

**Perfluoroalkyl-substituted ethylene carbonates:
novel electrolyte additives for high-capacity lithium-ion batteries**

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High-capacity lithium- and manganese-rich metal oxides are gaining increased attention because of their ability to deliver high rechargeable capacities; when cycled between 2.0 and 4.7 V vs. Li, a rechargeable capacity of 270 mAh·g⁻¹ can be routinely obtained.[1] Hence lithium-ion cells containing the Li₂MnO₃-stabilized LiMO₂ (M = Mn, Ni, Co) positive electrodes, graphite negative electrodes and EC:EMC (3:7 by wt.) + 1.2 M LiPF₆-based electrolyte (henceforth referred as Gen2 electrolyte) can be designed to meet the target cell specific capacity of ~250 Wh·kg⁻¹ for transportation applications.[2, 3] However, the target battery cycle life of up to 1000 charge-discharge cycles at 80% depth of discharge (DOD) can only be achieved through new electrolyte formulations because these cells show significant performance degradation on extended cycling.[4] Extensive diagnostic studies indicate that cell impedance rise mainly arises at the positive electrode, and cell capacity fade mainly results from lithium trapping in the solid electrolyte interphase (SEI) at the negative electrode.[4-6] During electrochemical aging, both electrodes undergo a cycle of surface film formation, decomposition, dissolution, and redeposition; this process results in continuous consumption of lithium ions, thereby reducing cell capacity and often increasing cell impedance.

Electrolyte additives are known to be an effective and economic approach to improving the stability of electrode surface films.[7] In the past two decades, many organic and inorganic compounds have been identified as effective electrolyte additives: examples include vinylene carbonate (VC), ethylene sulfite (ES), vinyl ethylene carbonate (VEC), and fluoroethylene carbonate (FEC). In recent years, with the emergence of many high-voltage cathode materials, the anodic stability of common electrolytes is recognized as the main bottleneck limiting the calendar- and cycle- life of high-energy lithium-ion cells.[8] Therefore, more attention has been devoted to improving stability of the cathode-electrolyte interface. As part of DOE's Advanced Battery Research (ABR) program, we have been examining ways to mitigate performance degradation of cells containing Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O₂-based positive electrodes (LMR-NMC) that are cycled at voltages beyond 4.5 V versus Li. Initial studies indicate that common electrolyte additives such as VC, VEC, and FEC are not effective at enhancing long-term cycling performance of these cells, i.e. stable electrode passivation could not be achieved with traditional SEI-forming additives. This observation underscores the need for new electrolyte additives that effectively form stable electrode passivation films in high-energy and high-voltage lithium-ion cells.

Polyfluoroalkyl (PFA) compounds are well known for their high chemical stabilities, and exhibit both hydrophobic and lipophobic behaviors. Upon dispersing in organic solvents, solvophobic PFAs tend to aggregate and form micelles in solution.[9] In light of these facts, we envision that PFA compounds can serve as a new type of electrolyte additive. In our design, the PFA additive has two components: (i) a reactive head-group for attachment onto electrode surfaces via either reductive or oxidative decomposition, so that it becomes an integral part of the surface layer; (ii) a polyfluoroalkyl chain that

self-assembles on the electrode surface into a solvophobic passivating layer that reduces both surface degradation and electrolyte decomposition.

To explore this novel idea, we synthesized a series of PFA-substituted ethylene carbonates and studied them as electrolyte additives in our high-voltage lithium-ion cells. The battery cycling performance was characterized using a combination of galvanostatic cycling and electrochemical impedance spectroscopy (EIS) techniques, and supplemented by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and Raman spectroscopy data. Within this series of compounds studied, we determined that perfluorooctyl-substituted ethylene carbonate (PFO-EC) most significantly improved the long-term cycling performance of our cells. (Figure 1)

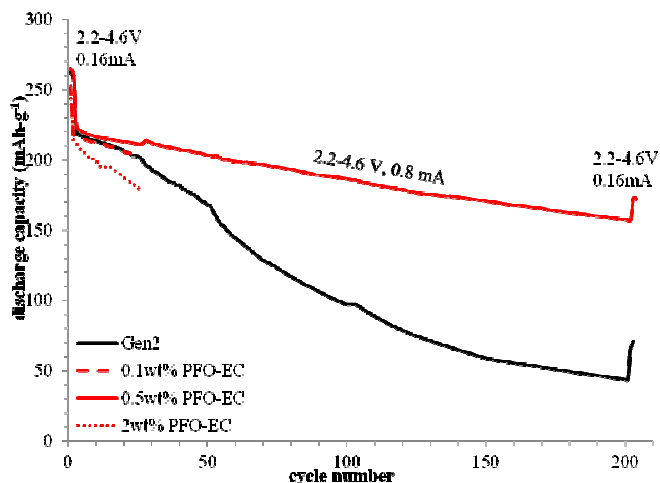


Fig 1. Capacity vs. cycle number plots for Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O₂/graphite full cells using Gen2 electrolyte containing various concentrations of PFO-EC. Two low-current cycles are run before and after the rapid cell aging cycles.

The details of our experiments, results and our mechanistic interpretation will be presented.

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