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Monolithic solid-electrolyte interphases formed in fluorinated orthoformate-based electrolytes minimize Li depletion and pulverization

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Supplementary information

Monolithic Solid-electrolyte Interphases Formed in Fluorinated Orthoformate-based Electrolytes Minimize Li Depletion and Pulverization

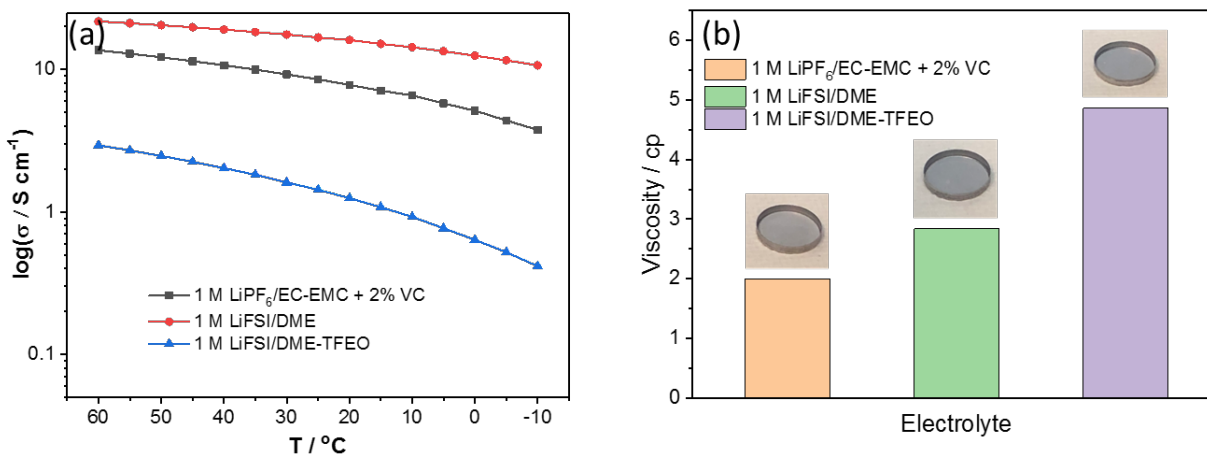
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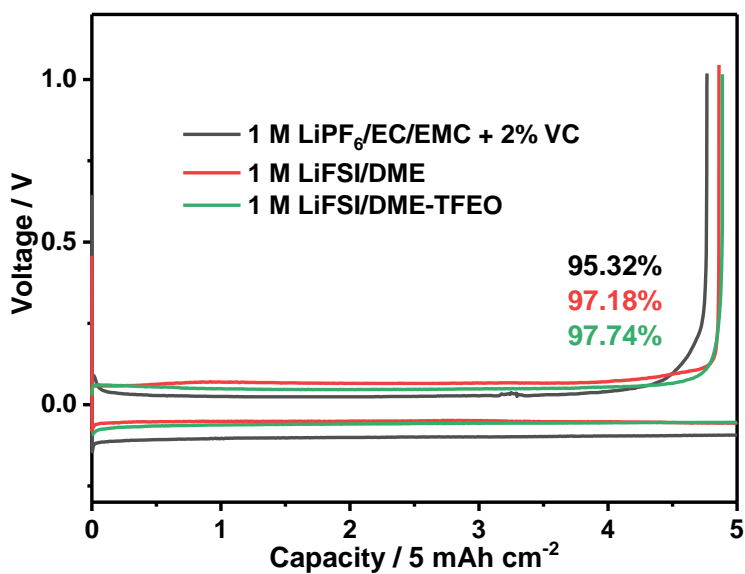
² Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States

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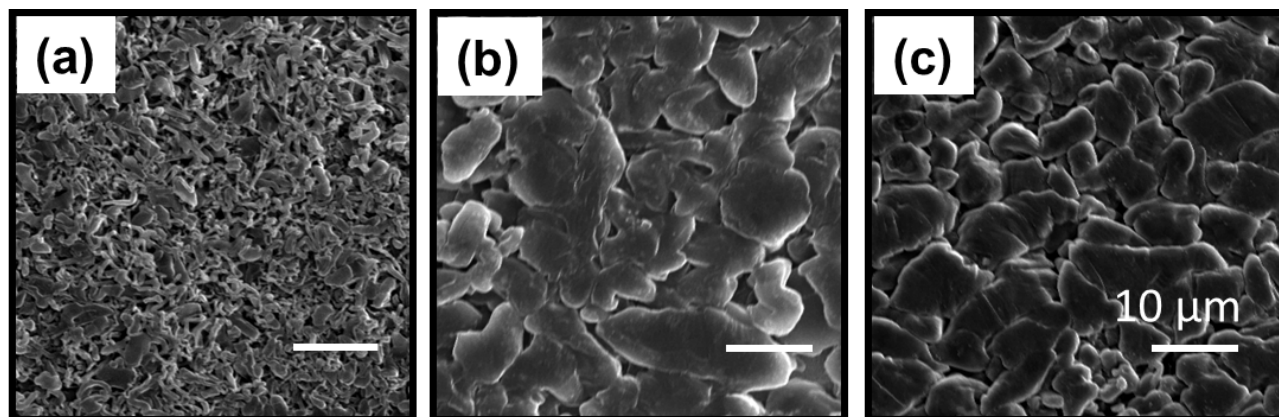
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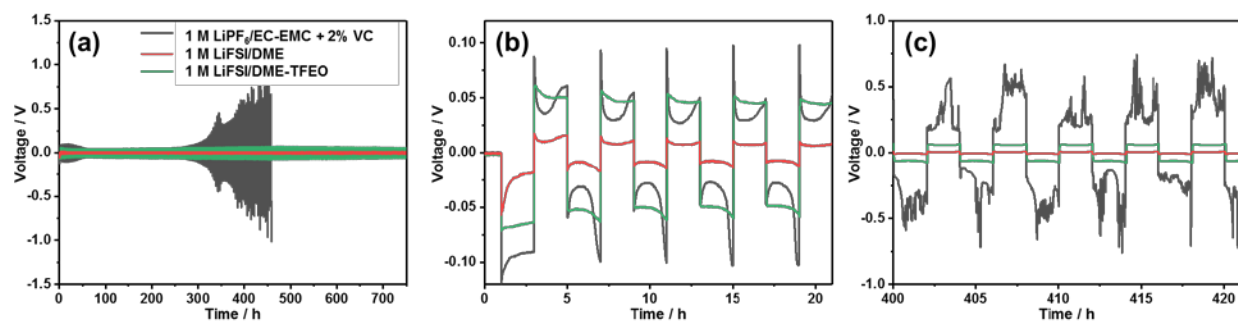
Supplementary Figure 1. (a) Conductivity and (b) viscosity and wettability of the three investigated electrolytes.



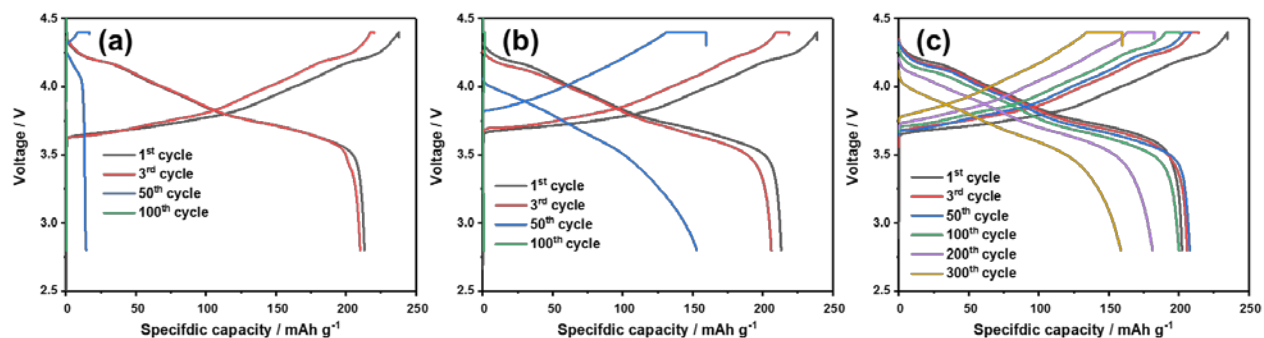
Supplementary Figure 2. First-cycle voltage profiles of Li plating/stripping in Li||Cu cells with the three investigated electrolytes at a current density of 0.5 mA cm^{-2} .



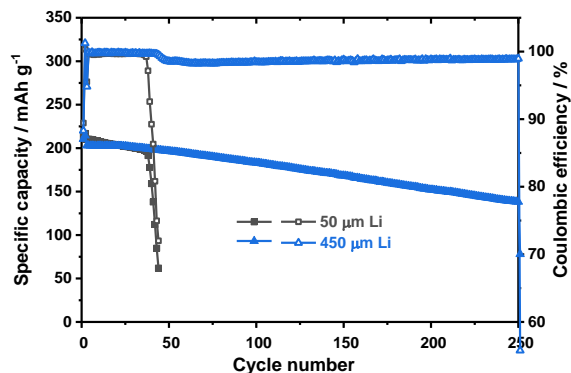
Supplementary Figure 3. SEM images of Li deposited in (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI/DME, and (c) 1 M LiFSI/DME-TFEO at a current density of 0.5 mA cm⁻² and capacity of 1 mAh.



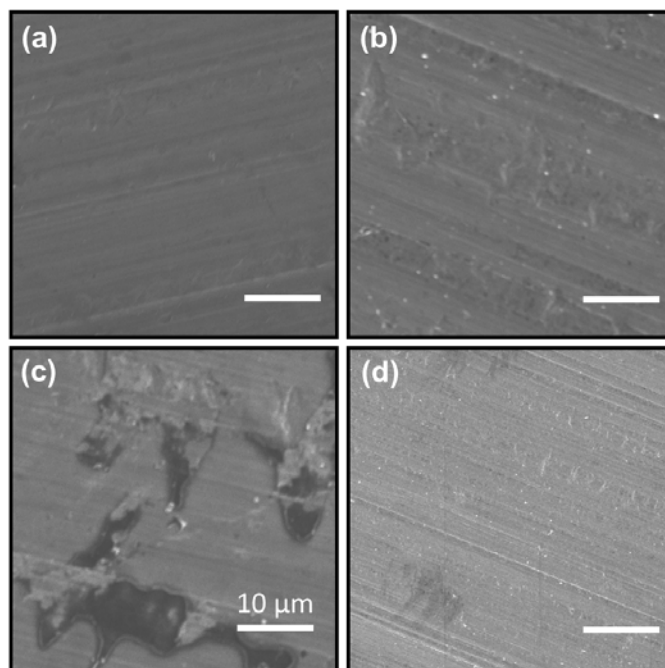
Supplementary Figure 4. (a) Cycling performance of Li||Li cells with the three electrolytes, and magnification of selected periods of (b) 0–22 h and (c) 400–422 h. The cycling was performed at a current density of 0.5 mA cm⁻² and an areal capacity of 1 mAh cm⁻² for each plating or stripping step.



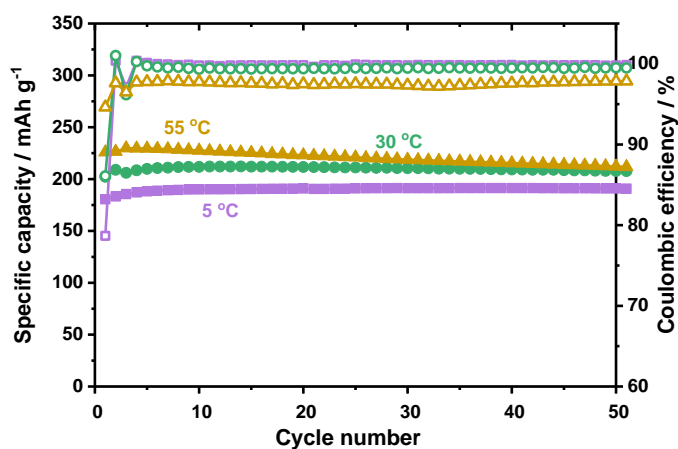
Supplementary Figure 5. Voltage profiles of the Li||NMC811 cells with electrolytes of (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI-DME, and (c) 1 M LiFSI/DME-TFEO.



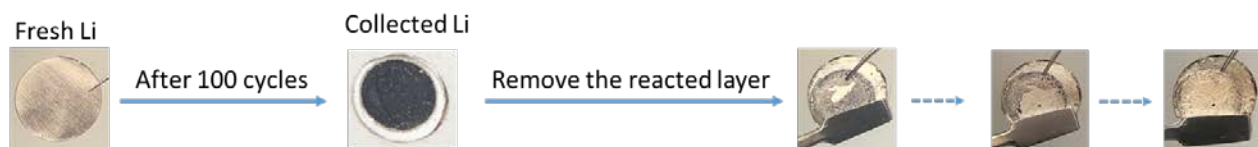
Supplementary Figure 6. Li||NMC811 cell cycling performances with 1 M LiPF₆/EC-EMC + 2% VC electrolyte, where the lines with full and hollow circles represents specific capacity and CE of the cells, respectively. Li||NMC811 cells consist of a NMC811 cathode (1.5 mAh cm^{-2}) and a thin Li foil ($50 \mu\text{m}$) or thick Li foil ($450 \mu\text{m}$). They were charged and discharged between 2.8 and 4.4 V at C/3 rate after two formation cycles at C/10, where $1\text{C} = 1.5 \text{ mA cm}^{-2}$.



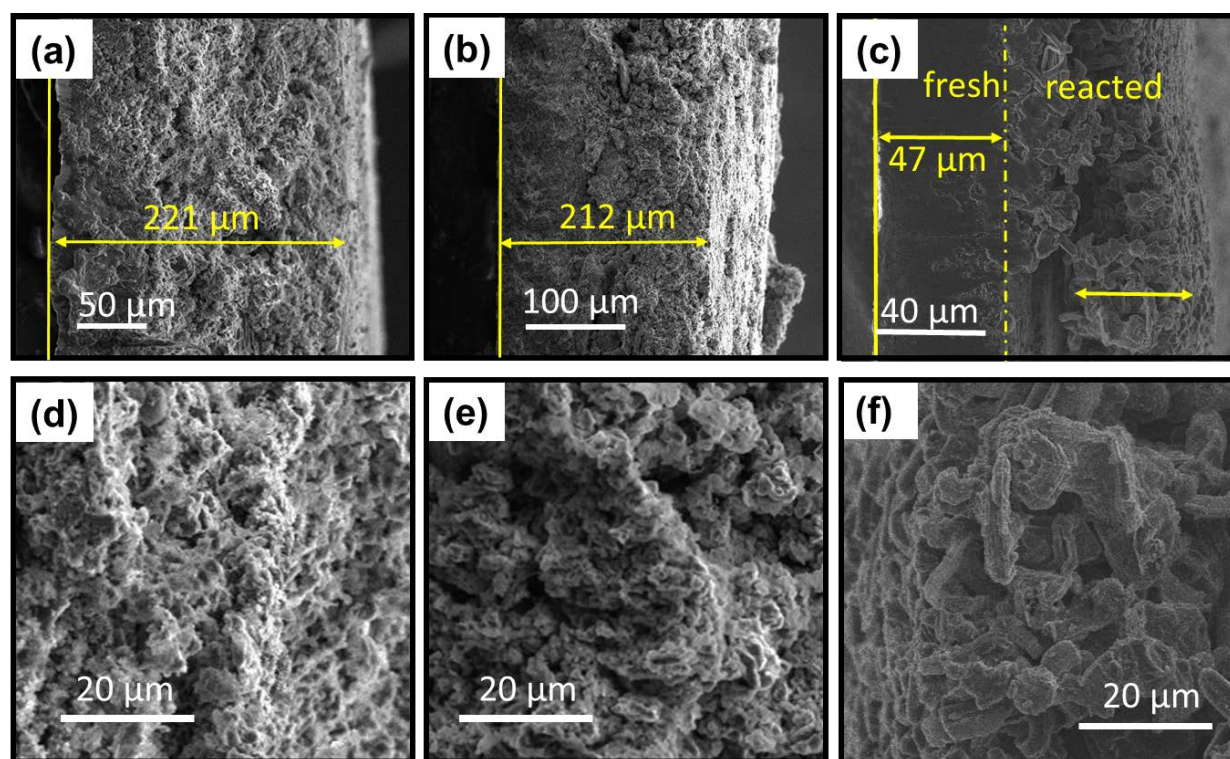
Supplementary Figure 7. SEM images of Al current collectors of (a) fresh foil and (b–d) foil after 100 cycles with electrolytes (b) 1 M LiPF₆/EC-EMC +2% VC, (c) 1 M LiFSI/DME, and (d) 1 M LiFSI/DME-TFEO



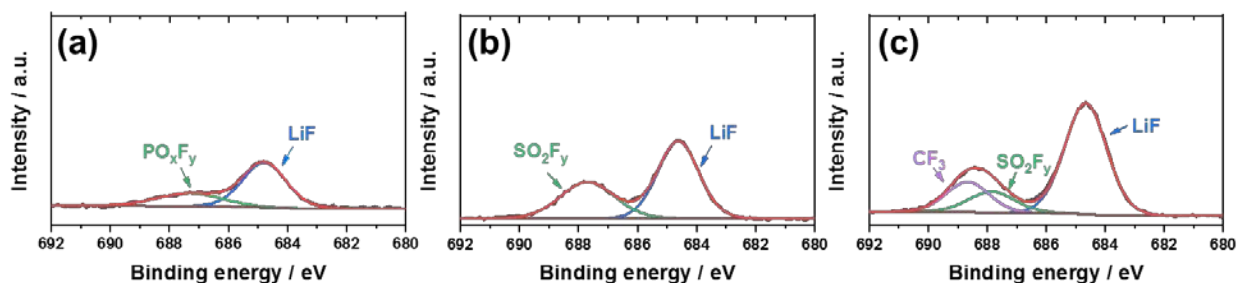
Supplementary Figure 8. Li||NMC811 cell cycling performances with 1 M LiFSI/DME-TFEO electrolyte at 5, 30 and 55 °C, where the lines with full and hollow circles represents specific capacity and CE of the cells, respectively. Li||NMC811 cells consist of a NMC811 cathode (1.5 mAh cm⁻²) and a thin Li foil (50 μm). They were charged and discharged between 2.8 and 4.4 V at C/3 rate after two formation cycles at C/10, where 1C = 1.5 mA cm⁻².



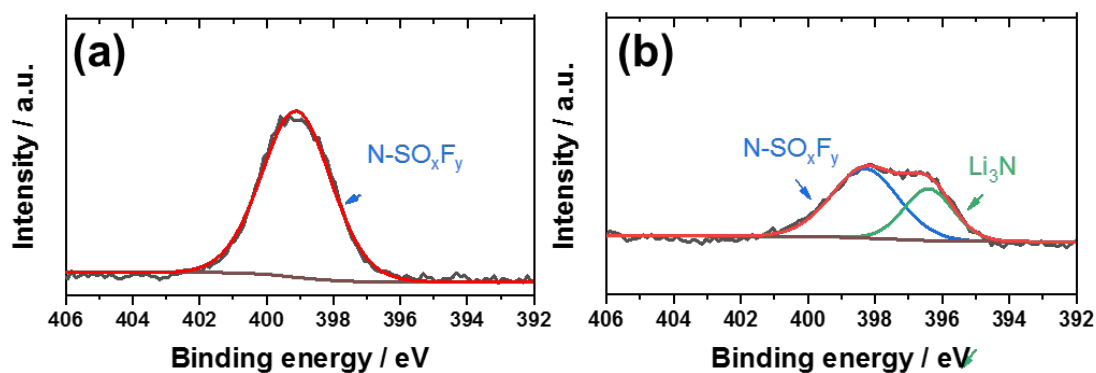
Supplementary Figure 9. Images of the collected Li after 100 cycles. Fresh Li remains under the reacted Li.



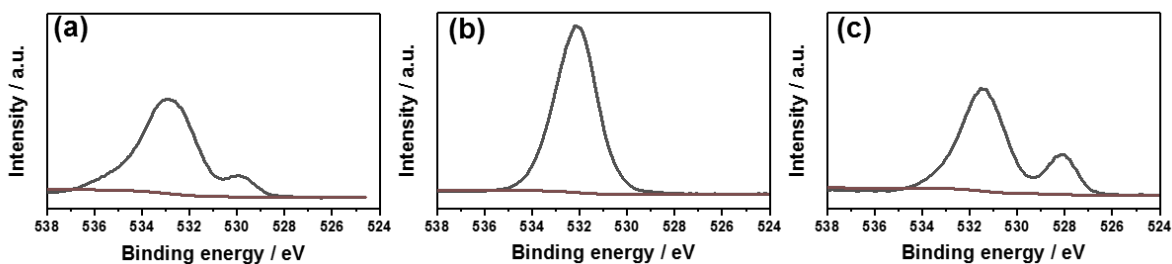
Supplementary Figure 10. Cross-sectional views (a–c) and magnified views (d–f) of SEM images of Li metal electrodes after 100 cycles in Li||NMC811 cells with electrolytes of (a, d) 1 M LiPF₆/EC-EMC +2% VC, (b, e) 1 M LiFSI/DME, and (c, f) 1 M LiFSI/DME-TFEO.



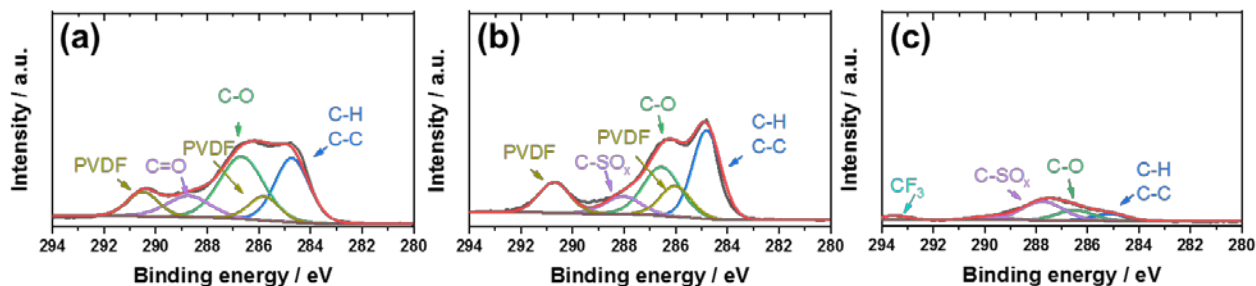
Supplementary Figure 11. F 1s XPS spectra of the Li SEI formed in (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI-DME, and (c) 1 M DME-TFEO after 100 cycles.



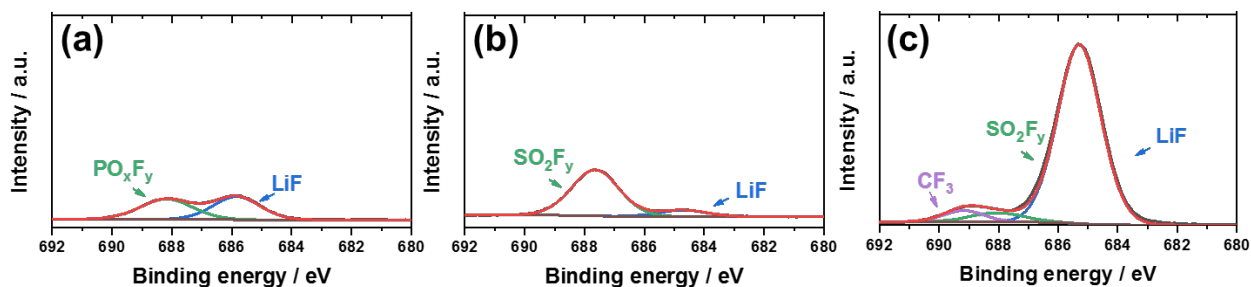
Supplementary Figure 12. N 1s XPS spectra of the Li SEI formed in (a) 1 M LiFSI/DME and (b) 1 M LiFSI/DME-TFEO after 100 cycles.



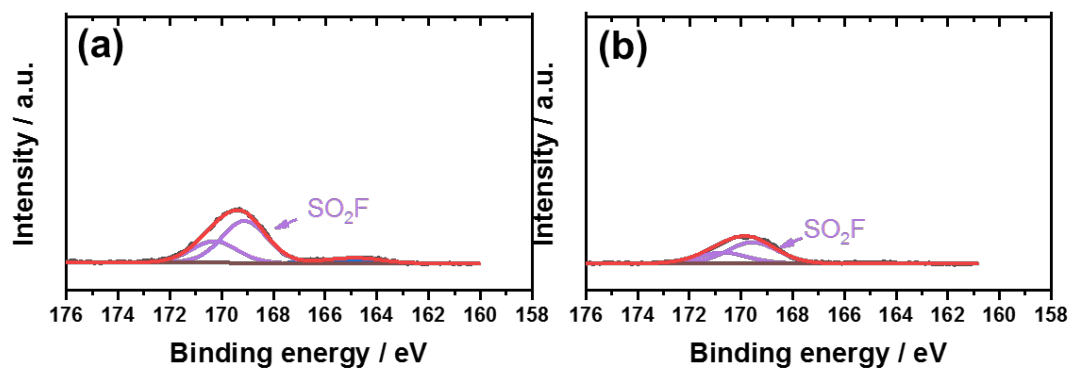
Supplementary Figure 13. O 1s XPS spectra of the Li SEI formed in (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI/DME, and (c) 1 M LiFSI/DME-TFEO after 100 cycles



Supplementary Figure 14. C 1s XPS spectra of the NMC811 CEI formed in (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI/DME, and (c) 1 M LiFSI/DME-TFEO after 100 cycles.



Supplementary Figure 15. F 1s XPS spectra of the NMC811 CEI formed in (a) 1 M LiPF₆/EC-EMC + 2% VC, (b) 1 M LiFSI/DME, and (c) 1 M LiFSI/DME-TFEO after 100 cycles.



Supplementary Figure 16. S 2p XPS spectra of the NMC811 CEI formed in (a) 1 M LiFSI/DME and (b) 1 M LiFSI/DME-TFEO after 100 cycles.