Supporting Information

Suppression of electrolyte decomposition and protection of the lithium metal anode *via* a lactone additive

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Experimental section

Materials: Lithium hexafluorophosphate ($LiPF_6$, 99.9%), diethyl carbonate (DEC, 99.99%) and ethylene carbonate (EC, 99.95%), were provided by Meryer Chemical Reagent Co., Ltd. 1,4-Dioxane-2,5-dione (1,4-DD, 97%) was provided by Adamas Beta Reagents Co., Ltd. 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), $LiNi_{0.8}Co_{0.1}Mn_{0.1}$ (NCM811), commercial $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, ~8.3 mg cm^{-2}) electrode, polyethylene (PE) separators, and Super P conductive carbon black were obtained from Guangdong Canrd New Energy Technology Co., Ltd.

Electrolyte preparation: The electrolyte used in the experimental group consisted of a mixture of 1 M $LiPF_6$ in EC/DEC (v/v = 1:1) (CCE + 1,4-DD), and 1wt% 1,4-DD. The control electrolytes included 1 M $LiPF_6$ in EC/DEC (v/v = 1:1) (CCE).

Electrochemical Testing: The battery configuration is as follows: Li-Cu half-cell, Li-Li symmetric cell, Li-NCM811 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 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 0.5 mA cm^{-2} and 1 mAh cm^{-2}, 1 mA cm^{-2} and 1 mAh cm^{-2}, 1 mA cm^{-2} and 3 mAh cm^{-2}, 3 mA cm^{-2} and 1 mAh cm^{-2}. NCM811 cathodes were prepared by scraping a blend of NCM811, Super P, and PVDF in a ratio of 8:1:1 (1.5 mg cm^{-2}). The Li-NCM811 cell was assembled from an NCM811 cathode (φ8 mm, 1.5 mg cm^{-2}), a ceramic 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 4.4 V at a rate of 2 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, ~8.3 mg cm^{-2}), a ceramic separator (φ19 mm), and a Li foil (φ14 mm, 400 μm) with the addition of 40 μL of electrolyte for cycling tests at 0.5 C charging and 1 C discharging. A 0.3 Ah Li-$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) pouch cell was assembled using an NCM811 cathode with a loading of 18 mg cm^{-2} and a 20 μm thick lithium foil anode. The cell was filled with 1.5 g of modified electrolyte, corresponding to 4.12 g Ah^{-1}, and subjected to cycling tests under 0.2 C charging and 1 C discharging conditions. 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. 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 in the frequency range of 100 kHz-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. Conductivity was determined with DDS-307A. The viscosity of the electrolyte was measured using the KF10.

Density functional theory (DFT) calculations of energy levels were performed using the Vienna ab-initio Simulation Package (VASP).

Supplementary Figures

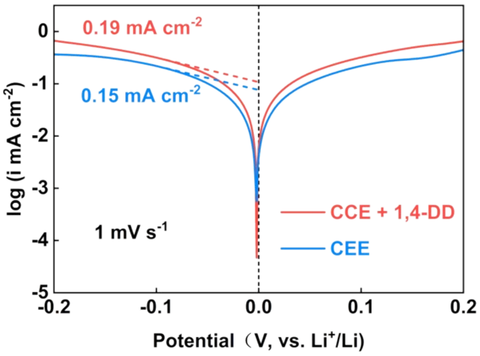

Fig. S1 Tafel plots of studied electrolytes. (Scan rate: 1 mV s^{-1})

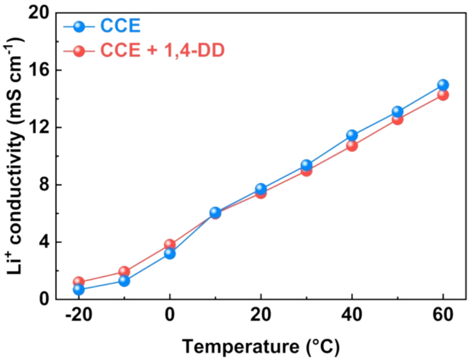

Fig. S2 Li$^+$ conductivity of different electrolytes at various temperatures.

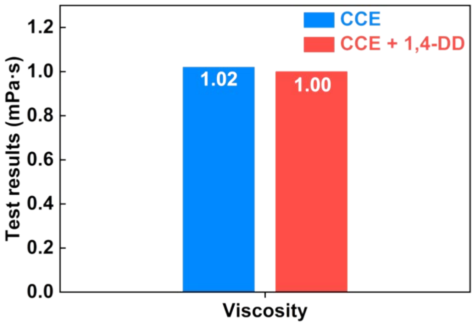

Fig. S3 Comparison of the viscosity of different electrolytes.

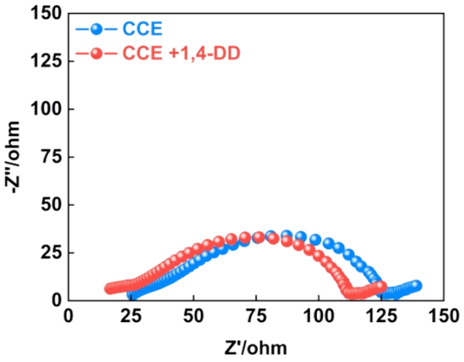

Fig. S4 EIS plots of Li-Li symmetric cells using different electrolytes after 50 cycle at 0.5 mA cm^{-2} and 1 mAh cm^{-2}.

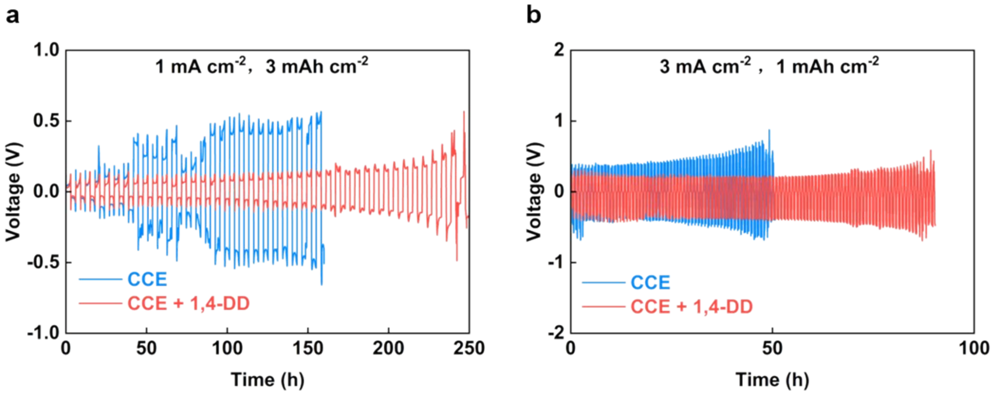

Fig. S5 Cycling performance of Li–Li symmetric cells using different electrolytes, test conditions: (a) 1 mA cm^{-2}, 3 mAh cm^{-2} and (b) 3 mA cm^{-2}, 1 mAh cm^{-2}.

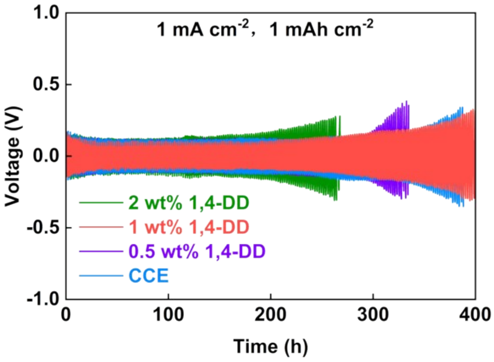

Fig. S6 Long-term cycling tests of Li-Li cells using CCE adding with different concentrations of 1,4-DD (1 mA cm^{-2}, 1 mAh cm^{-2}).

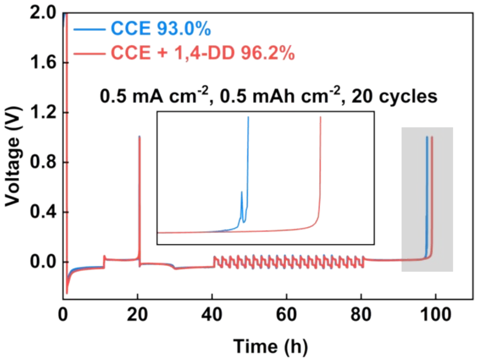

Fig. S7 CE test of Li-Cu half cells using different electrolytes (0.5 mA cm^{-2}, 0.5 mAh cm^{-2}, 20 cycles).

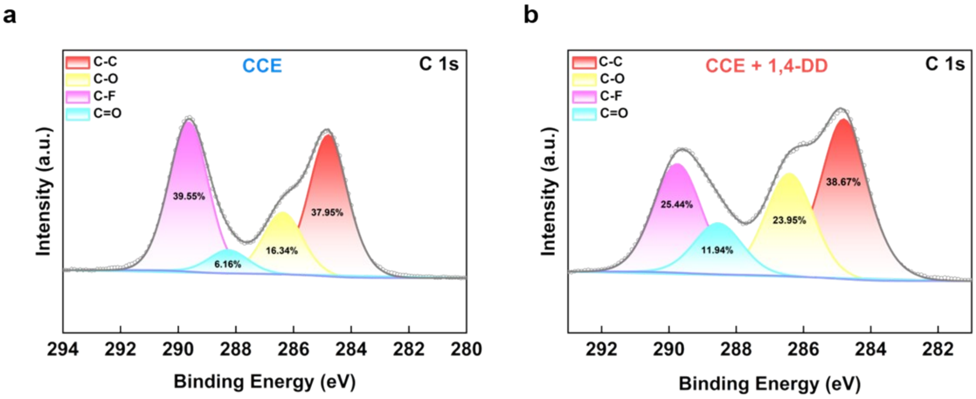

Fig. S8 (a) and (b) XPS C 1s spectra of cycled Li using different electrolytes (Cycling conditions are 0.5 mA cm^{-2} for 3 mAh cm^{-2}).

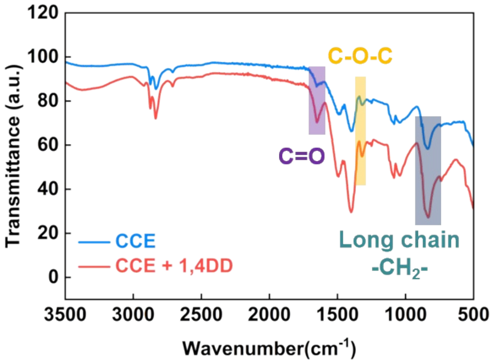

Fig. S9 FTIR spectra of deposited Li using various electrolytes.

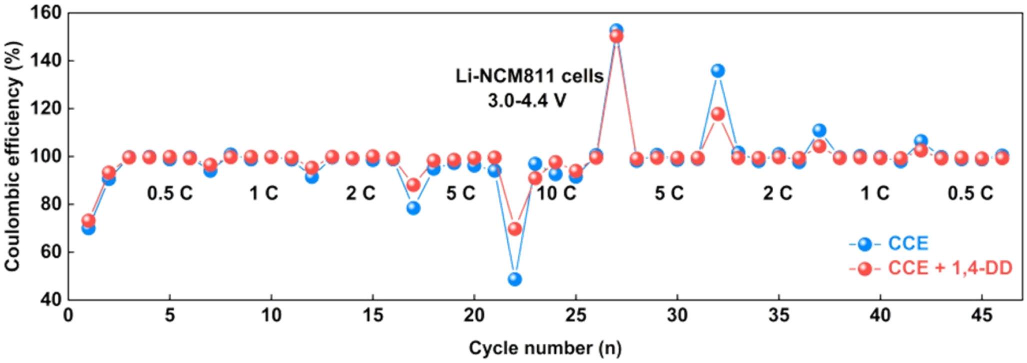

Fig. S10 The corresponding CE of Li-NCM811 cells in rate tests with different electrolytes.

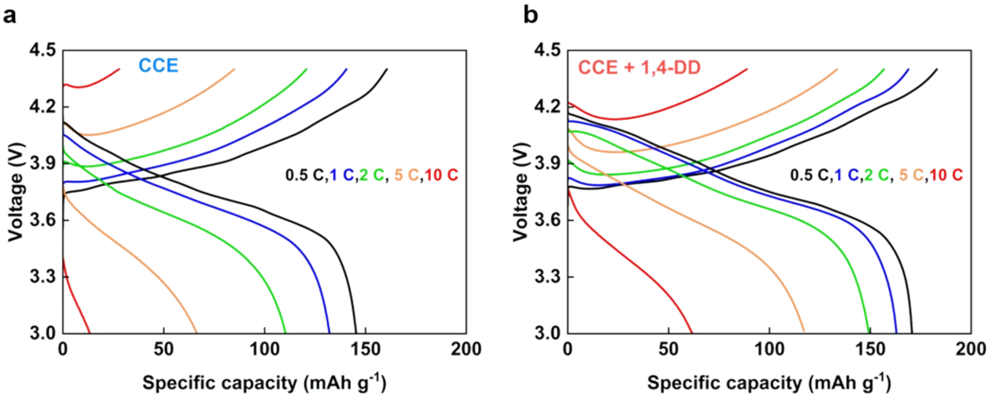

Fig. S11 Voltage profiles of the Li-NCM811 cells cycled with rates using various electrolytes. (a) CCE, (b) CCE + 1,4-DD.

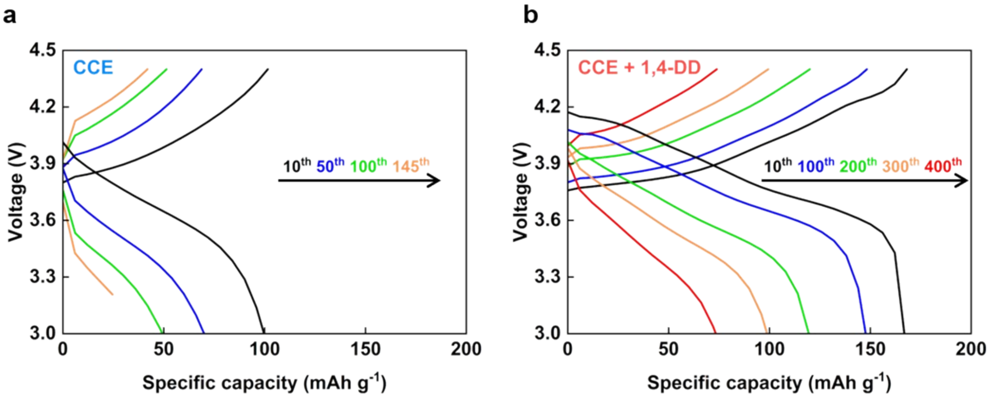

Fig. S12 Typical voltage profiles of the Li-NCM811 cells cycled at 2 C using different electrolytes. (a) CCE, (b) CCE + 1,4-DD.

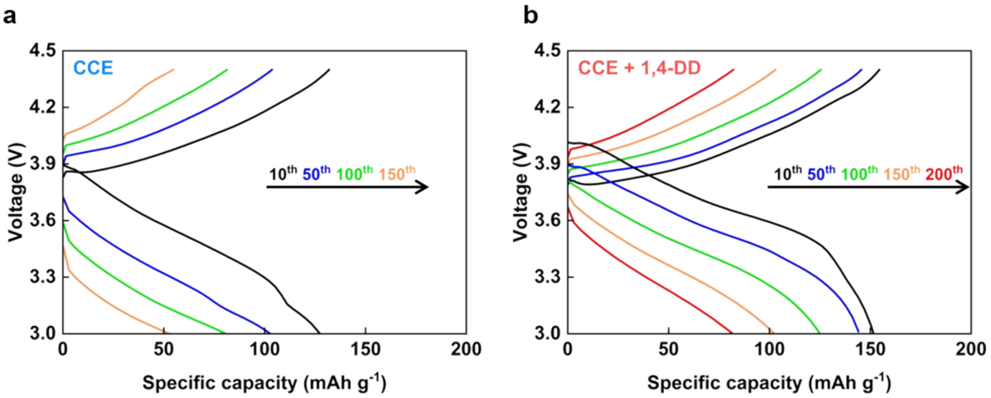

Fig. S13 Typical voltage profiles of the Li-NCM811 full cells using (a) CCE, (b) CCE + 1,4-DD.

Supplementary Tables

Table. S1 Comparison of cycling times of Li-Li symmetric cells using carbonate electrolyte with various additives.

Electrolyte	**Additive**	**Test condition of Li-Li symmetric cells**	**Cycling time**	**Reference**
1M $LiPF_6$ in EC/DEC (1:1)	1vt% 4-MeDOL	0.5 mA cm^{-2}/1 mAh cm^{-2}	800 h	*Chem. Commun.*, **2024**, *60*, 8435–8438
1M $LiPF_6$ in EC/DMC (1:1)	1wt% HFAC	1 mA cm^{-2}/0.5 mAh cm^{-2}	500h	*Angew. Chem. Int. Ed.,* **2022**, *61*, e202205091
1M $LiPF_6$ in EC/DEC (1:1)	20% $Cu(NO_3)_2$	0.5 mA cm^{-2}/1 mAh cm^{-2}	700 h	*Energy Storage Mater.* **2021**, *37*, 1-7
0.6 M LiTFSI + 0.4 M LiBOB in EC/EMC (7:3)	0.6 wt% $LiPF_6$ + 2.0 wt% VC + 2.0 wt% FEC	0.5 mA cm^{-2}/0.5 mAh cm^{-2} (30°C)	800 h	*Adv. Energy Mater.* **2018**, *8*, 1703022
1M $LiPF_6$ in EC/EMC/DMC (1:1:1)	2wt% TEOS + 3wt% TEOT	1 mA cm^{-2}/0.5 mAh cm^{-2}	200 h	*Adv. Funct Mater.* **2022**, *32*, 211034
1M $LiPF_6$ in EC/DMC (1:1)	5wt% FEC	3 mA cm^{-2}/1 mAh cm^{-2}	200 h	*ACS Energy Lett.* **2021**, *6,* 1839−1848
1M $LiPF_6$ in EC/DEC (1:1)	2wt% 15-Crown-5	1 mA cm^{-2}/0.5 mAh cm^{-2}	190 h	*Adv. Funct Mater.* **2021**, *31*, 2002578
1M $LiPF_6$ in EC/DEC (1:1)	**1wt% 1,4-DD**	**0.5 mA cm^{-2}/1 mAh cm^{-2}**	**800 h**	**This work**