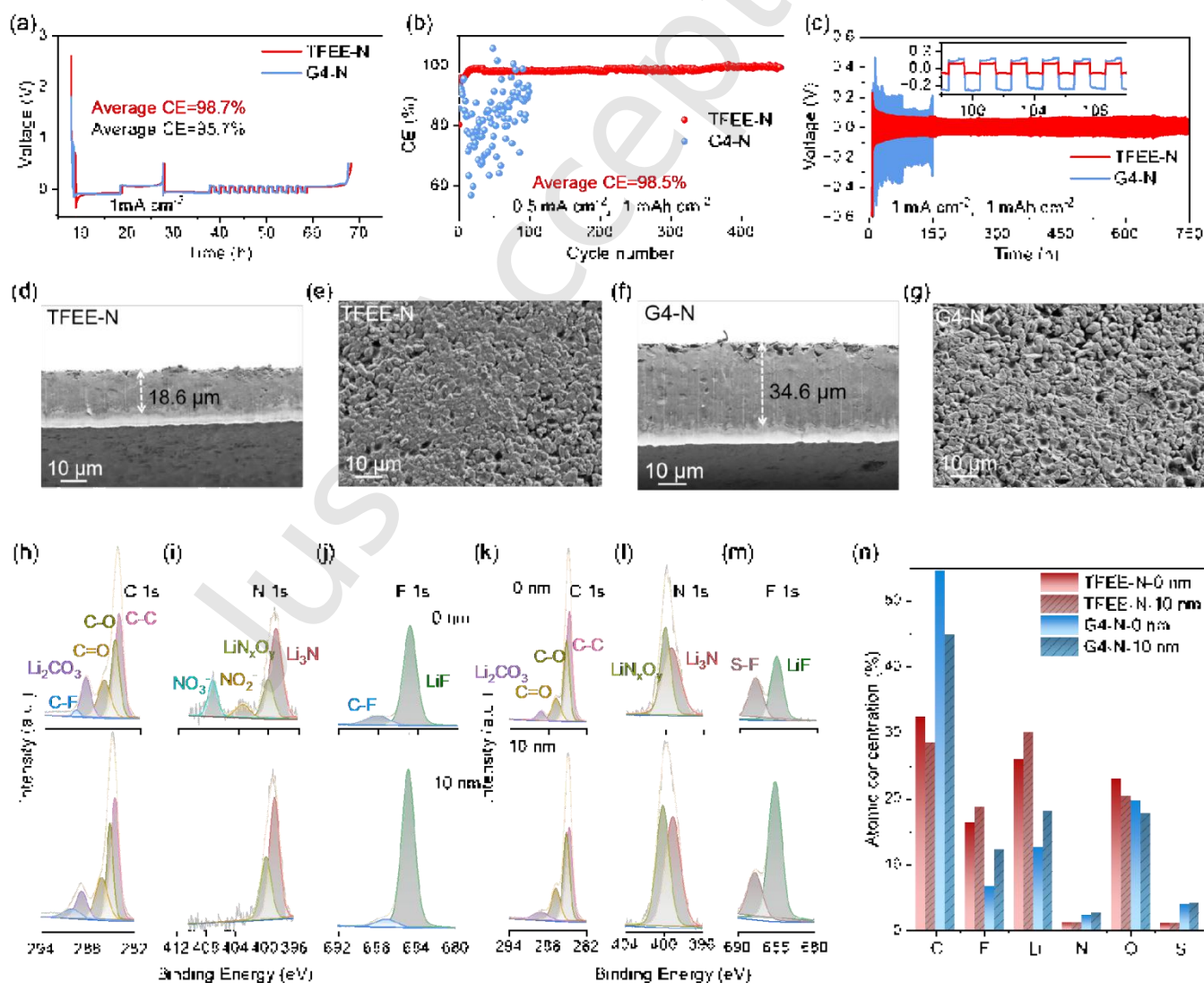


Figure 3 (a) Average CE test of Li||Cu cells with TFEE-N and G4-N electrolytes. (b) long-term cycling performances of Li||Cu cells with different electrolytes under a current density of 0.5 mA cm^{-2} . (c) Voltage–time profiles of Li||Li symmetric cells performed with different electrolytes at 1 mA cm^{-2} current density. Li deposition morphologies and section images of the Li deposition in (d–e) TFEE-N and (f–g) G4-N electrolytes with a capacity of 3 mAh cm^{-2} ; C 1s, F 1s, Li

1s XPS depth etching spectra of the deposited Li on Cu current collector with (h-j) TFEE-N and (k-m) G4-N electrolyte; (n) atomic concentration of C, N, Li, O, F, S detected on the deposited Li before and after etching with different electrolyte.

3.3 Li deposition behaviors and interface analysis of Li anode

Then the Li||Cu cell with TFEE-N was further evaluated, and it delivered an average CE of 98.7% at 1 mA cm^{-2} current density that was close to that without LiNO_3 (**Fig. 3(a)**). However, the polarization voltage significantly decreased in compared to that without LiNO_3 electrolyte, which was close to that with G4-N electrolyte, indicating the presence of LiNO_3

could modify the interfacial components and increase the ion transfer rate across the interface. The long-term cycling results of Li||Cu cell revealed that the TFEE-N based cell could stably cycle for 455 cycles with an average CE of 98.5% at 0.5 mA cm^{-2} current density, outperforming the G4-N-based, and other counterparts, which showed fluctuant CEs due to the dendritic growth and unstable interface (**Fig. 3(b)**). The symmetric cell with TFEE-N electrolyte could also keep stable

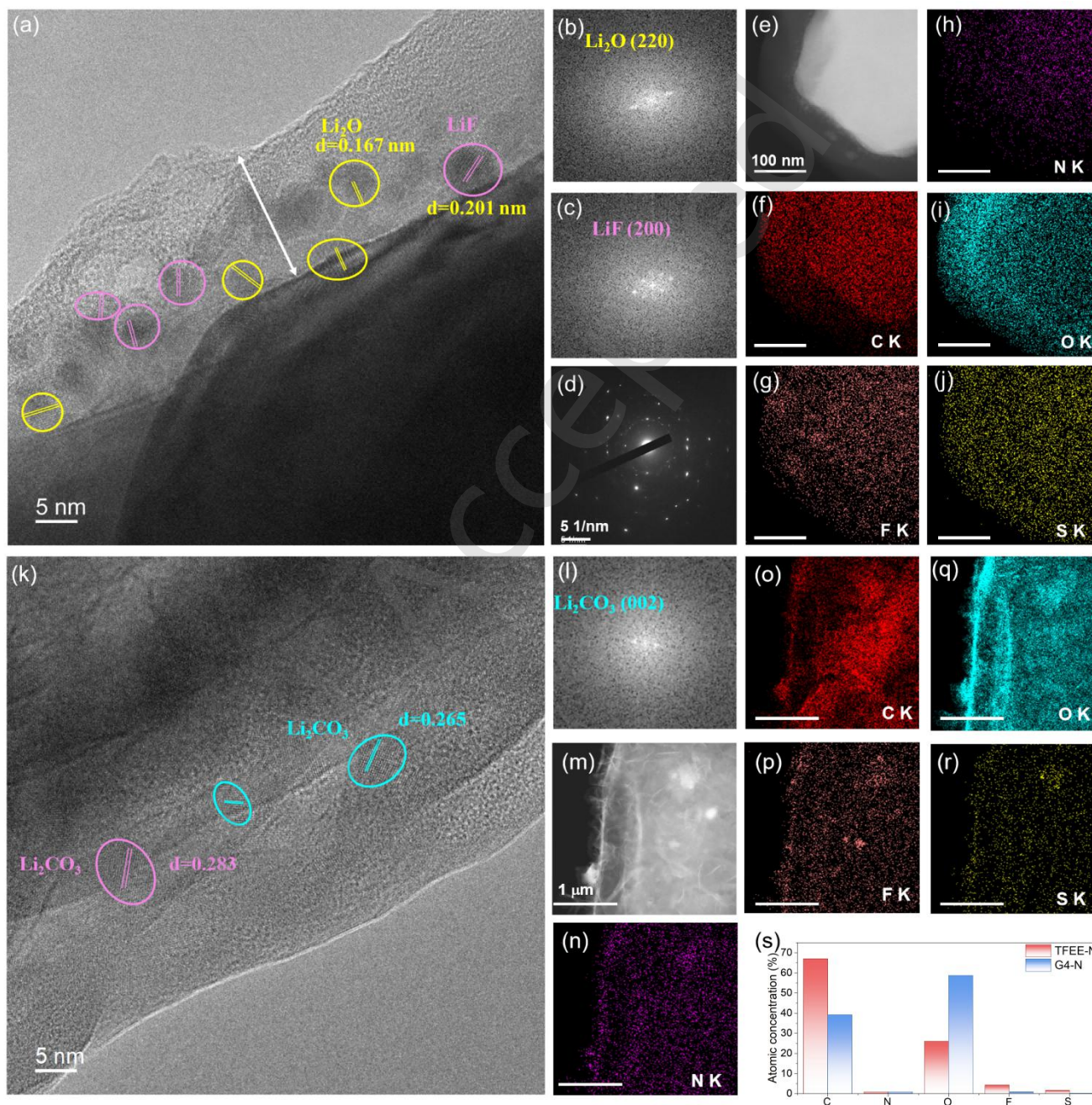


Figure 4 Cryo-TEM of deposited Li (inset the selected area electron diffraction). Local magnification of the interface between Li metal and vacuum with (a) TFEE-N and (k) G4-N electrolyte, highlighting the composition and nanostructure of the SEIs. (b-c) The corresponding inverse FFT (Li_2O and LiF and Li_2CO_3) crystallites images of SEI, EDS mappings for (f-j) TFEE-N and (n-r) G4-N. Li metal deposited on Cu TEM grid with 0.5 mAh cm^{-2} capacity under 0.5 mA cm^{-2} current density. (e, m) Low-magnification cryo-TEM images showing plated Li metal and SEI. (s) Comparison of atomic concentration of C, N, Li, O, F, S in SEI derived from different electrolytes.

with lower polarization voltage for 750 h at 1 mA cm^{-2} current density. In contrast, the G4-N-based cell could only cycle for

150 h with larger polarization voltage due to the severe interfacial side reactions (**Fig. 3(c)**). The improved cycling stability may be accounted for the enhanced interfacial ion transfer rate through the electrolyte regulation. SEM results revealed dense and flat deposition with a thickness of 18.6 μm in the TFEE-based cell (**Figs. 3(d)–3(e)**), demonstrating the tame electrolyte could form stable SEI film on anode and promote the uniform Li deposition. In contrast, a porous and dendritic morphology with a deposition thickness of 34.6 μm were observed in G4-N-based cell (**Figs. 3(f)–(g)**). The corresponding SEI film was analyzed by X-ray photoelectron spectroscopy (XPS). As shown in **Figs. 3(h)–3(j)**, for TFEE-N based SEI film, many inorganics consisting of LiF, LiN_xO_y , Li_3N , NO_3^- and Li_2CO_3 were detected in F 1s, N 1s and C 1s spectra, respectively. After etching, the content of LiF and Li_3N derived from the decomposition of FSI^- anions and LiNO_3 increased in TFEE-N electrolyte. The high ionic conductive Li_3N greatly accelerates Li-ion transport and alleviates cell polarization. Together with a high content of LiF, which offers excellent electronic insulation, and mechanical strength. Such high content of inorganics could accelerate the ion migration and enhance the mechanical strength of the SEI film. Although the components of the SEI film were similar between the two samples (**Figs. 3(k)–3(m)**). However, it showed a large difference in C, F, Li and S element contents between TFEE-N and BE based cells, the percentage of F element increased from 16.4% to 18.7% after etching for 10 nm in depth, which was much higher than that of BE with 6.7% to 12.3%, respectively. Conversely, the C contents in G4-based cell were much higher than that of TFEE-N (**Fig. 3(n)**), revealing severe decomposition of solvents by forming a high content of organics.

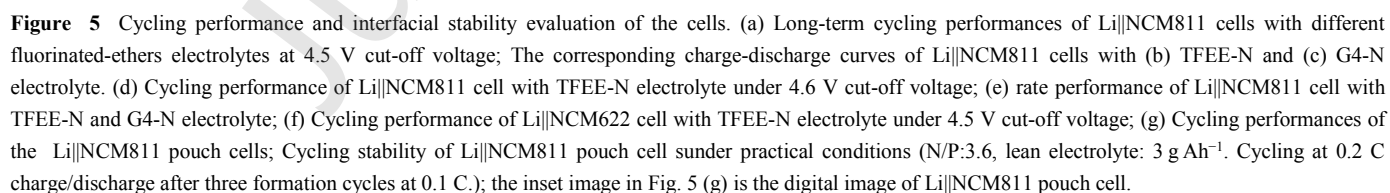
To elucidate the composition and nanostructure of the SEI film formed in different electrolytes, cryogenic transmission electron microscopy (cryo-TEM) was employed to characterize the morphology and microstructure of the SEI layer. High-resolution TEM images revealed an uniform and dense SEI layer covered on Li surface with a thickness of 18.3 nm in the cell using TFEE-N based electrolyte (**Fig. 4(a)**). The SEI layer features an amorphous matrix embedded with evenly distributed inorganic nanoparticles possessing clear lattice fringes (**Figs. S14(a)–S14(d)**). Magnified views of the local interface, combined with lattice spacing analysis and Fast Fourier transform (FFT), identified these nanoparticles as Li_2O and LiF, with measured lattice spacings of 0.167 nm corresponding to the {220} planes of Li_2O and 0.201 nm corresponding to the {200} planes of LiF (**Figs. 4(b)–4(c)**). Electron diffraction identified the SEI film consists of many nanocrystals with several polycrystalline rings (**Fig. 4(d)**). These structural findings are consistent with the XPS results presented in **Fig. 3(e)**. The element mapping images were also performed to visualize the spatial distribution of key components. As shown in **Figs. 4(e)–4(j)**, a homogeneous distribution of C, F, O, S and N was observed in the SEI layer throughout the SEI layer formed in the TFEE-N-based electrolyte. This uniform elemental arrangement is expected to enhance the mechanical robustness of the SEI and suppress electrolyte-induced corrosion on the Li anode. In sharp contrast, the SEI formed in the G4-N electrolyte exhibited a predominantly amorphous structure with a considerably greater thickness (**Fig. 4(k)** and **Figs. S14(e)–S14(h)**). High-resolution TEM images revealed sparsely dispersed inorganic nanoparticles, identified as Li_2CO_3 based on lattice spacings of 0.265 nm and 0.283 nm (corresponding to the $\{-211\}$ and $\{002\}$ planes, respectively). In addition, small amount of Li_2O based on lattice

spacings of 0.165 nm (corresponding to the {220} planes) was also found. Cryo-EDS elemental mapping further confirmed a uniform distribution of C, O, N, F, and S across the interface in this system (**Figs. 4(m)–4(q)**). Quantitative elemental analysis, however, indicated that the SEI derived from G4-N contains a higher proportion of organic species, as evidenced by significantly elevated C and O contents relative to the TFEE-N system (**Fig. 4(r)**). Conversely, the TFEE-N-derived SEI exhibited a markedly higher F content. Collectively, these cryo-TEM observations provide direct nanoscale evidence that the weakly solvating, anion-philic TFEE-mediated interfacial chemistry promotes the formation of an uniform, inorganic-rich SEI layer, which facilitates rapid charge transfer and enables dendrite-free, high-rate lithium deposition [37–40].

3.4 Electrochemical performances and interface analysis of the cathode

Based on the high interfacial stability of fluorinated-ether on anode, the high-voltage performance was further evaluated in Li||NCM811 cells. Li||NCM811 cells employing monofluorinated ether-based electrolyte (BFMP) failed during the first charging process due to continuous electrolyte decomposition at a cut-off voltage of 4.5 V (**Fig. S15(c)**). The G4-N cell delivered lower capacity and poor cycling stability, attributable to the inferior oxidation resistance of G4 solvent and inadequate interfacial passivation (**Figs. 5(a)–5c**). Although the TFEE based cell could initially cycle at 4.5 V, it suffers from rapid capacity decay after 60 cycles (**Fig. S15(a)**), indicating limited interfacial durability. The TFEE-based cell failed after only 14 cycles, showing a sudden overcharge phenomenon ascribed to α -H-induced side reactions (**Fig. S15(b)**). In contrast, the TFEE-N-based cell demonstrated exceptional cycling stability, retaining 79.2% of its initial capacity after 410 cycles at 0.5 C, with a high Coulombic efficiency of 99.4% (**Fig. 5(a)**). Charge-discharge profiles revealed superior reversibility and lower polarization for TFEE-N compared to G4-N (**Figs. 5(b)–5(c)**). Cyclic voltammetry further confirmed these trends: both cells exhibited three redox pairs corresponding to $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ oxidation and the $\text{M} \rightarrow \text{H}_2$ and $\text{H}_2 \rightarrow \text{H}_3$ phase transitions (**Fig. S16**). However, the TFEE-N system showed positively shifted reduction peaks (4.25, 4.05, 3.87 V) and negatively shifted oxidation peaks (3.63, 3.95, 4.14 V) relative to G4-N (reduction: 4.13, 3.94, 3.67 V; oxidation: 3.87, 4.05, 4.25 V), resulting in smaller polarization gaps and indicating faster ion transport across the interface. Consequently, the TFEE-N cell delivered outstanding rate performance, with specific capacities of 164.1 mAh g^{-1} at 2 C and 110.6 mAh g^{-1} at 5 C, significantly surpassing the G4-N system (120.2 and 1.1 mAh g^{-1} , respectively) (**Fig. 5(e)**). The self-discharge test also demonstrated that the TFEE-N cell exhibited markedly reduced self-discharge behavior, maintaining higher voltage and capacity after storage compared to G4-N (**Fig. S17**), underscoring its robust interfacial stability and practical viability under high-voltage operation. To further evaluate the oxidation stability, the cells were performed under 4.6 V cut-off voltage, as displayed in **Fig. 5(d)**, it delivered a capacity of 197.8 mAh g^{-1} and remained 72.4% capacity retention after 235 cycles at 0.5 C rate, while other fluorinated-ether based cells could not work normally under such a condition. Additionally, the electrolyte was used in Li||NCM622, TFEE-N-based cell could still remain a high cycling stability with 80.2% capacity retention after 470 cycles under 4.5 V (**Fig. 5(f)**). The Li||LiCoO₂ cell was also assembled and evaluated with TFEE electrolyte under 4.5 V. The result demonstrated that the cell delivered a capacity of 195 mAh g^{-1} and remained a capacity retention of 80.6% after 300 cycles under 4.5 V (**Fig. S18**), indicating the good compatibility

remaining an energy density of 246 Wh kg⁻¹ by calculating the whole mass of the pouch cell (**Fig. 5(g)** and **Tab. S2**).



47.6 Ω and 34.8 Ω after 20 and 40 cycles, respectively, markedly lower than those of the G4-N cell (138.2 Ω and 244.2 Ω for the same cycles). These results confirm the superior interfacial stability of the TFEE-N electrolyte and highlight the highly efficient ion transport across the TFEE-N-derived CEI layer. Therefore, the superior performance of TFEE-N arises from the synergistic combination of (i) molecular design (trifluoromethylation + methylation) ensuring high solvent stability, and (ii) the resulting anion-enhanced solvation structure optimizing interfacial chemistry, enabling excellent low-temperature and high-voltage cycling stability.

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the oxidation stability of the electrolyte. Inadequate oxidative resistance typically triggers severe interfacial side reaction at the cathode under high-voltage operation. To further validate the role of the TFEE in enhancing cathode interfacial stability, high-resolution transmission electron microscopy (HRTEM) was performed on cycled cathodes [41]. As displayed in **Figs. 6(a)-6(b)**, a dense and compact cathode electrolyte interphase (CEI) with a thickness of 6.48 nm was covered on the TFEE-N-derived cathode, in contrast to the uneven and thicker CEI film (17.87 nm) formed in the G4-N system. Furthermore, cross-sectional focused ion beam scanning electron microscopy (FIB-SEM) images revealed that the TFEE-N-derived cathode performed under 4.5 as well as 4.6 V cut-off voltage maintained structural integrity with no visible cracks, indicating that the robust CEI effectively mitigates electrolyte corrosion under high voltage (**Fig. S22**). Concurrently, HR-TEM revealed a uniform CEI film covering the cathode surface, with a thickness of approximately 5.4 nm (**Figure S22b**), which is comparable to that formed at 4.5 V. In comparison, the G4-N-derived cathode exhibited extensive cracking, reflecting severe structural degradation and interfacial instability. X-ray diffraction (XRD) analysis further corroborated these findings: the G4-N cathode

showed pronounced peak shifts for the (101), (003), and (104) crystal planes, indicative of substantial structural deterioration (**Fig. S23**). In contrast, the TFEE-N cathode exhibited only minimal peak shifts relative to the pristine material for the cathode after cycling under 4.5 V, underscoring its superior structural reversibility with the robust TFEE-N derived CEI film. To further clarify the failure mechanism with TFEE-N electrolyte operated under 4.6 V, XRD of the cathode was performed. All characteristic diffraction peaks of the cathode cycled under 4.6 V are retained, with only slight shifts in diffraction angles and minimal changes in full width at half maximum (FWHM). However, compared with the pristine cathode, the peak intensities are drastically reduced, indicating an increase in the amorphous phase within the cathode. This amorphous phase likely originates from the decomposition of G4, which occupies the first solvation sheath with a high coordination number to Li^+ . This is consistent with the poor cycling performance of the G4-N-based cell which failed to work under 4.6 V. To elucidate the composition of the CEI layers, XPS depth profiling was conducted on cathodes after 100 cycles in $\text{Li}||\text{NCM811}$ cells with 4.5 V cut-off voltage.

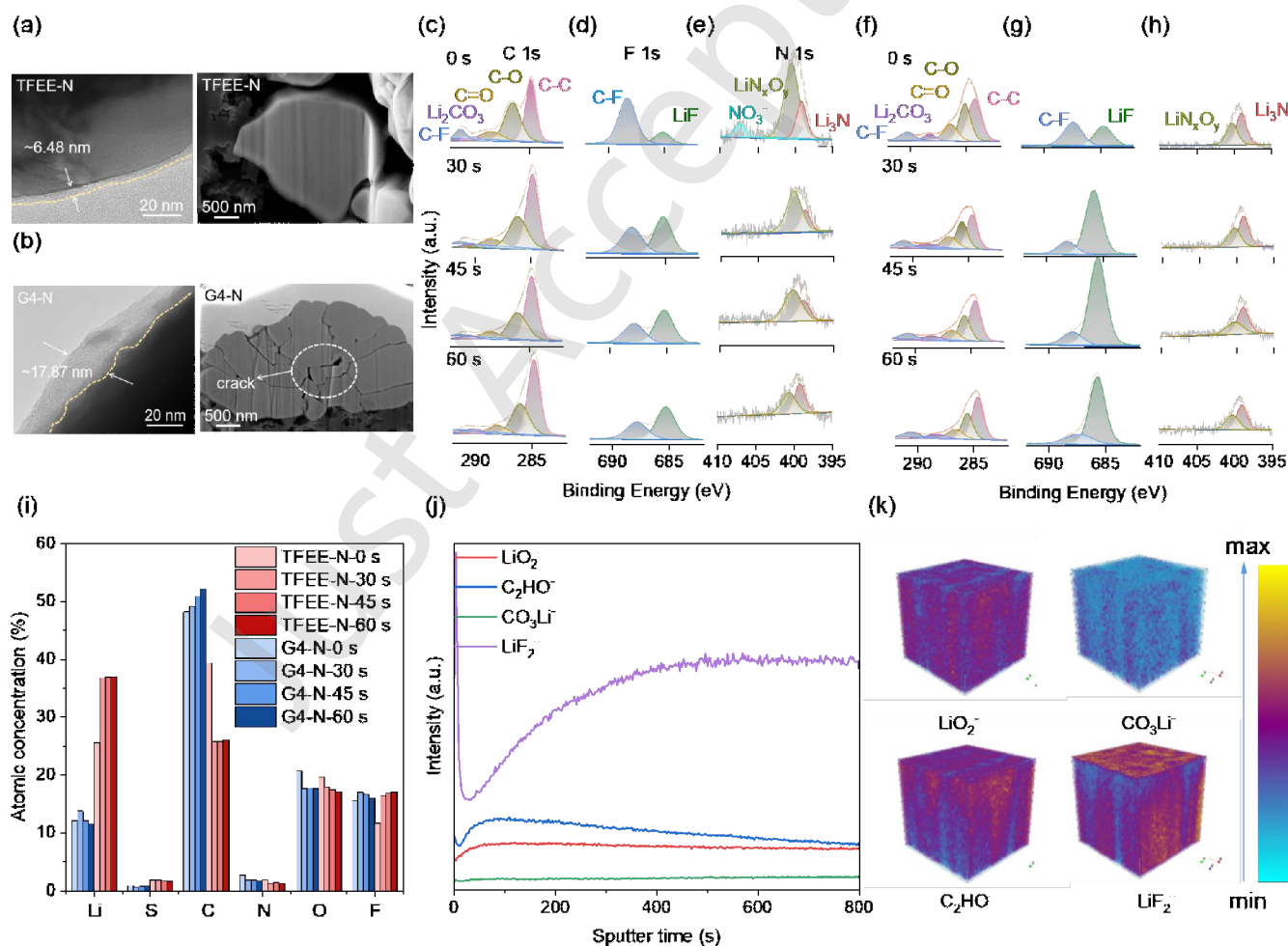


Figure 6 CEI chemistry and the structural evolution of NCM811. high-resolution TEM images of NCM811 particles and the corresponding cross-sectional SEM images of the NCM811 nanoparticles in (a)TFEE-N and (b) G4-N electrolytes, respectively. XPS analysis for the NCM811 cathodes cycled for 50 cycles in (c-e) TFEE-N and (f-h) G4-N electrolytes. (i) The corresponding element contents for TFEE-N and G4-N-based samples. (j) Evolution of representative SEI components at the TFEE-N interface as a function of sputtering time. (k) 3D reconstruction of TOF-SIMS secondary ion fragments sputtered from lithium electrodes after 50 cycles in an $\text{Li}||\text{NCM811}$ cell employing TFEE-N electrolyte.

As illustrated in **Fig. 6(i)**, the G4-N-derived surface exhibited

higher carbon content (48%) and lower lithium content (12%) compared to the TFEE-N system (C: 25%, Li: 25%) before

etching. With increasing etching depth, the C content rose and Li kept stable in the G4-N sample, suggesting an organic-rich CEI. In contrast, the TFEE-N-derived CEI showed lower and relatively stable C and Li profiles throughout the depth, indicating the interface was stable with the element distribution homogeneously across the whole CEI film. Concurrently, the C 1s, F 1s and N 1s XPS fitting result revealed that many inorganics with LiF, Li₂CO₃ and Li₃N embedded inside of the CEI film in both TFEE-N and G4-based cells (**Figs. 6(c)-6(h)**)[42]. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was further employed to probe the chemical composition and spatial structure of the CEI film formed in the TFEE-N electrolyte (**Figs. 6(j)-(k)**). Three-dimensional mapping of a selected region (100 × 100 μm) revealed a homogeneous distribution of LiF₂⁻ and C₂HO⁻ fragments across the CEI surface. Signals of Li₂O⁻ and CO₃Li⁻ were also detected throughout the film, though at comparatively lower intensities than those of LiF₂⁻ and C₂HO⁻. Depth profiling indicated that the LiF₂⁻ signal intensified during initial etching, subsequently decreased, and eventually stabilized with increasing sputtering time, suggesting a LiF-enriched outer region of the CEI. Based on the consistent C₂HO⁻ intensity profile and the depth-dependent LiF₂⁻ distribution, the CEI formed in TFEE-N electrolyte is described as an organic-dominated matrix with LiF nanoparticles concentrated in the outer region. Atomic force microscopy (AFM) characterization revealed that the TFEE-N-derived cathode electrolyte interphase (CEI) exhibited a smoother surface morphology and superior mechanical properties, as reflected by its higher average Young's modulus of 1.15 GPa (**Fig. S24**). This enhanced mechanical behavior is attributed to the higher inorganic content in the CEI layer. The resulting dense and robust interfacial structure effectively suppressed the dissolution of transition metal ions from the cathode. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of electrolytes cycled for 100 cycles confirmed significantly lower concentrations of dissolved Ni²⁺, Co²⁺, and Mn²⁺ in the TFEE-N system compared to the G4-N system (**Fig. S25**), further validating the protective quality of the CEI formed in the TFEE-N electrolyte.

4. Conclusion

In summary, a series of fluorinated ether solvents was investigated to elucidated the effects of fluorination and alkylation on electrochemical performance in high-voltage LMBs. The synergistic combination of trifluoromethylation and α-H substitution with a methyl group was found not only to enhance the oxidation stability (5.62 V) and ionic conductivity, but also to effectively suppress α-H related side reactions. MD calculations reveal that the tailored TFEE-N electrolyte, incorporating the newly synthesized TFEE solvent, forms an anion-enhanced solvation structure. This structure promotes the formation of a highly ion-conductive SEI film, consisting of an amorphous matrix embedded with inorganics nanoparticles such as LiF and Li₂O. Consequently, the Li deposition/stripping efficiency is significantly enhanced, achieving a CE of 98.5% over 450 cycles. Furthermore, the TFEE-N electrolyte exhibits high oxidation resistance, enabling Li||NCM811 cell to cycle stably for 235 cycles with 72.4% capacity retention at a cut-off voltage of 4.6 V, outperforming electrolytes containing non-methylated or monofluorinated ether analogs. Therefore, this

work proposed a structure modification strategy to balance ionic conductivity, oxidation stability and chemical stability in fluorinated ethers, providing a rational design guide for high-voltage LMB electrolytes.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909087>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

Heng Zhang: Writing – original draft, Data curation. **Kang Bo:** Data curation. **Qiyuan Huang:** Data curation. **Xin Guo:** Investigation. **Huguo Zhou:** Data curation, Methodology. **Weilong Kong:** Software. **Sheng Cheng:** Investigation. **Xiaoya Wang:** Investigation. **Hongfa Xiang:** Supervision. **Zhimei Huang:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Molecular design of methylated fluorinated-ether electrolytes for high-voltage lithium-metal batteries

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Figures:

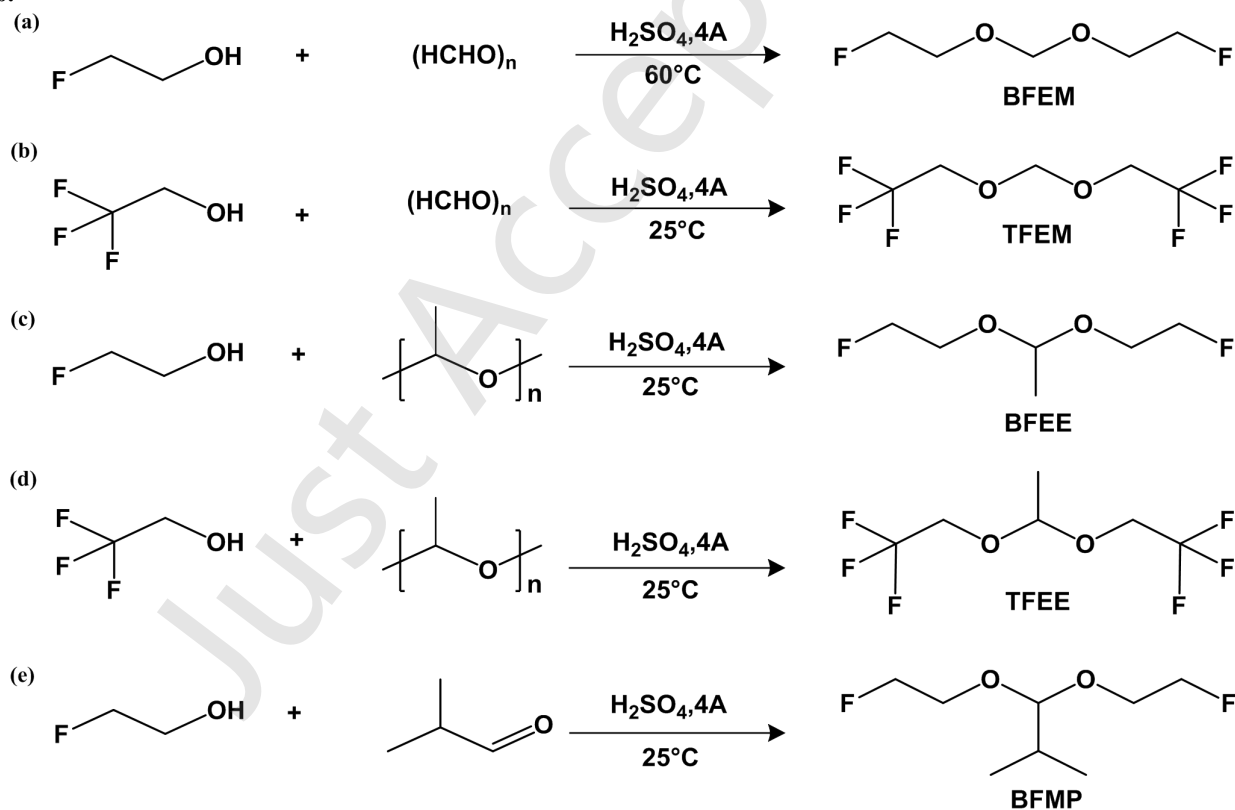
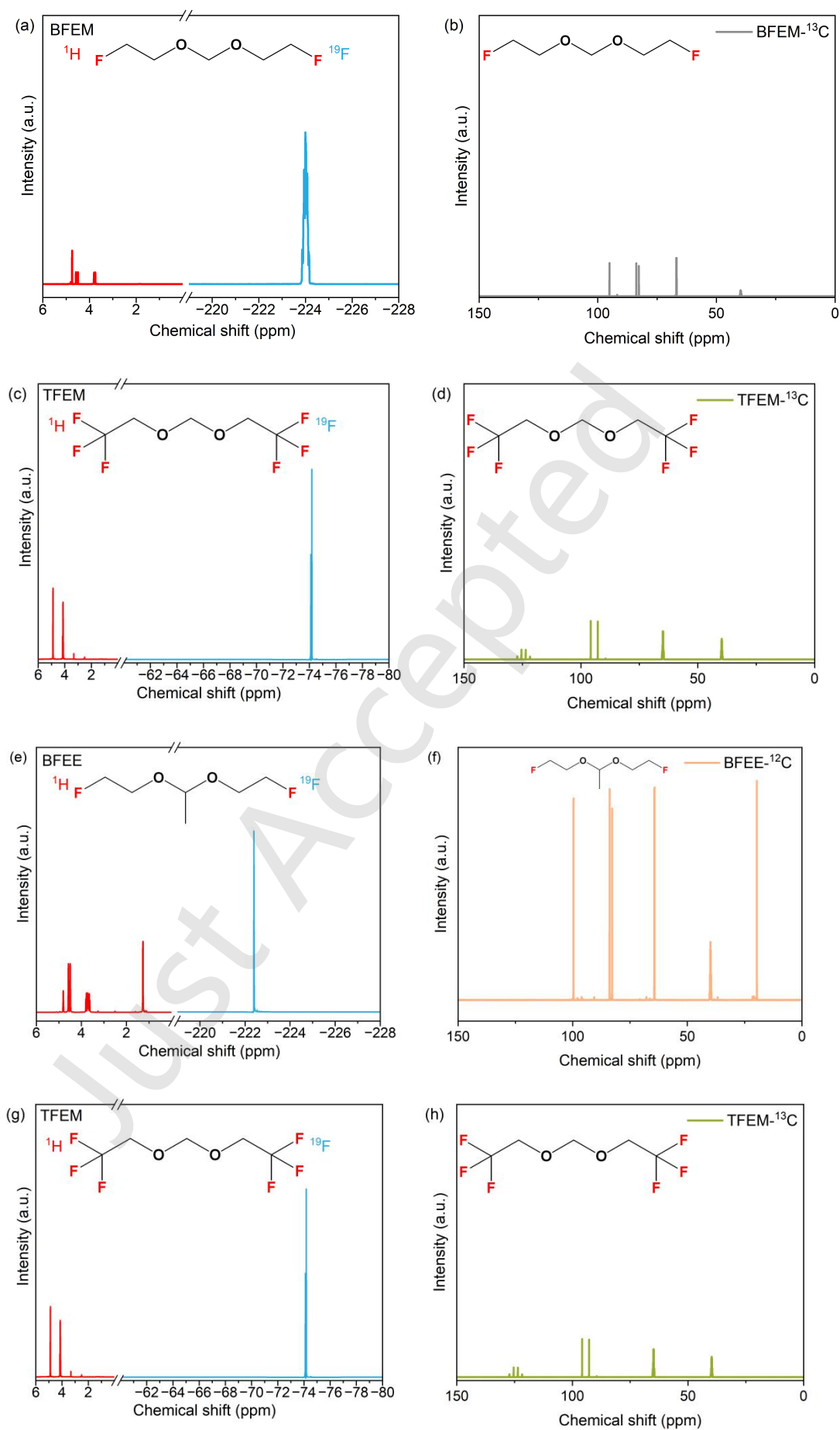


Figure. S1 Synthetic route of the designed (a) BFEM, (b) TFEM, (c) BFEE, (d) TFEE and (e) BFMP.



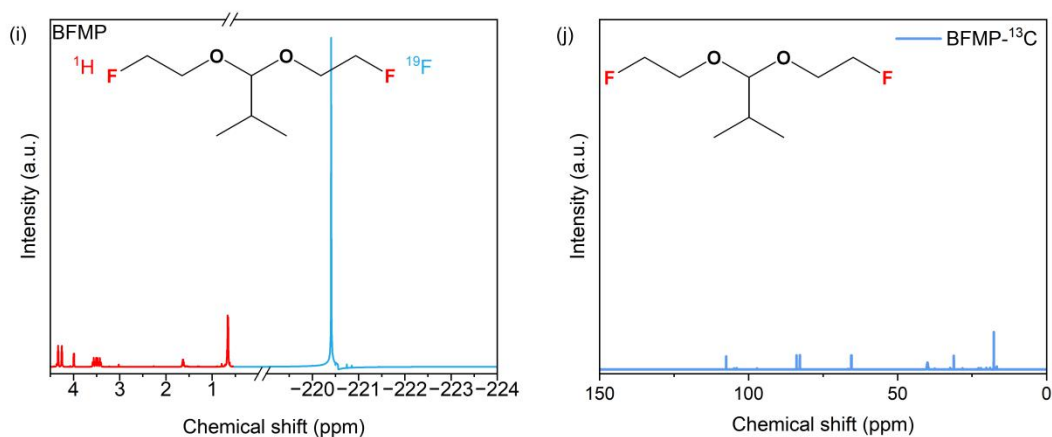
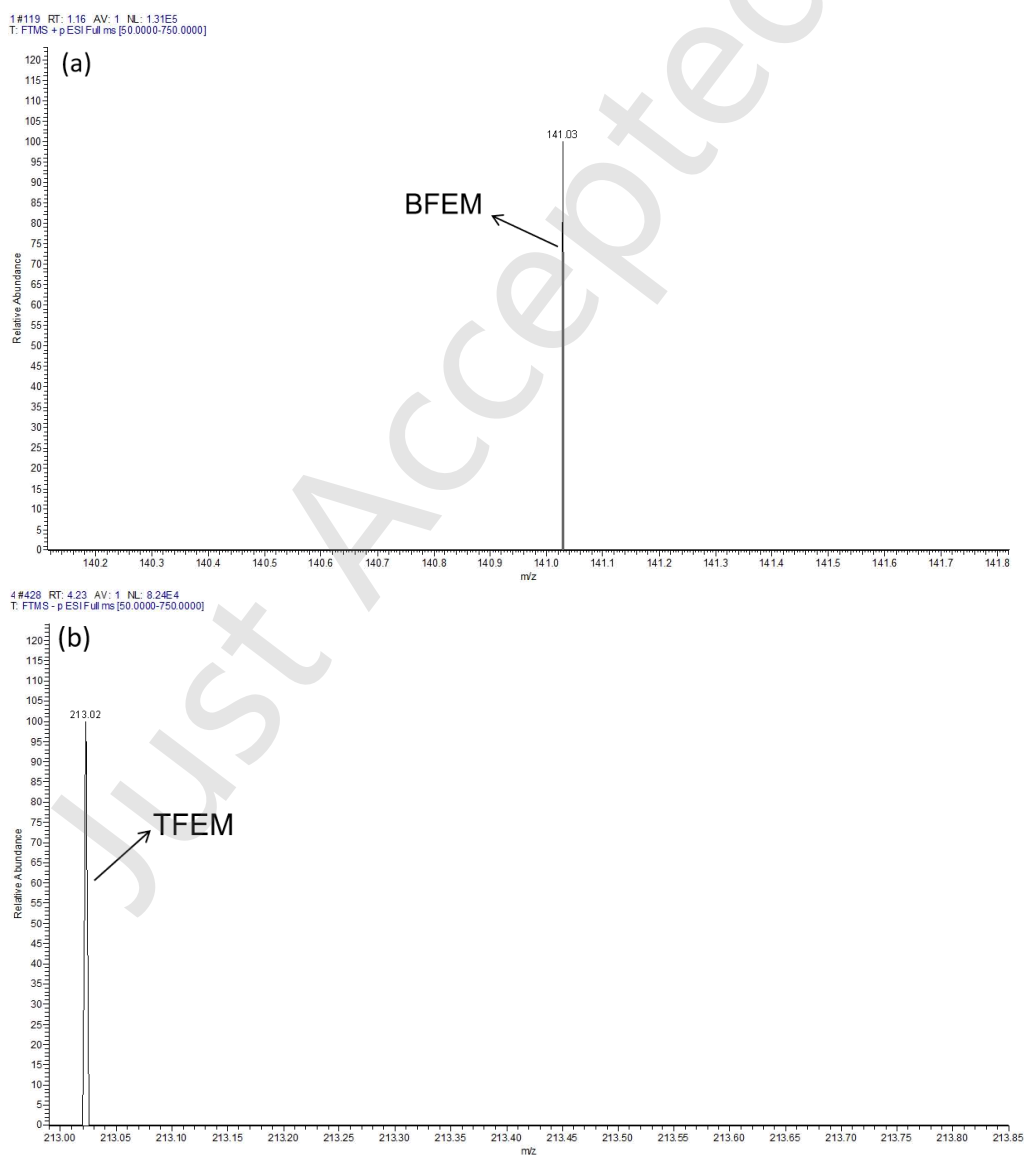


Figure. S2 ^{13}C , ^1H NMR and ^{19}F NMR spectra of (a, b) BFEM, (c, d) TFEM, (e, f) BFEE, (g, h) TFEE, (i, j) BFMP solvent.



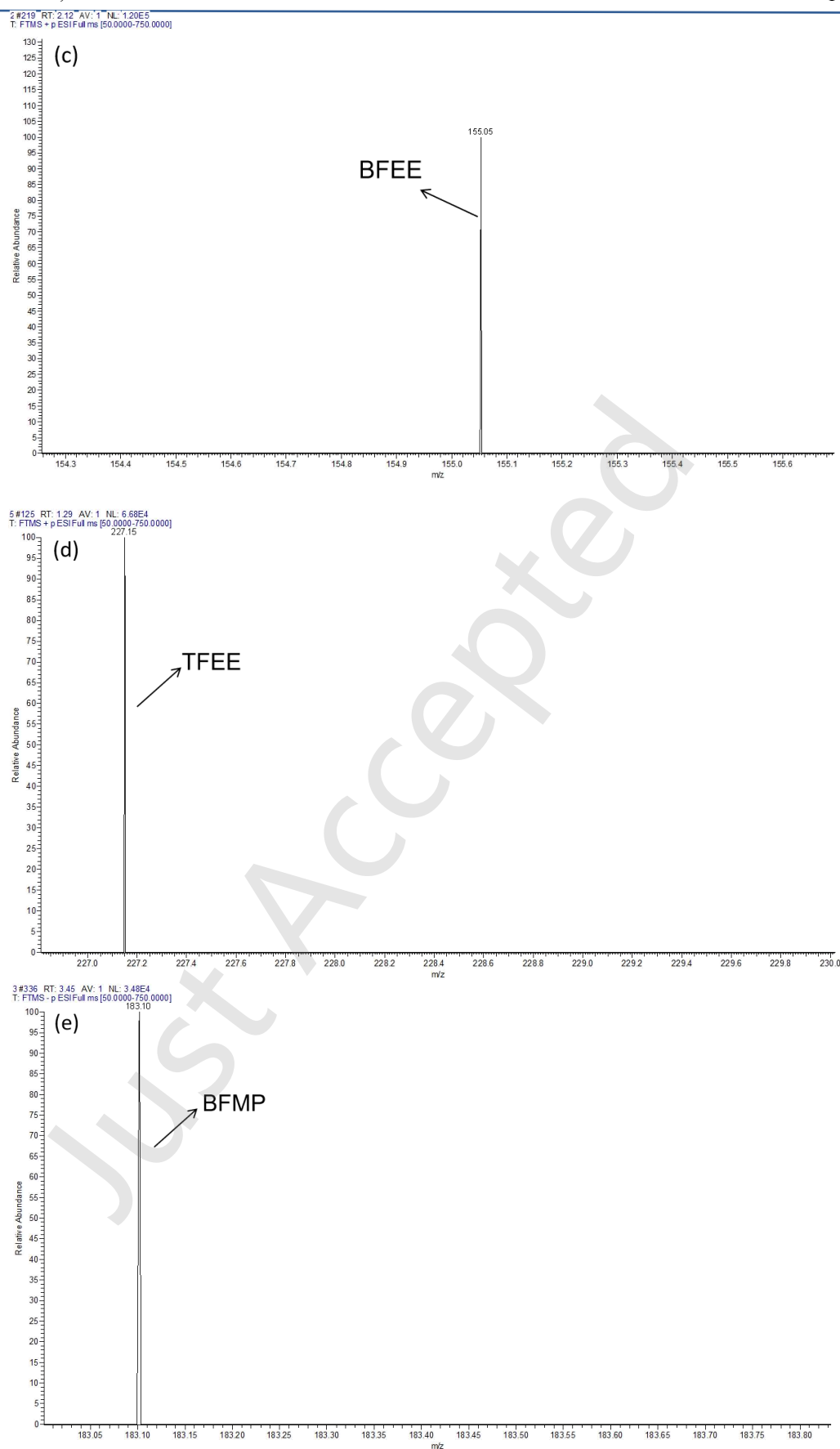


Figure. S3 Electrospray ionization mass spectrometry (ESI-MS) of (a) BFEM, (b) TFEM, (c) BFEE, (d) TFEE, (e) BFMP solvent.

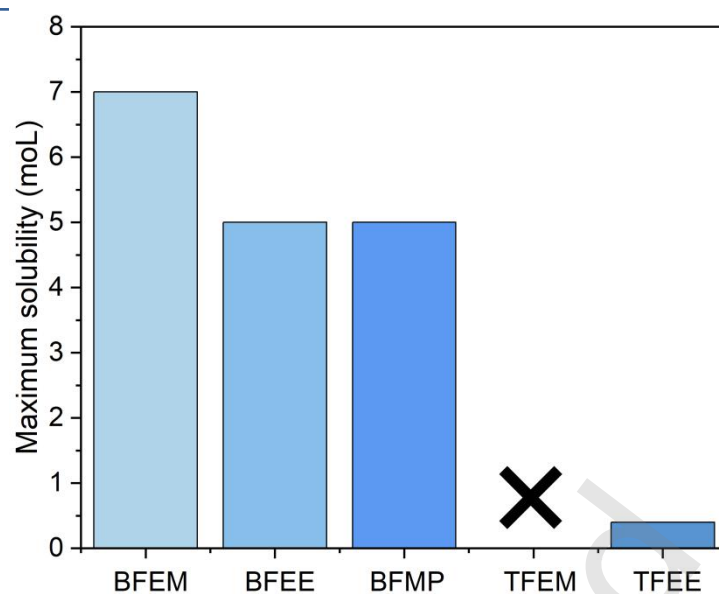


Figure. S4 The maximum solubility of LiFSI in different solvents.

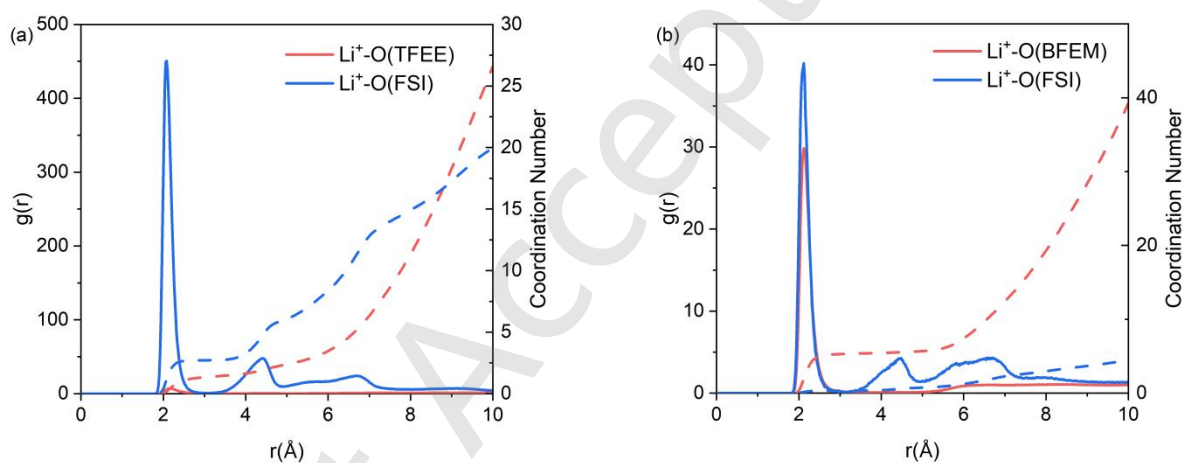


Figure. S5 RDF curves and the corresponding coordination number of the Li^+ solvation structures in (a) 0.2 M LiFSI/TFEE and (b) 0.2 M LiFSI/BFEM electrolyte.

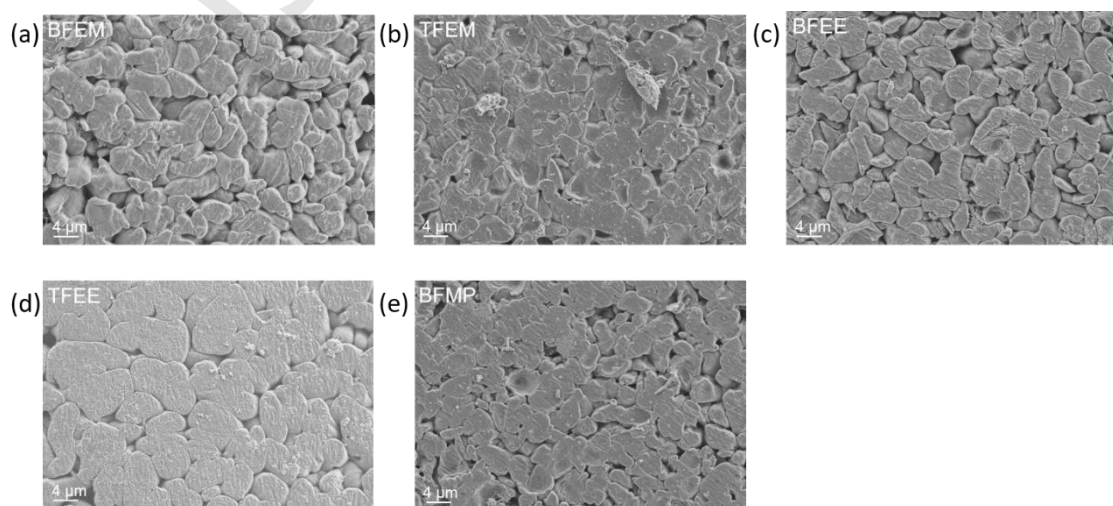


Figure. S6 Li deposition morphologies images in (a) BFEM, (b) TFEM, (c) BFEE, (d) TFEE and (e) BFMP electrolytes with a deposition capacity of 3 mAh cm^{-2} .

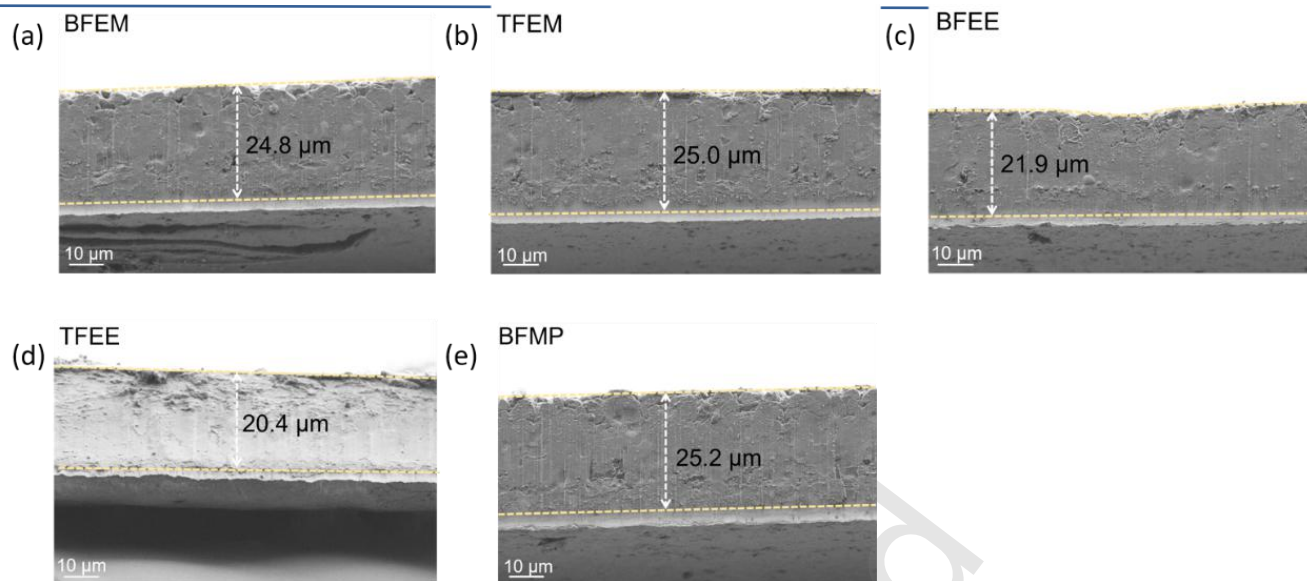


Figure. S7 Section images of the Li deposition on Cu current collector in (a) BFEM, (b)TFEM, (c) BFEE, (d) TFEE and (e) BFMP electrolytes with a capacity of 3 mAh cm^{-2} .

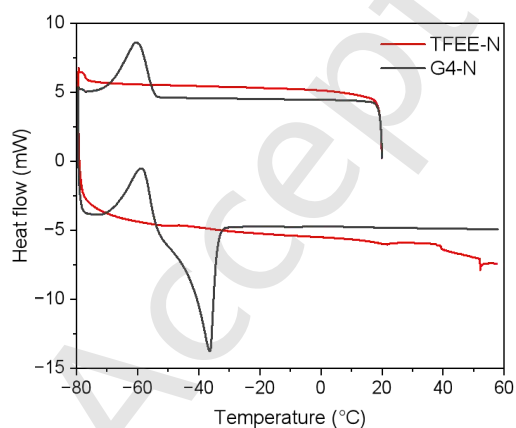


Figure. S8 DSC curves of the selected electrolytes at the temperature range of from 60 to -80°C with a heating rate of -5°C/min .

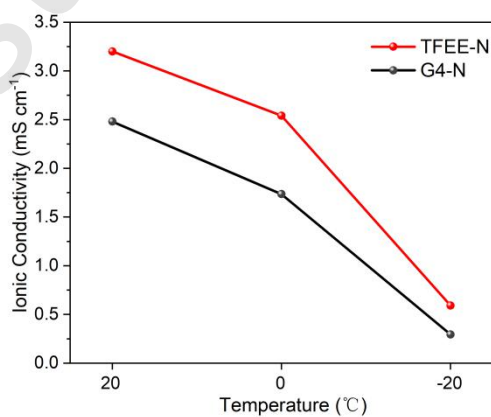


Figure. S9 Ionic conductivities of the selected electrolytes at different temperature.

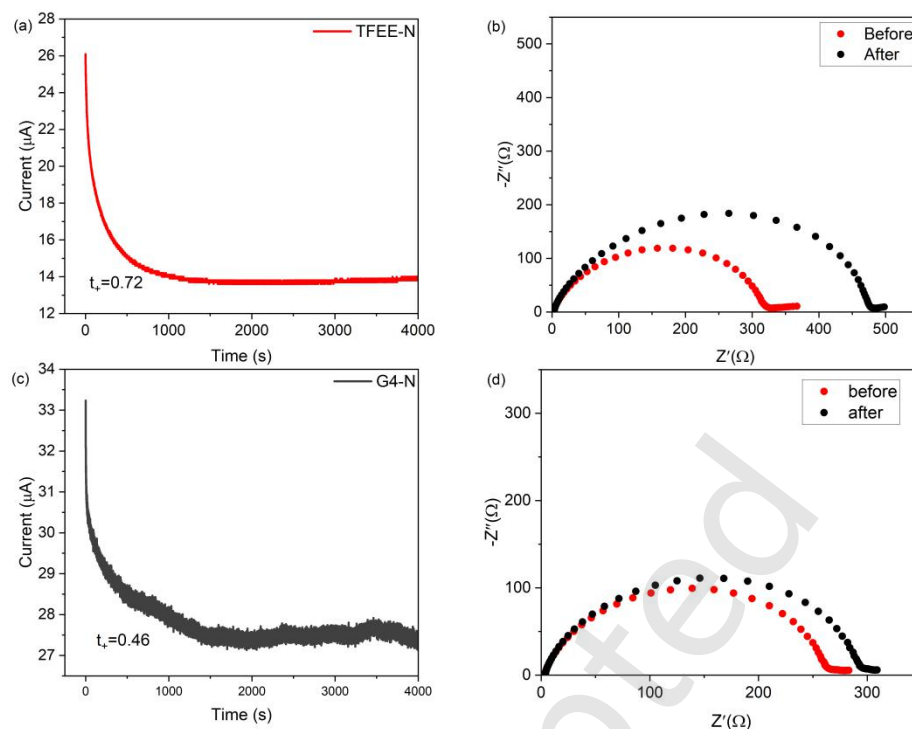


Figure. S10 Current time profiles of the symmetrical Li||Li cells with (a) TFEE-N, (c) G4-N electrolytes. the Nyquist impedance spectra of the (b) TFEE-N, (d) G4-N electrolytes before and after polarization.

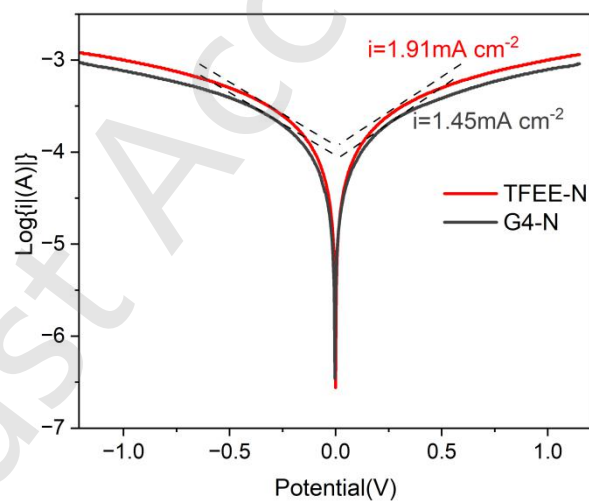


Figure. S11 Tafel curves of the electrolytes.

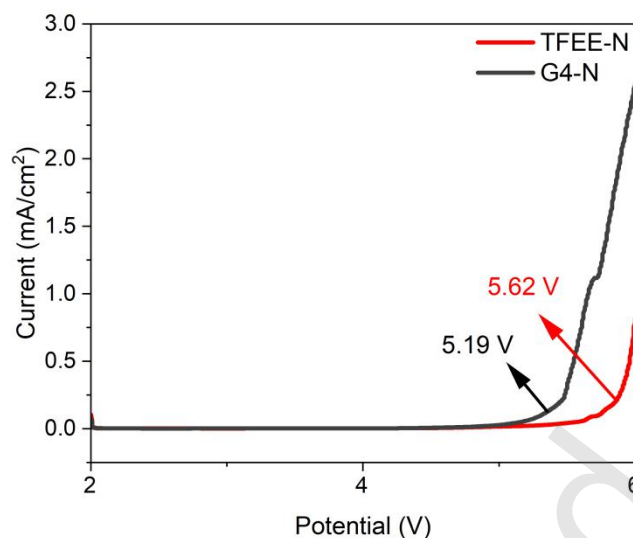


Figure. S12 LSV curves of the Li-stainless steel (SS) cells with the two electrolytes from 2 V up to 6.0 V versus Li/Li⁺.

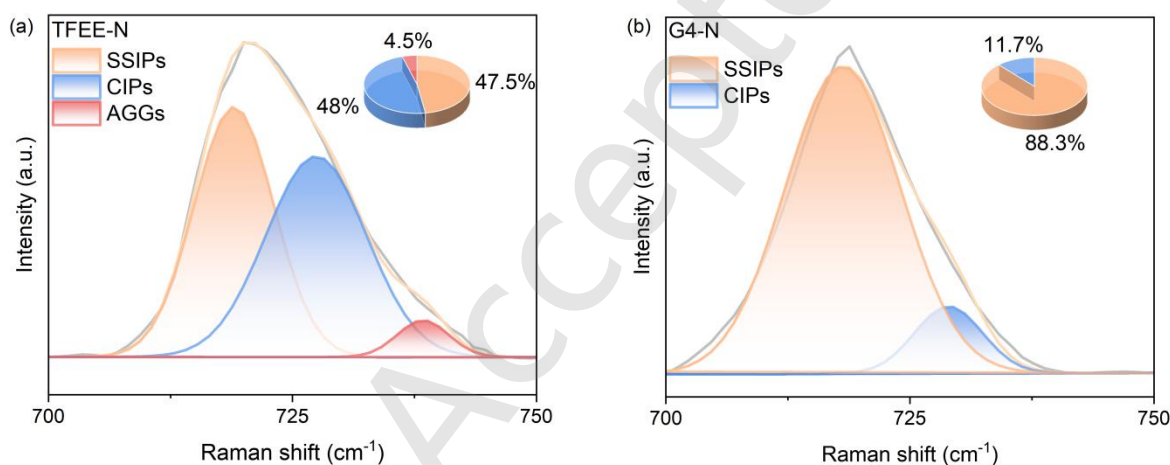


Figure. S13 The Raman spectrum of (a) TFEE-N, and (b) G4-N electrolytes, respectively.

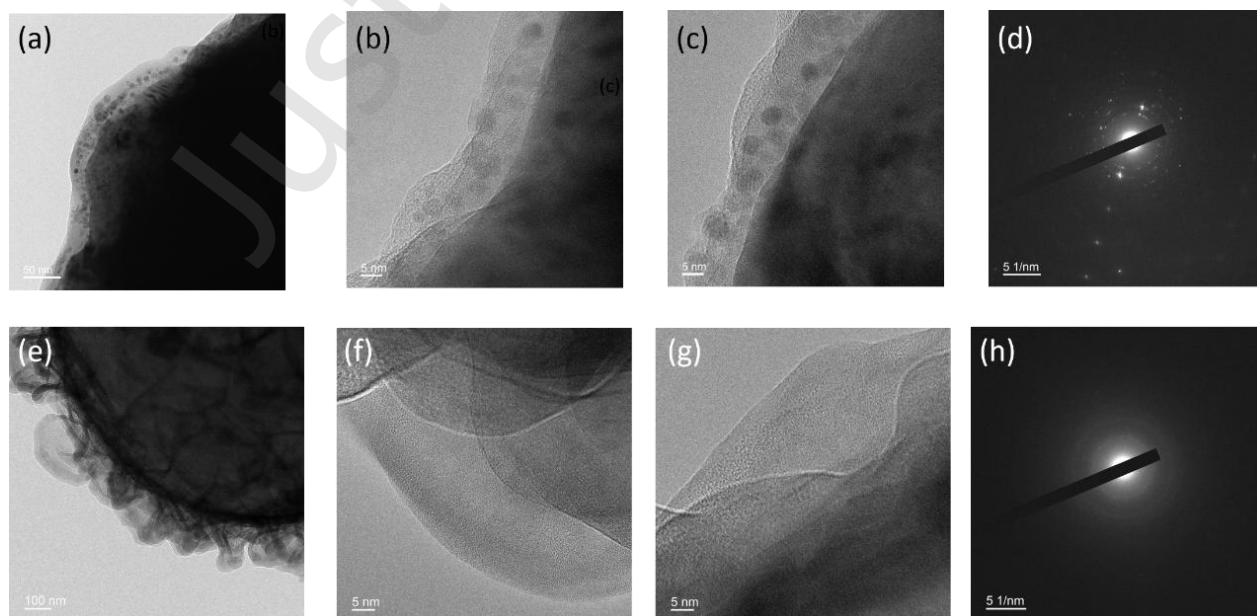


Figure. S14 Low-magnification cryo-TEM images showing plated Li metal in (a) TFEE-N and (e) G4-N electrolytes. (b-c) High resolution TEM showing Li nanocrystal and (d) the corresponding FFT diagram in TFEE-N electrolytes. (f-g) High resolution TEM showing Li nanocrystal and (h) the corresponding FFT diagram in G4-N electrolytes.

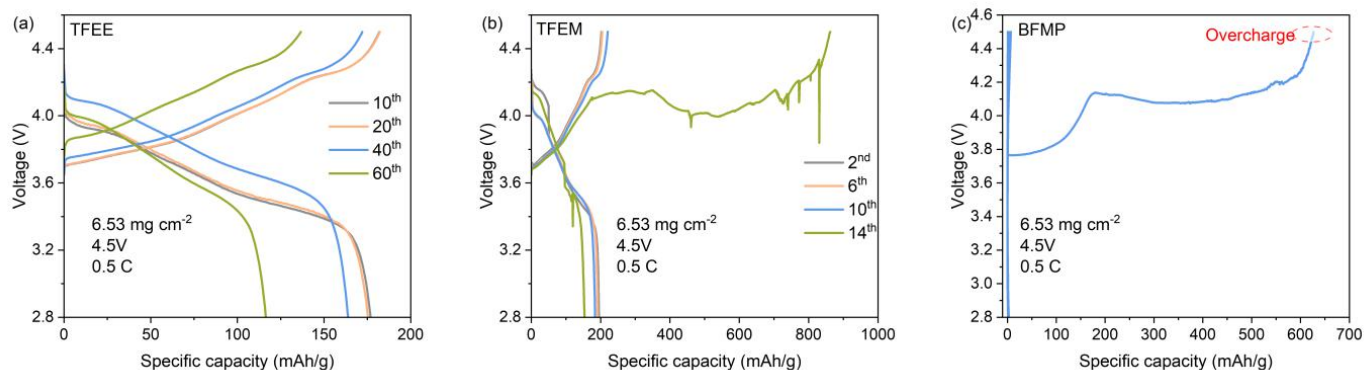


Figure. S15 Charge-discharge curves of the Li||NCM811 cell with (a) TFEE, (b) TFEM and (c) BFMP.

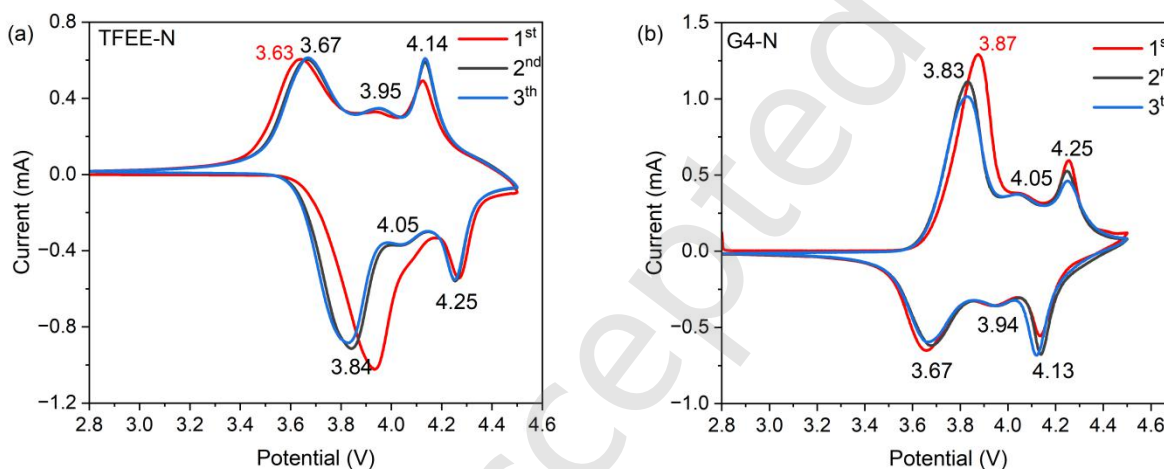


Figure. S16 Cyclic voltammetry analyses of Li||NCM811 cells with (a) TFEE-N and (b) GE-N electrolytes.

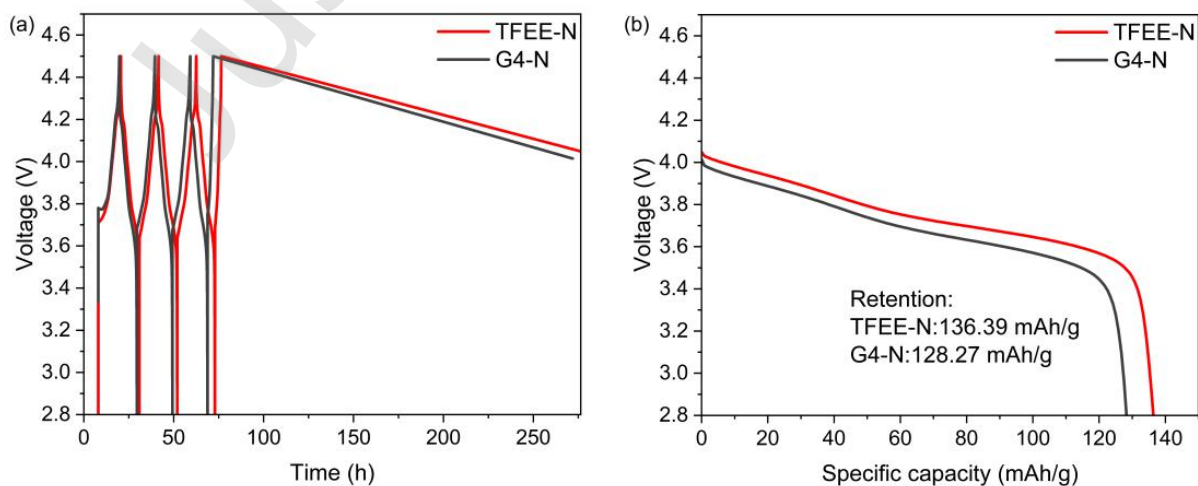


Figure. S17 The self-discharge behaviors of the Li||NCM811 cell after charging to 4.5 V with different electrolytes at selected cycles.

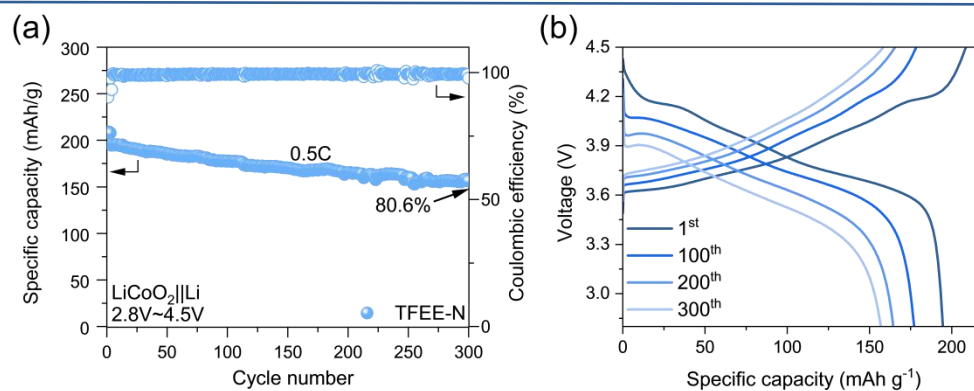


Figure. S18 (a) Long-term cycling performance of Li||LiCoO₂ cell with TFEE-N electrolyte under 4.5V cut-off voltage and 0.5 C rate. (b) The corresponding charge-discharge curves with different cycles.

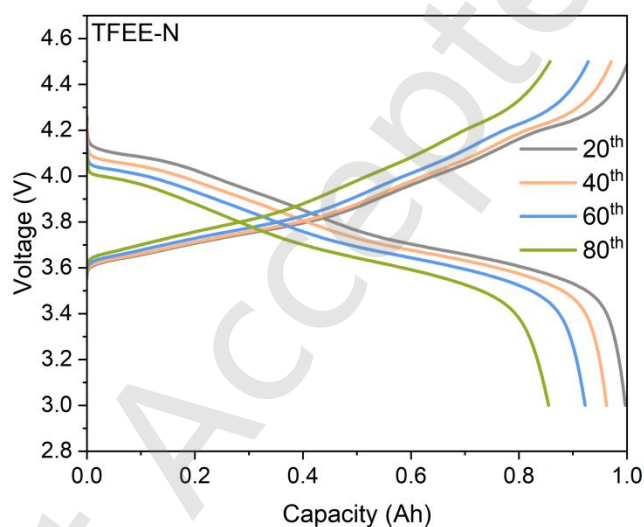


Figure. S19 The corresponding charge-discharge curves of Li||NCM811 pouch cell with TFEE-N electrolyte at selected cycles.

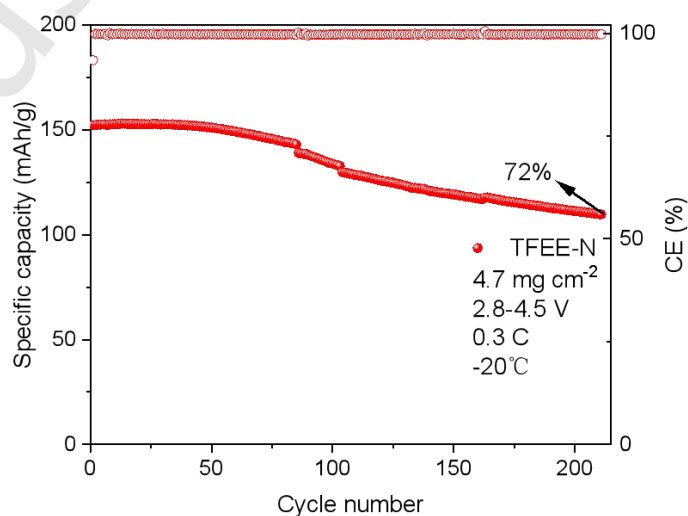


Figure. S20 Cycling performances of the Li||NCM811 cell with TFEE-N electrolytes at -20 °C under 0.3 C rate.

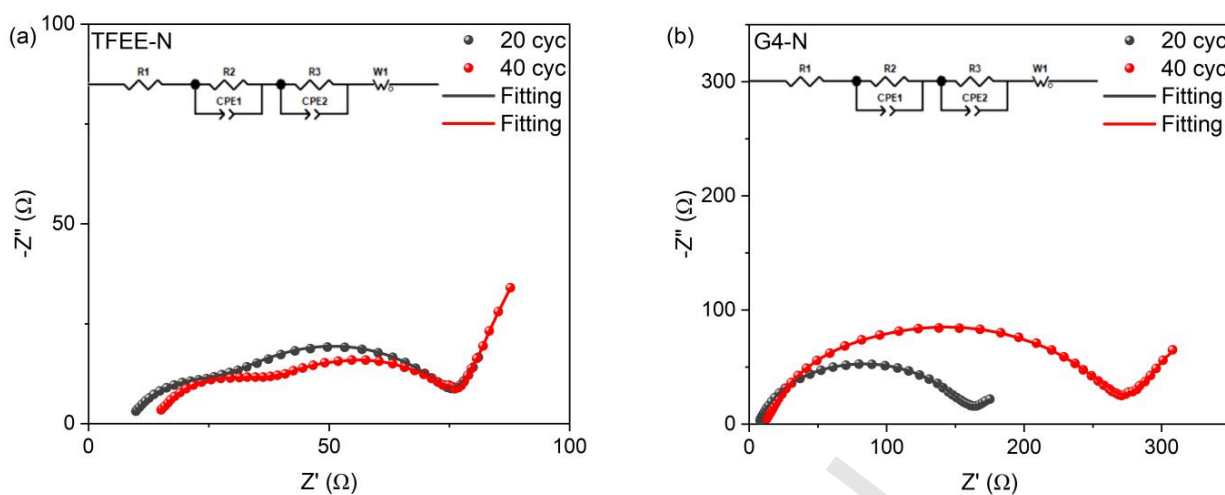


Figure. S21 Electrochemical impedance spectra of the Li||NCM811 cells after cycling for different cycles with (a) TFEE-N and (b) G4-N electrolytes.

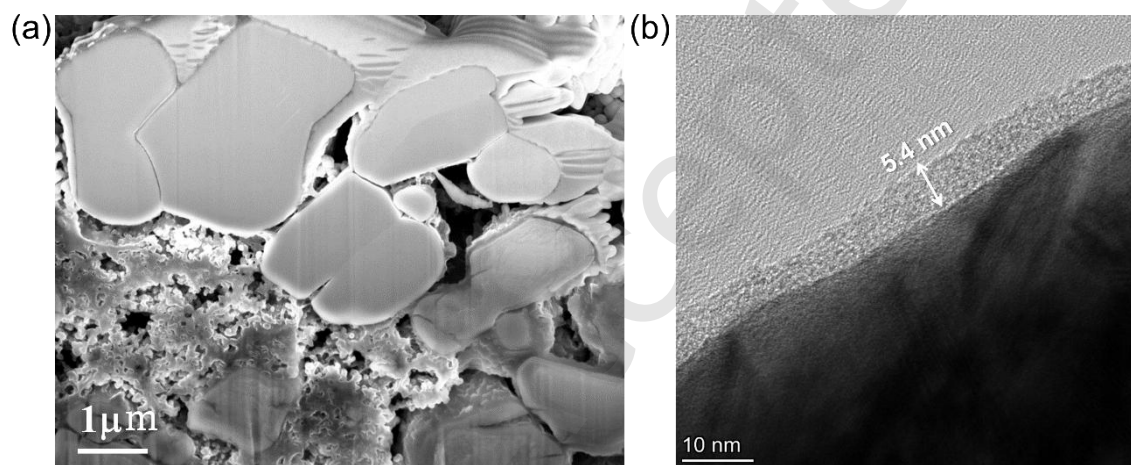


Figure. S22 (a) FIB-SEM cross-sectional image of the NCM811 cathode after 50 cycles with TFEE-N electrolyte at a cut-off voltage of 4.6 V. (b) HR-TEM analysis of the cycled cathode in TFEE-N electrolyte.

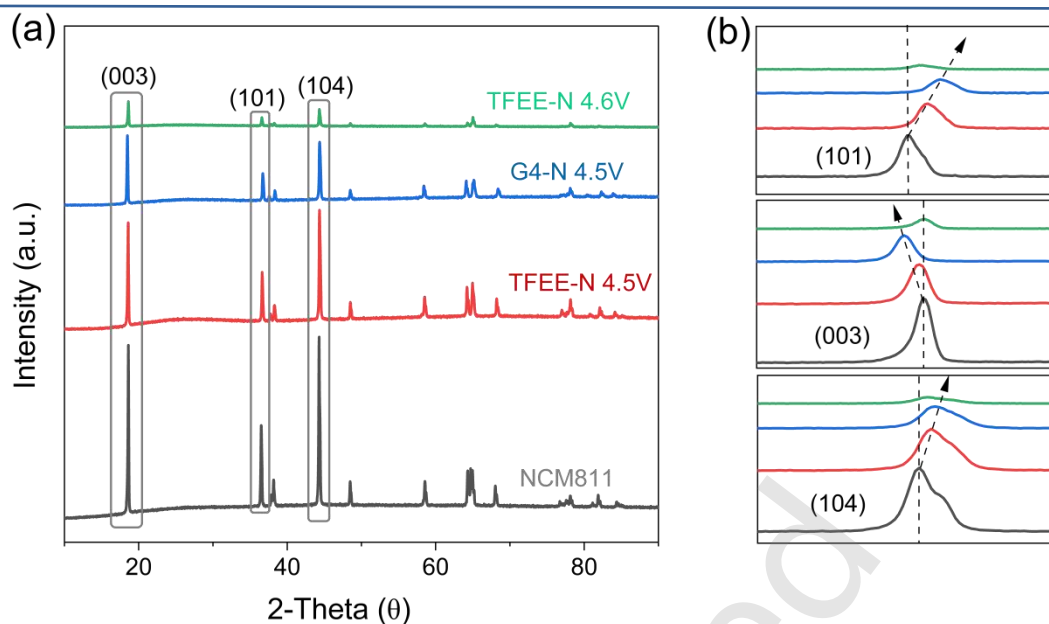


Figure. S23 (a) XRD analysis of the NCM811 cathodes after cycling with G4-N, TFEE-N electrolyte under different cut-off voltages; (b) Enlarged crystal facets for the XRD spectra at selected degrees.

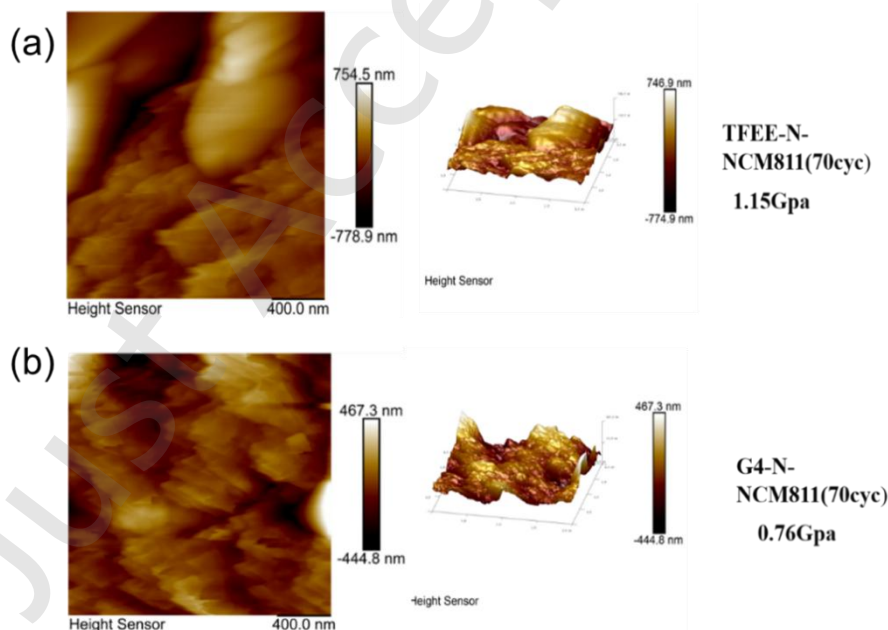


Figure. S24 AFM images of the NCM811 cathode after cycling in (a) TFEE-N and (b) G4-N electrolytes, respectively.

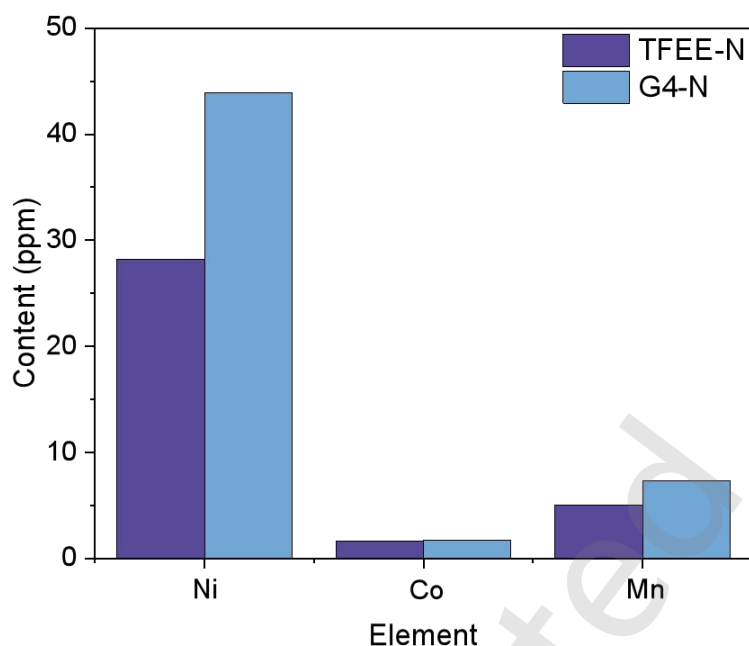


Figure. S25 The dissolution contents of transition metal ions for the cycled cells with different electrolytes.

Table S1 Impedance parameters of Li||NCM811 cells before and after cycling for different cycles with TFEE-N and G4-N electrolytes.

		Rs	R _{cei}	R _{ct}
20 cyc	BE	6.657	138.2	12.42
	BTTE	8.617	47.59	19.65
40 cyc	BE	11.08	244.2	15.66
	BTTE	13.6	34.82	23.95

Table S2 the detail parameters of the Li||NCM811 pouch cell.

Cell component	Specifications	Parameters
NCM811 cathode	Active material ratio (wt%)	94.5
	Areal weight (mg cm ⁻²)	15.12
	Compact density (g cm ⁻³)	3.35
	Areal capacity (mAh cm ⁻²)	4.76
	Length (mm)	52
	Width (mm)	59
Li/Cu anode	Thickness (mm)	0.5
	Length (mm)	54
	Width (mm)	61.5
Electrolyte	E/C (g Ah ⁻¹)	3
Full cell	Capacity (Ah)	1.1
	Plateau voltage (V)	3.8
	Total weight (g)	17
	Actual specific energy (Wh kg ⁻¹)	246