Supporting Information

A low-concentration all-fluorinated electrolyte for stable lithium metal batteries

Jisheng Mo,[a†] Yiqing Yao,[a†] Chen Li,[a] Hanxu Yang,[a] Haiwen Li,[c] Qingan Zhang,[ab] Zhipeng Jiang[*ab] and Yongtao Li[*ab]

[a] School of Materials Science and Engineering & Low-Carbon New Materials Research Center, Anhui University of Technology, Maanshan 243002, China

[b] Key Laboratory of Green Fabrication and Surface Technology of Advanced Metal Materials of Ministry of Education, Anhui University of Technology, Maanshan 243002, China

[c] Hefei General Machinery Research Institute, Hefei 230031, China

[†] These authors contributed equally to this work.

[*] Corresponding author.
E-mail: jzp1994@ahut.edu.cn; liyongtao@ahut.edu.cn

Experimental section

Materials. lithium hexafluorophosphate ($LiPF_6$, 99.9%), lithium difluorosulfonimide (LiFSI, 99.9%), fluoroethylene carbonate (FEC, 99%), ethylene carbonate (EC, 99%), diethyl carbonate (DEC, 99%) were purchased from Dodo chem. 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE, 99%) was bought from innochem. $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), and superconducting carbon black conductive agent (Super P) were ordered from the Kelude website. Polyvinylidene fluoride (PVDF) was purchased from Aladdin Technology Co., Ltd. Li foil (φ 14 mm, 400 μm, China Energy Lithium Co., Ltd.), Cu foil (12 μm, Shenzhen Jingliang Copper Industey Co., Ltd.), carbon-coated Al foil (8 + 2 μm, Shenzhen Kejing Star Technology Co., Ltd.), separator (Alumina Ceramic Diaphragm 16 + 4 μm). Commercial NCM622 electrode were purchased from Guangdong Canrd New Energy Technology Co., Ltd. (20.8 mg cm^{-2}). All these materials used without further purification.

Electrolyte Preparation. LCAFE was prepared by dissolving 0.5 M LiFSI in 1 ml mixed solvent of FEC and TTE with the volume ratio of 1: 1. The convention carbonate electrolyte is 1 M $LiPF_6$ in EC/DEC (v/v = 1: 1). Besides, 0.5 M LiFSI in pure FEC, and 1 M LiFSI in pure FEC were prepared as the control groups.

Characterizations. Raman spectra were obtained using HORIBA LabRAM HR Evolution. Conductivity was obtained using DDS-307A. Disassemble the cycled Li-Cu cells, the Cu foil was washed with DEC and dried in an Ar-atmosphere glovebox. NANO SEM430 field emission SEM system was employed to observe the morphologies of the deposited Li. XPS was conducted with Thermo Fisher Scientific K-Alpha. The Li-NCM622 cells were charged to 4.3 V and then dissembled. The cathode was washed with DEC and dried in an Ar-atmosphere glovebox. To characterize the CEI formed after cycling, transmission electron microscopes were obtained using F200X. The contact angle was measured using JY-82B Kruss DSA.

Electrochemical Tests. Li-Cu, Li-NCM622 and Cu-NCM622 cells were fabricated in CR2032-type coin cells with 40 μL of electrolyte for electrochemical tests. The electrochemical performance of the CR2032-type coin cells was conducted on the LANHE CT3002A battery test instrument at 25 °C. Li-Cu half cells were constructed using a Cu foil (φ 16 mm) and a Li foil (φ14 mm, 400 μm). The NCM622 cathode was prepared by slurrying NCM622 powder, Super P, and PVDF in an 8: 1: 1 weight ratio in NMP solution, and then coating on the carbon-coated Al foil. After overnight drying at 60 °C in a vacuum, electrodes with areal mass loadings of 2~3 mg cm^{-2} were obtained. Li-NCM622 cells were assembled by an NCM622 cathode (φ 8 mm, 2.5 mg cm^{-2}) and a Li foil (φ 14 mm, 400 μm, 80 mAh cm^{-2}) using various electrolytes (40 μL) for rate and long-term cycling tests. Cu-NCM622 anode-free cells were assembled by a commercial NCM622 cathode (φ 12 mm, 20.8 mg cm^{-2}) and Cu foil (φ 16 mm) for using various electrolytes (20 μL) cycling test. The above Li/Cu-NCM622 cells are galvanostatically cycled between 3 and 4.3 V. Linear sweep voltammetry (LSV) plot was tested by the CHI660E electrochemical workstation with a scan rate of 1 mV s^{-1}. Electrochemical impedance spectrometry (EIS) (100 kHz to 0.1 Hz) was conducted using the CHI660E with a voltage amplitude of 5 mV, and the cycled Li-NCM622 cells need to be rested 10 min to obtain a steady voltage before EIS tests.

Supplementary Figures

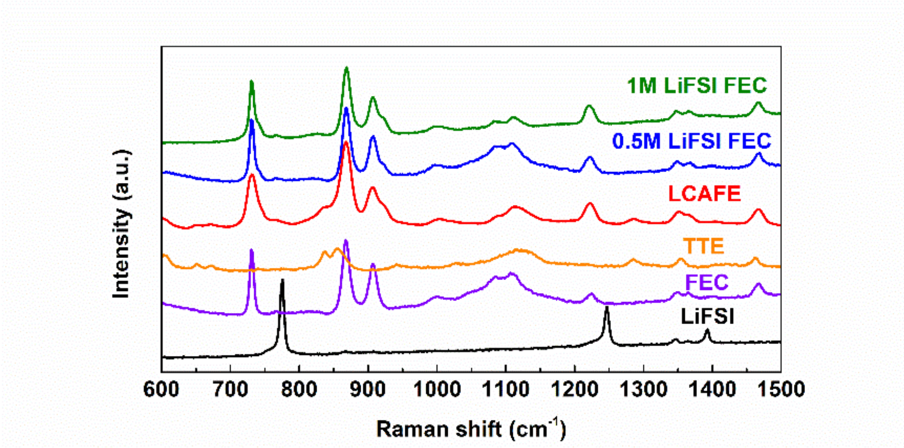

Fig. S1 Raman spectra of various solvent systems.

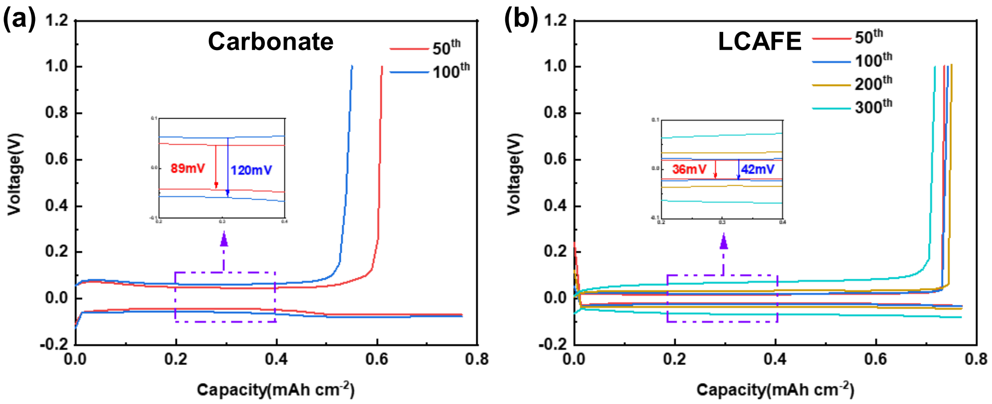

Fig. S2 Voltage response curves of Li-Cu cells in different electrolytes. (a) carbonate electrolyte and (b) LCAFE.

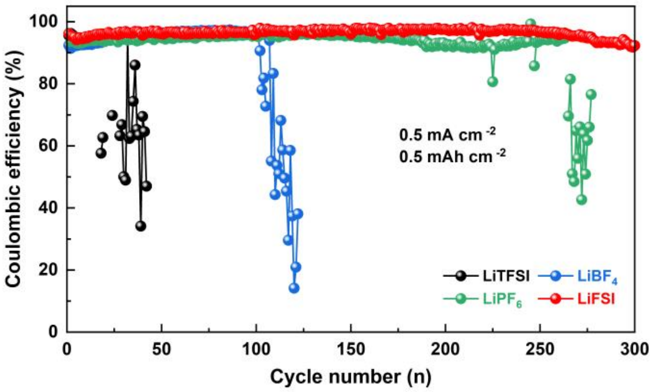

Fig. S3 Li-Cu half cell tests of various LCAFEs with different Li salts.

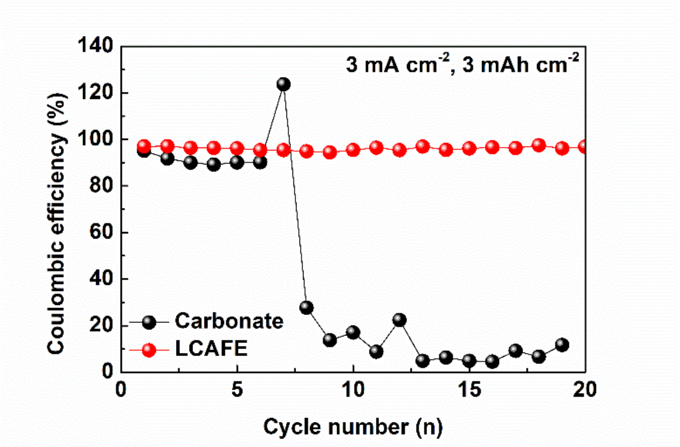

Fig. S4 CE tests using different electrolytes under the conditions of 3 mA cm^{-2}, 3 mAh cm^{-2}.

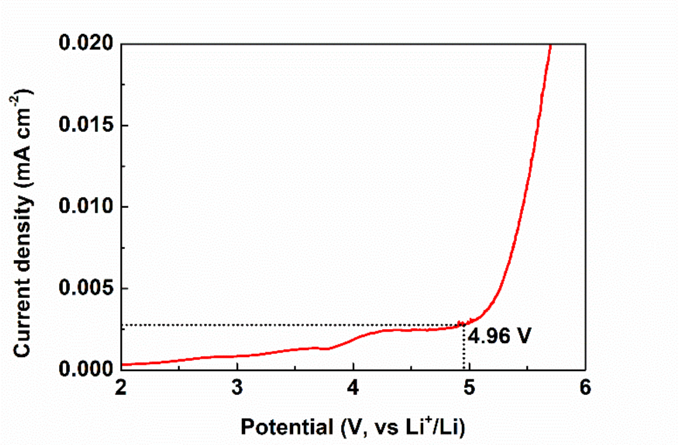

Fig. S5 LSV plot of LCAFE (Scan rate: 1 mV s^{-1}).

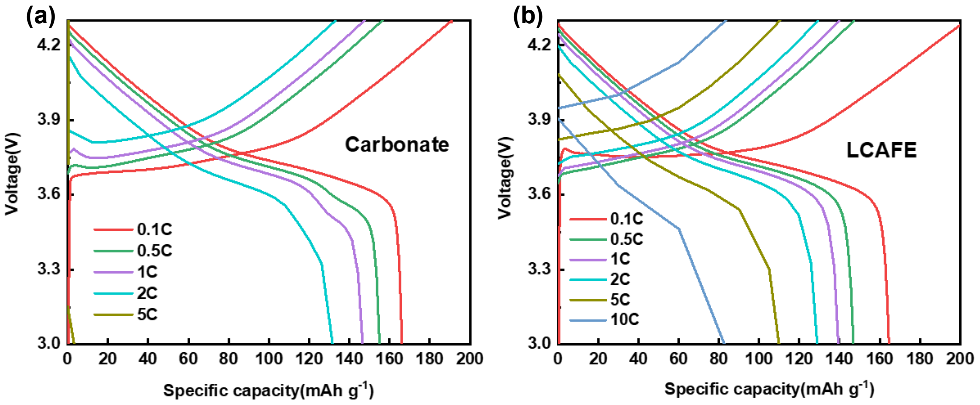

Fig. S6 Charge-discharge curves of rate tests of Li-NCM622 cells using (a) carbonate electrolyte and (b) LCAFE.

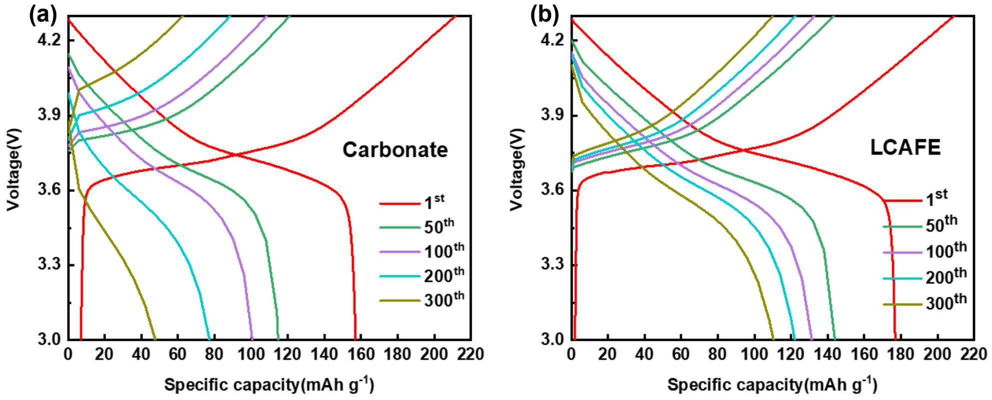

Fig. S7 Charge-discharge curves of long-term cycling tests of Li-NCM622 cells using (a) carbonate electrolyte and (b) LCAFE.

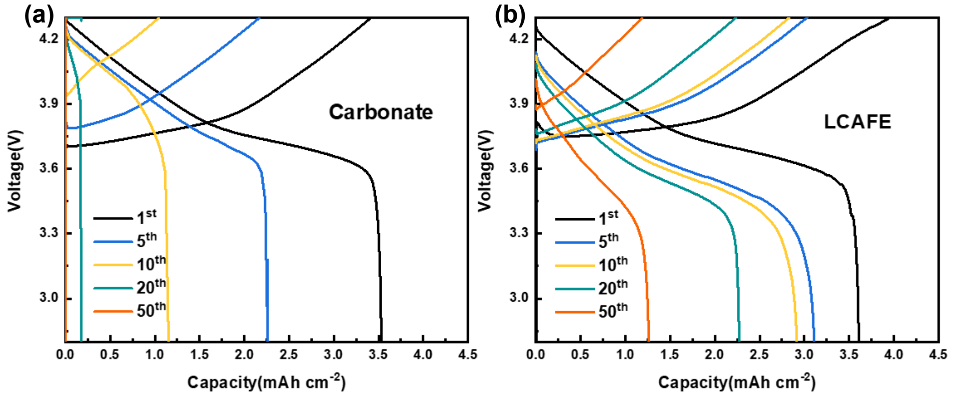

Fig. S8 Charge-discharge curves of Cu-NCM622 anode-free cell cycling tests using (a) carbonate electrolyte and (b) LCAFE.

Supplementary Tables

Table S1. Comparison of Li^+ conductivity of various electrolytes at room temperature.

Electrolytes	**Li^+ conductivity**
LCAFE	3.76 ms cm^{-1}
0.5M LiTFSI in FEC: TTE=1:1	2.60 ms cm^{-1}
0.5M $LiBF_4$ in FEC: TTE=1:1	11.60 µs cm^{-1}
0.5M $LiFP_6$ in FEC: TTE=1:1	3.67 ms cm^{-1}
0.5M LiFSI in FEC	4.45 ms cm^{-1}
1M LiFSI in FEC	5.60 ms cm^{-1}
Carbonate electrolyte	7.77 ms cm^{-1}

Table S2. Fitted results of the R_e, R_{sei} for Fig 3c-d.

Electrolyte	**R_e(Ω)**	**R_{sei} (Ω)**
Carbonate 0th	5.194	450.806
Carbonate 1st	3.848	515.952
Carbonate 10th	7.211	221.389
Carbonate 100th	4.305	54.875
Carbonate 200th	5.153	355.147
LCAFE 0th	5.394	345.606
LCAFE 1st	5.981	260.819
LCAFE 10th	6.214	128.186
LCAFE 100th	8.788	118.512
LCAFE 200th	5.447	161.853