

Toward Understanding the Electrode-Electrolyte Interface in Li-Ion Batteries

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Understanding electrochemical and chemical reactions at the electrode-electrolyte interface is of fundamental importance to increase the safety and cycle life of advanced Li-ion batteries. There is a growing body of research showing that carbonate-based electrolytes can be oxidized preferably by positive electrodes¹ in pursuit of high energy such as increasing nickel² in the layered transition metal oxides and increasing upper voltage limit on charge.

By DFT calculations we examined the thermodynamic tendency of the ethylene carbonate (EC) solvent for dissociative adsorption on the Li_xMO_2 surface, through the generation of reactive acidic OH groups on the oxide surface, which could lead to salt decomposition. EC dissociation became energetically more favorable on the oxide surfaces with transition metal ions from left to right on the periodic table or by increasing transition metal valence in the oxides, where higher degree of EC dissociation was found as the Fermi level was lowered into the oxide O $2p$ band (with increasing transition metal oxidation and/or increasing nickel in NMC).

Ex situ Raman and FT-IR spectroscopy of oxide-only electrodes provided evidence for the deprotonation of EC by chemisorbing on NMC oxide surface, forming surface hydroxyl groups. The greater nickel in NMC, the lower voltage for the appearance of deprotonated EC, and decomposed salt species such as PF_5 and PF_3O , which can be attributed to the reactivity between acidic groups such as OH and LiPF_6 . These results are in agreement with XPS findings, where increasing Ni significantly increased the P-F salt decomposition and metal fluorides found at the surfaces, suggesting that the salt decomposition can be triggered by solvent deprotonation.

We will discuss a detailed oxide-mediated decomposition pathway of carbonate solvents and LiPF_6 salt, which potentially guides the rational design of high-energy positive electrode materials and surfaces for more stable electrode-electrolyte interface.

References:

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