Supporting Information

A multifunctional phosphite-containing electrolyte for 5 V-class LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes with superior electrochemical performance

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Fig. S1. XRD patterns of fully charged Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ cathode before and after stored at 60°C for 1 day. The XRD pattern of fresh LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode is displayed for comparison. The XRD data reveals that a fully charged cathode stored in the TMSP-added electrolyte at 60°C experiences less re-lithiation (self-discharge).
Fig. S2. Comparison of cycling stability of LiNi_{0.5}Mn_{1.5}O_4 cathodes with various electrolytes at 60°C at a current density of 60 mA/g.
Fig. S3. (a) Discharge capacity, (b) Coulombic efficiency of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes in baseline and TMSP-added electrolytes at 30°C at a current density of 60 mA/g.
**Fig. S4.** EIS spectra for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes precycled in baseline or 0.5% TMSP-added electrolyte.

**Fig. S5.** Si 2p XPS spectra of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled in TMSP-added electrolyte.
Fig. S6. $^{19}$F and $^{31}$P NMR spectra of the electrolyte with and without 0.5wt% TMSP after hydrolysis tests at room temperature. HF was completely removed from the electrolyte in the presence of TMSP.
**Fig. S7.** O 1s XPS spectra of the LiNi_{0.5}Mn_{1.5}O_{4} cathodes before and after 5 cycles in the baseline and TMSP-added electrolytes at 60°C.

**Fig. S8.** Voltage profiles of the graphite anode with or without 0.5% TMSP for a current density of 35 mA/g (electrode capacity = 2.55 mAh/cm^2) during precycling.
Fig. S9. (a) Discharge capacity, (b) Coulombic efficiency of graphite/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ full cells in baseline and TMSP-added electrolytes at 45°C at a rate of C/2.
**Fig. S10.** FE-SEM images of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes after 5 cycles at 60°C: (a) pristine cathode, (b) baseline electrolyte, (c) 1% VC-added, (d) 5% FEC-added, and (e) 0.5% TMSP-added.
Fig. S11. O 1s and C 1s XPS spectra of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes cycled in baseline and VC-added electrolytes during 5 cycles at 60°C.
Fig. S12. (a) Potentiostatic profiles of Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ half cells maintained at charging voltage of 5.0 V after charging up to 5.0 V at 30°C. (b) Linear sweep voltammetry of electrolytes with and without 0.5% TMSP additive. Stainless steel was used as a working electrode and the scan rate was 1 mV/s.