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Supporting Information

Stabilizing electrode-electrolyte interface for high-voltage Li||LiCoO₂ cells by dual electrolyte additives

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1.Experimental section

Materials

Lithium cobalt oxide (LCO) (98%) was purchased from Tianjin Guoan Mengguli New Materials Science&Technology Co.,Ltd, and used directly for all measurements without any processing. Trans-4,5-difluoro-1,3-dioxolan-2-one (DFEC) (99.9%), bis(2,2,2-trifluoroethyl) carbonate (TFEC) (99.9%), fluoroethylene carbonate (FEC) (99.9%) and lithium hexafluorophosphate (LiPF₆) (99.9%)were purchased from Duoduo-Chem. Tri-(trimethylsilyl) phosphite (TMSPi) (95%) was hased from Aladdin. All the chemicals and reagents were used without further purification.

Preparation of electrolyte and coin assembly: All operations are carried out under an Ar-filled glove box with an index of $O_2/H_2O < 1$ ppm. (1) EDV-base electrolyte: 1.0 M LiPF₆ salt was dissolved in blended ethylene carbonate (EC) and diethyl carbonate (DEC) solvents with a volume ratio of 3:7. Then, add 1 vol.% vinylene carbonates into above mixed solvent, and stir until transparent to obtain EDV electrolyte. (2) TFDT electrolyte (1 M): 1M LiPF₆ solution was prepared by bis(2,2,2-trifluoroethyl) carbonate (TFEC) as the main solvent and fluoroethylene carbonate (FEC) as the cosolvent (volume ratio: 4:1). Afterwards, equal volume of trans-4,5-Difluoro-1,3dioxolan-2-one (DFEC) and tri-(trimethylsilyl) phosphite (TP) was added into above solution to form a uniform and stable electrolyte. The LiCoO₂ electrode was obtained by coating the slurry of LiCoO₂ powders, acetylene black and poly (vinylidene difluoride) with a weight ratio of 8: 1: 1 in N-methyl-2-pyrrolidone solvent onto an aluminum current collector. Dry the slurry for 6 h at 80 °C and punch into disks with diameter of 12 mm. CR2025 coin cells with different electrolytes were encapsulated according to the sequence of cathode, separator, and anode in a glove box for further testing. The mass loading is about $2.5 \sim 5 \text{ mg cm}^{-2}$.

Electrochemical characterization: The voltage range was set to 3.0 - 4.60 V for the Li||LCO cells. An electrochemical workstation (Corrtest, CS3104, Wuhan) was used to evaluate the AC impedance, electrochemical stability window of the electrolyte, and

the oxidation-reduction behavior of Li||LCO cell. Linear sweep voltammetry (LSV) was carried out on a coin cell with a scan rate of 1 mV s⁻¹. The charge and discharge tests were operated by using LAND system. The Li||LCO cells were charged and discharged at 1/3 C and 1 C (1 C = 274 mA h g⁻¹) between 3.0 - 4.6 V to assess electrochemical performance. The cell was cycled at continuous 8 cycles with various currents of 0.1 C, 0.2 C, 0.33 C, 0.5 C, 1 C, 2 C, 5 C, 0.1 C respectively for rate capability.

Combustion test of the electrolyte: It is mainly conducted through two types of combustion experiments. (1) **Ignition tests:** In a typical measurement process, electrolyte was soaked into a porous nonflammable matrix, constant area glass fiber (1.5 cm * 6 cm). After holding the ignition for 6 s, the time was recorded until completely extinguished after removal of fire source. Time to ignition (TTI) and self-extinguishing time (SET) are used to measure the flammability of electrolyte. They are generally normalized to the mass and represented by s g^{-1} . (2) **Cone calorimeter experiment:** The sample is placed on the sample support of the loading table, and the outer surface is exposed to the thermal radiation of the conical heater with rated heat flow intensity of 25 kW m⁻². The volatilized combustible gas is ignited by an igniter after heated, and various parameters are obtained through the detector.

2. Materials characterization

Interface testing: A field-emission scanning electron microscope (SEM, JEOL-7100F) was used to observe the surface morphology of cathode and anode at an acceleration voltage of 10 kV. The high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F) was utilized to observe the CEI layer. The surface information of the produced samples was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The atomic force microscopy (AFM) is used to observe the appearance of the anode surface. The crystal structure of prepared samples was analyzed using the X-ray diffraction (XRD) technique, specifically employing a Bruker D8 Advance X-ray diffractometer with Cu K α radiation (2 θ from 10 to 80°).

DSC measurement: Differential scanning calorimetry (DSC) measurement were performed on a thermal analysis system (Simultaneous Thermal Analysis, STA449F3, NETZSCH). Delighted LiCoO₂ cathode with around 25 mg mass loading were retrieved from cells after charged to 4.6V vs. Li⁺/Li, and then repeatedly rinsed with dimethyl carbonate (DMC) for three times to absolutely remove the residual electrolyte. After overnight drying, the electrode powder was mixed with selected electrolyte solutions and placed into a 100 μ L high-pressure gold DSC capsule with a seal. The DSC profiles were recorded between 100 and 500 °C with a scan rate of 5 °C min⁻¹. An empty stainless-steel vessel was used as a reference in all tests. The calculated heat generation during the measurement is expressed in the manuscript with the unit J g⁻¹, and the latter part of which (g) refers to the mass of the active cathode materials.

Solvation structures characterization: Electrolyte solvation structures were characterized using nuclear magnetic resonance spectroscopy (NMR, Avance III HD 500 MHz). The ¹H NMR spectra were acquired in the case of deuterated acetone with TMS used as an internal reference.

Molecular dynamics (MD) simulations: The molecular dynamics (MD) simulations were conducted by using the Forcite package in Materials Studio. The COMPASS

forcefield was applied for the all simulations. The summation method of Ewald was set for describing the electrostatic and van der Waals interactions in the systems. The Nose themostat and Berendsen barostat were selected for controlling the temperature and pressure. All electrolyte supercells were firstly annealed with the temperature ranging from 300 to 500 K for 5 cycles. The obtained supercells were then pre-equilibrated by using the NPT ensemble with the time step of 0.5 fs and total time of 1000 ps. The supercells were further equilibrated by applying the NVT ensemble with the same time step and equilibrium time. The statistical analyses were performed at the second half of this equilibration process.

3. Supplementary figures



Fig. S1 XRD spectra of LCO from different electrolytes before and after cycling.



Fig. S2 Charge-discharge curves of Li $\|$ LCO cells with the TFDT electrolyte at 0.3 C

for the first and second cycle in the voltage range 3-4.6 V.



Fig. S3 Charge-discharge curves of Li||LCO cells with the EDV electrolyte at 0.3 C

for the first and second cycle in the voltage range 3-4.6 V.



Fig. S4 Average discharge voltage of LCO||Li cell as a function of cycle number.



Fig. S5 Galvanostatic intermittent titration test curve of EDV and TFDT

electrolytes.



Fig. S6 Tafel plots of symmetric Li cells in different electrolytes.

4. Supplementary tables

electrolyte cycles					
Electrolyte	003(18.9°)	012(44.9°)			
TFDT	0.389	0.526			
EDV	0.742	0.765			
Pristine	1	1			

Table S1. The relative peak intensities of LCO cathodes after different

Table S2.	Summary	of the	roughness	parameters	of lithium	metal	surfaces	after
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Electrolyte	R _q (nm)	R _a (nm)
TFDT	3.95	2.01
EDV	38.7	28.7

50 cycles of different electrolytes

Electrolyte	CO ratio (kg/kg)	CO ₂ ratio (kg/kg)
TFDT	0.0124	0.1
EDV	0.005	0.01

Table S3. Summary of various parameters from Cone calorimeter experiment