Supplementary Information

Regulation of the Cathode Inner Helmholtz Plane in Dilute Ether

Electrolytes Using Electric-Field-Responsive Solvent for High-

Voltage Lithium Metal Batteries

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Fig. S1. The LUMO and HOMO energy values of LiDFOB, DFOB⁻, DME and DTS molecules.



Fig. S2. The dipole moment (μ) and dielectric constant (ϵ) of (a) DME and (b) DTS molecule.



Fig. S3. (a) The optical picture of Li salt dissolution in electrolytes with different ratio of DME and DTS (by volume). (b) Ionic conductivity and (c) t_{Li}^+ values of different electrolytes. (d) Cycling performance of cell using different electrolytes. (e, f) Intensity sputter profiles of (e) C₂H⁻ and (f) LiF₂⁻ measured by TOF-SIMS. The insets show the 3D reconstruction distribution map of C₂H⁻, and LiF₂⁻ showing the CEI structure and chemistry of cathodes retrieved from Li||LiCoO₂ cells after 100 cycles in different electrolytes.

Firstly, 1 mol L⁻¹ LiDFOB was dissolved in pure DME solvent or the mixtures of DME and DTS with different volume ratios. When the ratio of DME and DTS reaches 1:4, the salt appears to be insoluble (**Fig. S3**a). As for the property of electrolytes, with the amount of DTS increases, the ionic conductivity of electrolytes decreases from 9.69 for LiDFOB-DME and 4.03 mS cm⁻¹ for LiDFOB-DME:DTS (1:3 by vol.) (**Figs. S3**b and S9) but the t_{Li}^+ increases from 0.43 for LiDFOB-DME and 0.66 for LiDFOB-DME:DTS (1:3 by vol.) (**Figs. S3**c and S11). This suggests that the addition of DTS facilitates the Li ion de-solvation and ion transfer kinetics. In addition, the Li||LiCoO₂ cells using LiDFOB-DME:DTS (1:3 by vol.) shows the best cycling performance among these four samples (**Fig. S3**d). Interfacial analysis validated by TOF-SIMS indicates the formation of stable CEI film with less organics from ether oxidation and more LiF species from DTS decomposition (**Figs. S3**e, f, and **5**e, g). Based on the comprehensive consideration, the ratio of 1:3 for DME to DTS is deemed as the optimum.



Fig. S4. MD simulation snapshots of (a) LiDFOB-DME and (c) LiDFOB-DME:DTS electrolyte and corresponding DFOB⁻ distribution in (c) LiDFOB-DME and (d) LiDFOB-DME:DTS electrolytes, respectively. (e) Molecular number density of DFOB⁻ along with the distance from the electrified $LiCoO_2$ cathode in different electrolytes.



Fig. S5. (a, b) ESP of (a) DME, and (b) DTS solvent. (c) The binding energy of Li⁺-solvent complexes.



Fig. S6. (a, b) Li⁺ radial distribution functions obtained from MD simulations of (a) LiDFOB-DME and (b) LiDFOB-DME:DTS electrolytes.



Fig. S7. Raman spectra of LiDFOB salt, pure DME, DTS solvent, LiDFOB-DME and LiDFOB-DME:DTS electrolytes.



Fig. S8. FTIR spectra of pure LiDFOB salt, DME, DTS solvent, LiDFOB-DME and LiDFOB-DME:DTS electrolytes.



Fig. S9. Ionic conductivity of different electrolytes.



Fig. S10. Oxidation stability of different electrolytes evaluated by linear sweeping voltammetry at a scanning rate of (a) 5 mV s⁻¹ and (b) 0.5 mV s^{-1} .

As depicted in **Fig. S10**a, in LiDFOB-DME electrolyte, the oxidatively unstable DME molecule prevail in the IHP, leading to oxidative decomposition of electrolyte after the 3.5 V and maintaining a relatively high oxidation current of about 15 μ A before 4.5 V. After the addition of DTS, most of oxidatively unstable DME are extruded from the IHP by anti-oxidation DTS, allowing the preferential adsorption on the electrode surface of DTS molecules. Consequently, the oxidation of DME molecules is significantly inhibited, and therefore, a low oxidation current for LiDFOB-DME:DTS electrolyte is observed until 5.5 V. LSV measurements with a lower sweep rate of 0.5 mV s⁻¹ have been carried out to avoid the large polarization of the system (**Fig. S10**b), and the similar trend is observed between them. The oxidation decomposition of DME molecules was intensified at lower sweep rates, with a slow and persistent increase in the oxidative current after about 3 V. In contrast, DTS-containing electrolyte still presents wide electrochemical window (up to 5.2 V vs. Li/Li⁺).



Fig. S11. The chronoamperometry profile of the symmetric Li||Li cells using (a) LiDFOB-DME and (b) LiDFOB-DME:DTS electrolytes. The applied polarization voltage is 10 mV. The EIS spectra before and after the polarization are shown in inset. (The values of R_b/R_i are seen Table S3)



Fig. S12. CV curves of Li||LiCoO₂ cell using (a) carbonate, (b) LiDFOB-DME and (c) LiDFOB-DME:DTS electrolytes at $0.1 \text{mV} \text{ s}^{-1}$ within the voltage range between 3 and 4.55 V.



Fig. S13. (a) Typical galvanostatic charge/discharge curves of different cycles in $Li||LiCoO_2$ batteries with carbonate electrolyte. (b) The charge and discharge average voltage of $Li||LiCoO_2$ batteries with carbonate electrolytes during cycling.



Fig. S14. Typical galvanostatic charge/discharge curves of different cycles in Li||LiCoO₂ batteries with (a) LiDFOB-DME electrolyte and (b) LiDFOB-DME:DTS electrolytes.



Fig. S15. Charge-discharge voltage profiles of Li||LiCoO₂ cells using (a) carbonate, (b) LiDFOB-DME and (c) LiDFOB-DME:DTS electrolytes under different C rates.



Fig. S16. (a) The initial charge curve of 50 μ m-thin Li||4.2 mAh cm⁻² LiCoO₂ cells using LiPF₆-EC:EMC electrolyte. (b) Cycling performance of 50 μ m-thin Li||4.2 mAh cm⁻² LiCoO₂ cells with 10 μ L electrolyte (E/C~2.9 g Ah⁻¹, N/P~2.4).



Fig. S17. FE-SEM images of the cross-sections and the surfaces of $LiCoO_2$ cathode cycled in carbonate electrolyte.



Fig. S18. HRTEM images of $LiCoO_2$ electrode after 100 cycles within the voltage range of 3.0–4.55 V in carbonate electrolyte.



Fig. S19. EIS spectra of $LiCoO_2 \parallel LiCoO_2$ cells using (a) LiDFOB-DME and (b) LiDFOB-DME:DTS electrolytes.



Fig. S20. (a) C 1s (b) O 1s (c) F 1s (d) P 2p and Li 1s XPS in-depth spectra and corresponding quantified atomic concentrations of the detected elements of SEI layers formed on Li metal anode in carbonate electrolyte.



Fig. S21. S 2p XPS in-depth spectra and corresponding quantified atomic concentrations of the detected elements of SEI layers formed on Li metal anode in LiDFOB-DME:DTS electrolyte.



Fig. S22. (a-c) 3D reconstruction distribution map of (a) C_2H^2 , (b) PO_2^2 and (c) LiF_2^2 showing the CEI structure and chemistry of LCO cathoDTS retrieved from cycled Li||LiCoO₂ cells with carbonate electrolyte. (d) Corresponding intensity sputter profiles of C_2H^2 , PO_2^2 and LiF_2^2 measured by TOF-SIMS. (e) Schematic of CEI formation and cycled LiCoO₂ cathode particles in carbonate electrolyte.



Fig. S23. FE-SEM images of Li anode disassembled from Li||LiCoO₂ cells in (a) carbonate, (b) LiDFOB-DME, and (c) LiDFOB-DME: DTS electrolytes after 100 cycles



Fig. S24. (a) C 1s, (b) O 1s, (c) F 1s, and (d) P 2p XPS in-depth spectra and corresponding quantified atomic concentrations of the detected elements of SEI layers formed on Li metal anode in carbonate electrolyte.



Fig. S25. (a) C 1*s*, (b) O 1*s*, (c) F 1*s*, and (d) B 1*s* XPS in-depth spectra and corresponding quantified atomic concentrations of the detected elements of SEI layers formed on Li metal anode in LiDFOB-DME electrolyte.



Fig. S26. (a) C 1*s*, (b) O 1*s*, (c) F 1*s*, and (d) B 1*s* XPS in-depth spectra and corresponding quantified atomic concentrations of the detected elements of SEI layers formed on Li metal anode in LiDFOB-DME:DTS electrolyte.



Fig. S27. Voltage profiles of LillLi symmetric cells with different electrolytes at 25 °C



Fig. S28. The variation of (003) peak of $LiCoO_2$ electrode using LiDFOB-DME electrolyte at different charged/discharged state.



Fig. S29. The variation of (003) peak of LiCoO₂ electrode using LiDFOB-DME:DTS electrolyte at different charged/discharged state.

| | Peak position (cm ⁻¹) | Full Width at Half Maximum (FWHM) | Peak area percentage (%) |
|-------|--------------------------------------|---|-----------------------------|
| SSIPs | 702.5 | 12.60781 | 82.47043 |
| CIPs | 710.0 | 12.10180 | 17.52957 |

Table S1. Fitted results of Raman spectrum in LiDFOB-DME electrolyte (R²=0.9887).

Table S2. Fitted results of Raman spectrum in LiDFOB-DME:DTS electrolyte(R2=0.9866).

| | Peak position (cm ⁻¹) | Full Width at Half Maximum (FWHM) | Peak area percentage (%) |
|-------|--------------------------------------|---|-----------------------------|
| SSIPs | 702.5 | 12.60781 | 55.76834 |
| CIPs | 710.0 | 12.10180 | 39.98809 |
| AGGs | 718.0 | 5.61031 | 4.243520 |

| Electrolytes | R_b^{θ} | $R_i^{\ \theta}$ | R_b^{SS} | R_i^{SS} | I ⁰ | I ^{SS} | t_{Li}^+ |
|--------------|----------------|------------------|------------|------------|----------------|-----------------|------------|
| LiDFOB-DME | 2.55 | 132 | 2.55 | 135 | 0.063 | 0.05 | 0.43 |
| LiDFOB- | | | | | | | |
| DME:DTS (1:1 | 5.6 | 406.4 | 2.7 | 419 | 0.022 | 0.0188 | 0.45 |
| by vol.) | | | | | | | |
| LiDFOB- | | | | | | | |
| DME:DTS (1:2 | 2.044 | 450 | 2.044 | 496 | 0.020 | 0.017 | 0.55 |
| by vol.) | | | | | | | |
| LiDFOB- | 20.10 | 164.95 | 42 79 | 105 | 0.051 | 0.040 | 0.66 |
| DME:DTS | 29.19 | 104.83 | 42.70 | 195 | 0.031 | 0.040 | 0.00 |

Table S3. The t_{Li}^+ values of different electrolytes (**Fig. S3**c, **S11**).

Table S4. Shrinkage in the *c*-axis direction (%) of LiCoO₂ in different electrolytes (**Fig. S28, S29**).

| | Pristine | Lowest (003) | Highest (003) | Shrinkage in the |
|--------------|--------------|---------------|---------------|------------------|
| Electrolytes | position (°) | peak position | peak position | c-axis direction |
| | | (°) | (°) | (%) |
| LiDFOB-DME | 18.83 | 18.359 | 18.934 | 3.01% |
| LiDFOB- | 18 83 | 18.337 | 18 885 | 2 880/ |
| DME:DTS | 10.05 | | 10.003 | 2.0070 |