Electronic supplementary information

Fluorinated carboxylate ester-based electrolyte for lithium ion batteries operated at low temperature

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Experimental Section

1. Fabrication of Electrodes and Assembly of cell

Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) salt and ETFA solvent were provided by Aladdin. The commercial standard electrolyte 1M $LiPF_6$ in EC/DMC/DEC (1/ 1/ 1, in volume) was purchased from Capchem company. For the ETFA electrolyte, 1.435 g LiTFSI was dissolved into 10 g ETFA solvent. All solvents and salt were storied and handled in a glove box filled with ultrahigh purity argon with O_2 and H_2O level <1 ppm.

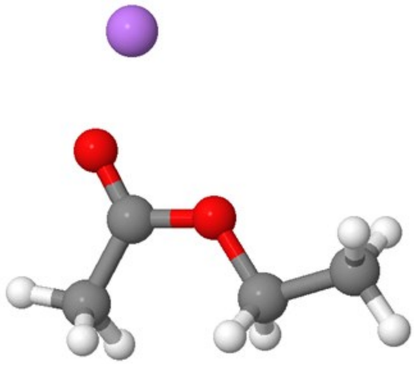
The intercalation compounds (LMO, NMC and LTO) electrode was prepared by coating the mixture of 80% active material,10% conductive carbon (super-P) and 10% PVDF on Al/Cu current collector, and then the samples were dried in a vacuum oven overnight at $80^{o}C$ and then roll-pressed. The mass loading of active material was about 2-4 mg cm^{-2} for intercalation compounds electrodes with the area of 1.13 cm^2. Lithium self-battery were constructed using these intercalation compounds electrodes, a foil of Li metal anode, one piece of Celgard 2400 poly-propylene membrane as the separator and the prepared electrolytes. The full cell was fabricated with LMO and NMC electrodes as cathode, LTO electrode as anode. All cell assembly was done under an argon atmosphere.

2. Electrochemical investigation

The freezing point of the ETFA electrolyte was measured by differential scanning calorimetry (DSC) with a DSC 2003 F3 Maia (NETZSCH, Germany). Viscosity of the different electrolytes at low temperatures were obtained with rotational viscosity test with a rotary rheometer HAAKE MARS III (Thermofisher, USA). The ionic conductivities of the electrolyte at different temperatures were calculated based on the electrochemical impedance spectroscopy measurements with two titanium plate electrodes (1*1 cm^2) symmetrically placed in the electrolyte solutions. The applied frequency range was set within 100 kHz to 0.01 kHz with an AC amplitude of 5 mV. Cyclic voltammetry was investigated with a three-electrode system at the scan rate of 0.5 mV s^{-1} to measure the electrochemical stable potential window, in which Cu foil/Al foil was applied as the working electrode, two Li plates were used as counter and reference electrode, respectively.

Charge/discharge performance of the well-prepared rechargeable battery based on intercalation compounds were measured using CR2016 coin cells on a Landt CT 2001A battery cycler controlled by a computer. The NMC||Li cells were charged/discharged with a rate of 0.05C for initial three cycles, and then cycled at 0.2C rate. For the low temperature performance test, cells were transferred into a low-temperature chamber (MEILING biology & medical), kept under -40^{o}C, -50^{o}C, -60^{o}C and -70^{o}C for at least 2 h, and then charged/discharged under these temperatures.

Supplementary Figures



Li^+ - EA: -28.18 kJ mol^{-1}

Fig. S1 Molecule dynamics calculation of the binding energy of Li^+- EA solvent.

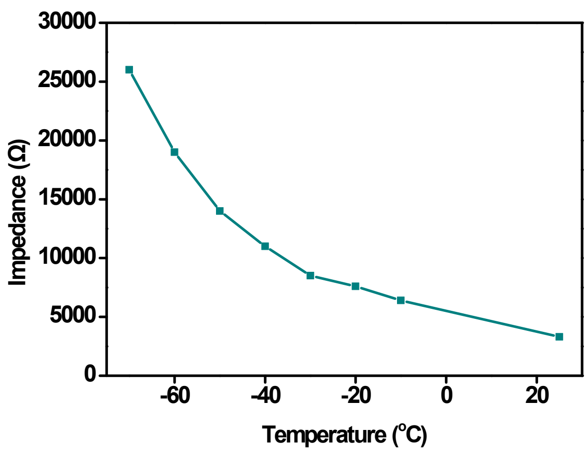


Fig. S2 Impedance at different temperatures of ETFA electrolyte evaluated through electrochemical impedance spectroscopy (EIS) measurement.

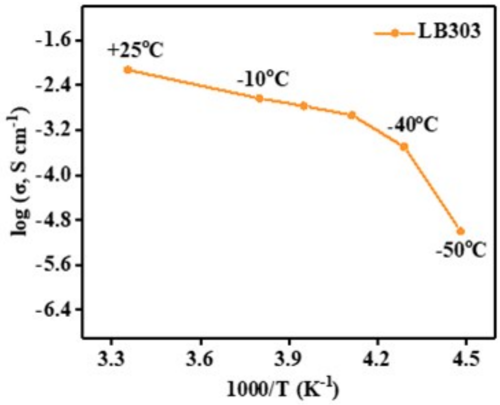


Fig. S3 Ionic conductivity of commonly used LB303 electrolyte at various temperatures.

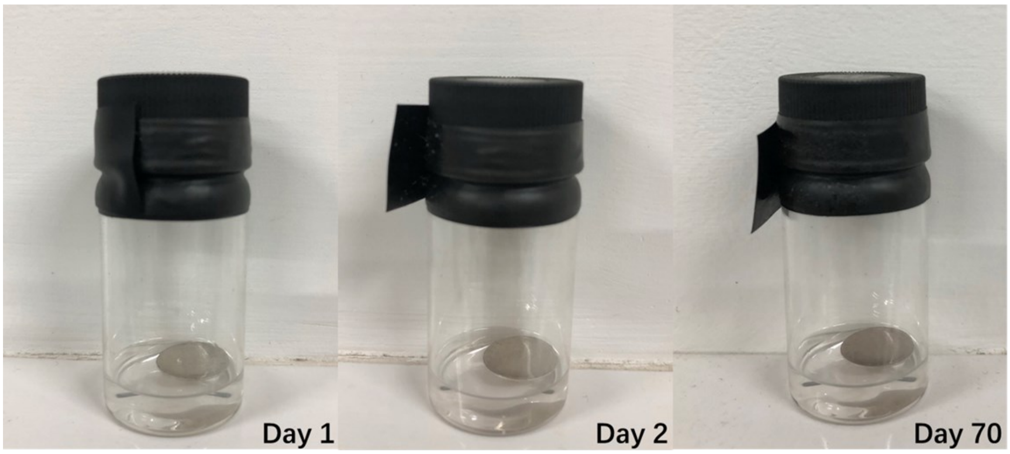


Fig. S4 Chemical stability of the ETFA electrolyte with Li metal tested through immersing Li metal in the electrolyte for days.

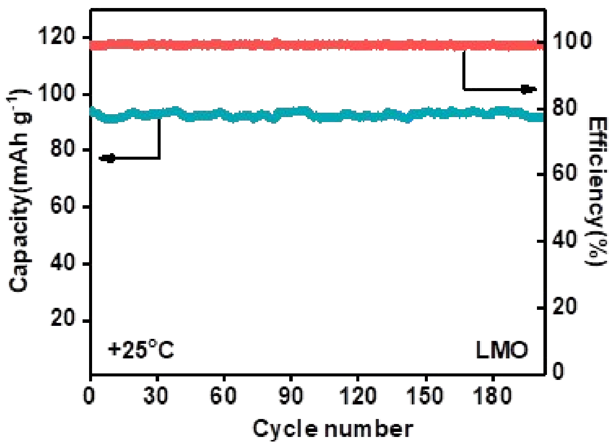


Fig. S5 Cycle performance of LMO||Li cell using ETFA electrolyte under 1C.

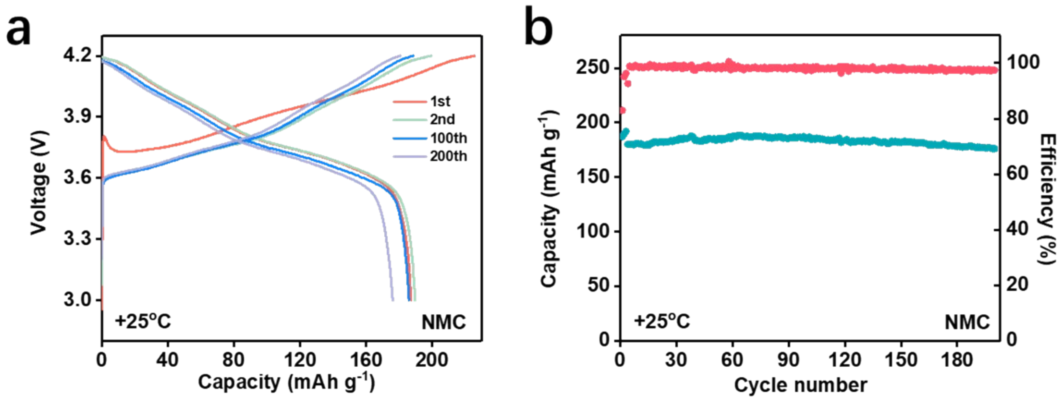


Fig. S6 (a) Voltage profiles as a function of cycle number of NMC||Li cells at 1st, 2nd, 100th and 200th cycle; (b) Cycle performance of NMC||Li cell using ETFA electrolyte. The cell was cycled at 0.2C after the first three cycles at 0.05C.

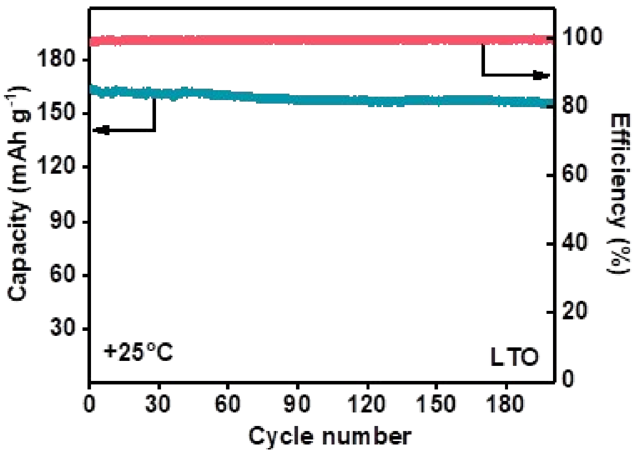


Fig. S7 Cycle performance of LTO||Li cell using ETFA electrolyte at 1C.

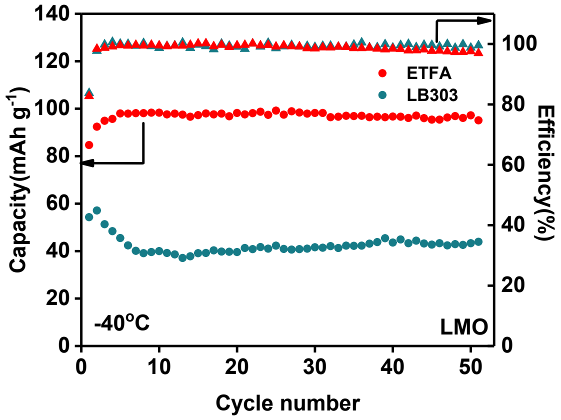


Fig. S8 Cycle performance of LMO||Li using different electrolytes under 0.05C at a low temperature (-40°C).

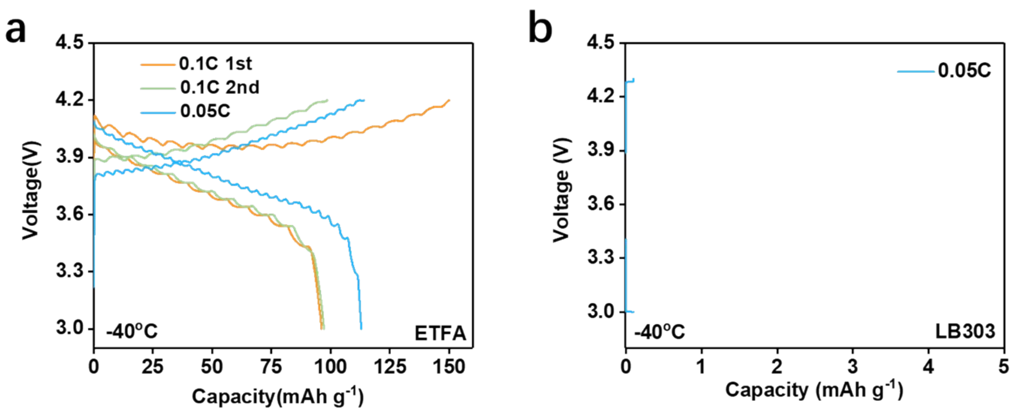


Fig. S9 Charge/discharge profiles of NMC||Li cells in (a) ETFA electrolyte and (b) LB303 electrolyte at -40°C.

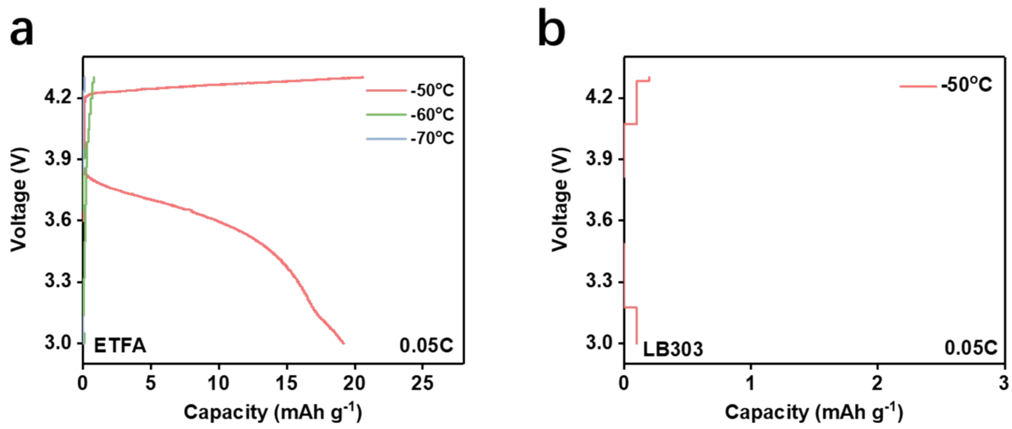


Fig. S10 Charge/discharge profiles of LMO||Li cells in (a) ETFA electrolyte and (b) LB303 electrolytes at various temperature.

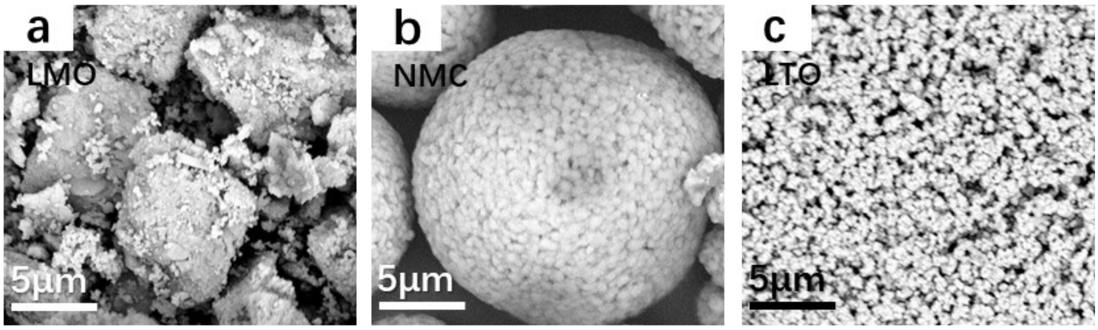


Fig. S11 SEM photograph of (a) LMO, (b) NMC and (c) LTO materials.

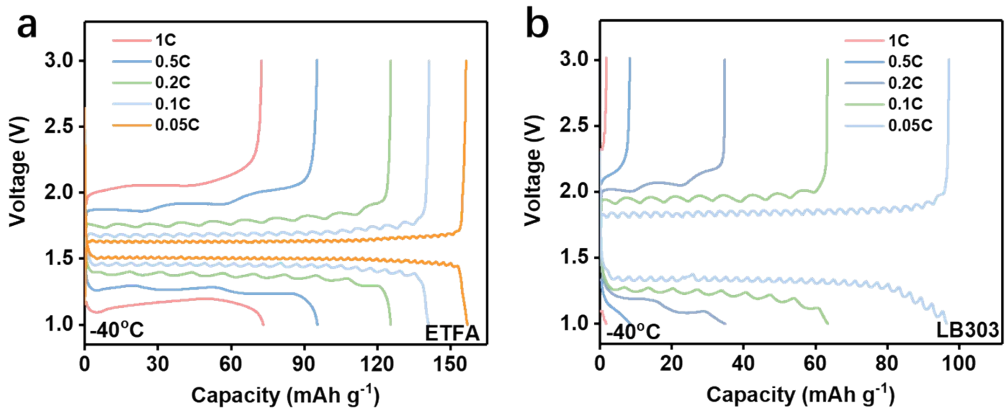


Fig. S12 Charge/discharge curves of LTO||Li cells in (a) ETFA electrolyte and (b) LB303 electrolyte at various rates at -40°C.

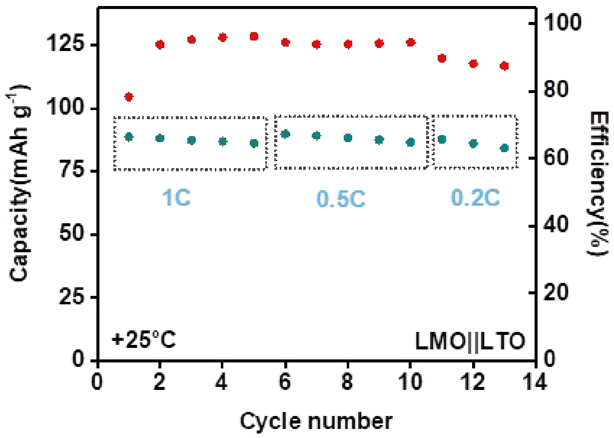


Fig. S13 Rate performance of the LMO||LTO full-cell using ETFA electrolyte at room temperature.

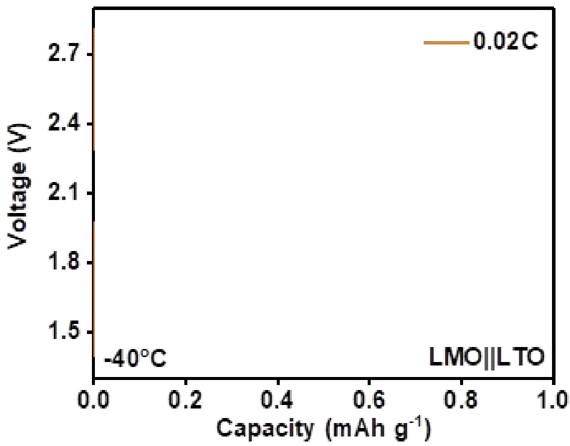


Fig. S14 Electrochemical performance of the LMO||LTO full-cell using LB303 electrolyte at -40°C.

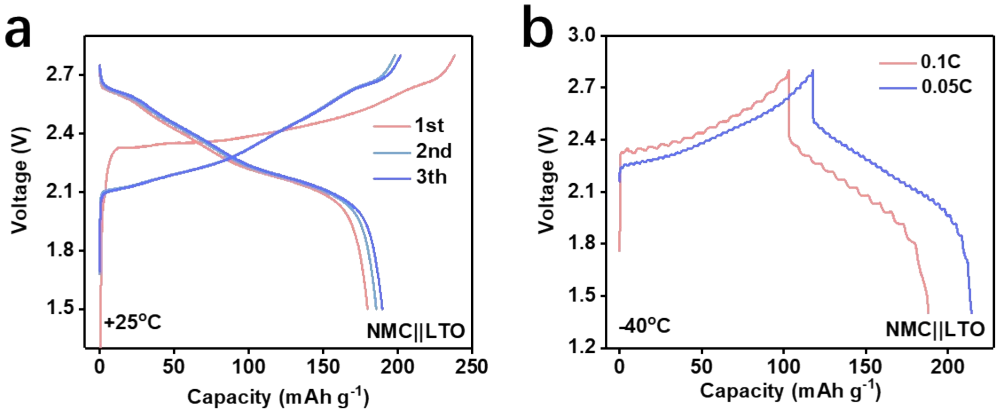


Fig. S15 Charge/discharge profiles of NMC||LTO full-cell using ETFA electrolyte at different C rates (1C = 200 mA g^{-1}) at (a) +25 °C and (b) -40 °C. The mass ratio of anode and cathode was set as 1.2: 1 (N/P = 1.1), and hereby the capacities were calculated based on the mass of cathode.

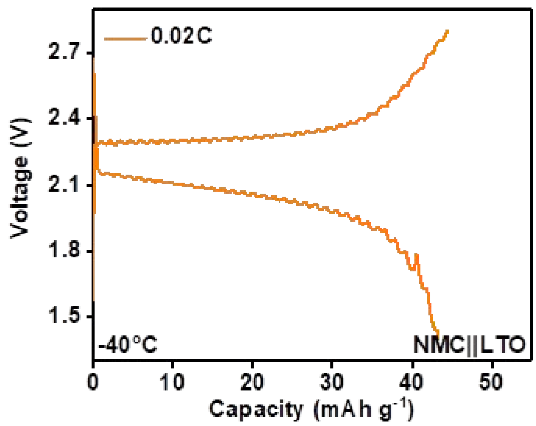


Fig. S16 Charge/discharge curves of the NMC||LTO full-cell using LB303 electrolyte at -40°C.

Table S1 Energy densities and power densities of the LMO||LTO full cells using ETFA electrolyte at room temperature and low temperature.

Temperature (^{o}C)	Current density (C rate)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})
+25	1	102	139
	0.5	106	71
	0.2	105	29
-40	0.05	80	7
	0.02	95	3

Table S2 Energy densities and power densities of the NMC||LTO full cells using ETFA electrolyte at room temperature and low temperature.

Temperature (^{o}C)	Current density (C rate)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})
+25	0.1	204	22
-40	0.1	85	20
□	0.05	102	10

The energy density and power density of the full-cells can be calculated based on the total mass of cathode material (LMO, NMC) and anode material (LTO), which can be obtained with Equation 1 and Equation 2 as follows:

$$E = \frac{Q \times m_{(cathode)} \times V}{m_{(cathode + anode)}}$$ (Equation 1)

$$P = \frac{I \times V}{m_{(cathode + anode)}}$$ (Equation 2)

Herein, E and P are the energy density and power density based on the total mass of LMO(NMC) cathode and LTO anode, respectively. Q is the discharge capacity of cathode material LMO(or NMC), V is the average voltage of the full-cell, I is the applied current, $m_{cathode}$ is the mass of cathode material (LMO, NMC) and $m_{cathode+anode}$ is the total mass of LMO (or NMC) cathode and LTO anode.