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Supporting Information

Methodology for understanding interactions between electrolyte additives and cathodes: a case of the tris(2,2,2-trifluoroethyl) phosphite additive

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Figure S1. XPS of pure TTFPa drop-casted onto a LTO electrode (contains LTO, carbon black, and PVDF binder). Panels (a), (b), (c), and (d) plot the high-resolution spectra of the C1s, O1s, F1s and P2p regions. Dotted lines indicate binding energy of the atoms present in a TTFPa molecule which are highlighted in red. The spectra were aligned based on the Ti 3p/2 peak in LTO at 458.6 eV.¹



Figure S2. HPLC/ESI-MS chromatograms of uncycled 0% TTFP-, 10% TTFP-, and 10% TTFPacontaining Gen2 (EC/EMC (3:7) with 1M LiPF₆) electrolytes after undergoing the salt-removal step described in the Experimental Section. Very few ions could be detected in these electrolyte samples compared to the aged electrolyte samples described in the manuscript, which confirms that all those ions were actually generated as a result of electrochemical aging and, therefore, were not sample-preparation artifacts. It is to be noted that in this result the TTFPa peak shows up at ~20 min instead of ~30 min compared to rest of the results, which is likely due to aging of our HPLC column over time. However, this does not affect our analysis, since we only rely on m/z and the number of Cs for species identification and not on column retention time.



Figure S3. HPLC/ESI-MS chromatograms of pure EC, TTFP, and TTFPa performed without the presence of electrolyte and without performing the salt-removal sample preparation step. This control experiment was done to obtain the characteristic signals of EC, TTFP, and TTFPa molecules.



Figure S4. Signal versus time of the pseudomolecular ions detected via HPLC/ESI-MS as a function of initial TTFP concentrations: 0% TTFP (black), 0.5% TTFP (red), 1% TTFP (blue), 3% TTFP (pink), 5% TTFP (green), and 10% TTFP (navy). Each panel corresponds to a particular m/z as indicated by the label.

Identification of type of adduct in a molecular ion detected via ESI-MS

Even though our mobile-phase solvents each contained 0.1 vol.% formic acid, it was found that a detected pseudomolecular ion would not necessarily have a proton (H⁺) adduct. Na⁺ and NH₄⁺ ions are among the commonly encountered contaminants in mass spectrometry that could also act as adducts.² To screen for whether a detected ion mass (M) has H⁺ as an adduct or Na⁺ or NH₄⁺, we started with the assumption that it was a proton adduct if the mass (m/z) was an odd number. In that case, we looked for the presence of ions with masses (M-1+23), i.e., with Na⁺, or (M-1+18), i.e., with NH4⁺, with elution time the same as that of M. If any of these ions were present, the mass M was confirmed to be with a proton adduct. If none of the above two masses were present, the mass very likely turned out to have a Na⁺ adduct. This was also confirmed by checking for masses (M-23+1), i.e., with H⁺, or (M-23+18), i.e., with NH₄⁺, at the same elution time as M. If the mass was odd but none of the four abovementioned modifications of M existed, the mass was assumed to have an H⁺ adduct. If the detected mass of an ion was even, it was assumed to have NH₄⁺ as an adduct, since that is the only way the final mass would be even.



Figure S5. Normalized areas of signal peaks of ions that were present in the TTFP-free aged electrolyte as a function of TTFP concentration.



Figure S6: ¹⁹F spectra of 10 wt% TTFP and 10 wt% TTFPa reference solutions and cycled electrolyte. The spectra on the right are enlargements of selected regions from those above.



Figure S7. ¹⁹F (a) and ³¹P (b) NMR spectra of additive-free (0% TTFP) aged electrolyte.

Thermodynamic calculations of the reaction energy of TTFP's reaction with water.



	G (kJ/mol)	H (kJ/mol)
TTFP	-4414300.8	-4414113.2
H ₂ O	-198704.42	-198651.18
TTFPa	-4609985.4	-4609795
H ₂	-3041.6542	-3005.6624
$(TTFPa + H_2) - (TTFP+H_2O)$	-21.905	-36.27

 $TTFP + H2O \rightarrow TTFPa + H2$

References

- 1.
- J. Lu, C. Nan, Q. Peng and Y. Li, *Journal of Power Sources*, 2012, **202**, 246-252. B. O. Keller, J. Sui, A. B. Young and R. M. Whittal, *Analytica Chimica Acta*, 2008, **627**, 2. 71-81.