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Design and electrochemical properties of novel fluorinated electrolytes for lithium metal batteries

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General remarks: 1D NMR ^{1}H and ^{13}C were registered at a spectrometer Bruker Fourier 300 (300 MHz/54m), NMR ^{19}F spectra were registered at a Bruker VRX-400 spectrometer. Chemical shifts for ^{1}H NMR spectroscopic data were referenced to internal tetramethylsilane ($\delta = 0$ ppm); chemical shifts for ^{13}C NMR spectroscopic data were referenced to $CDCl_3$ ($\delta = 77$ ppm); chemical shifts for ^{19}F NMR spectroscopic data were referenced to $CFCl_3$ ($\delta = 0$ ppm). ESI MS was registered at a DuoSpray AB Sciex TripleTOF 5600+ spectrometer. Samples were injected through a direct injection loop into a 100 μl min^{-1} flow of methanol.

Viscosities measurements were conducted at 25°Cusing an Electro Magnetically Spinning Viscocometer EMS-1000 by Kyoto Electronics Manufacturing Co. Ltd. Typically, the liquid sample volume is 0.3 cm^3.

Linear sweep voltammetry was performed using a Versatile Multichannel Potentiostat (Biologic S.A) piloted by an ECLab V9.97 interface in Li||stainless steel CR2032 coin-type cells with a potential sweep of 0.2 mV s^{-1} from 2.5 V to 5.5 V. Galvanostatic charge/discharge tests and voltage tests of Li||Li symmetric cells were carried out in the potential range of 2.7–4.5 V *vs*. Li^+/Li using a battery testing system (Neware) with a C-rate of C/10 for first three cycle and C/2 rate for the rest of the experiment in a set of three coin cells for each experiment. The two-electrode CR2032 coin-type cells were assembled in an argon-filled glovebox (MBraun, $p(O_2) = 0.1$ ppm, $p(H_2O) = 0.1$ ppm) with Li metal (Gelon Lib, 99.9%) as an anode and polypropylene separators. Round-shaped electrodes with an area of 1.54 cm^2 and an average mass loading of NMC622 (Rustor, Russia) or NMC811 (Rustor, Russia) of 10–15 mg cm^{-2} were used as cathodes.

Electrolytes used were 1 M $LiBF_4$ (Sigma-Aldrich, 98%, anhydrous), 1 M $LiPF_6$ (GelonLib, ≥99.95%) in a 9:1 v/v mixture of synthesized α-methoxy-ω-(2,2,2-triluoroethoxy)alkanes **1-3** and fluoroethylene carbonate (Xiamen TOB New Energy Technology, ≥99.95%). Coin cells NMC622||Li and NMC811||Li with 1 M $LiPF_6$ (GelonLib, ≥ 99.95%) in 1:1 v/v ethylene carbonate (Sigma-Aldrich, 99%, anhydrous) and dimethyl carbonate (Xiamen TOB New Energy Technology, ≥ 99.9%) were used for reference. THF (Rushim, ≥ 99.8%, grade 'for synthesis') was dried by distillation with sodium. 2,2,2-Trifluoroethyl tosylate was synthesized from 2,2,2-trifluoroethanol and *p*-toluenesulfonyl chloride (W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, 1955, **77**, 4899).

General Procedure for the synthesis of α-methoxy-ω-(2,2,2-triluoroethoxy)alkanes 1-3: To a round-bottom flask were added dry THF (150 ml) and the corresponding ω-methoxyalkanol (0.172 mol, 1 equiv.). The solution was cooled to 0°C, and then sodium hydride (60% dispersion in mineral oil, 7.60 g, 0.190 mol, 1.10 equiv.) was added slowly in portions. Bubbling was observed upon sodium hydride addition. Then, 2,2,2-trifluoroethyl tosylate (45.91 g, 0.181 mol, 1.05 equiv.) was added to the stirred suspension, followed by heating to reflux overnight. The solid residue was filtered off, the solvents were removed from the filtrate, and the crude sample was distilled under reduced pressure to yield the final products.

1-Methoxy-2-(2,2,2-trifluoroethoxy)ethane **3FEME (1)**, colorless liquid, bp = 65°C (170 Torr.), yield 80% (23.66 g). ^{1}H NMR ($CDCl_3$): δ 3.39 (3H, s, CH_3), 3.55 – 3.58 (2H, m, CH_2), 3.76 – 3.78 (2H, m, CH_2), 3.86 – 3.94 (2H, m, CH_2). ^{13}C NMR ($CDCl_3$): δ 59.1, 68.6 (q, J = 33.53 Hz, C-CF_3), 68.7 (q, J = 33.53 Hz, C-CF_3), 71.89, 71.90, 123.9 (q, J = 279.4 Hz, CF_3).^{19}F NMR ($CDCl_3$): δ -74.20 (t, J = 8.7 Hz, CF_3). ESI-MS calculated for $C_5H_{10}F_3O_2^+$ [M+H$^+$] 159.0628, found 159.0630.

1-Methoxy-3-(2,2,2-trifluoroethoxy)propane **3FEMP (2)**, colorless liquid, bp = 65°C (120 Torr.), yield 47% (15.00 g). ^{1}H NMR ($CDCl_3$): δ 1.89 (2H, qt, J = 6.24 Hz, C-CH_2-C), 3.36 (3H, s, CH_3), 3.47 – 3.51 (2H, m, CH_2), 3.69 – 3.74 (2H, m, CH_2), 3.83 (2H, q, J = 8.75 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 29.8, 58.6, 58.5, 68.4 (q, J = 33.8 Hz, C-CF_3), 69.0, 69.7, 124.1 (q, J = 279.6 Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ -74.29 (t, J = 8.9 Hz, CF_3). ESI-MS calculated for $C_6H_{12}F_3O_2^+$ [M+H$^+$] 173.0784, found 173.0785.

1-Methoxy-4-(2,2,2-trifluoroethoxy)butane **3FEMB (3)**, colorless liquid, b*p* = 76-77°C (50 Torr.), yield 59% (20.29 g). ^{1}H NMR ($CDCl_3$): δ 1.60 – 1.77 (4H, m, 2CH_2), 3.36 (3H, s, CH_3), 3.38 – 3.46 (2H, m, CH_2), 3.60 – 3.70 (2H, m, CH_2), 3.82 (2H, q, J = 8.75 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ26.0, 26.2, 58.5, 68.2 (q, J = 33.8 Hz, C-CF_3), 72.3, 72.6, 124.1 (q, J = 279.6 Hz, CF_3). ^{19}F NMR ($CDCl_3$): δ -74.23 (q, J = 8.6 Hz, CF_3). ESI-MS calculated for $C_7H_{14}F_3O_2^+$ [M+H$^+$] 187.0941, found 187.0939.

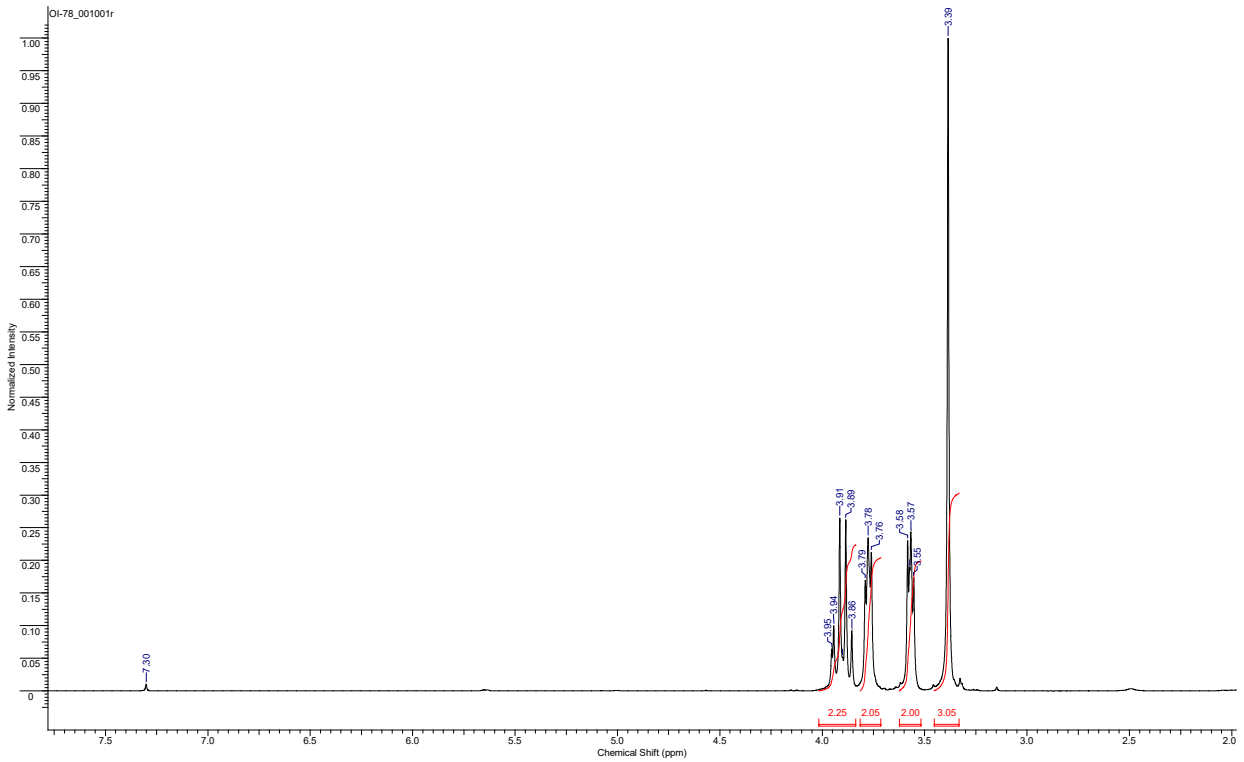
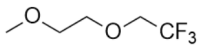


Figure S1. ^{1}H NMR for 3FEME **1**  .

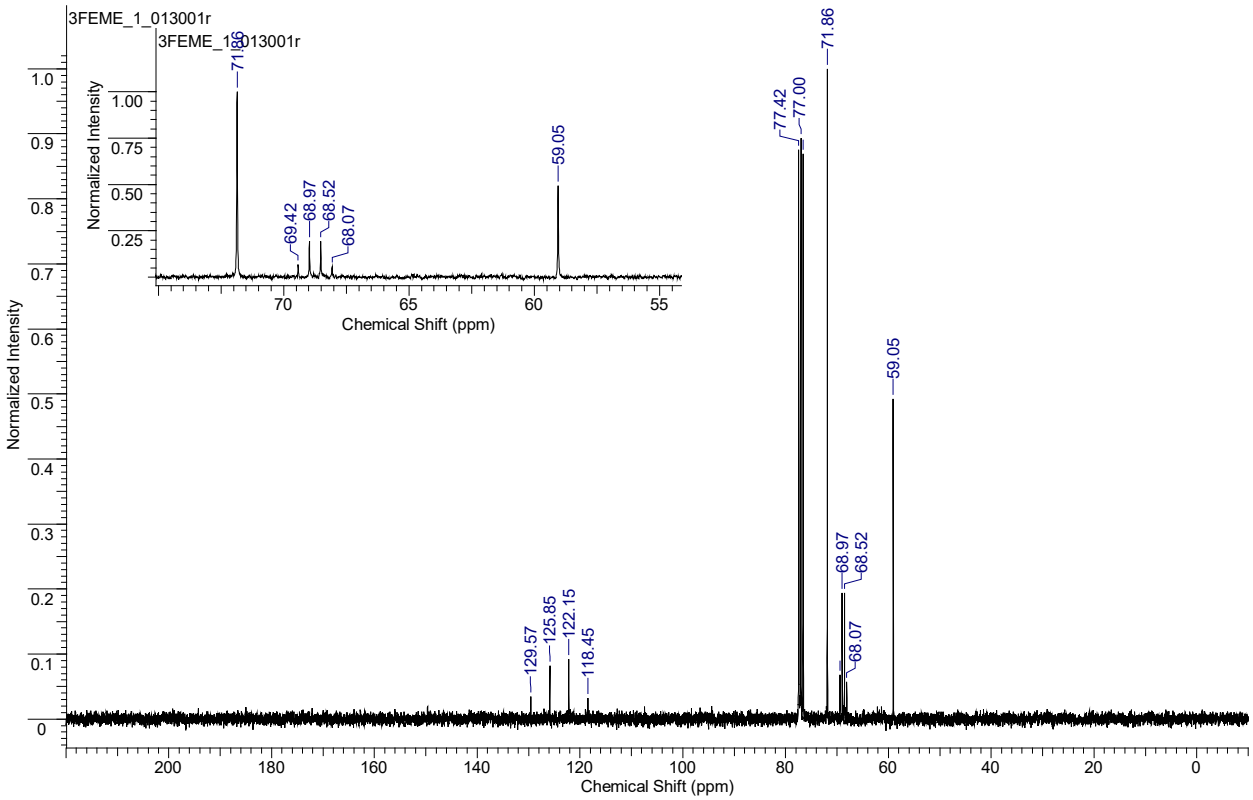
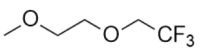


Figure S2. ^{13}C NMR for 3FEME **1**  .

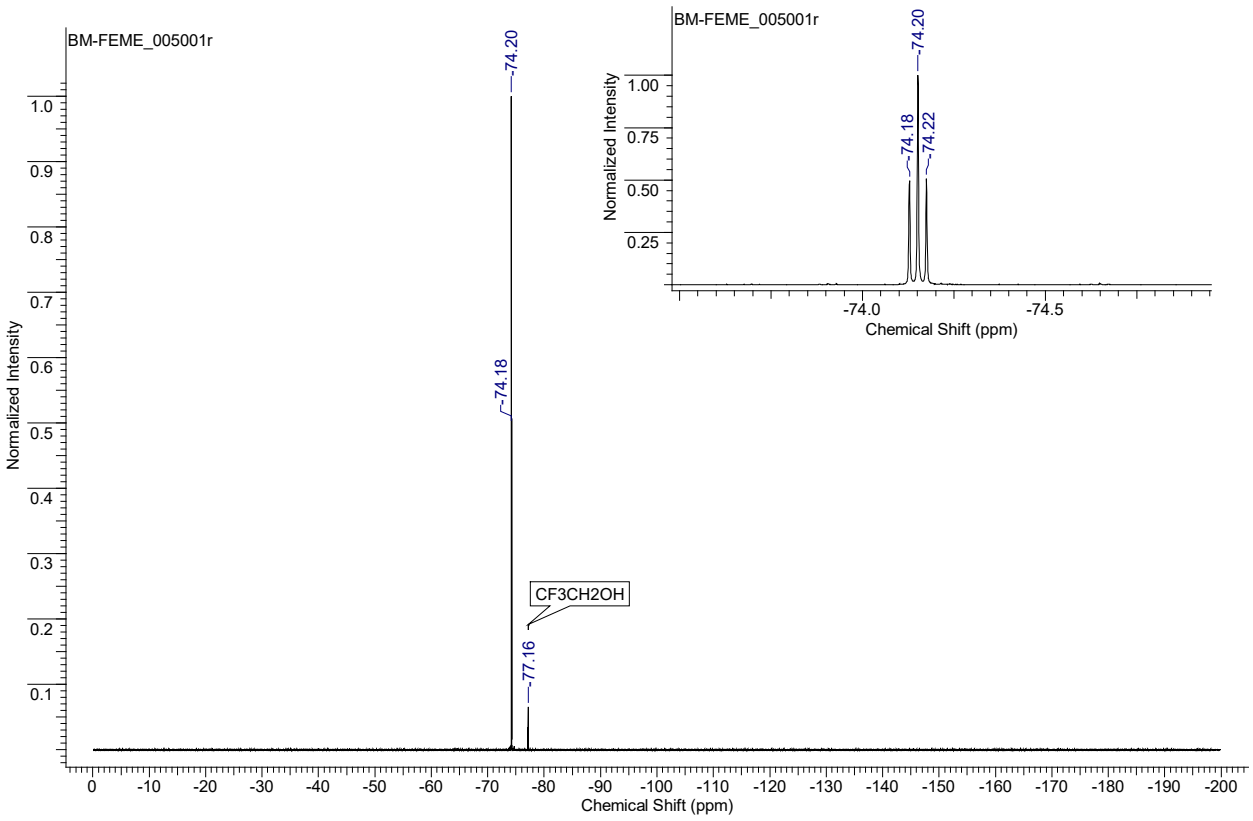
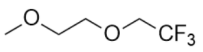


Figure S3. ^{19}F NMR for 3FEME **1**  .

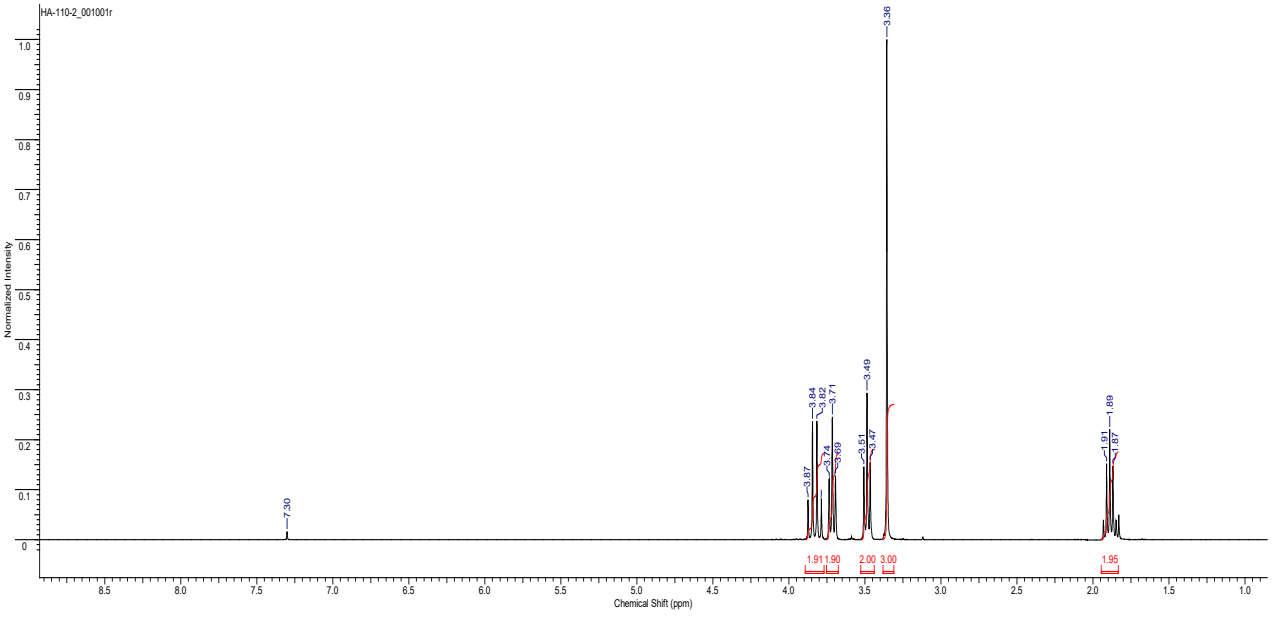
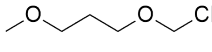


Figure S4. ^{1}H NMR for 3FEMP **3**  .

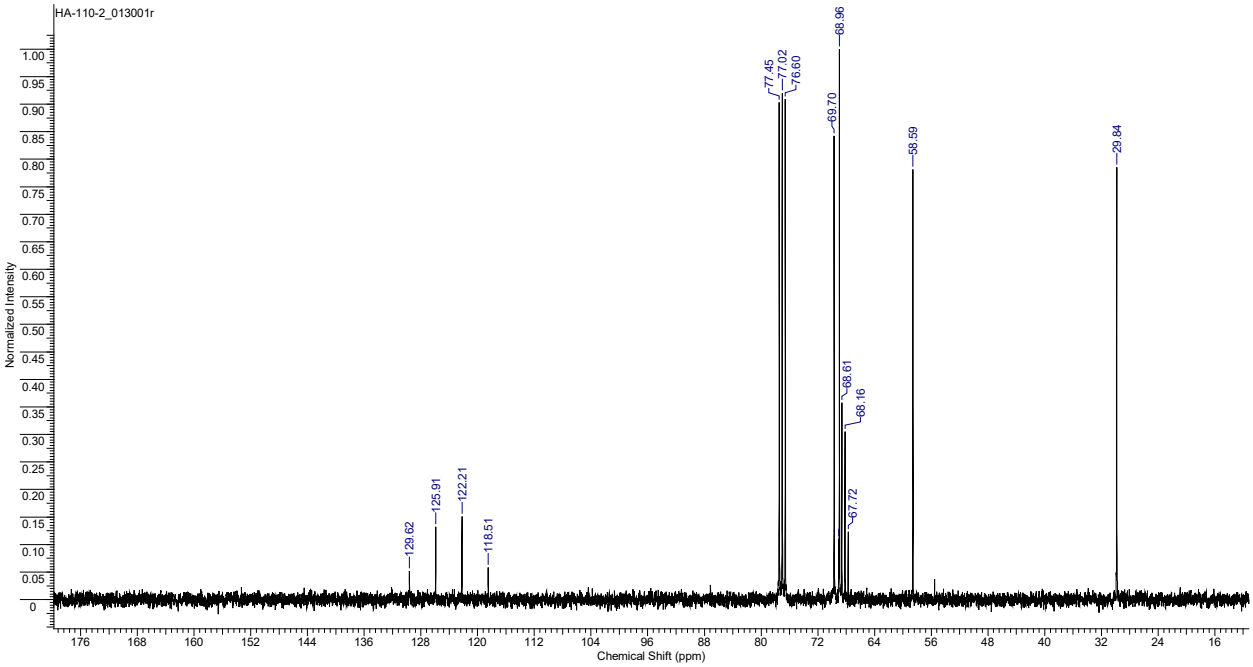
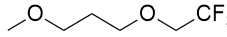


Figure S5. ^{13}C NMR for 3FEMP **2**  .

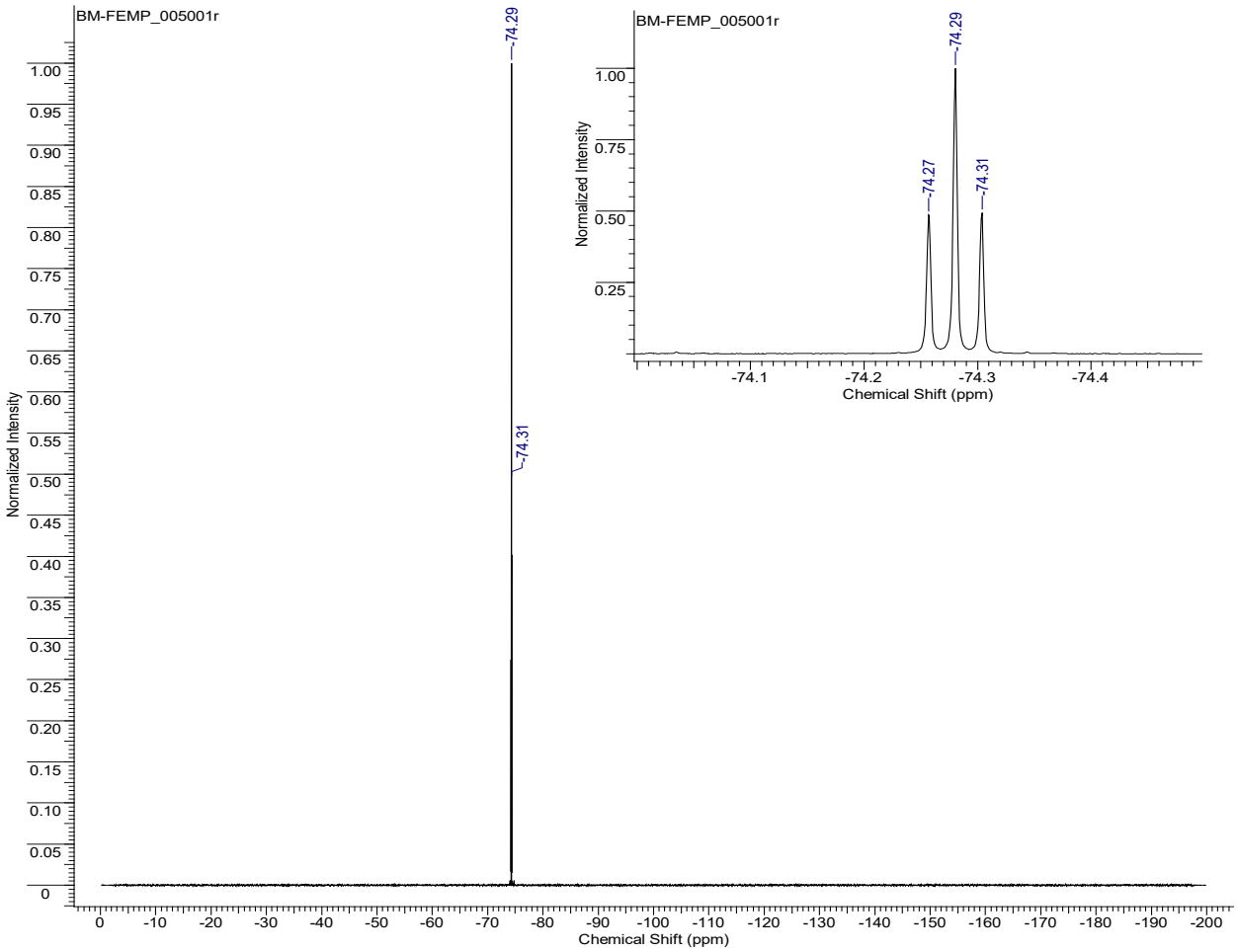
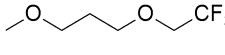


Figure S6. ^{19}F NMR for 3FEMP **2**  .

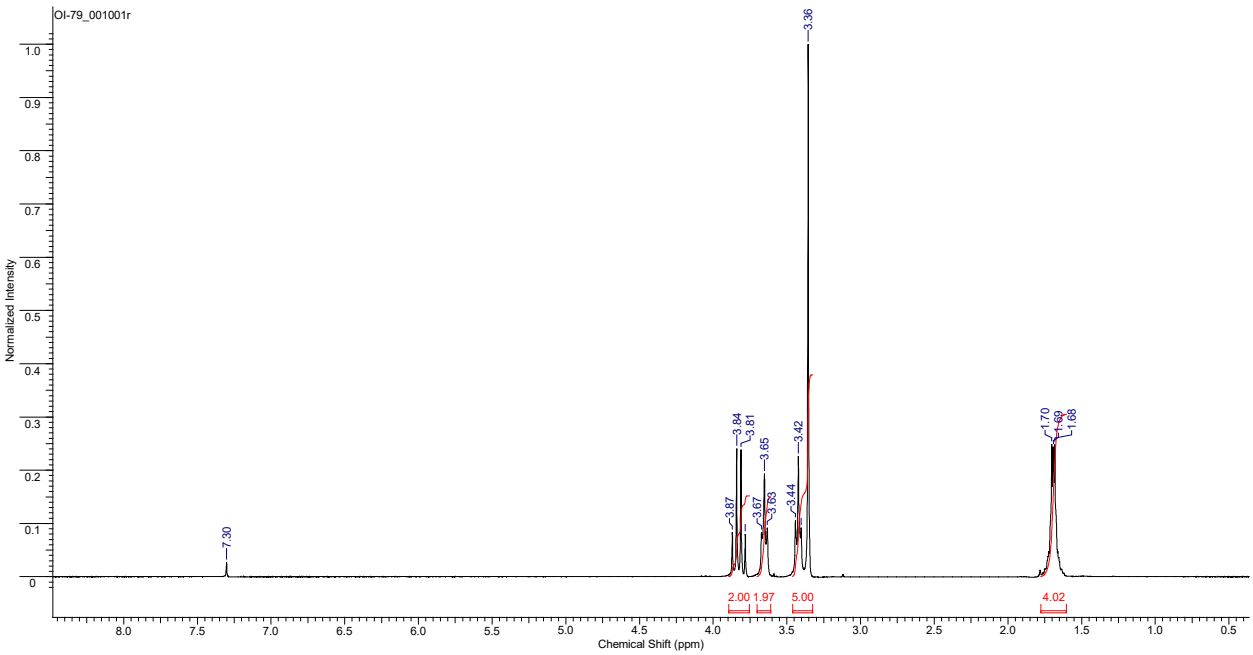
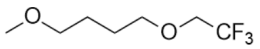


Figure S7. ^{1}H NMR for 3FEMB **3** 

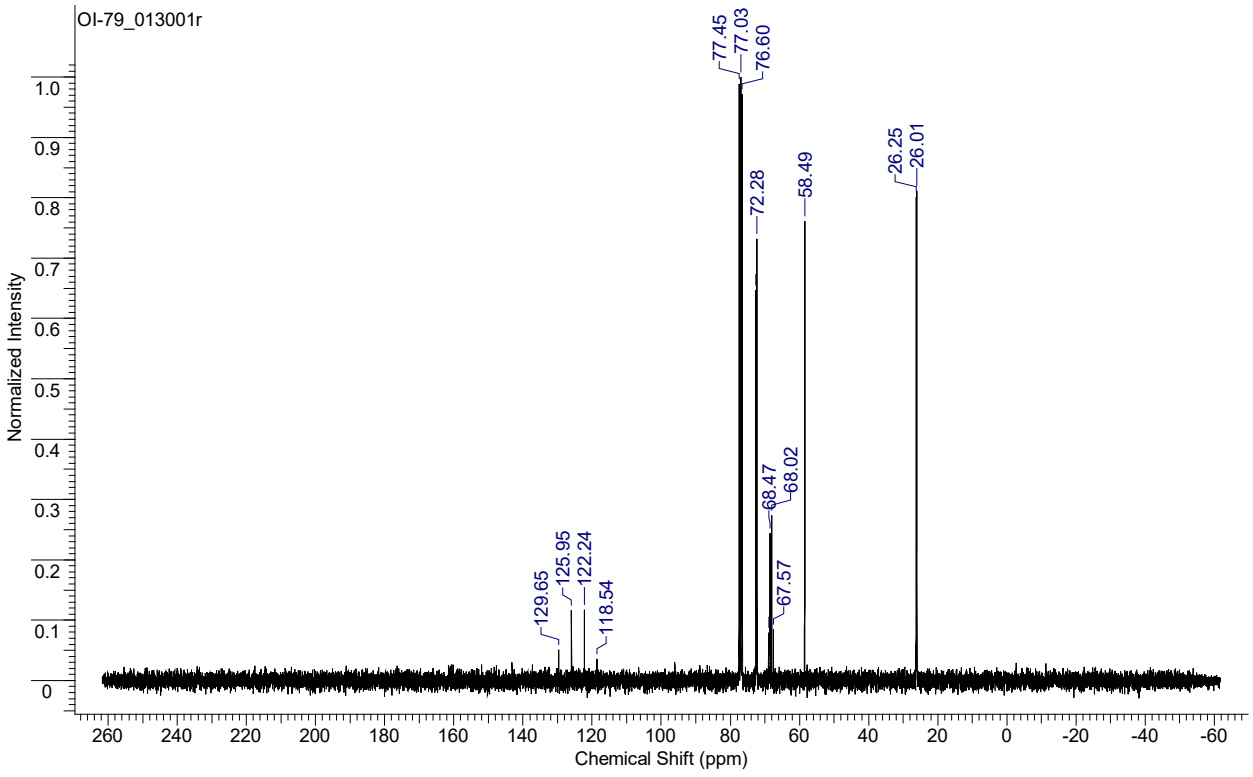
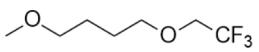


Figure S8. ^{13}C NMR for 3FEMB **3** 

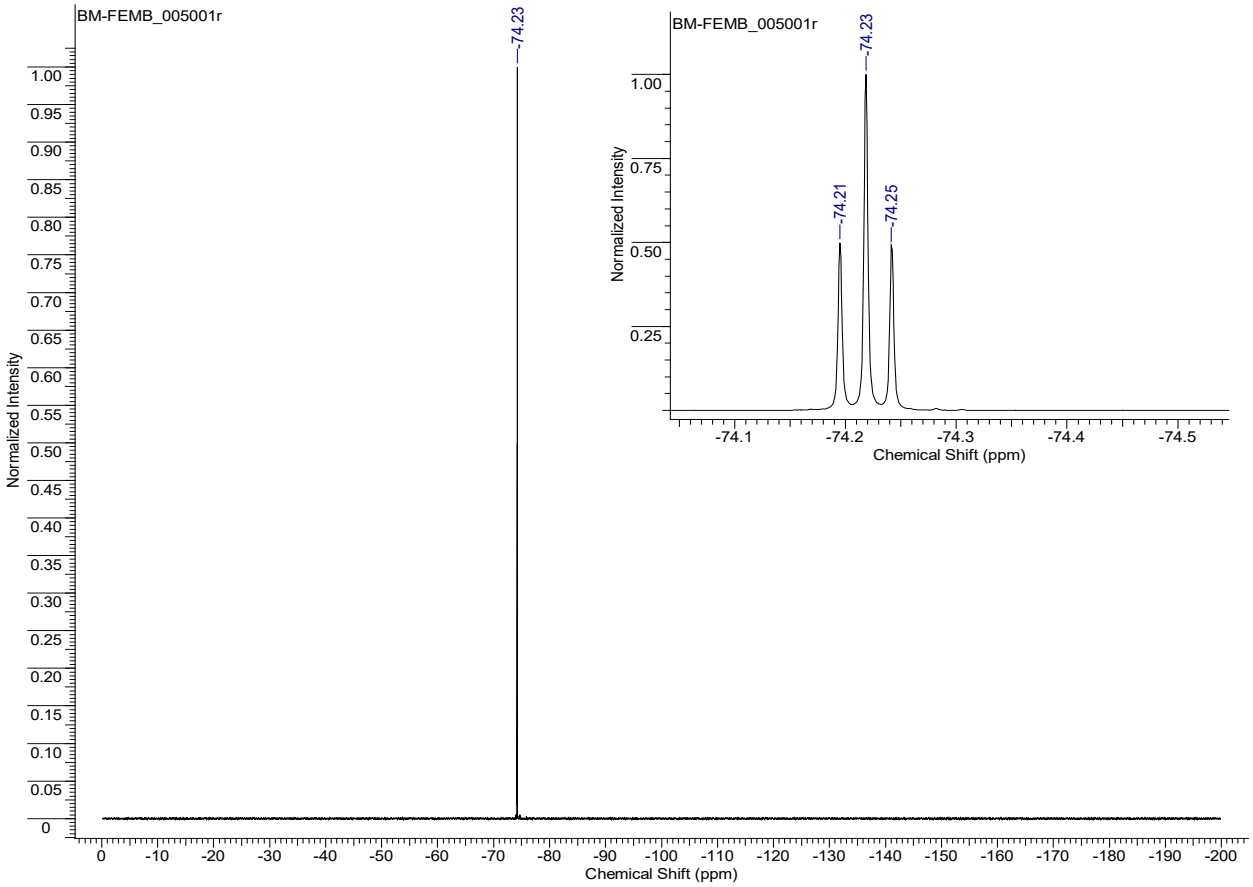
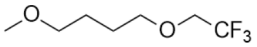


Figure S9. ^{19}F NMR for 3FEMB **3**  .

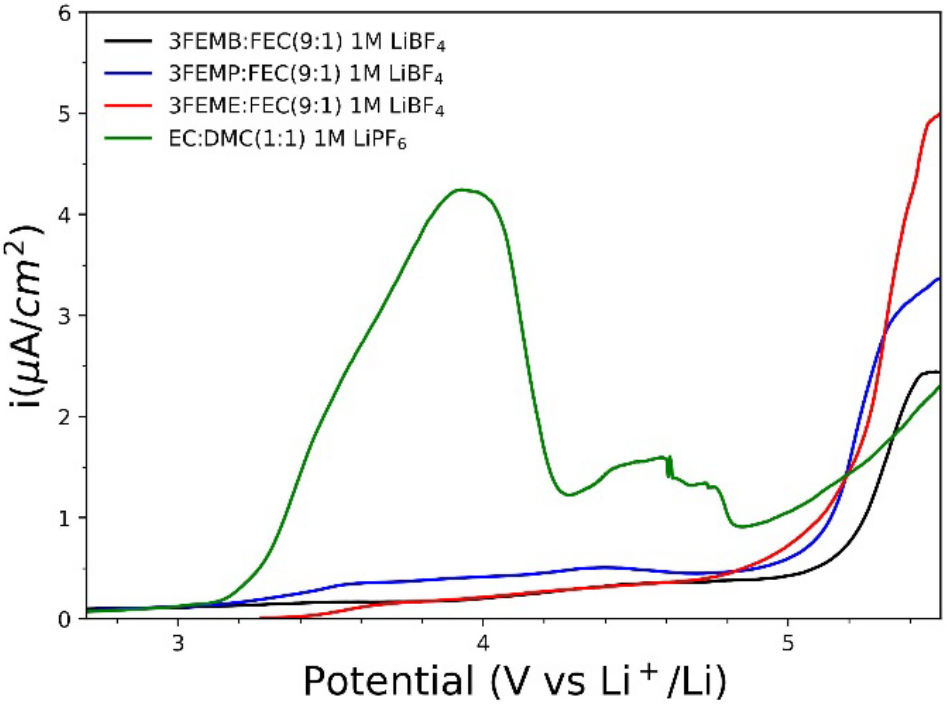


Figure S10. LSV of Li||stainless steel coin-cells cycled at 0.5 mA h cm^{-2}.

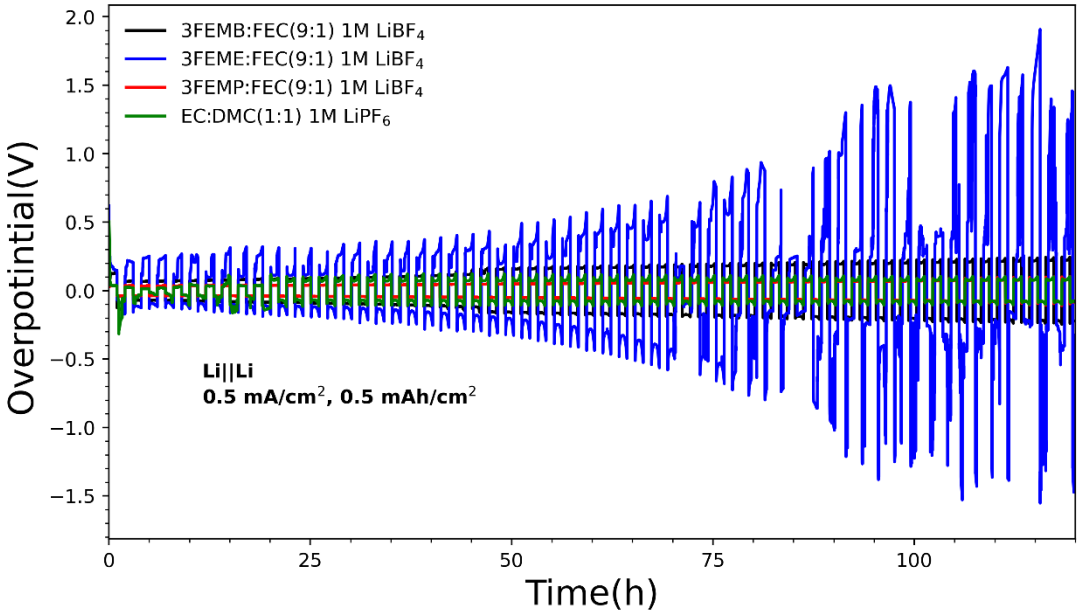


Figure S11. Voltage profiles of Li||Li symmetric cells cycled at 0.5 mA h cm^{-2}.

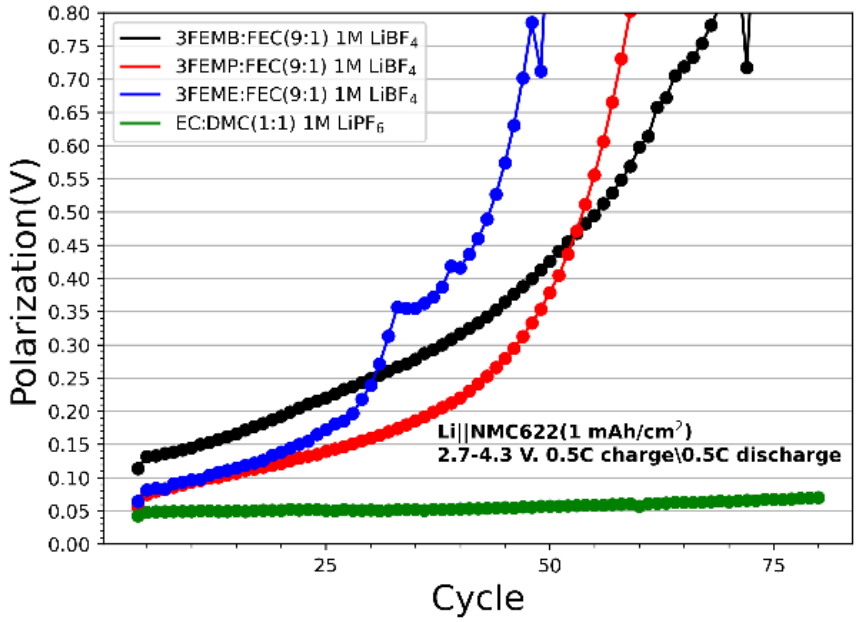


Figure S12. Voltage polarization of Li||NMC622 with 1M $LiBF_4$ in 3FEME(**1**)/FEC, 3FEMP(**2**)/FEC and 3FEMB(**3**)/FEC electrolytes.

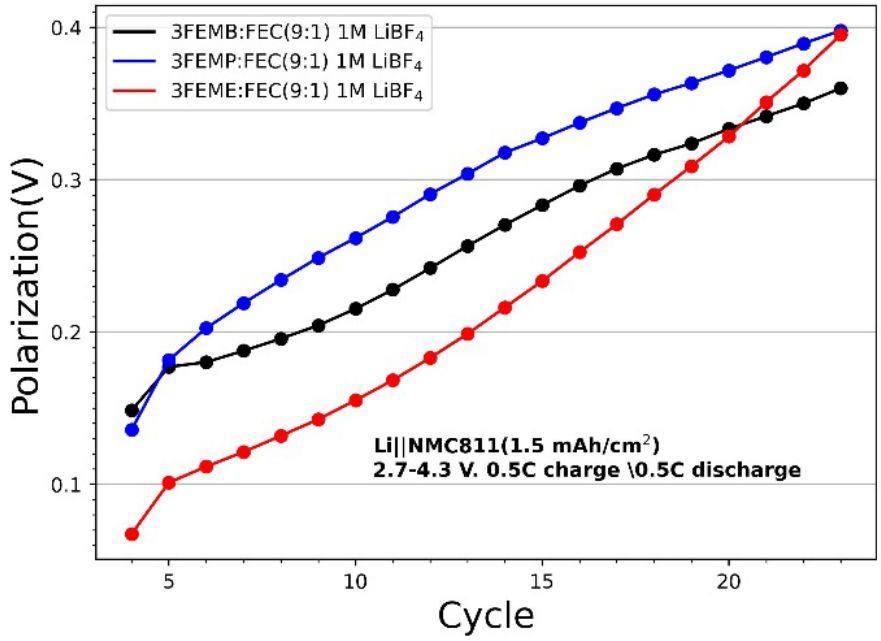


Figure S13. Voltage polarization of Li||NMC811 with 1M $LiBF_4$ in 3FEME(**1**)/FEC, 3FEMP(**2**)/:FEC and 3FEMB(**3**)/FEC electrolytes.

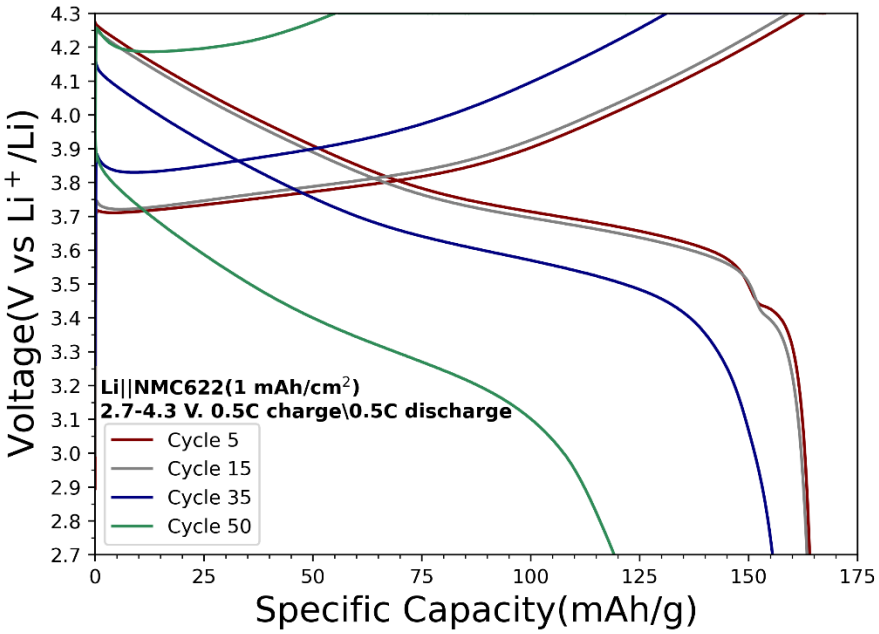


Figure S14. Cycling performance of 1M $LiBF_4$ 3FEME(**1**)/FEC electrolyte in Li||NMC622 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CCCV charge CC discharge, current cut-off 2%.

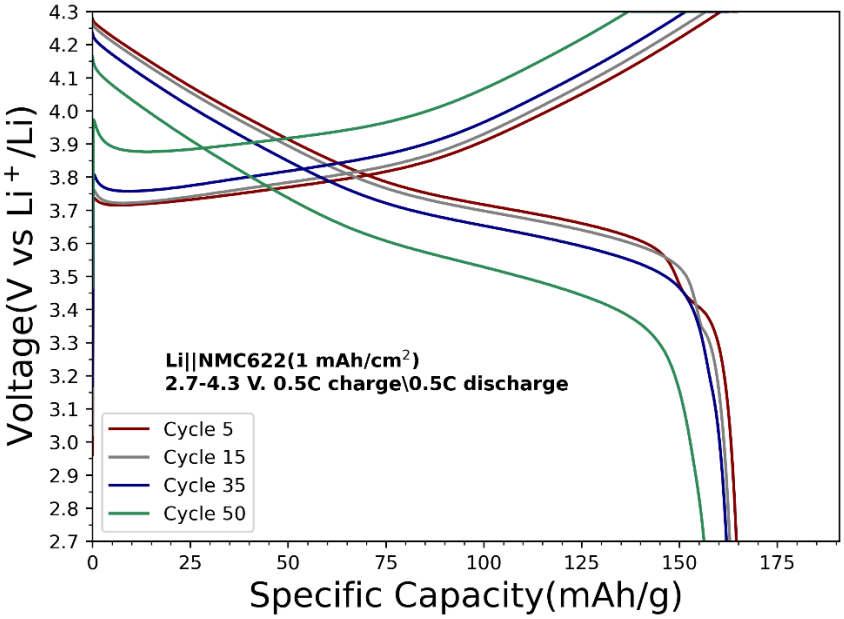


Figure S15. Cycling performance of 1M $LiBF_4$ 3FEMP(**2**)/FEC electrolyte in Li||NMC622 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CCCV charge CC discharge, current cut-off 2%.

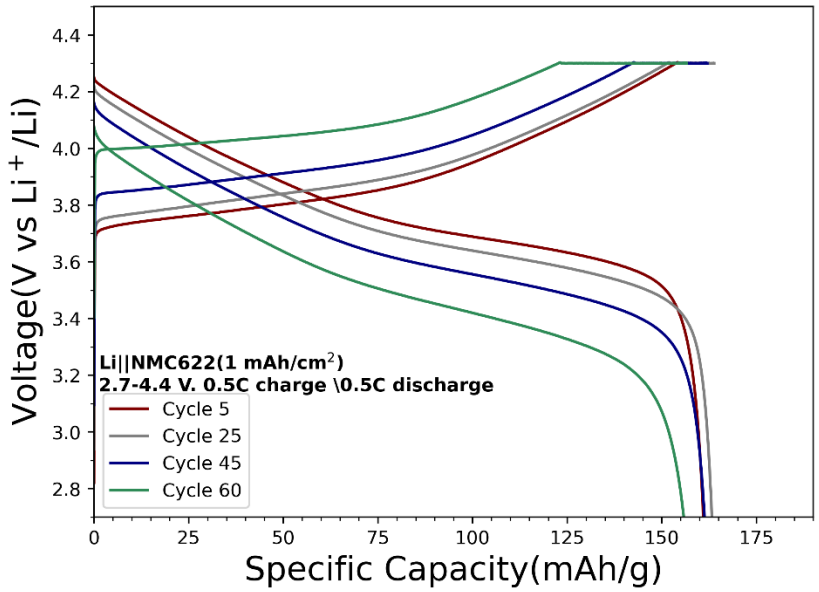


Figure S16. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC622 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CCCV charge CC discharge, current cut-off 2%.

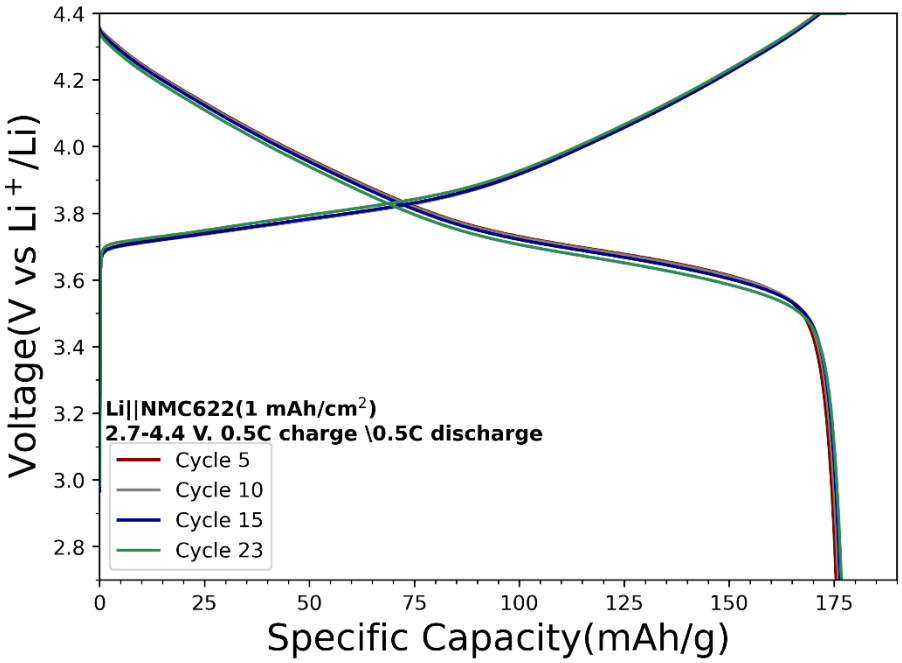


Figure S17. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC622 (1 mAh/cm^2) cells from 2.7 V to 4.4 V. CCCV charge CC discharge, current cut-off 2%.

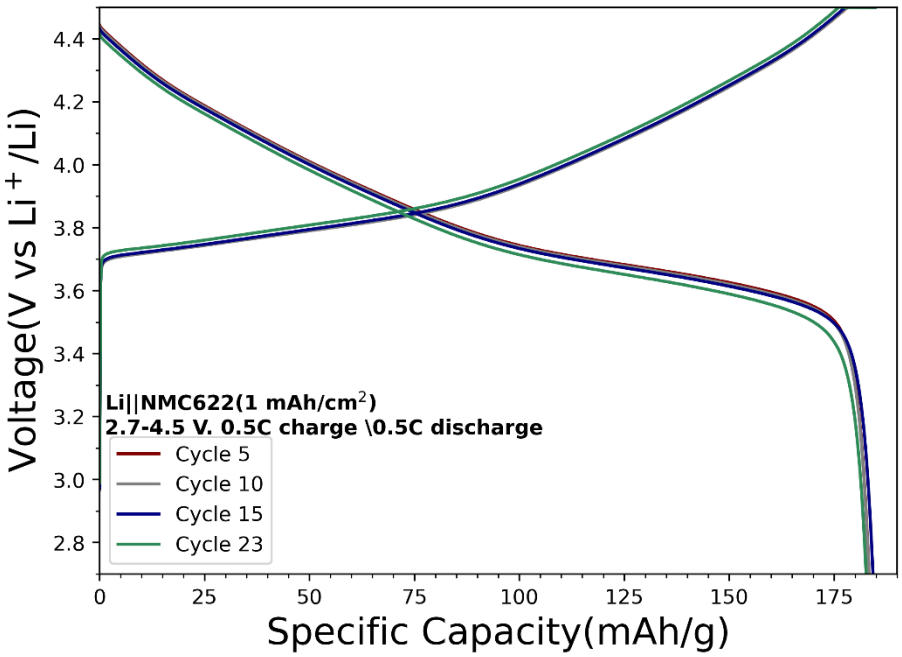


Figure S18. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC622 (1 mA h cm^{-2}) cells from 2.7 V to 4.5 V. CCCV charge CC discharge, current cut-off 2%.

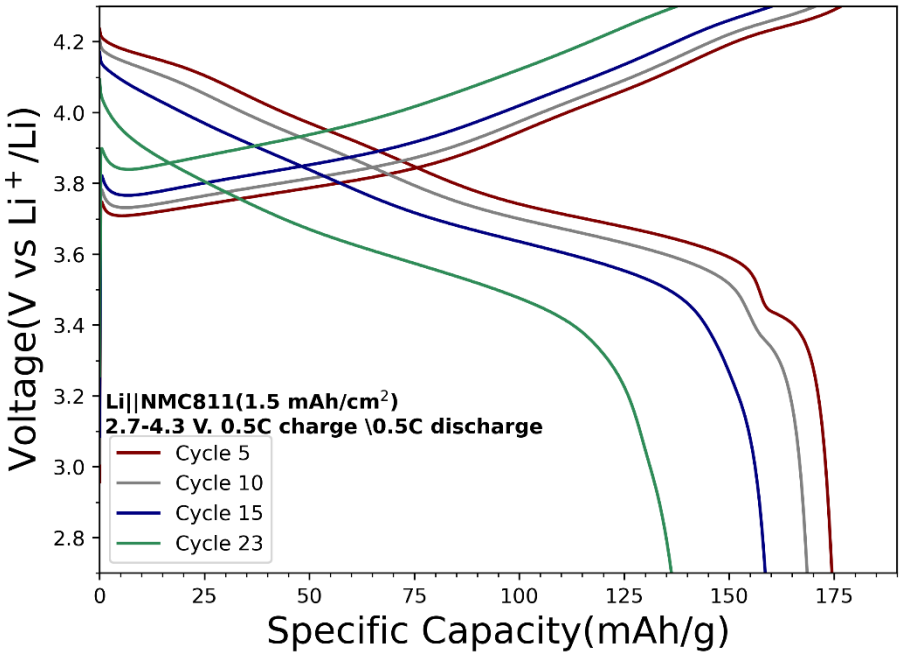


Figure S19. Cycling performance of 1M $LiBF_4$ 3FEME(**1**)/FEC electrolyte in Li||NMC811 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CC charge/discharge.

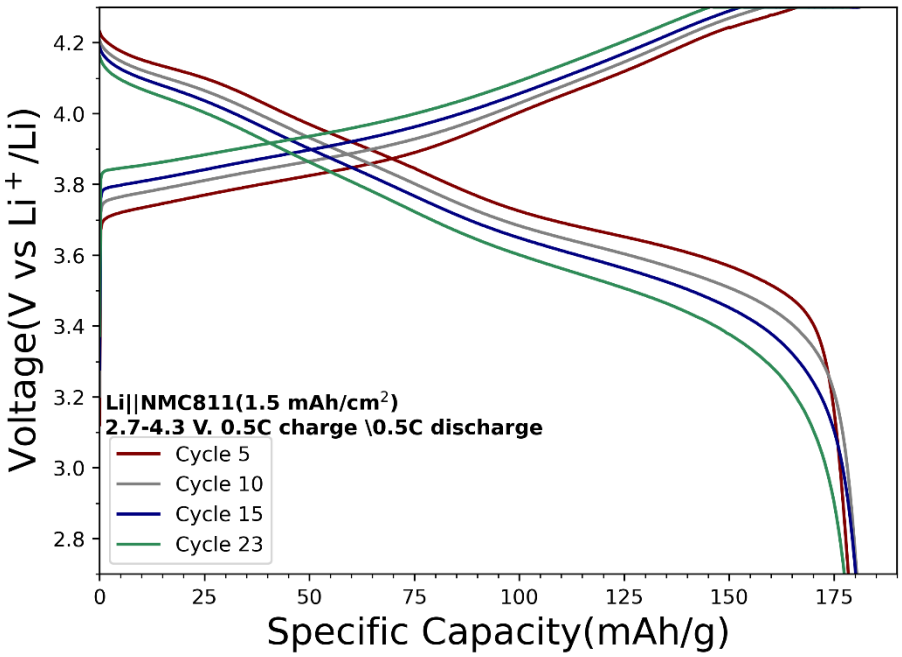


Figure S20. Cycling performance of 1M $LiBF_4$ 3FEMP(**2**)/FEC electrolyte in Li||NMC811 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CCCV charge CC discharge, current cut-off 2%.

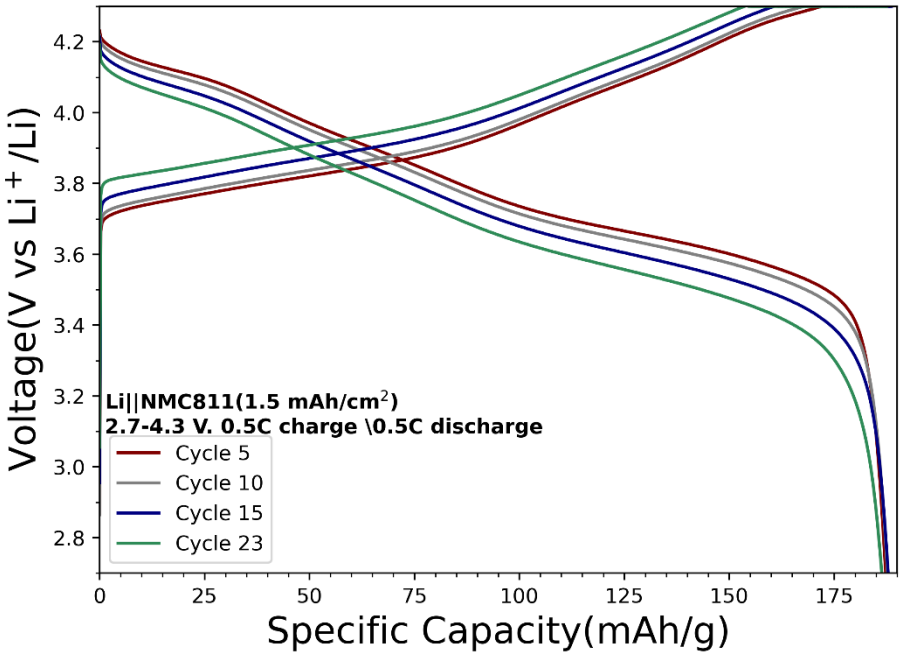


Figure S21. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC811 (1 mA h cm^{-2}) cells from 2.7 V to 4.3 V. CCCV charge CC discharge, current cut-off 2%.

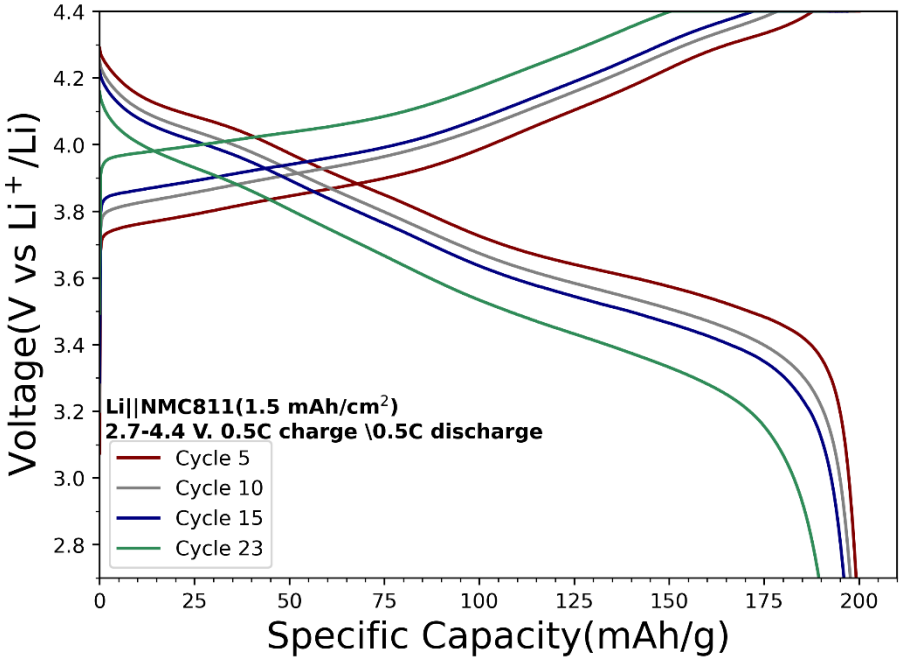


Figure S22. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC811 (1 mA h cm^{-2}) cells from 2.7 V to 4.4 V. CCCV charge CC discharge, current cut-off 2%.

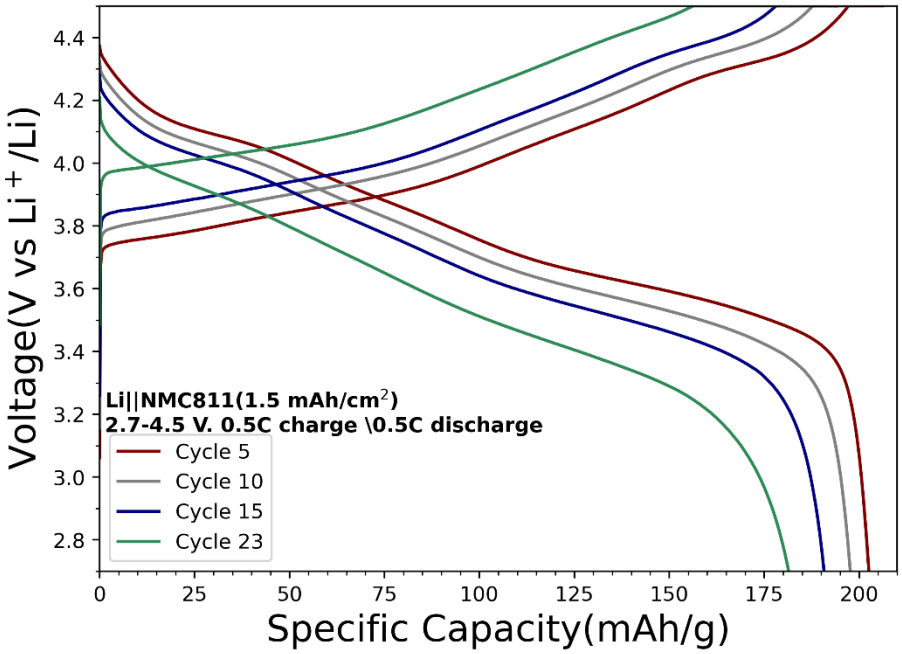


Figure S23. Cycling performance of 1M $LiBF_4$ 3FEMB(**3**)/FEC electrolyte in Li||NMC622 (1 mA cm^{-2}) cells from 2.7 V to 4.5 V. CCCV charge CC discharge, current cut-off 2%.