Experimental Section

Computational Details: To allow the best comparison to the oxidative decomposition mechanism of $EC^{\bullet+}$, [1] we performed DFT calculations to investigate the possible decomposition pathways of $FEC^{\bullet+}$, and the geometry optimizations and transition state searches were performed on the B3LYP [2] level with 6-311++G (d, p) basis set [3]. All calculations were performed with Gaussian 09 program package. [4] All transition states were confirmed by intrinsic reaction coordinate (IRC) toward a set of pre- and postreaction structures. [5, 6] The computed structures are displayed with IQmol.

Preparation of Materials and Electrolytes: High-voltage positive electrode powders, spinel $LiNi_{0.5}Mn_{1.5}O_4$ was prepared using solid state reaction as reported elsewhere. [7] The solvent-fluoroethylene carbonate (FEC) was purchased from BASF SE (purity 99.9%, $H_2O \leq 10$ ppm) without any additional in-house purification process. Li battery grade ethyl methyl carbonate (EMC, purity 99.99%, $H_2O \leq 10$ ppm) and lithium hexafluorophosphate ($LiPF_6$, purity 99.95%, $H_2O \leq 20$ ppm) were obtained from Zhangjiagang Guotai Huarong New Chemical Materials Co. Ltd, China, and used without further purification. The electrolyte used in this work was prepared in an argon filled glove box with an oxygen and water level below 5 ppm by dissolving 1 mol L^{-1} $LiPF_6$ in a binary mixture solution of fluoroethylene carbonate (FEC) and ethylmethyl carbonate (EMC) with different volume ratios. The conventional EC-based electrolyte selected as the baseline electrolyte was composed of 1.0 mol L^{-1} $LiPF_6$ dissolved in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (EMC) in a 3:7 volume ratio.

Electrochemical Tests: The ion conductivity of the selected electrolyte was measured on DDS-307 (INESA Scientific Instrument Co., Ltd, Shanghai, China) in 25°C room temperature. The oxidative stability of the electrolytes was measured by cyclic voltammetry (CV) experiments. CVs were tested on Autolab Electrochemical Analytical Instrument (ECO CHEMIE, B. V. Utrecht, The

Netherlands) using three-electrode electrochemical cell (Pt as working electrode, Li foil as both reference electrode and counter electrode) at a scan rate of 5 mV s^{-1}.

The positive electrode consisted of $LiNi_{0.5}Mn_{1.5}O_4$ active powder (85 wt %), conductive carbon: Super P carbon black (7 wt %) and poly (vinylidene fluoride) (PVDF) (8 wt %). The 2032 type coin cells were assembled in an argon-filled glove box with an oxygen and water level below 5 ppm using different electrolytes, and the lithium sheets was used as the counter electrode and reference electrode. Celgard 2400 microporous membrane was used as the separator. Then, the charge and discharge measurements were carried on a computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China). $LiNi_{0.5}Mn_{1.5}O_4$/Li coin cells were cycled at a potential range of 3.0~5.0 V with a current rate of 20 mA g^{-1} and 40 mA g^{-1}.

Characterization Techniques: To test the electrochemical impedance spectroscopy (EIS) measurement of the cells, we used an Autolab Electrochemical Analytical Instrument (ECO CHEMIE, B. V. Utrecht, The Netherlands) with oscillation amplitude of 5 mV, and the frequency range is from 10 mHz to 100 kHz. Then, we characterised the surface morphology of the electrode using field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS) measurements (AXIS Ultra DLD spectrometer with Al-Ka (1253.6 eV) radiation). For these measurements, $LiNi_{0.5}Mn_{1.5}O_4$/Li coins cells were cycled 106 times and disassembled in a glove box. The fully discharged $LiNi_{0.5}Mn_{1.5}O_4$ samples were collected with pure DMC washing to remove the precipitates on the electrode surface.

Table S1. Comparison of fluoroethylene carbonate (FEC) with its nonfluorinated counterpart ethylene carbonate (EC).

Molecule	T_m / °C	T_b / °C	ε, 25°C	η/cP, 25°C	DFT Calculations[a]	
					HOMO/eV	LUMO/eV
EC	39	249	89.8	1.86	-8.47	-0.60
FEC	18	249	100.3	4.10	-8.97	-0.64

[a] All of the DFT calculations were performed with the B3LYP/6-311++G (d, p) basis sets using the Gaussian 09 program package.

Table S2. Atomic percentages (at. %) of elements measured at the surface of the $LiNi_{0.5}Mn_{1.5}O_4$ materials after 106 cycles with the EC- and FEC-based electrolyte solutions.

Electrolytes	C 1s	O1s	F 1s	Mn2p	Ni3p	P 2p	Li 1s
EC-based	55.6	18.5	18.3	1.9	0.3	1.4	3.9
FEC-based	51.5	24.8	8.5	1.1	0.2	1.3	12.5

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