Supporting Information

Stable cyclic ether as an electrolyte additive for high-performance lithium metal batteries

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Experimental section

Materials: Lithium hexafluorophosphate ($LiPF_6$, 99.9%), diethyl carbonate (DEC, 99%), ethylene carbonate (EC, 99%), and 1,3-dioxolane (DOL, 99%) were provided by Meryer Chemical Reagent Co., Ltd. 4-methyl-1,3-dioxolane (4-Me DOL, 99%) was provided by Aladdin. Lithium foil with a thickness of 400 μm was provided by China Energy Lithium Co., Ltd. Copper (Cu) foil with a thickness of 16 μm was purchased from Shenzhen Jingliang Copper Industry Co., Ltd. Carbon-coated aluminum (Al) foil (15 μm), $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), polyethylene (PE) separators, and Super P conductive carbon black were obtained from Guangdong Canrd New Energy Technology Co., Ltd. The commercial $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, ~18 mg cm^{-2}, 3 mAh cm^{-2}) electrode was supplied by Hunan Lifang New Energy Technology Co., Ltd.

Electrolyte Preparation: The electrolyte used in the experimental group consisted of a mixture of 1 M $LiPF_6$, EC/DEC (v/v = 1:1), and 1 vol% 4-Me DOL (BE + 4-Me DOL). The control electrolytes included 1 M $LiPF_6$ in EC/DEC (v/v = 1:1) (BE), and a mixture of 1 M $LiPF_6$ in EC/DEC (v/v = 1:1) with 1 vol% DOL (BE + DOL).

Electrochemical measurements: The battery configuration is as follows: Li-Cu half-cell, Li-Al cell, Li-Li symmetric cell, Li-NCM622 cell, and Li-NCM811 full cell. The Li-Cu half-cell consists of Li foil (14 mm, 400 μm), Cu foil (16 mm), and 40 μL of electrolyte. The structure of the Li-Al cell includes Li foil (14 mm, 400 μm) and Al foil (16 mm). The Li-Li symmetric cell was constructed using two Li foil (14 mm, 400 μm) with 40 μL of electrolyte. Constant current charge-discharge was performed at 3 mA cm^{-2}, 1 mAh cm^{-2}, and 0.5 mAh cm^{-2}. Additionally, rate capability charge-discharge was conducted at 0.5 mAh cm^{-2}, 1 mAh cm^{-2}, 2 mAh cm^{-2}, and 3 mAh cm^{-2} for the cell. NCM622 cathodes were prepared by scraping a blend of NCM622, Super P, and PVDF in a ratio of 8:1:1 (1.5 mg cm^{-2}). The Li-NCM622 cell was assembled from an NCM622 cathode (φ8 mm, 1.5 mg cm^{-2}), a PE separator (φ19 mm), and a Li foil (φ14 mm, 400 μm) with the addition of 40 μL of electrolyte for cycling and rate tests. Cycling tests were conducted at 25 °C within a voltage range of 3 to 4.3 V at a rate of 1 C, along with rate capability tests at 0.5 C, 1 C, 2 C, 5 C, and 10 C. The Li-NCM811 full cell was assembled from a commercial NCM811 cathode (φ8 mm, ~18 mg cm^{-2}, 3 mAh cm^{-2}), a PE

separator (φ19 mm), and a Li foil (φ14 mm, 400 μm) with the addition of 40 μL of electrolyte for cycling tests at 0.33 C charging and 0.66 C discharging. Cyclic voltammetry (CV) measurements of the Li-Cu half-cell were conducted using a CHI660E electrochemical workstation, and the scan rate was set to 1 mV s^{-1}, with a scan range from 3 to 0 V. Linear sweep voltammetry (LSV) measurements of the Li-Al cell were conducted using a CHI660E electrochemical workstation with a scan rate of 1 mV s^{-1}. Tafel plot analysis of the Li-Li symmetric cell was performed using the CHI660E electrochemical workstation within a voltage range of -0.2 to 0.2 V, also with a scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a CHI660E electrochemical workstation with a frequency range of 100 kHz to 0.1 Hz. All coin cells were assembled in a controlled environment inside a glovebox filled with Ar (H_2O content < 0.1 ppm, O_2 content < 0.1 ppm).

Material Characterization: The sample with deposited Li was rinsed three times with DEC solution before analysis to remove residual electrolytes and then air-dried at room temperature. SEM observation and X-ray photoelectron spectroscopy (XPS) analysis were conducted using a Field Emission NANO SEM430 and a Thermo Scientific K-Alpha from the United States, respectively, to observe the morphology and chemical composition of the deposited Li. FTIR spectra of the electrolyte were measured using a Nicolet iS20. Density functional theory (DFT) calculations of energy levels were performed using the Vienna ab-initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) was employed for the exchange-correlation functional.

Supplementary Figures

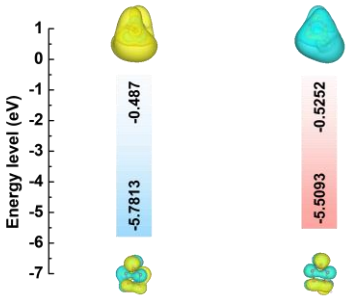

Fig. S1 LUMO–HOMO energy level diagram of DOL and 4-Me DOL.

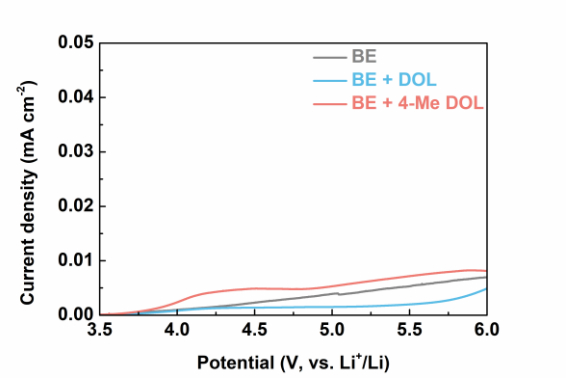

Fig. S2 LSV plots of different electrolytes.

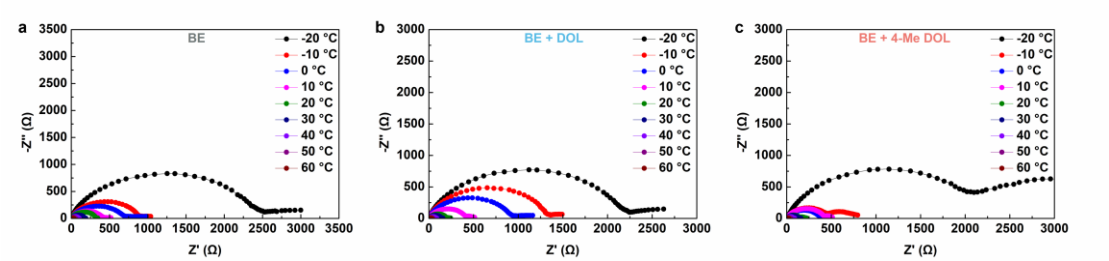

Fig. S3 EIS plots of the Li-Li cells using various electrolytes at different temperatures. (a) BE, (b) BE + DOL, (c) BE + 4-Me DOL.

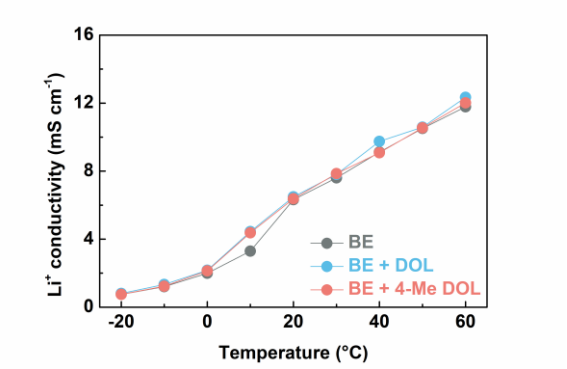

Fig. S4 Li$^+$ conductivity of different electrolytes at various temperatures.

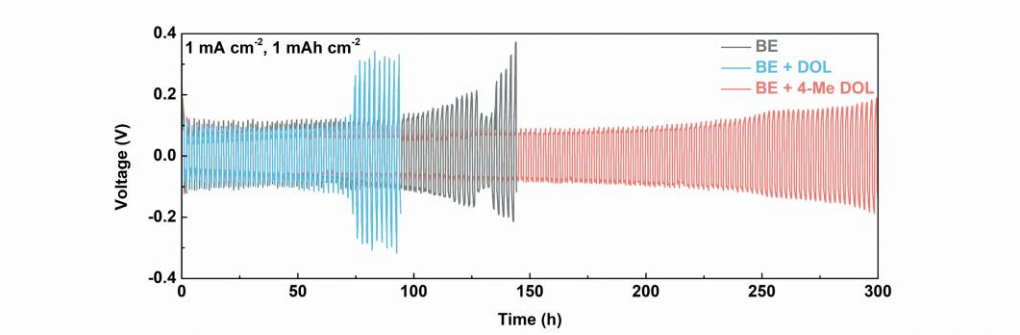

Fig. S5 Cycling tests of Li-Li cells using various electrolytes. (1 mA cm^{-2}, 1 mAh cm^{-2})

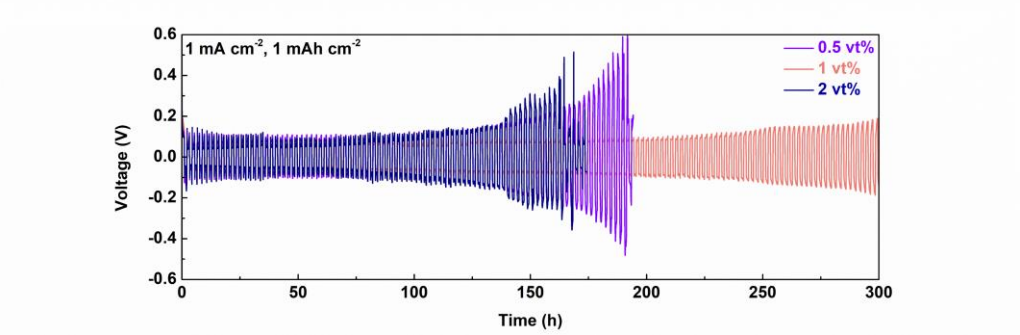

Fig. S6 Long-term cycling tests of Li-Li cells using BE adding with different concentrations of 4-Me DOL. (1 mA cm^{-2}, 1 mAh cm^{-2})

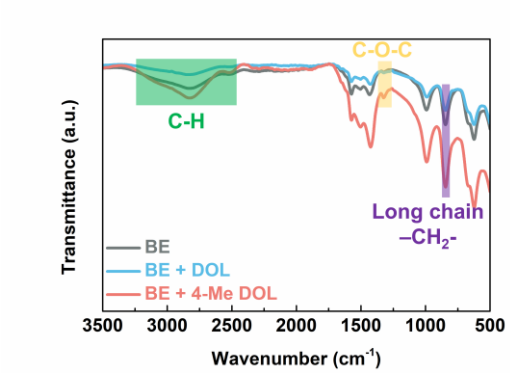

Fig. S7 FTIR spectra of deposited Li using various electrolytes.

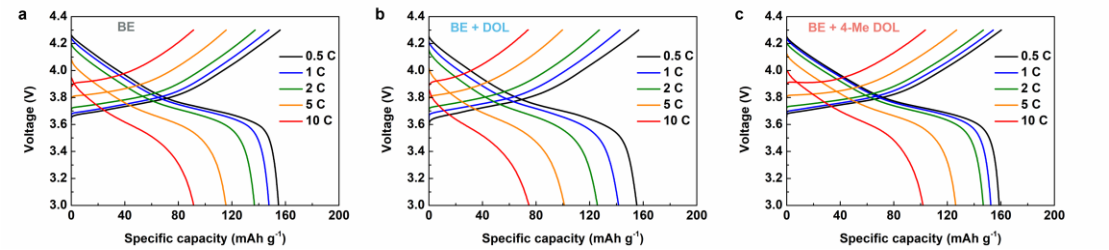

Fig. S8 Voltage profiles of the Li-NCM622 cells cycled with rates using various electrolytes. (a) BE, (b) BE + DOL, (c) BE + 4-Me DOL.

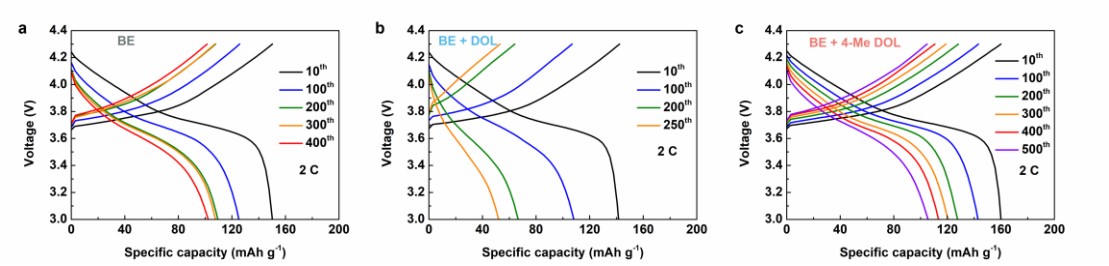

Fig. S9 Typical voltage profiles of the Li-NCM622 cells cycled at 2 C using different electrolytes. (a) BE, (b) BE + DOL, (c) BE + 4-Me DOL.

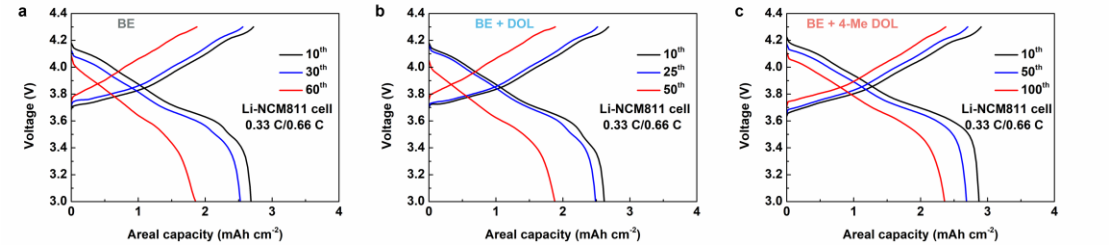

Fig. S10 Typical voltage profiles of the Li-NCM811 full cells using different electrolytes. (a) BE, (b) BE + DOL, (c) BE + 4-Me DOL.