Electronic Supplementary Material (ESI) for Energy Advances.

Support Information

Realizing a high voltage lithium metal battery in ether-based electrolyte by regulating the cathode electrolyte interphase

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AUTHOR INFORMATION

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Experimental Section

Materials. Commercially available tetrahydrofuran (THF) (purity: >99.9%, J&K Scientific), lithium nitrate ($LiNO_3$) (purity: >99.99%, Sigma-Aldrich), and lithiumbis(fluorosulfonyl)imide (>98%, TCI) were used without further treatment. $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ electrode (areal density: 15 mg cm^{-2}, nominal specific capacity: 185 mAh g^{-1}) and $LiFePO_4$ electrode (areal density: 16.88 mg cm^{-2}, nominal specific capacity: 155 mAh g^{-1}) were provided from Tianjin EV Energies Co., Ltd (JEVE). The lithium foil with a thickness of 50 μm was used as anode and Celgard film coated with Al_2O_3 was used as the separator.

Electrolyte Preparation. The preparation of the four electrolyte solutions was carried out in a glove box filled with Ar (MIKROUNA, H_2O< 0.1 ppm, O_2< 0.1 ppm).

Electrolyte formulations used in this work

Electrolyte nomenclature	formulation
THF Ele.	1 m LiFSI in 0.9 mL THF
+0.25 M $LiNO_3$ Ele.	1 m LiFSI + 0.25m $LiNO_3$ in 0.9 mL THF
+0.5 M $LiNO_3$ Ele.	1 m LiFSI + 0.5 m $LiNO_3$ in 0.9 mL THF
+1M $LiNO_3$ Ele.	1 m LiFSI + 1 m $LiNO_3$ in 0.9 mL THF

Characterizations and electrochemical tests. Coin 2032 type cells were assembled in glovebox to test the electrochemical properties. Galvanostatic discharge-charge measurement was carried out on LAND battery test system (Land CT3002A). Electrochemical workstation (CHI 760E) is used to collect EIS spectra. The surface information of anode and cathode were collected by an X-ray photoelectron spectrometer (XPS, Escalab 250Xi, ThermoFisher Scientific) using monochromatic Al Kα X-rays as excitation sources. The morphology and structure of the electrode were characterized by a focused ion beam-scanning electron microscope (FIB-SEM, Crossbeam340, Carl Zeiss AG) and a high-resolution transmission electron microscope (HRTEM, Talos F200 X, FEI). Raman spectra were collected on a confocal Raman spectrometer (alpha300 R, WITec) with 532 nm excitation wavelength in the range of 50-3600 cm^{-1}.

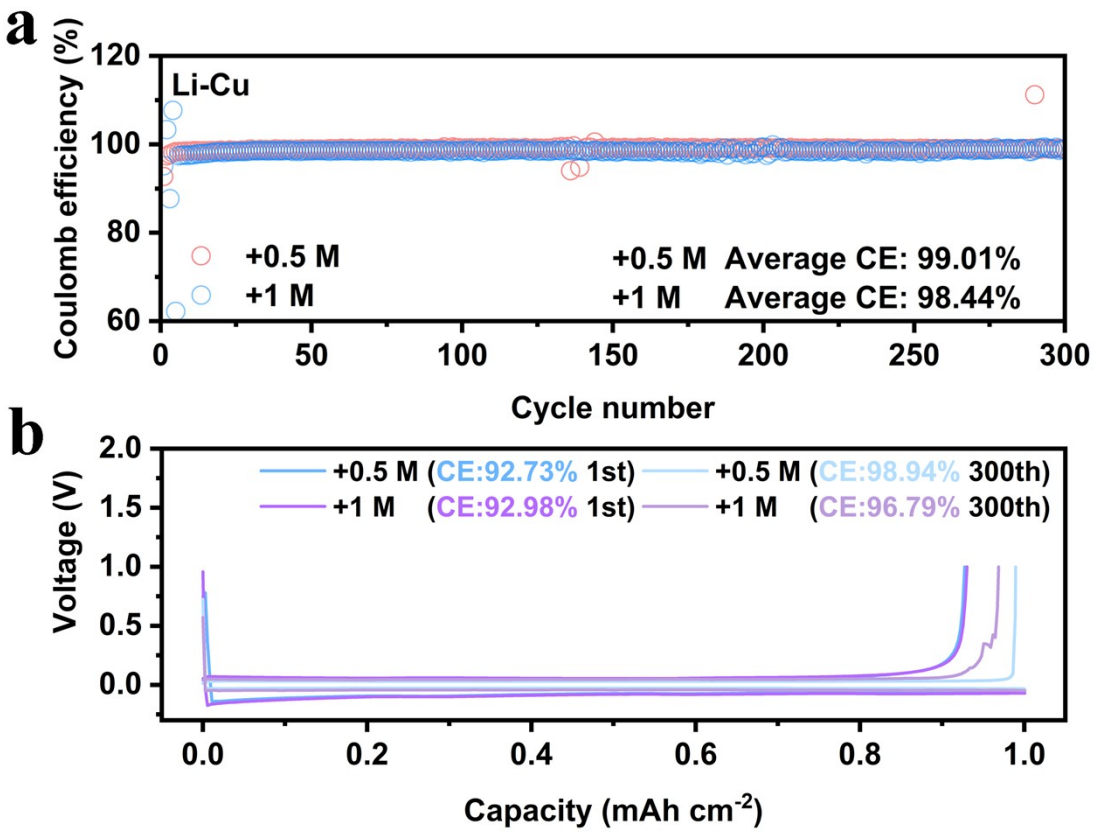

Fig. S1. (a) Long-term cycle performance of Li‖Cu electrochemical cells and (b) corresponding charge-discharge curves of different cycles in +0.5 M and +1 M $LiNO_3$ electrolyte at 0.5 mA cm^{-2}.

Table S1: **Coulombic efficiencies (CE) of Li||Cu batteries with carbonate electrolytes with $LiNO_3$ addition**

Electrolytes	CE
1 M $LiPF_6$ EC/DEC with 0.5 M $LiNO_3$ and 10mM $In(Otf)_3$	98.1%[1]
1.0 M $LiPF_6$ in EC/DEC with 0.2 wt.% CuF_2 and1.0 wt.% $LiNO_3$	98.1%[2]
1 M $LiPF_6$ in EC/DMC (1:1 vol.) with 5wt% $LiNO_3$ and 0.5wt% $Sn(Otf)_2$	98.4%[3]
1 M $LiPF_6$ in FEC/EMC (3:7 vol.) with 3 wt% $LiNO_3$ and 1 wt% TPFPB	98.5%[4]

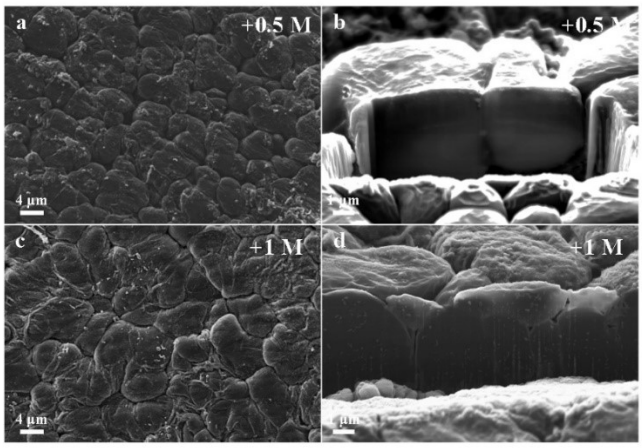

Fig. S2. Focused ion beam scanning electron microscope (FIB-SEM) images of lithium deposited in (a), (b) +0.5 M and (c), (d) +1M $LiNO_3$ electrolytes.

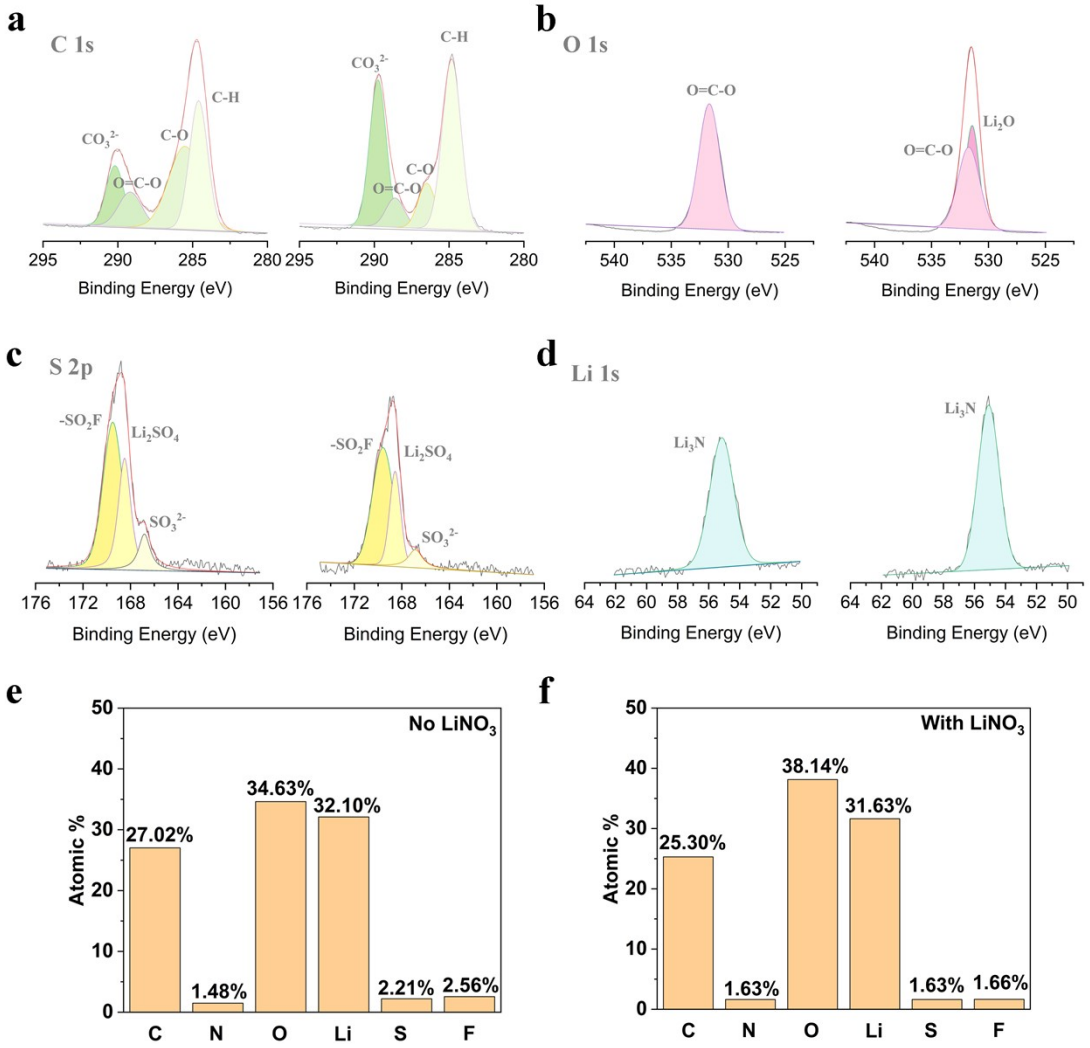

Fig. S3. The XPS spectrum of (a) C 1s, (b) O1s, (c) S 2p and (d) Li 1s of the SEI layer in THF electrolyte and +0.25 M $LiNO_3$ electrolyte. (e), (f) Atomic surface concentrations of two types of cathodes.

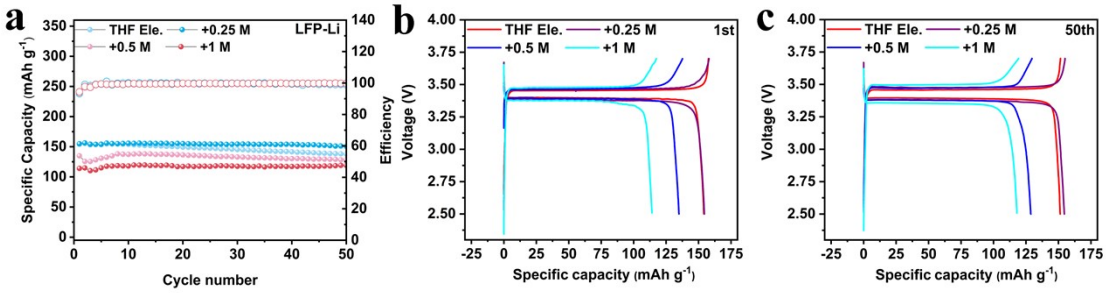

Fig. S4. (a) Long-term cycle performance of Li‖LFP battery with different electrolytes at 0.2 C rate. The charge-discharge curves of the corresponding (b) 1st and (c) 50th cycle.

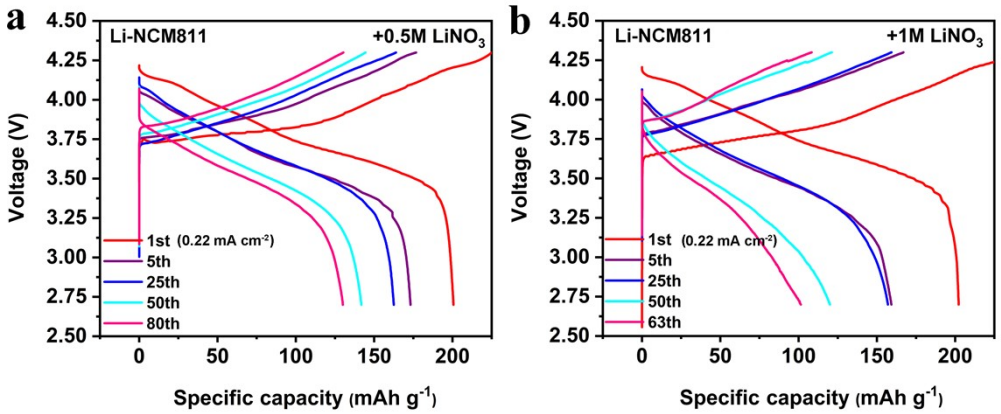

Fig. S5. The charge-discharge curves of Li‖NCM811 battery with (a) 0.5 M and (b) 1 M $LiNO_3$ electrolytes at 0.2 C rate.

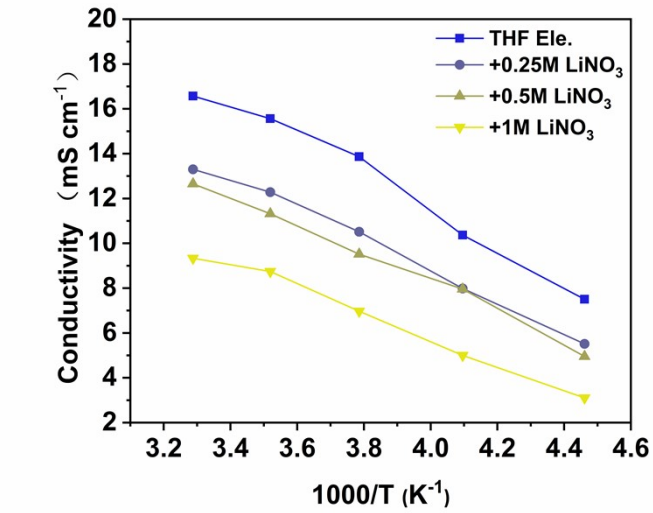

Fig. S6. Ionic conductivity of different electrolytes.

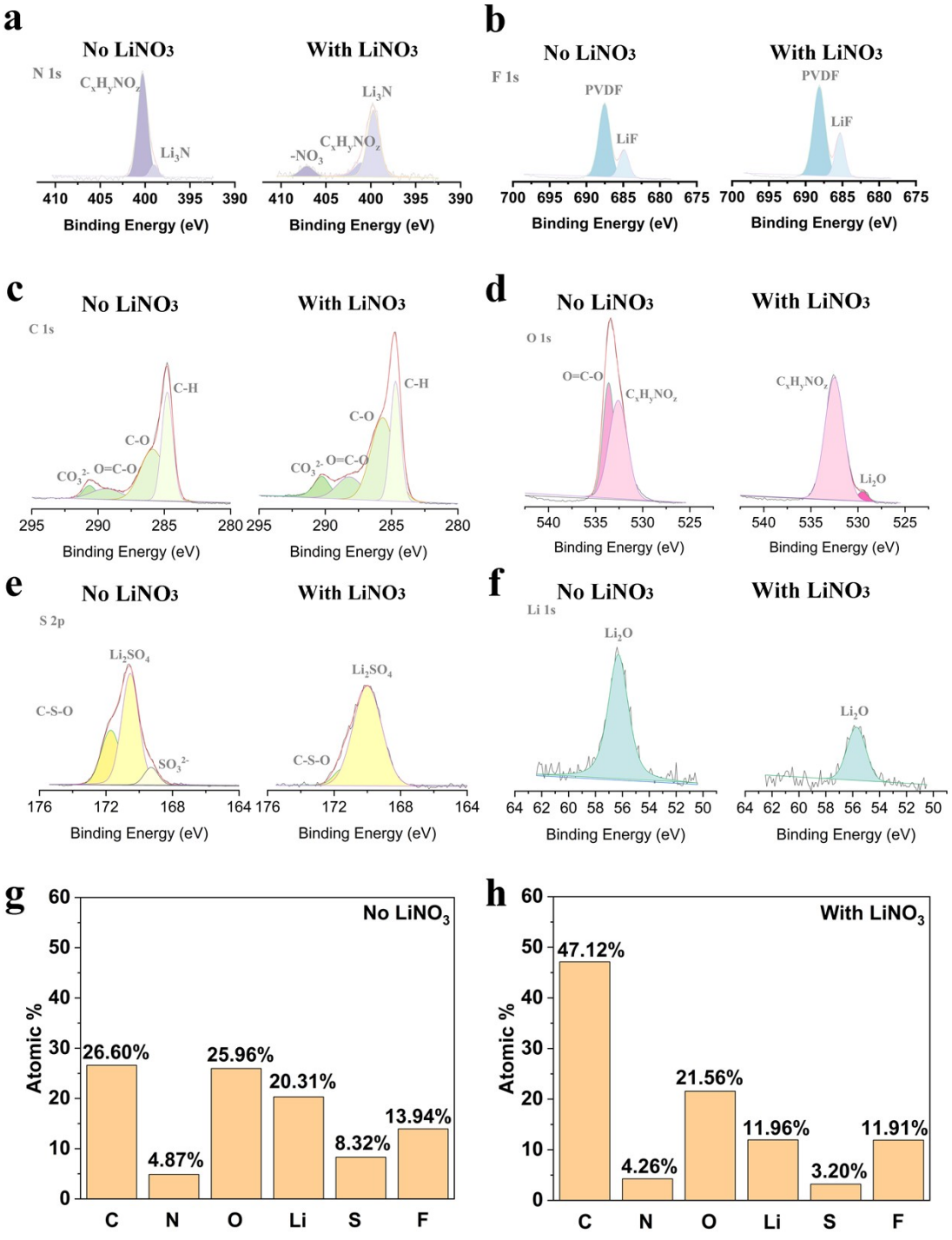

Fig. S7. The XPS spectrum of (a) N 1s, (b) F1s, (c) C 1s, (d) O 1s (e) S 2p and (f) Li 1s of the CEI layer in THF electrolyte and +0.25 M $LiNO_3$ electrolyte. (g), (h) Atomic surface concentrations of two types of cathodes.

References:

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