Experimental

1. Preparation of the fluorinated electrolytes:

Ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were purchased from Novolyte Technologies and dried over molecular sieves. Lithium hexafluorophosphate (LiPF₆) is purchased from Stella Chemifa Corporation and was used as received. Fluorinated carbonate F-AEC, F-EMC and F-EPE are provided by Daikin Industries, Ltd. (Japan). The F-compounds are dried over 4A molecular sieves to a moisture level of <10ppm measured by Karl-Fischer titration. 1.2M LiPF₆ in EC/EMC 30:70 (by weight) was selected as baseline electrolyte, while high voltage electrolytes were formulated by various ratios of fluorinated solvents. All procedures involving electrolyte preparation and cell assembly were carried out in an argon filled glove box with an oxygen level below 5 ppm.
2. NMR Characterization:

The purity of the fluorinated solvent F-AEC, F-EPE and F-EMC were identified by $^1$H, $^{13}$C and $^{19}$F NMR (Bruker model DMX 500 NMR spectrometer (11.7 T)) and their NMR spectra were shown in Fig. S1-S9.

![Fig. S1 $^1$H NMR spectrum of F-AEC.](image)

![Fig. S2 $^{13}$C NMR spectrum of F-AEC.](image)
Fig. S3 $^{19}$F NMR spectrum of F-AEC.

Fig. S4 $^1$H NMR spectrum of F-EPE.

Fig. S5 $^{13}$C NMR spectrum of F-EPE.
**Fig. S6** $^{19}$F NMR spectrum of F-EPE.

**Fig. S7** $^1$H NMR spectrum of F-EMC.

**Fig. S8** $^{13}$C NMR spectrum of F-EMC.
Fig. S9 $^{19}$F NMR spectrum of F-EMC.

3. Ionic conductivity of the fluorinated high voltage electrolytes was determined by YSI 3200 Conductivity Instrument equipped with an YSI 3253 conductivity cell. Conductivity at various temperatures were measured and summarized in Fig. S10.

Fig. S10 Conductivity measurement of Gen 2 and E1 to E6 electrolyte.

4. Electrochemical floating test:

The electrochemical floating test was performed in the argon filled glove box using a Solartron Analytical 1470E Cell Test System electrochemical analyzer. A three-electrode cell was custome-made using a 20 mL glass vial with platinum as the working electrode (1mm in diameter) and lithium foil as both the reference and counter electrodes. This test was run under various designated potentials relative to the lithium metal reference electrode for 10 minutes and
the corresponding currents were recorded. Fig. SX are the results of oxidation stability of Gen2, E5 and E6 electrolyte at high potentials up to 6.0V.

Fig. S11 Comparison of the floating test data of E5 and E6 with Gen 2 under different potentials.

5. LNMO/LTO cell cycling performance test:
To evaluate the performance of the fluorinated electrolyte, 2032 coin cells were fabricated with different electrolyte compositions and cycled on a Maccor Inc. Electrochemical analyzer using LiNi_{0.5}Mn_{1.5}O_4 as the cathode and Li_4Ti_5O_{12} (LTO) electrode as the anode. The separator, Celgard 3501, was soaked with the appropriate electrolyte sample before being placed in the cell. After one formation cycle, typically between 2.0 and 3.45V for LTO electrode at C/10 (0.2 mA)
rate, the coin cells were cycled continuously at room temperature or 55 °C, typically at a C/2 (1.0 mA) rate.

**Fig. S12** Capacity retention data of LTO/LNMO cells using Gen 2, E1 electrolyte under room temperature.

**Fig. S13** Extended capacity retention profile of LTO/LNMO cells using Gen 2, E1 and E2 electrolyte at 55°C. 200 cycles is close to the limit set by the lithium dendrite growth in a half cell.