

Supporting Information

A bifunctional surfactant-like electrolyte additive for a stable lithium metal anode

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Experimental section

Electrode Preparation: The cathode slurry, designated as NCM523, was formulated by blending LiNiCoMnO₂ sourced from Guangdong Canrd New Energy Technology Co., Ltd., Super-P obtained from the Kelude website, and polyvinylidene difluoride (PVDF, 99.9% purity, Macklin) at a mass ratio of 8:1:1. This mixture was dispersed in N-methyl-2-pyrrolidone (99.5% purity, Aladdin) to form a slurry, which was uniformly coated onto carbon-coated aluminum foil (provided by Guangdong Canrd New Energy Technology Co., Ltd.). The coated foil was then dried overnight at 60°C under vacuum. Subsequently, the material was cut into discs with a diameter of 12 mm, ensuring a consistent loading mass of the active NCM523 material on the cathode at $1 \pm 0.5 \text{ mg cm}^{-2}$.

Electrolyte Preparation: The based electrolyte (BE) consisted of 1M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC-DEC, v: v = 1: 1), procured from Suzhou Duoduo Chemical Technology Co., Ltd. Additionally, nonafluorobutanesulfonyl fluoride (NtF, 99.99%) from Admas was introduced into the base electrolyte at concentrations of 0.5 vt% and 1 vt% NtF, yielding different electrolyte formulations. Introduce lithium Lithium Bis(fluorosulfonyl)imide (LiFSI) from Suzhou Duoduo Chemical Technology Co., Ltd. and 1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE) from McLean Company into the base electrolyte to form the electrolyte formula for the control experiment. CR2032 coin cells and Li-Li symmetrical cells were assembled using NCM523 cathodes, lithium foils supplied by China Energy Lithium Co., Ltd. ($\phi 14 \text{ mm}$, $400 \mu\text{m}$), Al₂O₃-coated separators ($\phi 19 \text{ mm}$, $16 + 4 \mu\text{m}$), and the electrolytes. All assembly operations were conducted in a glovebox filled with argon (Ar) gas ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$).

Electrochemical Testing: The electrochemical tests encompassed Li-Li symmetric cell tests, Li Al battery testing, Li-NCM523 cell tests, Tafel curve tests, and electrochemical impedance spectroscopy (EIS) tests. CR2032 coin cells were assembled in a glovebox with 1 M LiPF₆ in EC: DEC and 0.5 vt% NtF as the electrolyte, with a fixed volume of 40 μL , unless otherwise specified. The Li-NCM523 half-cell is assembled with an NCM523 cathode ($\phi 8 \text{ mm}$, 1.5 mg cm^{-2}) and a lithium foil ($\phi 14 \text{ mm}$), along with 40 μL of electrolyte. These cells are cycled within the voltage range of 3 to 4.3 V. The Li-NCM523 full cell is assembled with a

commercial NCM523 cathode (φ 8 mm, 20.8 mg cm⁻²) and a lithium foil (φ 14 mm). They are subjected to cycling tests between 3 and 4.3 V at rates of 0.5 C/1 C. Li-Li symmetric cells were charged/discharged at constant currents of 1 mA cm⁻², 1 mAh cm⁻², and 0.5 mAh cm⁻², respectively. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a CHI660E electrochemical workstation in the frequency range of 100 kHz-0.1 Hz. Additionally, cyclic voltammetry (CV) measurements were performed on a Li-Cu half-cell at a scan rate of 1 mV s⁻¹ within the voltage range of 3 to 0 V. CV measurements were also carried out on the Li-NCM523 cell at a scan rate of 1 mV s⁻¹ (scan range: 3-4.3 V). The Li-Al cell configuration involved a Li foil (φ 14 mm, 400 μ m) and Al foils (φ 16 mm), with LSV testing conducted at a rate of 1 mV s⁻¹. Tafel curve analysis was performed on Li-Li symmetric cells using a CHI660E electrochemical workstation, with a voltage range of -0.2 to 0.2 V and a scan rate of 1 mV s⁻¹.

Theoretical calculations: The highest occupied molecular orbital (HOMO) energy and lowest unoccupied molecular orbital (LUMO) energy of various components were calculated using density functional theory (DFT). All calculations were performed using the B3LYP DFT method combined with the VASP program.

Material Characterization: SEM observations were conducted using a Field Emission NANO SEM430, and X-ray photoelectron spectroscopy (XPS) analysis was performed using Thermo Fisher Scientific K-Alpha to characterize the morphology and chemical composition of the deposited lithium. Prior to analysis, the electrode was rinsed with DEC solvent thrice to eliminate any residual electrolyte and subsequently air-dried at room temperature. The ionic conductivity of the electrolyte was measured using a DDS307A instrument. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is used to detect the hybrid layer on the surface of the treated Li. The instrument model used is ToF.SIMS 5-100 and the sputtering time is 1000 seconds.

Supplementary Figures

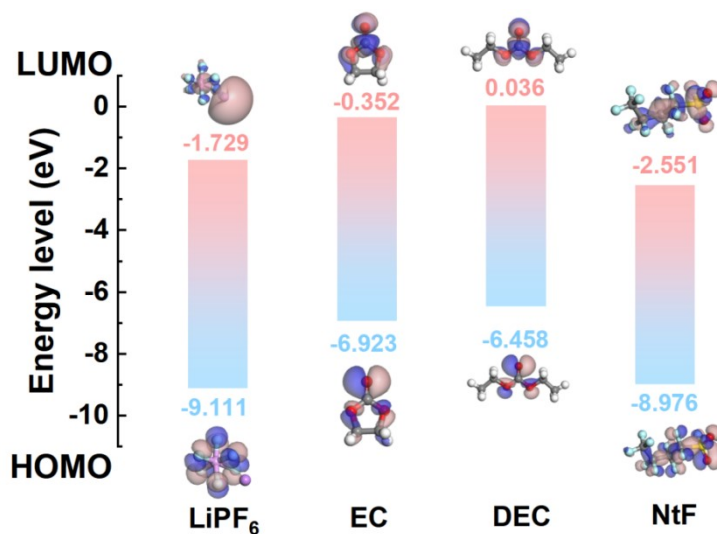


Fig. S1 HOMO and LUMO energies of LiPF₆, EC, DEC and NtF.

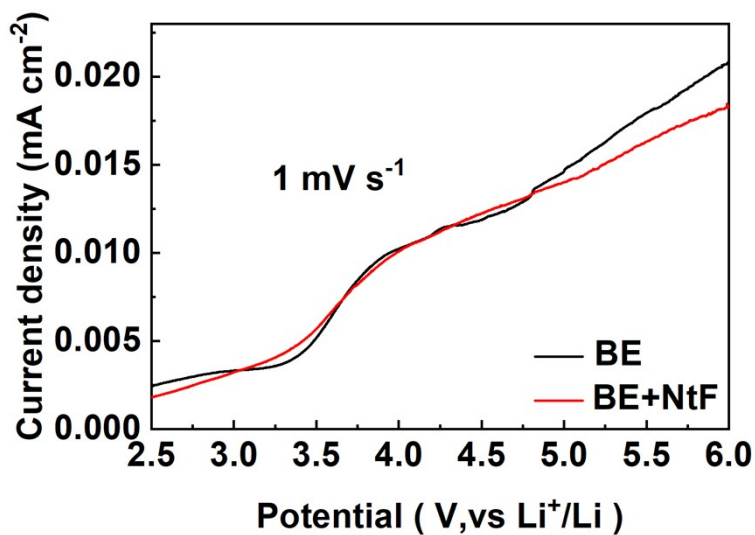


Fig. S2 LSV curves using different electrolytes. (Scan rate: 1 mV s⁻¹).

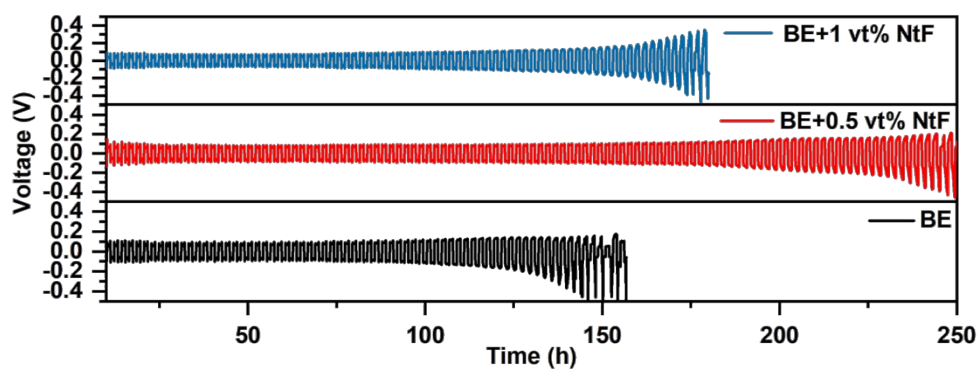


Fig. S3 Cycling performance of Li-Li symmetrical cells using BE with different concentrations of NtF (1 mA cm⁻², 1 mAh cm⁻²).

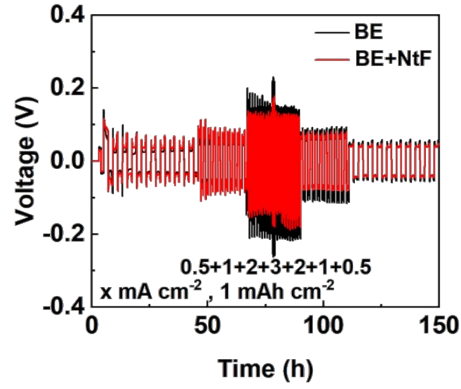


Fig. S4 Rate performance comparison of Li-Li symmetric cells using different electrolytes (The areal capacity is 1 mAh cm^{-2}).

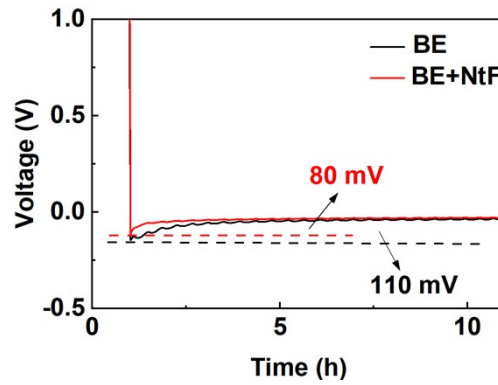


Fig. S5 Polarization curves of Li-Cu half-cells using different electrolytes.

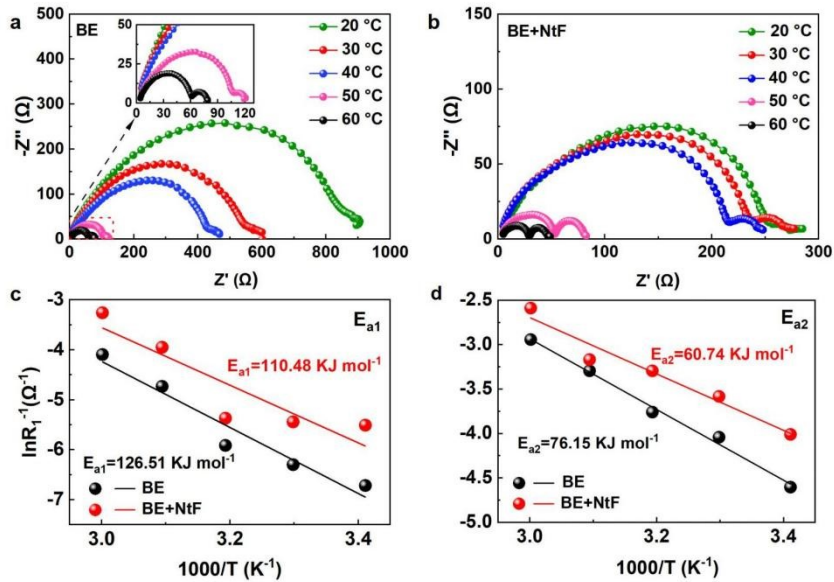


Fig. S6 (a and b) Nyquist plots of the Li-Li symmetric cells at different temperatures. (c and d) Arrhenius behavior and comparison of activation energies between the R1 and R2 derived in Nyquist plots of Li-Li symmetric cells.

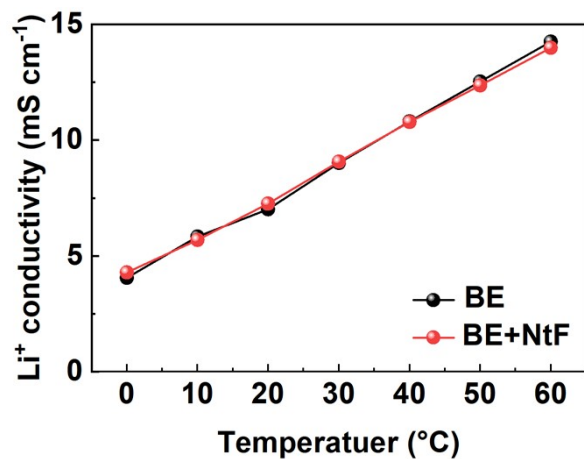


Fig. S7 Li⁺ conductivity of studied electrolytes under different temperatures.

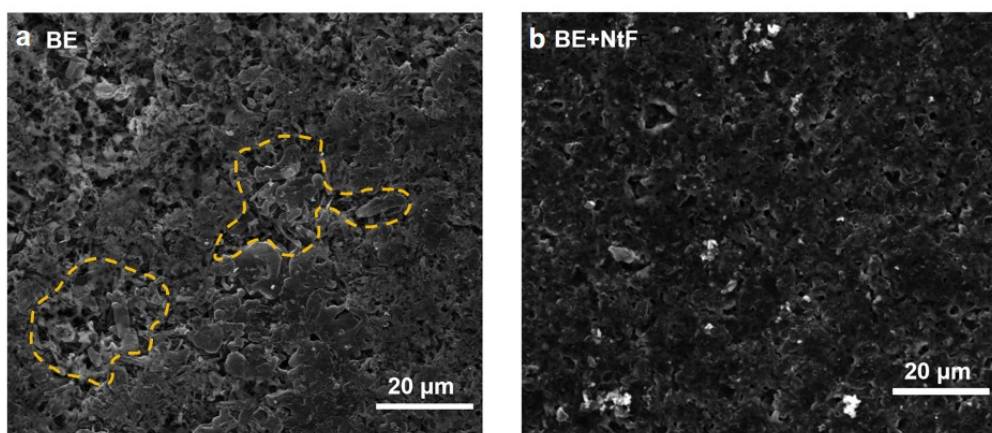


Fig. S8 SEM images of deposited Li using (a) BE and (b) BE + NtF (Deposition conditions are 0.5 mA cm⁻² for 3 mAh cm⁻²).

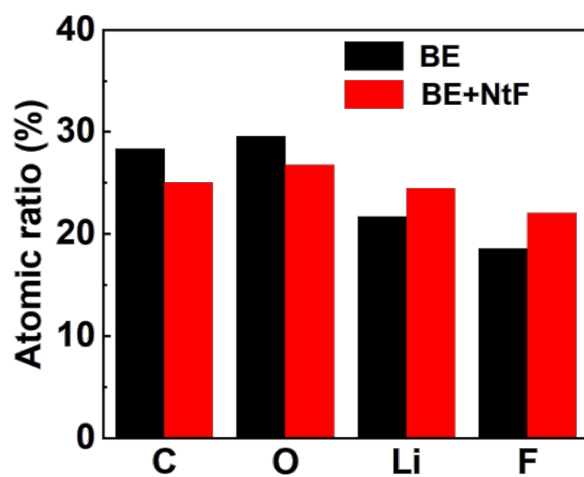


Fig. S9 XPS element distributions of cycled Li using different electrolytes.

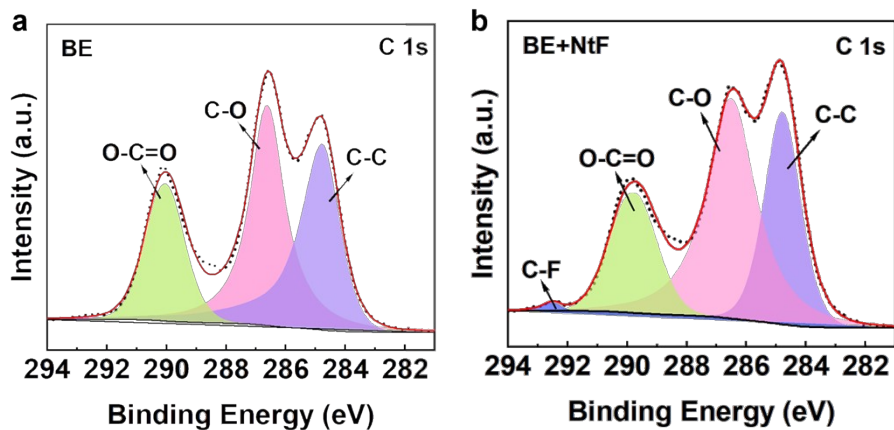


Fig. S10 XPS C 1s spectra of cycled Li using (a) BE and (b) BE + NtF (Cycling conditions are 1 mA cm⁻² and 1 mAh cm⁻² for 100 cycles).

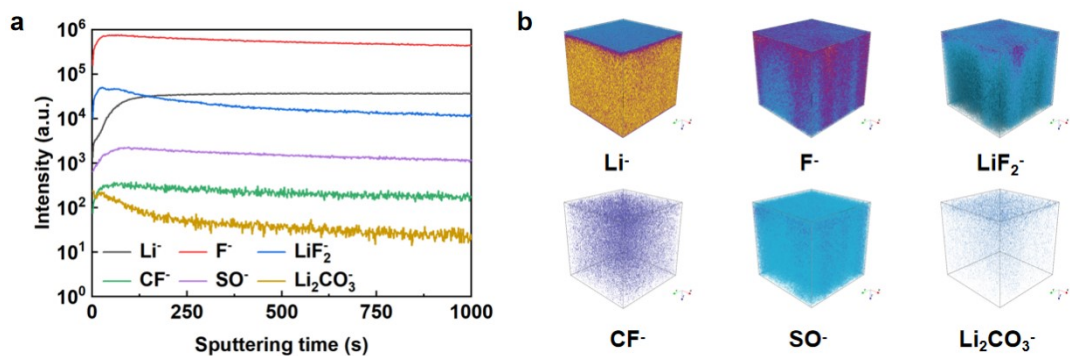


Fig. S11 (a) TOF-SIMS deep etching results of Li deposited with BE+NtF, and (b) the 3D compositional distribution (Deposition conditions are 0.5 mA cm⁻² for 3 mAh cm⁻²).

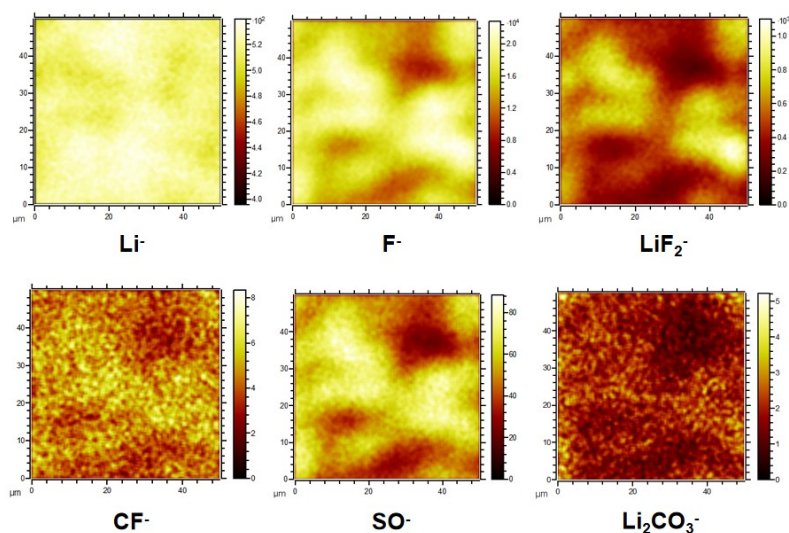


Fig. S12 TOF-SIMS deep sputtering cross-sectional image of Li deposited with BE+NtF (Deposition conditions are 0.5 mA cm⁻² for 3 mAh cm⁻²).

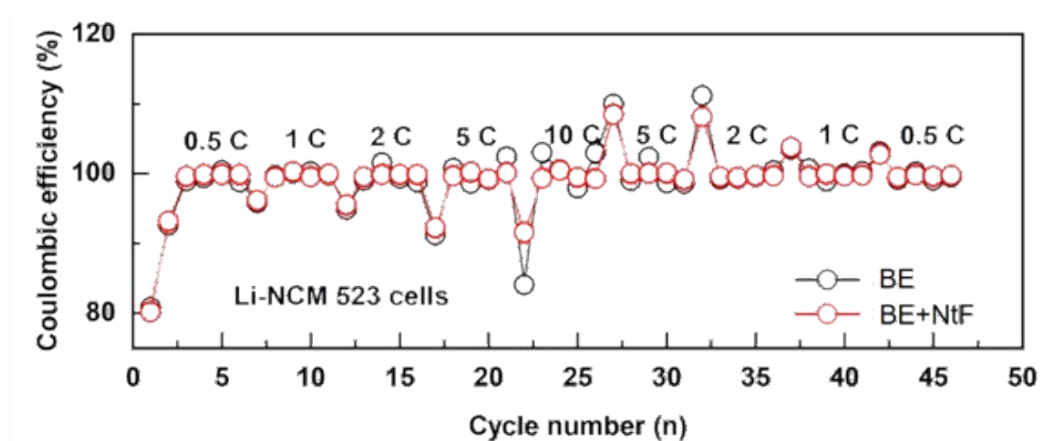


Fig. S13 The corresponding CE of Li-NCM523 cells in rate tests with different electrolytes.

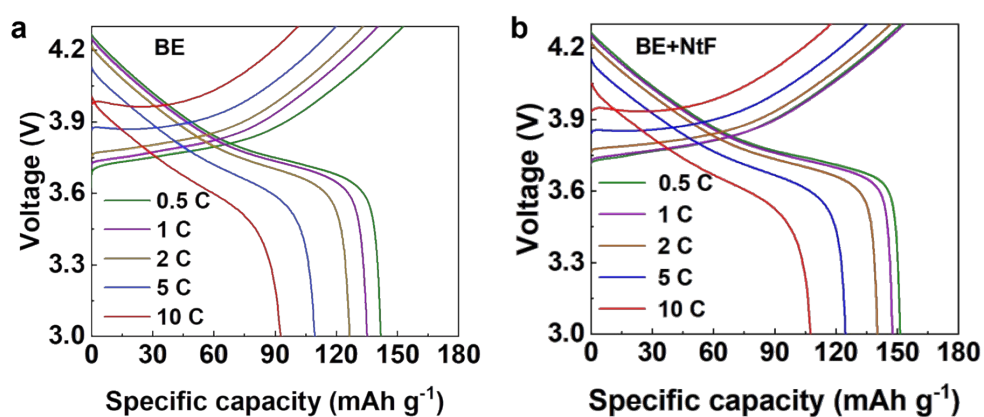


Fig. S14 Voltage profiles of the Li-NCM523 cells cycled with different rates using (a) BE and (b) BE + NtF.

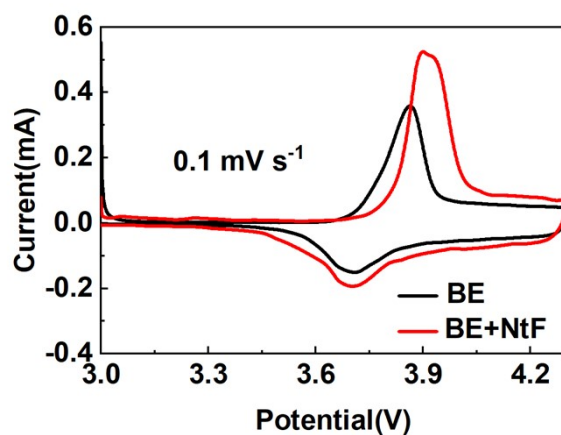


Fig. S15 CV curves of Li-NCM523 cells using different electrolytes.

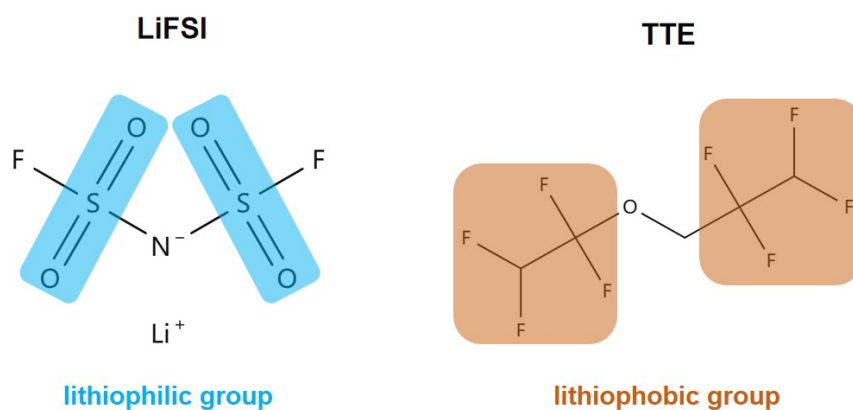


Fig. S16 The molecular formula of LiFSI and TTE.

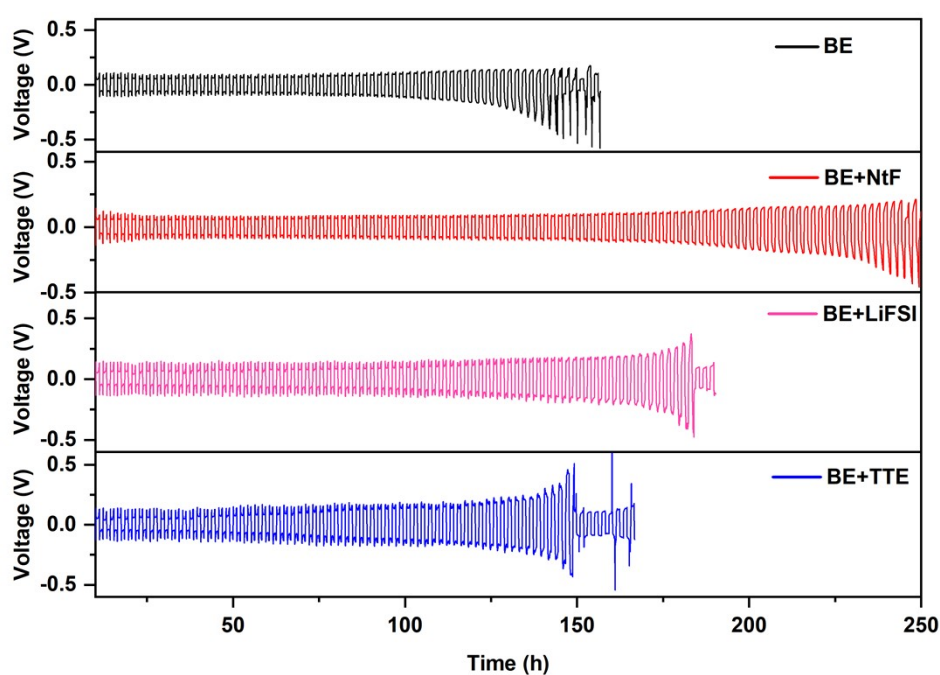


Fig. S17 Cycling performance of Li-Li symmetric cells using different electrolytes (1 mA cm^{-2} , 1 mAh cm^{-2}).

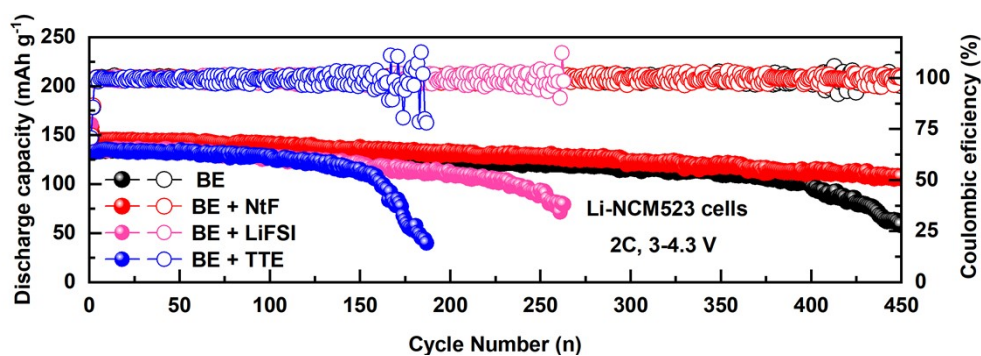


Fig.S18 Cycling performance of Li-NCM523 cells using different electrolytes.

Table S1. Performance comparison of LMBs using various additives.

| Additive | Electrolyte composition | LMA performance | Full cells performance | | Refs. |
|--|--|---|-----------------------------|---|----------|
| | | | Loading | performance | |
| pentafluorophenyl 4-nitrobenzenesulfonate (PFBNBS) | 1 M LiPF ₆ in EC/EMC + 1 wt% PFBNBS | Li-Li cell 1 mA cm ⁻² , 0.5 mAh cm ⁻² 250 h | 3 mg cm ⁻² | Li-NCM622 500 cycles 70.8% retention | 1 |
| isosorbide nitrate (ISDN) | 1M LiPF ₆ in FEC/DMC +0.3 M ISDN | Li-Li cell 1 mA cm ⁻² , 3 mAh cm ⁻² 200 h | 3.0 mAh cm ⁻² | Li-NCM523 Over 150cycles | 2 |
| flavone (FLA) | 1 M LiPF ₆ in EC/DMC + 1 wt% FLA | Li-Li cell 1 mA cm ⁻² , 1 mAh cm ⁻² 380 h | 5.0 mg cm ⁻² | Li-LNMO cell 200 cycles 91.2% retention | 3 |
| tris(4-fluorophenyl)phosphine (TFPP) | 1 M LiPF ₆ in EC/DMC + 1 wt% TFPP | Li-Li cell 1 mA cm ⁻² , 0.5 mAh cm ⁻² 400 h | 4 mg cm ⁻² | Li-NCM622 200 cycles 87.8% retention | 4 |
| tris(hexafluoroisopropyl) phosphate (THFP) | 1 M LiPF ₆ in PC/EMC/TEP + 2 wt% THFP | Li-Li cell 1 mA cm ⁻² , 0.5 mAh cm ⁻² 250 h | 3.5–4.5 mg cm ⁻² | Li-NCM622 200 cycles 82% retention | 5 |
| Li difluorophosphate (LiDFP) | 1 M LiPF ₆ in EC/DEC + 0.15 M LiDFP | Li-Li cell 1 mA cm ⁻² , 1 mAh cm ⁻² 200 h | 9.7 mg cm ⁻² | Li NMC cell Over 100 cycles | 6 |
| Nonafluorobutanesulfonyl fluoride (NtF) | 1 M LiPF ₆ in EC/DEC + 0.5vt% NtF | Li-Li cell 1 mA cm ⁻² , 0.5 mAh cm ⁻² 400 h | 1.5 mg cm ⁻² | Li-NCM523 450 cycles, 68 retention | Our work |
| | | | 20.8 mg cm ⁻² | Li-NCM523 Full cell over 100 cycles | |

References

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