Supporting information

Resolving the Phase Instability of a Fluorinated Ether, Carbonate-Based Electrolyte for the

Safe Operation of an Anode-free Lithium metal battery

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Table S1. Laboratory prepared and commercial electrolytes were used for comparison of

 electrochemical performance

| Electrolytes denoted by the volumetric ratio of solvents | Marked as |
|--|--------------|
| 1 M LiPF ₆ in EC/DEC (1:1) | EC/DEC |
| 1 M LiPF ₆ in FEC/TTE (3:7) | FEC/TTE |
| 1 M LiPF ₆ in FEC/TTE/EMC (3:6:1) | FEC/TTE/EMC1 |
| 1 M LiPF ₆ in FEC/TTE/EMC (3:5:2) | FEC/TTE/EMC2 |
| 1 M LiPF ₆ in FEC/TTE/EMC (3:4:3) | FEC/TTE/EMC3 |
| 1 M LiPF ₆ in FEC/TTE/EMC (3:3:4) | FEC/TTE/EMC4 |



Figure S1. The electrochemical performance of using anode-free CullNMC111 configuration cells when charged/discharged at 0.5 mA/ cm² with potential window of 2.5-4.5 V.



Table S2. Interaction of solvent complex with TTE

Figure S2. Critical current density test for EC/DEC and FEC/TTE/EMC2 using MCMBINMC111 cell cycled at different current density ranging from 0.1 to 10 mA/cm² within a potential window

of 2.5 - 4.5 V. (a) Critical density test of EC/DEC. (b) Critical density test of FEC/TTE/EMC2. (c) Critical density test comparison of EC/DEC and FEC/TTE/EMC2. (d) Enlarge graph of (c).



Video S1. Screenshot of the flame test video comparisons of EC/DEC and FEC/TTE/EMC2 electrolytes. (video available from <u>https://pubs.acs.org/doi</u>... or upon kind request)

Table S3. Laboratory prepared electrolytes were used for comparison of electrochemical performance

| Electrolytes denoted by the volumetric | Marked as |
|--|--------------|
| ratio of solvents | |
| 1 M LiPF ₆ in FEC/TTE/EMC (4:5:1) | FEC/TTE/EMC5 |
| 1 M LiPF ₆ in FEC/TTE/EMC (3:5:2) | FEC/TTE/EMC2 |
| 1 M LiPF ₆ in FEC/TTE/EMC (2:5:3) | FEC/TTE/EMC6 |
| 1 M LiPF ₆ in FEC/TTE/EMC (1:5:4) | FEC/TTE/EMC7 |



Figure S3. Electrochemical performance comparison using anode-free CullNMC111 configuration cells. (a) Discharge areal capacity. (b) Coulombic efficiency when charged/discharged at 0.5 mA/ cm² with a potential window of 2.5-4.5 V.



Figure S4. LSV test of the electrolyte in Li||Cu cell with the potential window from 2.5 to 0 V versus Li/Li⁺ at a scan rate of 1 mV/s. (a-b) LSV test for reductive stability of FEC/TTE/EMC2 and EC/DEC electrolyte, respectively.



Figure S5. Photograph of the wetting behavior of EC/DEC and FEC/TTE/EMC2 electrolytes with the MCMB and separator during cell assembly.