

Understanding the interface reactivity and reaction mechanisms between Ni-rich $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ cathodes and PF_6 -based carbonate electrolyte in Li-ion batteries

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The development of Ni-rich $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC, $x > 0.6$) positive electrodes for Li-ion batteries provides opportunity for long driving range electric vehicle applications, by delivering a first-cycle discharge capacity of more than 170 mAh/g, yet bearing relatively poor cycle life¹. Understanding the interfacial (electro-)chemical reactions between cathode and electrolyte is crucial to improve Li-ion batteries cyclability. For common electrolyte which comprises of carbonate solvent and LiPF_6 salt, it is usually proposed that during the charging process the carbonate solvent oxidation and polymerizes, accompanied by the release of CO_2 gas², while PF_6 salt decomposes through hydrolysis process, emitting PF_3O gas³. However, it remains largely unclear on how the degradation process of carbonates proceed and the exact source of water in the salt hydrolysis. Moreover, limited mechanistic understanding has been gained on the impact of cathode materials on the onsets and detailed pathways of these reactions.

In this study, we used LP57 electrolyte (1M LiPF_6 in EMC:EC 7:3) with different Ni-contents of NMC cathode materials to experimentally investigate how does the change in Ni contents in NMC cathodes affect the decomposition process of the electrolyte. Through *ex-situ* characterizations including Raman and FT-IR spectroscopy, we have captured that the EC molecule can proceed with the deprotonation process by chemisorbing on the surface with the ring structure intact, forming surface hydroxyl groups at high oxidation potential. The onset of this reaction is largely determined by the Ni contents of NMC, which is dictated by different O $2p$ band positions with regard to the Fermi level of the cathode materials⁴. We have also shown that the onset of PF_6 salt decomposition also correlates with the Ni-contents in the NMC, hinting that the salt decomposition is triggered by solvent deprotonation process. Here, we propose a detailed oxide-mediated decomposition pathway of solvent and salt, which potentially establish a new foundation for the rational design of high energy density cathode materials, as well as coating and electrolyte additives for more stable Li-ion battery interfaces.

References:

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