

Supporting Information

**Integrated Ring-Chain Design of a New Fluorinated Ether Solvent
for High-Voltage Lithium-Metal Batteries**

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1. Materials

Triethyl orthoformate (TOF) and anhydrous toluene were purchased from ACROS. 3,3,3-trifluoro methyl pyruvic acid was purchased from Fluorochem. *p*-Toluenesulfonic acid was purchased from TCI and then dried by Dean-Stark apparatus in toluene. Sodium borohydride was purchased from Sigma-Aldrich. Anhydrous tetrahydrofuran (THF) was taken from the solvent drying system. Lithium bis(fluorosulfonyl)imide (LiFSI) and NCM811 were purchased from Guangdong Canrd New Energy Technology. 20 μm Li foil was purchased from China Energy Lithium Co., Ltd.

2. Experimental procedures

Synthesis of the 1,1,1-trifluoro-2,3-propanediol: To the solution of sodium borohydride (11.8 g, 0.32 mol) and THF (50 mL), 3,3,3-trifluoro methyl pyruvic acid (50 g, 0.32 mol) was added slowly by using a syringe pump over 2 h at 50 °C, and refluxed for 1 h under Ar atmosphere. After cooling the reaction to room temperature, H₂O (11.5 mL, 0.64 mol) was slowly added into the mixture and refluxed for 1 h. Then, 95% sulfuric acid (0.32 mol), H₂O (50 mL) was added to this mixture at room temperature and refluxed for additional 1 h. The resulting mixture was extracted with ethyl acetate and the organic phase was washed with water twice and then the solvent was removed under reduced pressure. The residue was purified by vacuum distillation at 41 °C at 1.2 Torr with a yield of 44%.^[1] ¹H NMR (400 MHz, CD₃OD) δ = 3.98 (m, 1H), 3.74 (m, 1H), 3.64 (m, 1H) ppm.

Synthesis of the 2-ethoxy-4-(trifluoromethyl)-1,3-dioxolane (cFTOF): 1,1,1-trifluoro-2,3-propanediol (9.6 g, 73.7 mmol) was slowly (1 mL/h) added to the solution of triethyl orthoformate (10 g, 67 mmol) and *p*-toluenesulfonic acid (0.165 g, 0.96 mmol) in anhydrous toluene (10 ml) at 100 °C under Ar atmosphere. The reaction mixture was stirred for 3 h at 100 °C. Finally, the colorless liquid was obtained by vacuum distillation at 52-53 °C at 21 Torr with a yield of 56%. ¹H NMR (400 MHz, CDCl₃) δ = 5.98 and 5.92 (s, 1H), 4.58 and 4.53 (m, 1H), 4.21 (m, 2H), 3.64 (q, *J* = 7.09 Hz, 2H), 1.24 (t, *J* = 7.09 Hz, 3H) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ = -77.12 and -79.26 (d,

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$J = 6.81$ Hz, CF_3) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 124.9$ and 124.9 (q, $J = 280.23$ Hz, CF_3), 116.5 and 116.4 (s), 73.3 and 73.1 (q, $J = 34.48$ Hz, $\text{CF}_3\text{-CH}$), 65.6 and 63.4 (q, $J = 2.20$ Hz), 60.9 and 60.6 (s), 14.8 and 14.8 (s) ppm.

Preparation of 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes: 187 mg LiFSI were added into 1 mL TOF or 1 mL cFTOF solvents and stirred for 3 h to prepare the final 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes. Also, 374 mg LiFSI was added into 1 mL cFTOF solvent and stirred for 3 h for 2 M LiFSI-cFTOF electrolyte.

3. Material characterization

The morphologies of Li in both electrolytes were characterized by the field emission scanning electron microscopy (FE-SEM, Tescan Mira3 LM FE). TEM of cathode was conducted by FEI Tecnai spirit at 120 kV. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) using focused monochromatized Al $K\alpha$ radiation (1486.6 eV) with a beam size of $\sim 500 \mu\text{m}^2$ (power of 150 W). The calibration of the binding energy peak positions is applied according to C1s located at 284.8 eV. All of the electrodes were rinsed with DME prior to their analysis. Ar-filled sample transfer chamber was adopted to avoid the air exposure and surface modification for lithium during transferring process before characterization.

Raman spectra was measured on a RENISHAW inVia Raman Microscope with a 785 nm laser. Fourier transform infrared (FTIR) spectra was recorded on the Bruker TENSOR II. Density functional theory (DFT) calculations of the HOMO and LUMO levels (based on equilibrium geometry at ground state) were performed on Spartan software with a basis set of B3LYP/6-311++G**. ^1H , ^{19}F and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. ^{19}F and ^7Li NMR spectra of electrolytes were recorded on 500 MHz Bruker NMR spectrometer at ambient temperature using 1 M LiCl- D_2O as an internal standard in a coaxial NMR tube.

4. Electrochemical characterizations

The batteries were assembled in a glove-box as either CR2032-type coin cell or Swagelok-cell with Celgard 2400 as a separator. The electrolyte amount for each cell was 40 μL , and cycling performance was tested by Land 2001A battery system.

For the CE and symmetric Li|Li tests, all cells were first cycled at 50 μA between 0–1.5 V (versus Li^+/Li) for ten cycles to clean the Cu electrode surface and stabilize the interface. Cu foil (\varnothing 14 mm) and Li foil (\varnothing 16 mm) were used as the electrodes. For the CE test, 1 (or 3) mAh cm^{-2} Li was deposited on the Cu electrode and then stripped away up to 1 V at 1 mA cm^{-2} . For the symmetric Li|Li test, 5 mAh cm^{-2} Li was first predeposited on Cu electrode at 0.5 mA cm^{-2} , then cycled at 1 mA cm^{-2} for 1 h.

The electrochemical stability window was examined by linear sweeping voltammetry (LSV) on Li|Al cells using VMP3 (Bio Logic Science Instruments) at a scan rate of 5 mV s^{-1} . The anodic stability was determined by cyclic voltammetry (CV) over a voltage range of –0.1 to 2 V for three cycles in Li|Cu cells by using the VMP3 electrochemical working station at a scan rate of 0.5 mV s^{-1} . Al corrosion tests were conducted by Li|Al half cells with difference electrolytes by holding the cell voltage at 5 V for 48 hours. Electrochemical Impedance Spectroscopy (EIS) measurements were conducted at room temperature using VMP3, wherein the voltage amplitude was set to 5 mV in the frequency range of 100 kHz to 10 mHz on Li|Cu cells after 1 cycle and 10 cycles at 1 mA cm^{-2} with 1 mAh cm^{-2} . Li ion transference number (LTN) was measured on the symmetric Li|Li cells. The initial and steady polarization currents (I^o and I^{ss}) were recorded under a polarization potential of 10 mV. The LTN was calculated by the following equation:

$$t_{\text{Li}}^+ = \frac{I^{ss} R_b^{ss} (\Delta V - I^o R_i^o)}{I^o R_b^o (\Delta V - I^{ss} R_i^{ss})} \quad (\text{S1})^{[2]}$$

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Wherein, R_b^o and R_b^{ss} refer to the initial and steady bulk resistances, R_i^o and R_i^{ss} refer to the initial and steady interfacial resistances, which were tested by EIS before and after the potentiostatic polarization of 10 mV.

For the Li|NCM811 full cells, the cathode was prepared from NCM811 powder, Super-P and polyvinylidene difluoride (PVDF) at the ratio of 8: 1: 1 using N-methyl-2-pyrrolidone (NMP) as the solvent. The areal loading of NCM811 was about 5 mg cm⁻². The Al-coated cathode case with a piece of Al foil (Ø 14 mm) was used to suppress corrosion from the electrolyte. The Li foil anode was 20 µm. After the first formation cycle at C/10 of charge/discharge, the cells were cycled at 0.5 C between 3 and 4.3 V.

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5. Supporting figures and tables

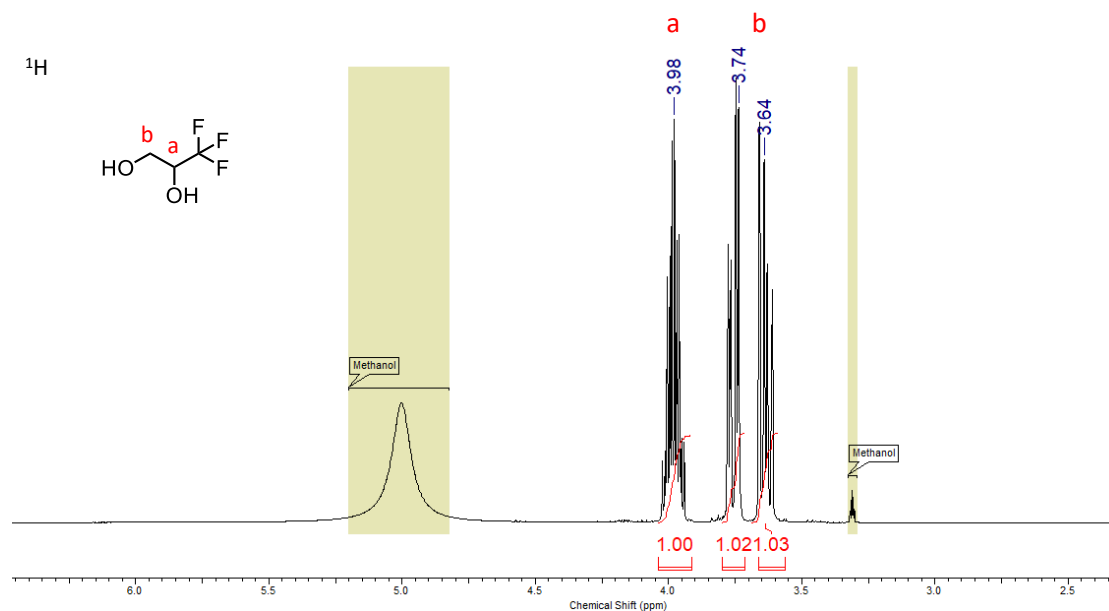


Figure S1. ¹H NMR (400MHz, CD₃OD, 298K) spectrum of 1,1,1-trifluoro-2,3-propanediol.

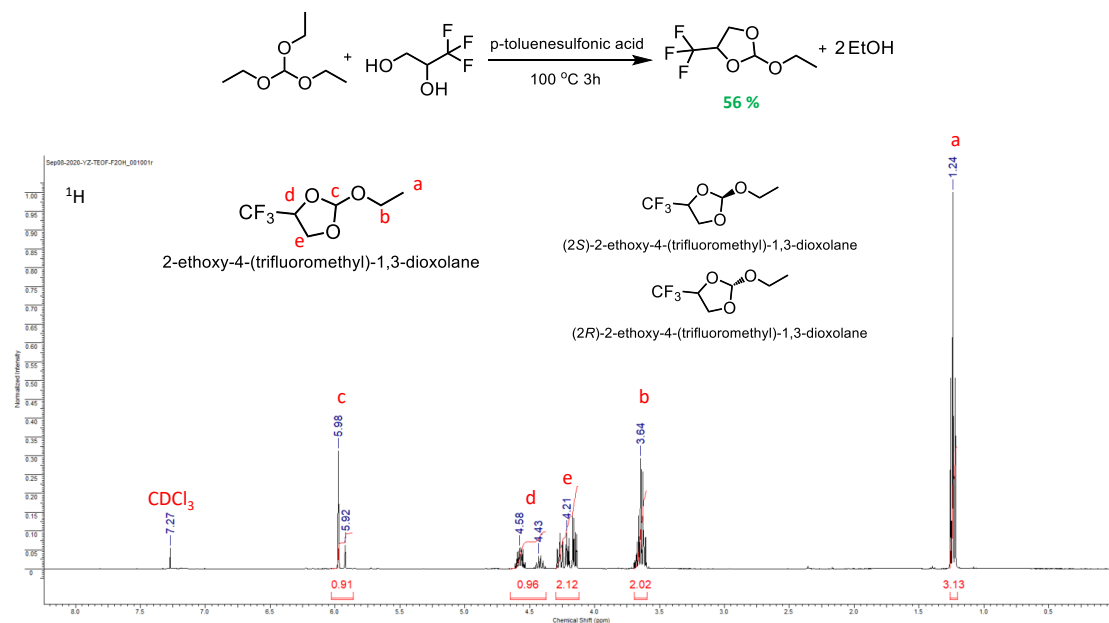


Figure S2. Synthesis procedure and ¹H NMR (400MHz, CDCl₃, 298K) spectrum of cFTOF.

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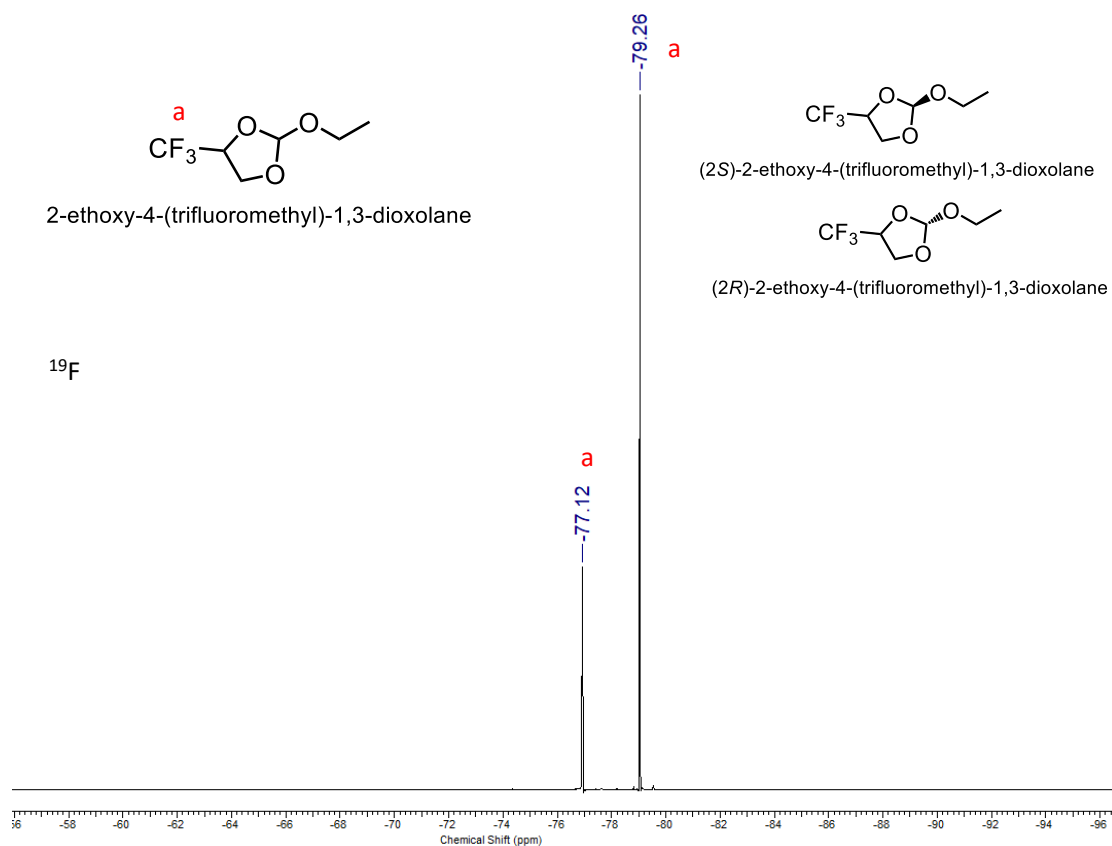


Figure S3. ^{19}F NMR (376 MHz, CDCl_3 , 298 K) spectrum of cFTOF.

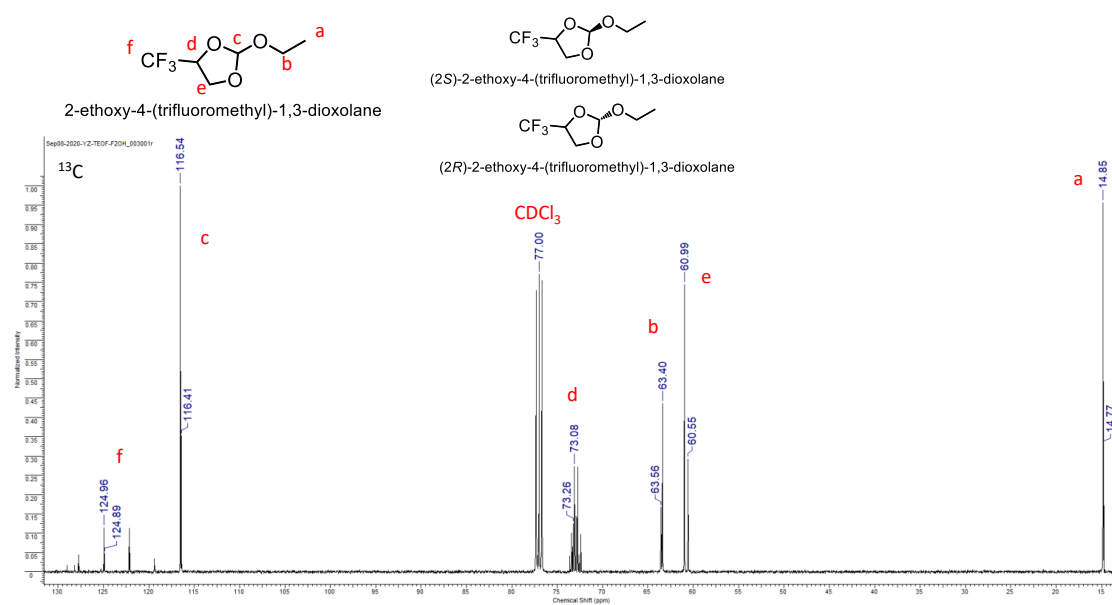


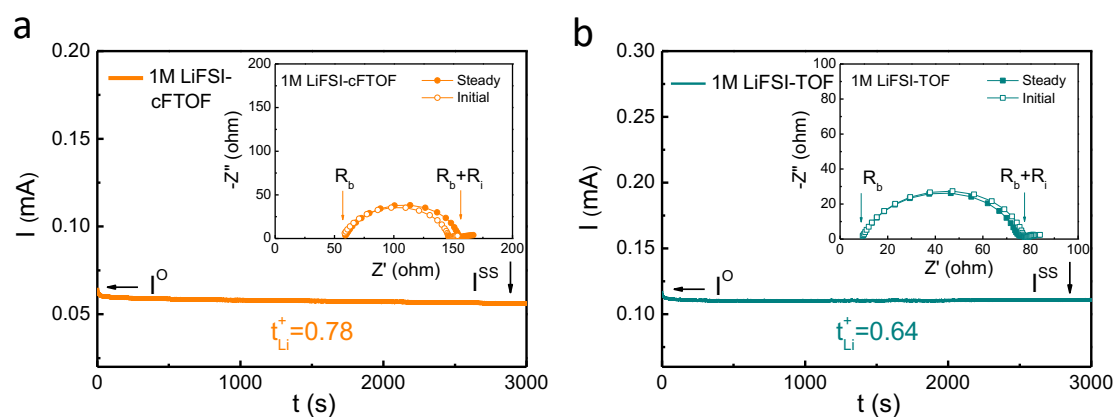
Figure S4. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) spectrum of cFTOF.

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Table S1. Physicochemical properties of cFTOF and TOF solvents, 1 M LiFSI-cFTOF and 1 M LiFSI-TOF electrolytes.

	TOF	cFTOF
Density (g mL ⁻¹)	0.891	1.26
Boiling point (°C)	146	52 (21Torr)
Viscosity (cp at 25 °C)	0.65	1.55

	1 M LiFSI-TOF	1 M LiFSI-cFTOF
Conductivity (mS cm ⁻¹)	5.5	0.7
Li ion transference number (LTN)	0.64	0.78
Viscosity (cp at 25 °C)	2	4.3

**Figure S5.** (a, b) The chronoamperometry profiles of Li|Li cells under a polarization voltage of 10 mV in (a) 1 M LiFSI-cFTOF and (b) 1 M LiFSI-TOF electrolytes, and the corresponding EIS profiles before and after polarization are shown as insets.

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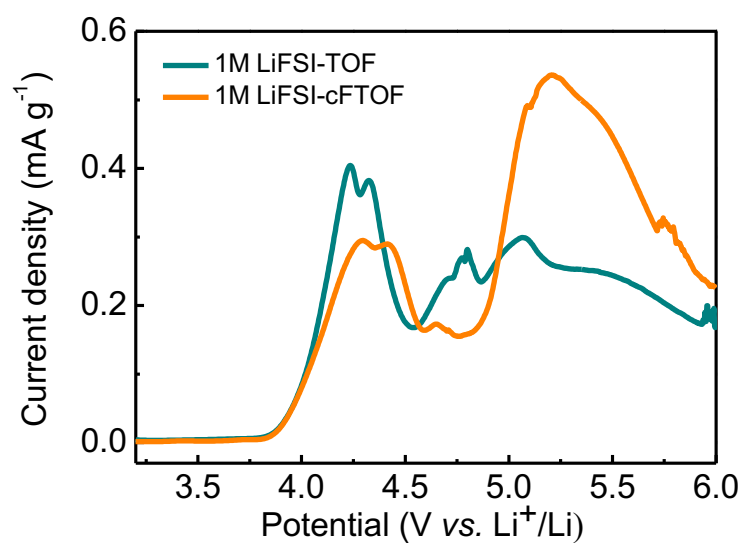


Figure S6. Oxidation stability of two electrolytes in Li||LMO cells tested by LSV from OCV to 6 V at a scan rate of 0.5 mV S^{-1} .

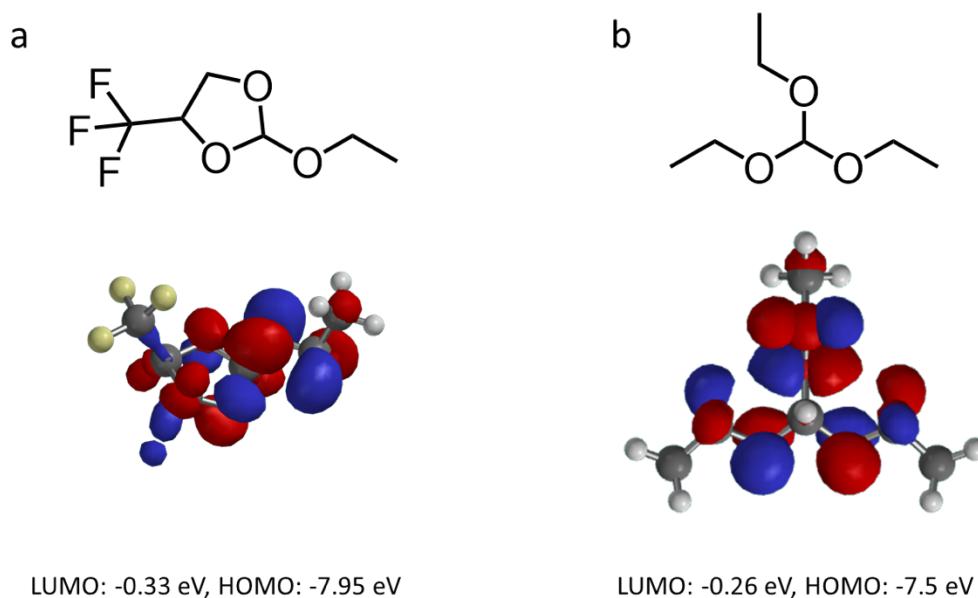


Figure S7. The HOMO and LUMO energy levels of cFTOF (a) and TOF (b) solvents.

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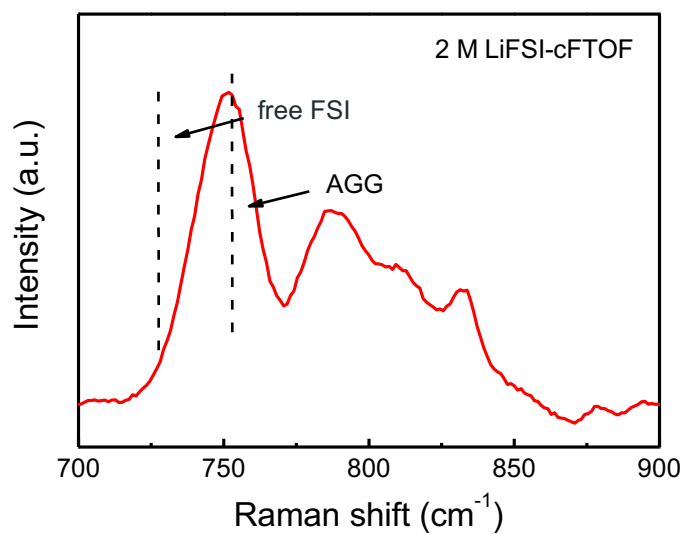


Figure S8. Raman spectra of 2 M LiFSI-cFTOF electrolyte.

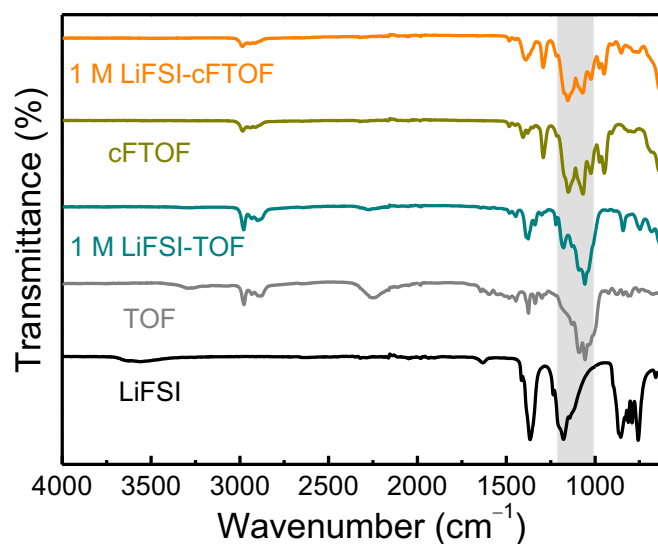


Figure S9. The FTIR spectra of cFTOF, TOF solvents, 1 M LiFSI-cFTOF, 1 M LiFSI-TOF electrolytes and LiFSI.

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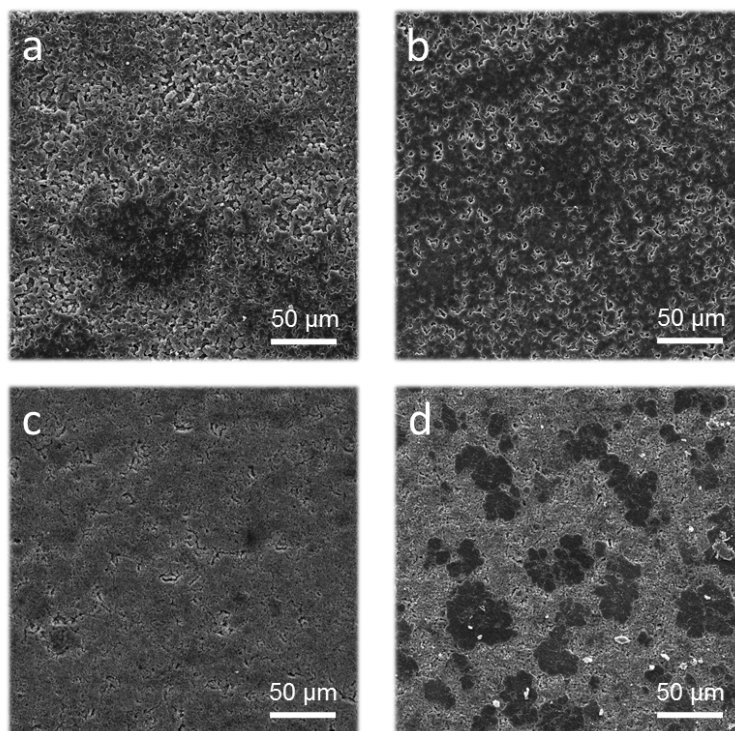


Figure S10. Low magnification SEM images of 4 mAh cm^{-2} Li plating morphology after 1st cycle at 1 mA cm^{-2} in (a) 1 M LiFSI-TOF and (b) 1 M LiFSI-cFTOF electrolytes and the morphology of Li surface after 50 cycles at 1 mA cm^{-2} with a cut-off capacity of 1 mAh cm^{-2} in (c) 1 M LiFSI-TOF and (d) 1 M LiFSI-cFTOF electrolytes.

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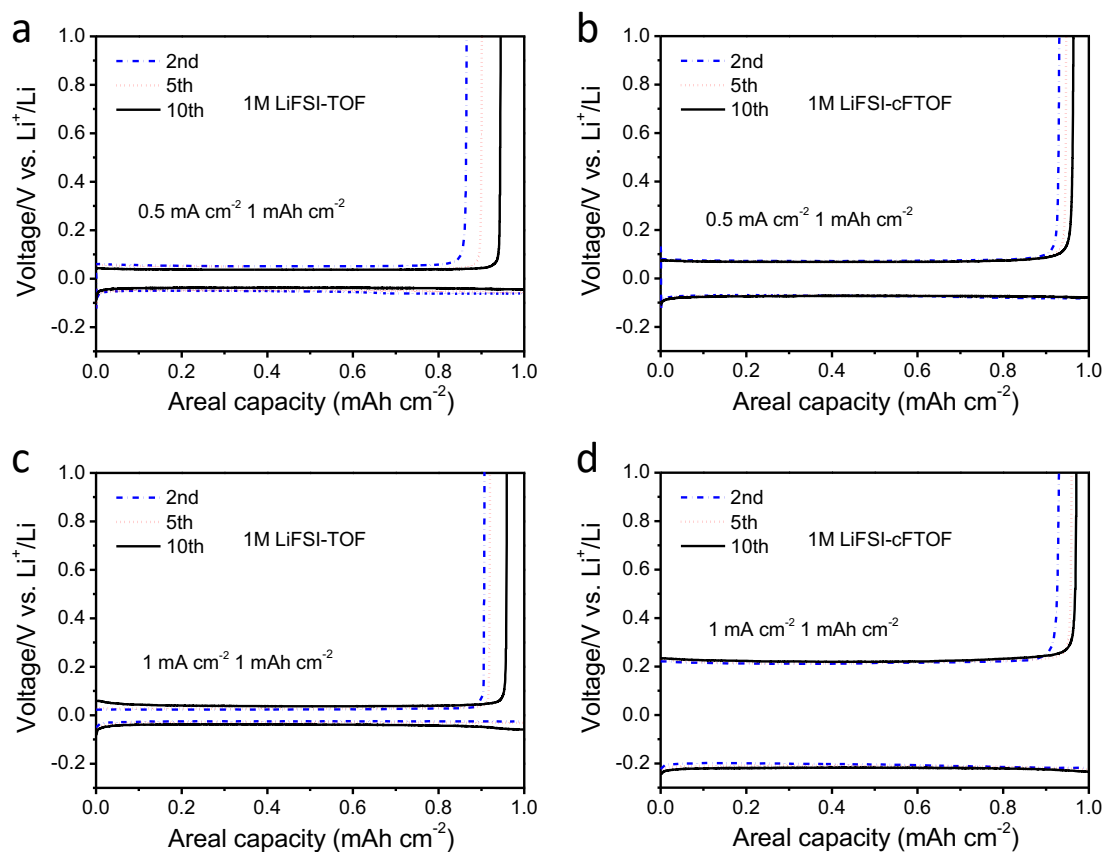


Figure S11. Charge-discharge profiles of the Li|Cu cells in 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes at (a, b) 0.5 mA cm^{-2} at a current density of 1 mAh cm^{-2} Li and (c, d) 1 mA cm^{-2} current density of 1 mAh cm^{-2} Li.

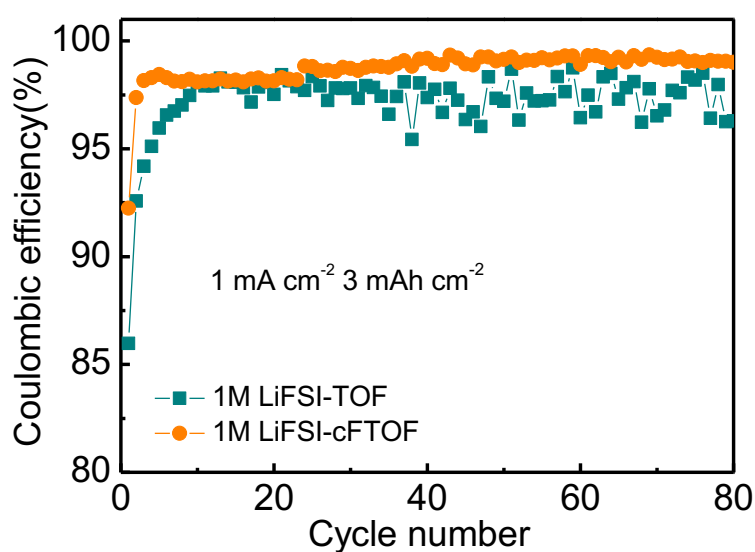


Figure S12. CE of Li plating/stripping in 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes at a current density of 1 mA cm^{-2} with a capacity of 3 mAh cm^{-2} .

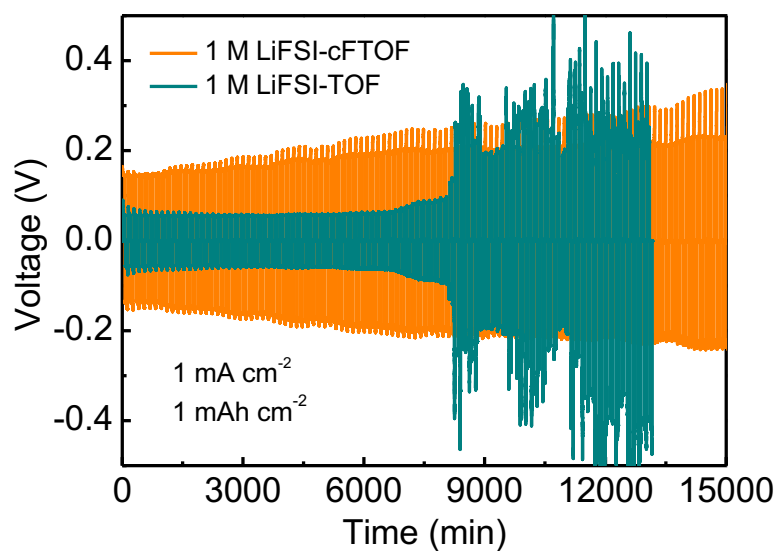


Figure S13. Voltage-time profiles of symmetric cells at 1 mA cm⁻² with a cut-off capacity of 1 mAh cm⁻² in 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes.

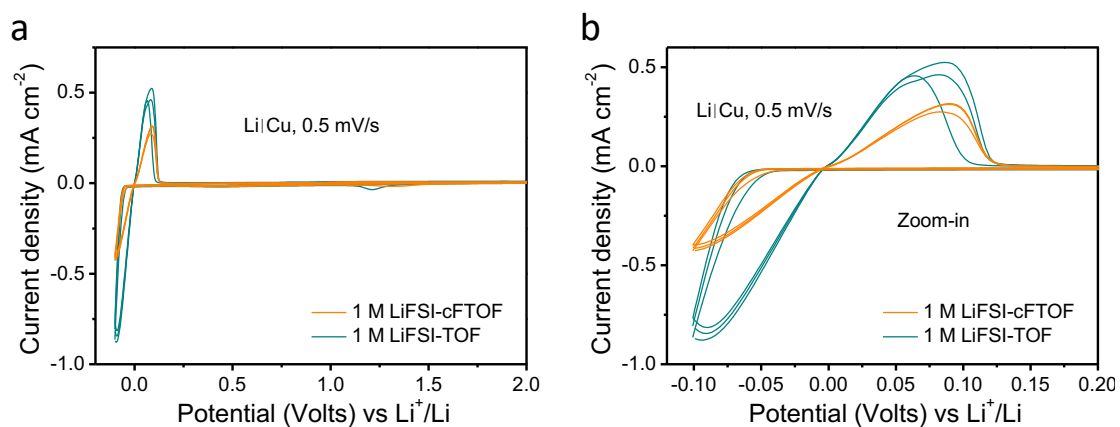


Figure S14. (a, b) The full and zoom-in cyclic voltammetry (CV) curves of 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes in Li|Cu half cells.

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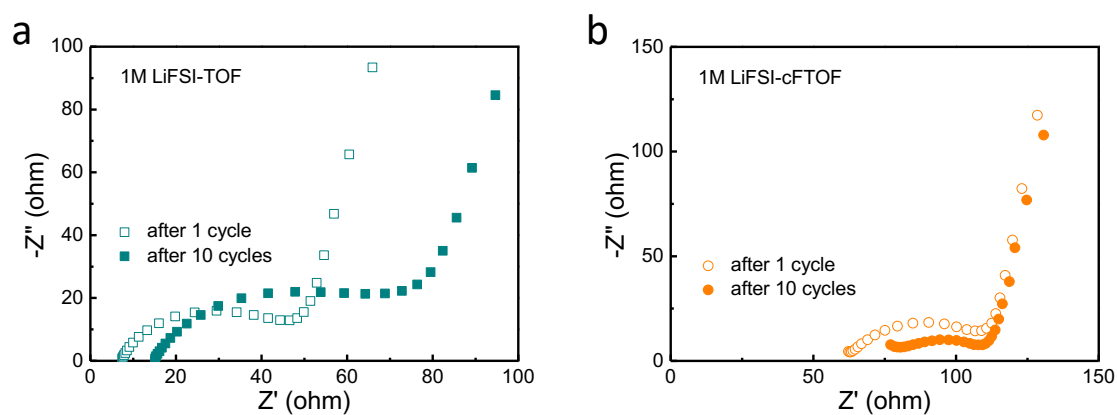


Figure S15. EIS curves of (a) 1 M LiFSI-TOF and (b) 1 M LiFSI-cFTOF electrolytes in Li|Cu half cells after 1 cycle and 10 cycles at 1 mA cm^{-2} with 1 mAh cm^{-2} .

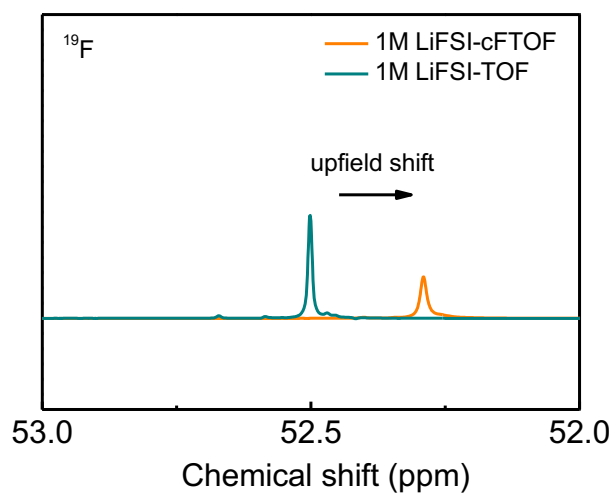


Figure S16. ^{19}F -NMR spectra of 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes.

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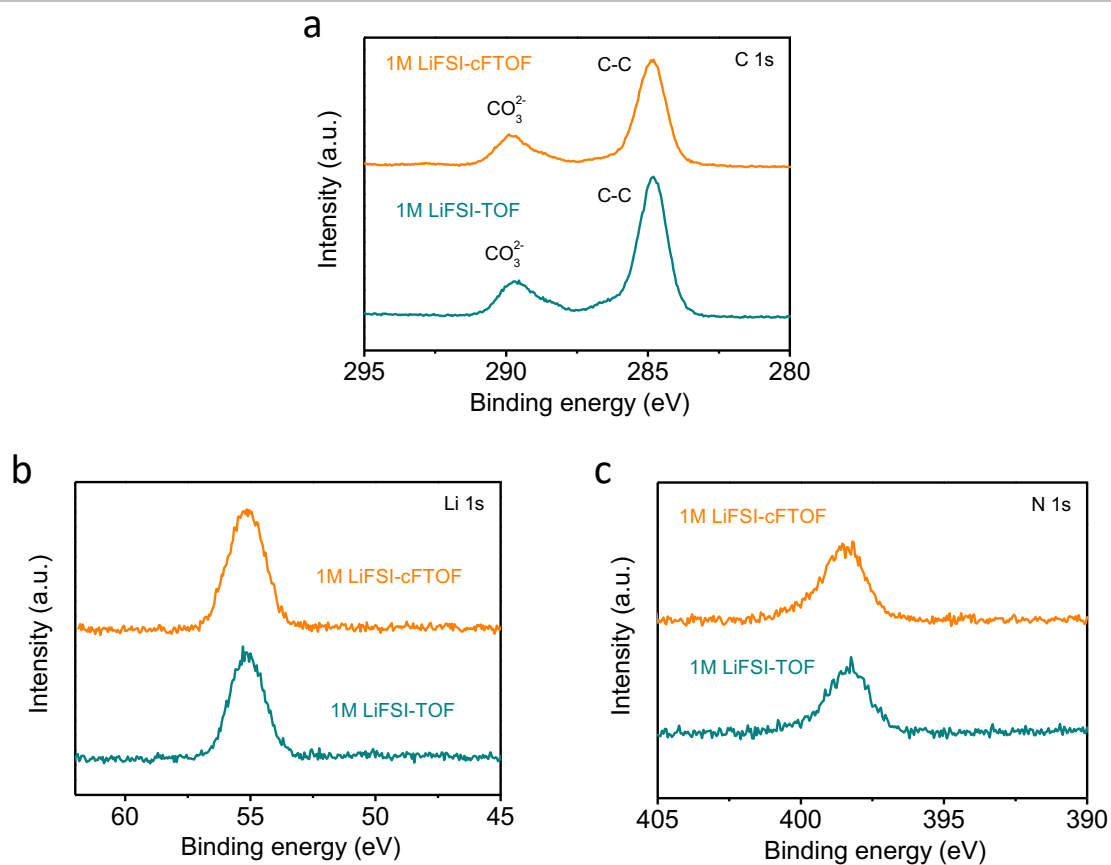


Figure S17. (a-c) XPS spectra of (a) C 1s, (b) Li 1s and (c) N 1s in 1 M LiFSI-TOF and 1 M LiFSI-cFTOF electrolytes after 20 cycles.

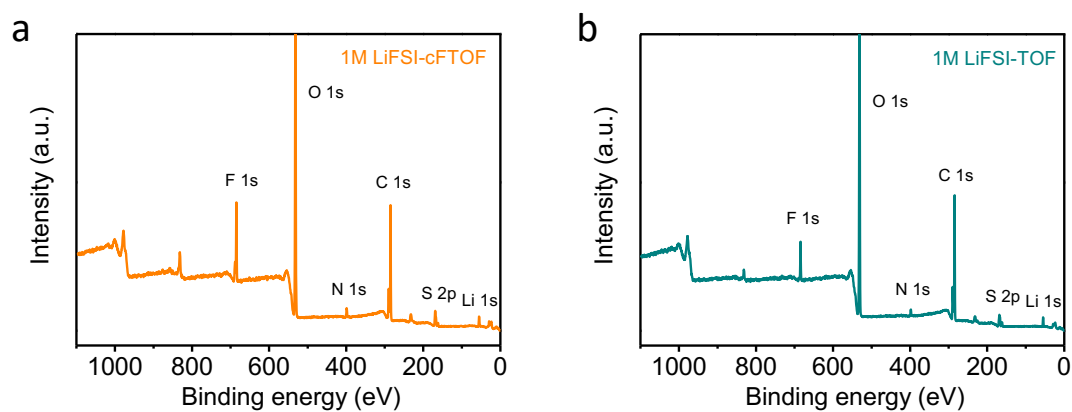


Figure S18. (a, b) Overall XPS survey spectra of (a) 1 M LiFSI-cFTOF and (b) 1 M LiFSI-TOF electrolytes after 20 cycles.

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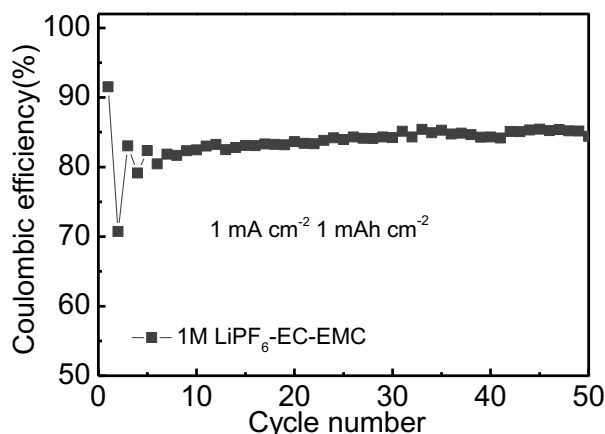


Figure S19. CE of Li plating/stripping in 1 M LiPF₆-EC-EMC electrolyte in Li|Cu half cell at a current density of 1 mA cm⁻² with a capacity of 1 mAh cm⁻².

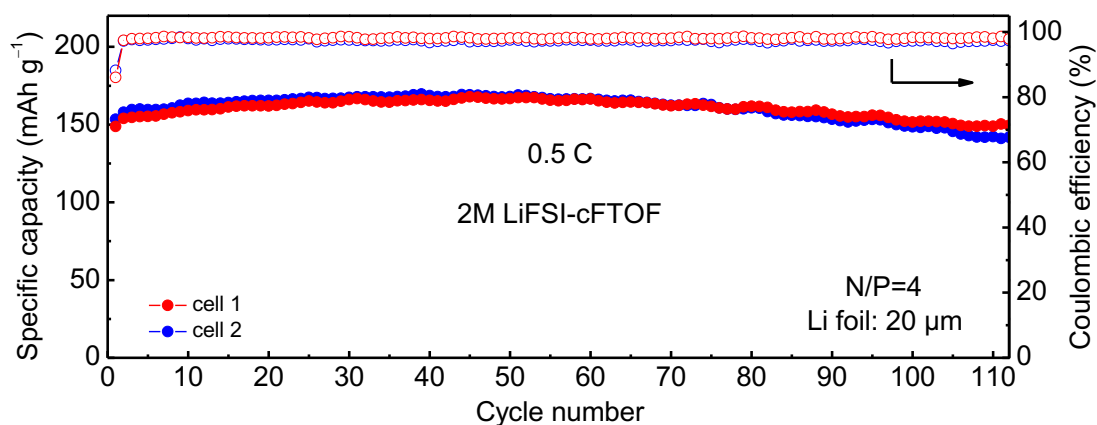


Figure S20. Reproducibility test of cycling performance of Li|NCM811 full cells at 0.5 C in 2 M LiFSI-cFTOF electrolyte.

Table S2. Comparison of performance of high-voltage lithium metal batteries with different electrolytes.

Reference	Electrolyte	cathode	Electrochemical performance
This work	2 M LiFSI-cFTOF	NCM811	0.5 C, N/P=4, 112 cycles, 149.4 mAh g⁻¹, (100% capacity retention);
<i>J. Am. Chem. Soc.</i> 2020, 142(16): 7393-7403.	1 M LiFSA in DEG-FTriEG	NCM811	0.5 C, 10 cycles, ~50 mAh g ⁻¹ ;
<i>Nature Energy</i> , 2020, 5(7): 526-533.	1 M LiFSI-FDMB	NCM523	1/3 C, N/P=2.5, ~215 cycles, ~155 mAh g ⁻¹ , (100% capacity retention);

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<i>Nature Energy</i> , 2022, 7: 94-106.	1.2 M LiFSI /F5DEE	NCM811	0.1C/0.3C, N/P=2, ~270 cycles, ~160 mAh g ⁻¹ , (80% capacity retention);
<i>Angew. Chem.</i> , 2020, 59(35): 14935-14941.	1 M LiPF ₆ /FEC- EMC with 3 wt% LiNO ₃ and 1 wt% TPFPB	NCM811	0.1C/0.3C, N/P=2.94, 140 cycles, (80% capacity retention);
<i>Advanced Functional Materials</i> , 2020, 30(39): 2003800.	1 M LiPF ₆ /EC- DEC with 10 mM In(OTf) ₃ and 0.5 M LiNO ₃	NCM811	0.3C/0.5C, N/P=2.09, 160 cycles, ~150 mAh g ⁻¹ , (80% capacity retention);
<i>Energy & Environmental Science</i> , 2020, 13(1): 212-220.	1 M LiFSI/FSA	NCM622	N/P=7.6, 200 cycles, (89% capacity retention);
<i>Nature Energy</i> , 2021, 6(5): 495- 505.	1 M LiFSI in DMTMSA	NCM811	0.5C, N/P=7.06, 100 cycles, (88% capacity retention);
<i>PNAS</i> , 2018, 115(6): 1156- 1161.	7 M LiFSI in FEC	LNMO	0.36C, N/P=1.4, 140 cycles, (70% capacity retention);
<i>Energy Storage Materials</i> , 2021, 34: 76-84.	1LiFSI- 1.3DME- 2TFEO	NCM811	0.1C/0.3C, N/P=2.38, 210 cycles, (80% capacity retention);
<i>Joule</i> , 2019, 3(7): 1662-1676.	1LiFSI- 1.2DME-3TTE	NCM811	1/3 C, N/P=2.38, 155 cycles, (80% capacity retention);
<i>Nature nanotechnology</i> , 2018, 13(8): 715-722.	1 M LiPF ₆ /FEC- FEMC-HFE	NCM811	0.5C, N/P=1, 120 cycles, (95% capacity retention);
<i>Angewandte Chemie</i> , 2020, 132(49): 22378- 22385.	1.3 M LiTFSI/LiNO ₃ - SL/HFE	NCM811	0.5C, N/P=5, 200 cycles, (99.5% capacity retention);
<i>Nat. Mater.</i> 10.1038/s41563- 021-01172-3	Li ₂ O suspension electrolyte	NCM811	0.5C/1C, N/P unknown, 150 cycles, (100% capacity retention);
<i>J. Am. Chem. Soc.</i> , 2021, 143(44): 18703- 18713.	4 M LiFSI/DEE	NCM811	0.17C (0.8 mA/cm ²), N/P=2.08, 182 cycles, (80% capacity retention);
<i>Adv. Mater.</i> 2021, 2008619.	1 M LiFSI/6FDMH- DME	NCM523	1/3 C, N/P=1.6, 250 cycles, (84% capacity retention);

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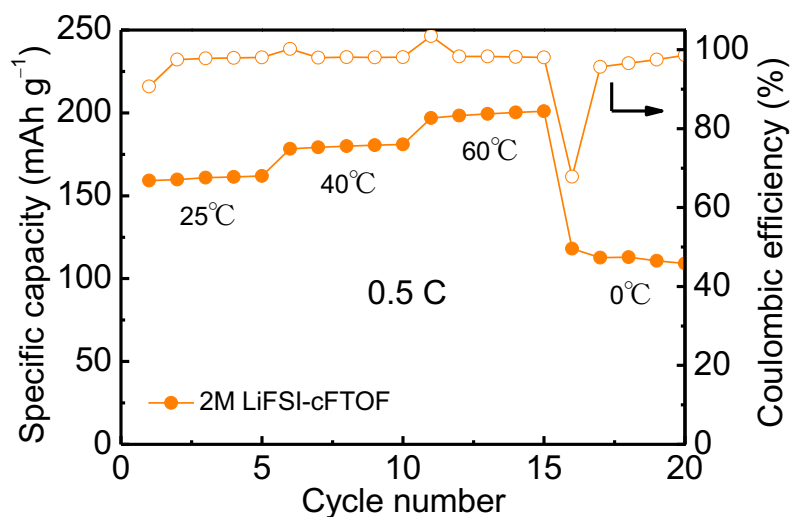


Figure S21. The Li|NCM811 full cell with 2 M LiFSI-cFTOF electrolyte at 0.5 C at different temperatures.

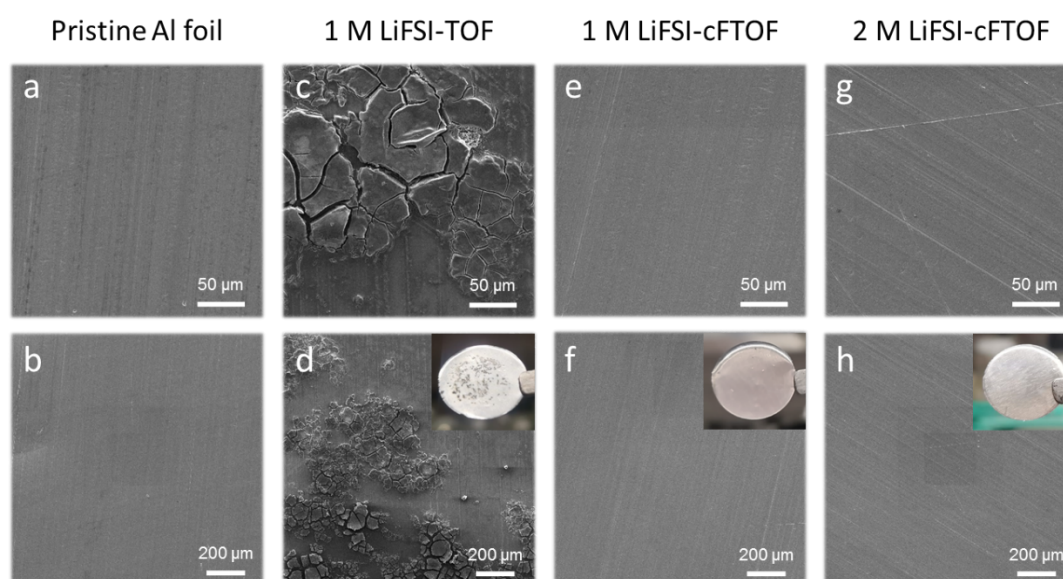


Figure S22. High and low magnification SEM images of (a, b) pristine Al foil and Al foil after constant-voltage at 5 V for 48 hours in (c, d) 1 M LiFSI-TOF, (e, f) 1 M LiFSI-cFTOF and (g, h) 2 M LiFSI-cFTOF.

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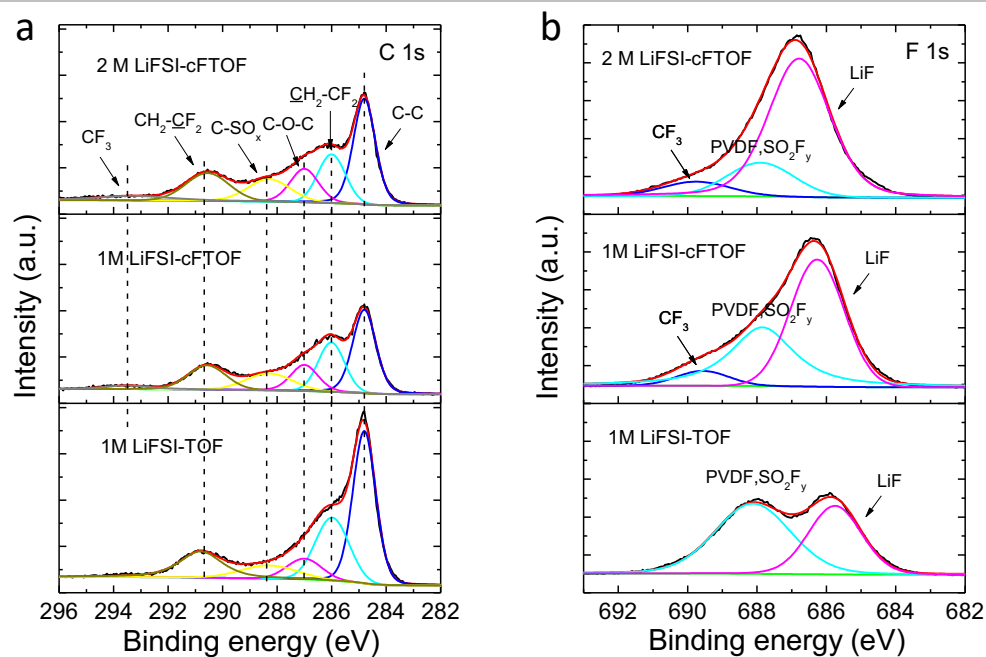


Figure S23. XPS profiles of (a) C 1s and (b) F 1s on NCM811 cathode surfaces in Li|NCM811 full cells after 20 cycles at 0.5 C with 1 M LiFSI-TOF, 1 M and 2 M LiFSI-cFTOF electrolytes.

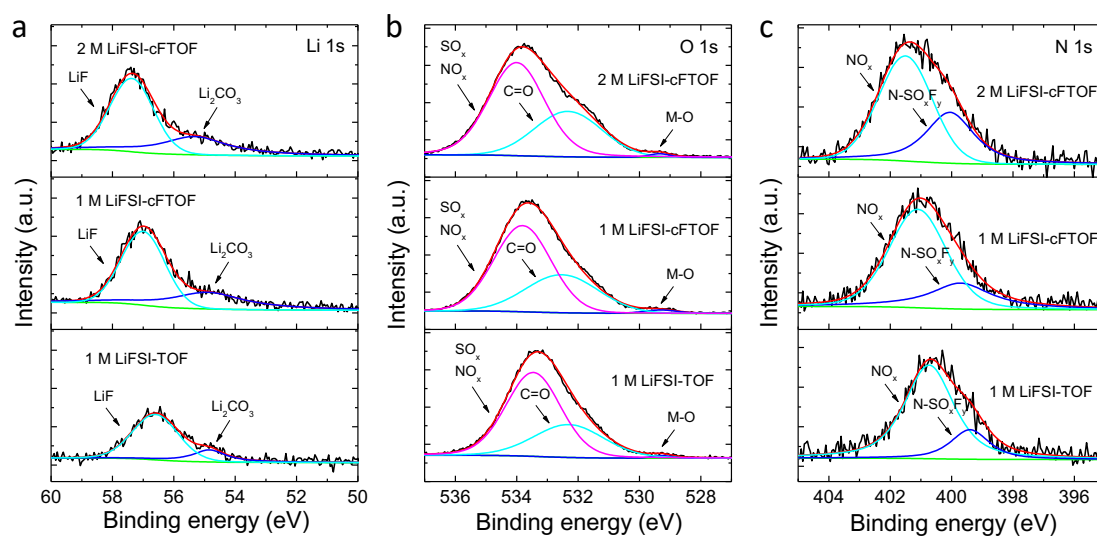


Figure S24. XPS profiles of (a) Li 1s, (b) O 1s and (c) N 1s on NCM811 cathode surfaces in Li|NCM811 full cells after 20 cycles at 0.5 C with 1 M LiFSI-TOF, 1 M and 2 M LiFSI-cFTOF electrolytes.

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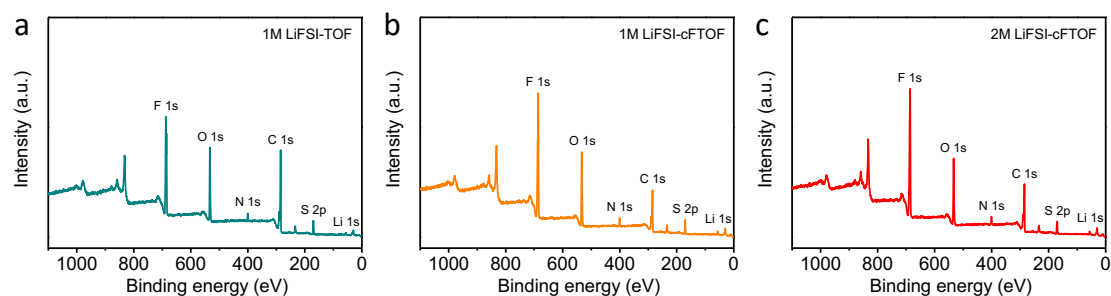


Figure S25. Overall XPS survey spectra of CEI in (a) 1 M LiFSI-TOF, (b) 1 M LiFSI-cFTOF and (c) 2 M LiFSI-cFTOF electrolytes after 20 cycles at 0.5 C in Li|NCM811 full cells.

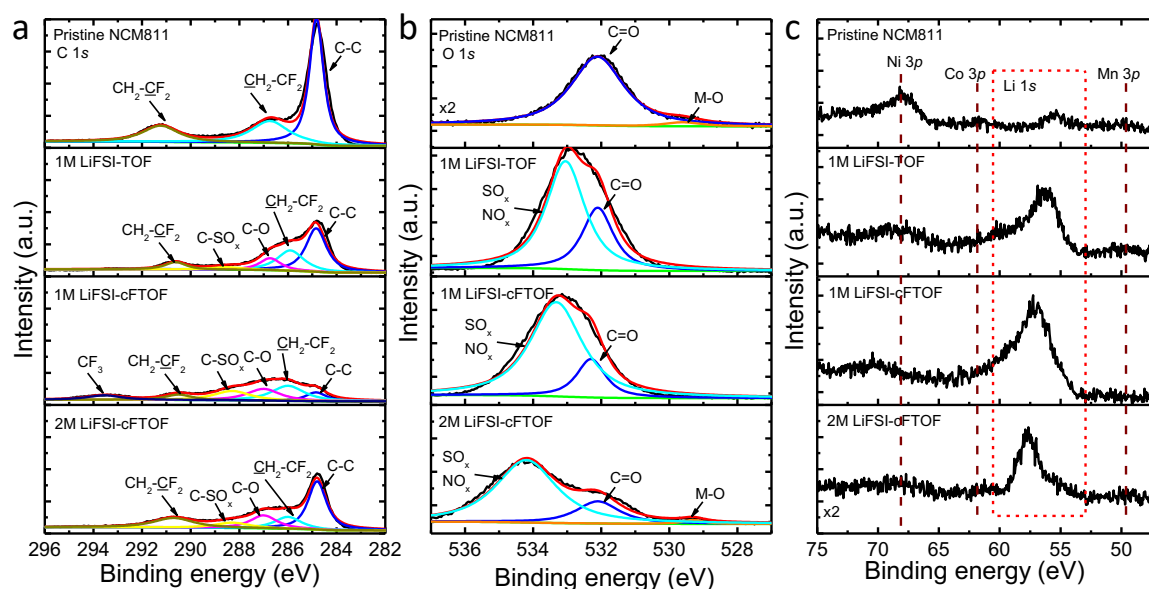


Figure S26. XPS profiles of (a) C 1s, (b) O 1s and (c) Li 1s-transition metals 3p on pristine NCM811 cathode surfaces and in Li|NCM811 full cells after 100 cycles with 1 M LiFSI-TOF, 1 M and 2 M LiFSI-cFTOF electrolytes.

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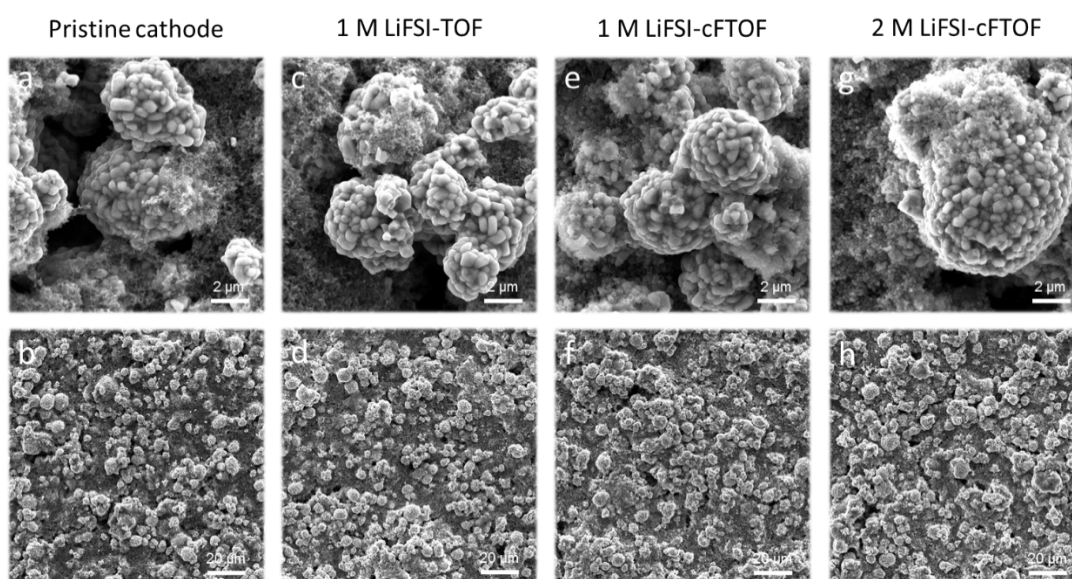


Figure S27. High and low magnification SEM images of (a, b) pristine cathode and the cathode in Li|NCM811 full cell after 20 cycles at 0.5 C in (c, d) 1 M LiFSI-TOF, (e, f) 1 M LiFSI-cFTOF and (g, h) 2 M LiFSI-cFTOF electrolytes.

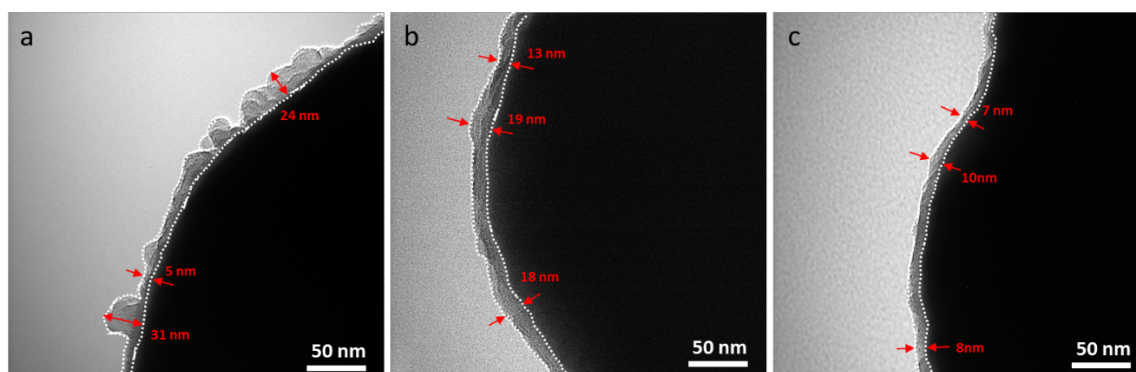


Figure S28. Bright-field TEM images of cathode in Li|NCM811 full cells after 100 cycles with (a) 1 M LiFSI-TOF, (b) 1 M LiFSI-cFTOF and (c) 2 M LiFSI-cFTOF electrolytes.

References

- [1] M. Y. Koh, Akiyoshi; Tanaka, Michiru; Saita, Tomohide, *Vol. JP2008230970 A*, Japan, **2008-10-02**.
- [2] K. Abraham, Z. Jiang, B. Carroll, *Chem. Mater.* **1997**, *9*, 1978-1988.