Supplemental information

Low concentration electrolyte with non-solvating cosolvent enabling high-voltage lithium metal batteries

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Supplementary Figures

**Figure S1.** Solubility test of a) LiDFOB and b) LiBF$_4$ in the DEC/FEC/FB system. Saturability test of a) LiDFOB and b) LiBF$_4$ in the DLCE. Related to Figure 1.

**Figure S2.** The comparison of density and viscosity of different electrolytes (25 °C). Related to Figure 1.
Figure S3. Wettability tests of the separator contact with a) CCE, b) LCE, and c) DLCE. Related to Figure 1.

Figure S4. Raman spectra of studied solvent systems. Related to Figure 1.

Figure S5. Raman spectra of different electrolytes in the wavenumber range of 720-736 cm\(^{-1}\) (DFOB\(^-\)). Related to Figure 1.
Figure S6. XPS F 1s spectra of the deposited Li in a) CCE, b) LCE, and c) DLCE. Related to Figure 2.

Figure S7. XPS C 1s spectra of the deposited Li in a) CCE, b) LCE, and c) DLCE. Related to Figure 2.

Figure S8. EDX element distribution of deposited Li in a) CCE, b) LCE, and c) DLCE. Related to Figure 2.
Figure S9. SEM cross-sectional view images of deposited Li in a) CCE, b) LCE, and c) DLCE.

Related to Figure 2.

Figure S10. Selected area electron diffraction images of deposited Li in a) CCE, b) LCE, and c) DLCE. Related to Figure 2.

Figure S11. The charge-discharge curves of Li-LCO cell at 1 C/25 °C using a) CCE, b) LCE, and c) DLCE. Related to Figure 3.
Figure S12. EIS plots of cycled Li-LCO cells in a) CCE, b) LCE, and c) DLCE. Related to Figure 3.

Figure S13. The charge-discharge curves of Li-LCO cell at 0.5 C/−20 °C using a) CCE, b) LCE, and c) DLCE. Related to Figure 3.

Figure S14. The charge-discharge curves of high-loading Li-LCO cell at different current densities using a) CCE, b) LCE, and c) DLCE. Related to Figure 4.
**Figure S15.** The charge-discharge curves of high-loading Li-LCO cell at 1 mA cm$^{-2}$ using a) CCE, b) LCE, and c) DLCE. Related to Figure 4.

**Figure S16.** $^{19}\text{F}$ NMR results for analysis of the consumption of LiDFOB after 100 cycles in high-loading Li-LCO cells with different electrolytes. Related to Figure 4.

**Figure S17.** TEM images of cycled LCO in a) LCE and b) DLCE. Related to Figure 5.
Figure S18. XRD patterns of different LCO (The range of diffraction angle: 10° to 90°). Related to Figure 5.

Figure S19. XPS C 1s spectra of the cycled LCO in a) LCE and b) DLCE. Related to Figure 5.
Supplementary Tables

**Table S1.** The mass of each part of the Li-LCO pouch cell. Related to Figure 4.

| Li-LCO pouch cell components                  | Weight (mg) |
|----------------------------------------------|-------------|
| Cathode (4.3×5.6 cm, two-sided)              | 982.5       |
| Al foil (10 μm, single-layer)                | 65.0        |
| Li foil (50 μm, double-layer)                | 124.7       |
| Cu foil (8 μm, double-layer)                 | 246.6       |
| Separator (20 μm, double-layer)              | 43.3        |
| Electrolyte (500 μL)                         | 555.0       |
| **All**                                      | **2017.1**  |
Table S2. The performance comparison of Li-LCO cells. Related to Figure 4.

| Strategies                  | Cutoff voltage (V) | Cathode loading (mg cm$^{-2}$) | Cycle number (n) | Capacity retention (%) | Ref.                        |
|-----------------------------|-------------------|---------------------------------|------------------|------------------------|-----------------------------|
| Li$_3$N-coated LMA          | 4.2               | 4                               | 100              | 96                     | Chen et al., 2019           |
| Li/0.2 M g-C$_3$N$_4$/CC    | 4.2               | 4                               | 300              | 71.9                   | Xu et al., 2019             |
| Li/MnF$_2$-PCNFs            | 4.2               | 17.34                           | 100              | 90                     | Qin et al., 2019            |
| Mg coated separator         | 4.3               | 8                               | 400              | 80                     | Liu et al., 2019            |
| PPE-Li                      | 4.5               | 3                               | 100              | 80                     | Liu et al., 2020            |
| AD-ether electrolyte        | 4.5               | 13.5                            | 800              | 80                     | Ren et al., 2020            |
| CMLCO                       | 4.6               | 1.5                             | 200              | 78                     | Wang et al., 2019           |
| LMCO                        | 4.6               | 3                               | 100              | 84                     | Huang et al., 2021          |
| TMA-LCO                     | 4.6               | 3                               | 100              | 86                     | Zhang et al., 2019          |
| LATP@LCO-700                | 4.6               | 3                               | 100              | 88.3                   | Wang et al., 2020           |
| DLCE                        | 4.3               | 3                               | 1000             | 87.1                   | This work                  |
|                             | 4.6               | 20.4                            | 120              | 85.6                   |                             |

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Transparent Methods

Materials
Li foil (China Energy Lithium Co., Ltd.), fluorobenzene (FB, 99%, Aladdin), LiCoO$_2$ power (Shenzhen Kejing Star Technology Co., Ltd.), separator (Celgard 2400). Lithium difluoro(oxalato)borate (LiDFOB, 99.5%), lithium tetrafluoroborate (LiBF$_4$, 99%), fluoroethylene carbonate (FEC, 99%), and diethyl carbonate (DEC, 99%) were purchased from Dodo Chem Co., Ltd. (Suzhou, China). Commercial LiCoO$_2$ electrode was supplied by Zhuhai COSMX power battery Co., Ltd. (Zhuhai, China). All these materials used without further purification.

Characterizations
The density and viscosity of various electrolytes was tested by Lovis 2000 M (Anton-Paar. Co., Ltd.) at 25 °C. Wettability reflected by contact angle difference between the various electrolytes and separators (Celgard 2400) measured by KRUSS DSA100 at 25 °C. Raman spectra were tested by LabRAM HR800 (HORIBA Jobin Yvon IBH Ltd.) with 785 nm laser. $^{11}$B nuclear magnetic resonance (NMR) results were carried out with Ascend 600 MHZ (Bruker. Co., Ltd.). A 1 M $\text{H}_3\text{BO}_3$ in $\text{D}_2\text{O}$ was hot sealed in quartz capillary for internal standard. And then, the quartz capillary and electrolyte were put into the NMR tube for test. Scanning electron microscopy (SEM) observations and X-ray energy dispersive spectrometer (EDX) were carried out with EPMA-8050G (SHIMADZU-KRATOS. Co., Ltd.). X-ray photoelectron spectroscopy (XPS) performed on an AXIS-ULTRA DLD-600W (SHIMADZU-KRATOS. Co., Ltd.). TEM images were observed by Talos F200X (Thermo Fisher Scientific). The ionic conductivities of the electrolytes were
recorded by DDS-307A (INESA Scientific Instrument Co. Ltd., Shanghai, China) at different temperatures. XRD patterns were recorded by X’Pert3 Powder (Malvern Panalytical. Co., Ltd.) using Cu-Kα radiation at room temperature.

**Electrolyte Composition**

The CCE is 0.6 M LiDFOB + 0.4 M LiBF₄ in DEC/FEC (7: 3 by volume). The LCE is 0.3 M LiDFOB + 0.2 M LiBF₄ in DEC/FEC (7: 3 by volume), and the DLCE is 0.3 M LiDFOB + 0.2 M LiBF₄ in DEC/FEC/FB (3.5: 1.5: 5 by volume). The preparation and storage of electrolytes are carried out in the glovebox. (H₂O< 0.1 ppm, O₂< 0.1 ppm).

**Electrochemical Measurements**

The electrochemical performance of the coin/pouch cells was conducted on Land battery test instrument. Electrochemical impedance spectrometry (EIS) (100 kHz to 0.1 Hz) was conducted using Solartron electrochemical workstation with voltage amplitude of 5 mV, and the EIS plots of cycled Li-LCO cells need to be rested 10 min to obtain a steady voltage before tests. The LSV plots were tested in Li-Cu half cells, and Tafel plots were carried by Li-Li symmetric cells, and were measured using a CHI 600D at a scan rate of 1 mV s⁻¹, and the voltage range is 2~6 V and 0.2~0.2 V, respectively. The amount of electrolyte is controlled as 40 µL in coin cell, and 500 µL in pouch cell. Li-Cu half cells assembled with Cu foil (φ 16 mm) as a cathode and Li foils as an anode in CR2032 coin cells. The calculation method of average Coulombic efficiency (CE) of the Li-Cu cells similar to previous report (Adv. Energy Mater. 8, 1702097; ACS Nano, 14, 13784). The LCO cathode was made by blending LCO powder, Super P, PVDF with a weight ratio of 8: 1: 1 in
NMP solution to form the slurry, and then coated on the Al foil. After drying at 80 °C under vacuum overnight, the obtained electrodes with areal mass loadings controlled to be 3~4 mg cm$^{-2}$. The Li-LCO cells were galvanostatically cycled between 3 and 4.3 V at 25 °C or −20 °C. The commercial LCO electrode has a mass loading of 20.4 mg cm$^{-2}$ and the high-loading Li-LCO cells were galvanostatically cycled between 3 and 4.6 V with long-term cycling and rate tests at 25 °C. For the Li-LCO pouch cell, a 50 μm Li foil as an anode, and the commercial LCO electrode (4.6×5.6 cm) as a cathode, the amount of DLCE was controlled at 500 μL (2.7 g Ah$^{-1}$), then, adding separator and packed with an aluminum-plastic film. The pouch cell was galvanostatically cycled between 3 and 4.6 V with a current density of 1 mA cm$^{-2}$ at 25 °C.