

ABSTRACT - POSTER

Phase Engineering Improves the Electrochemical Stability of Lithium-rich Cobalt-free Layered Oxides for Lithium-ion Batteries

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The growing demand for sustainable energy storage has intensified the search for cobalt-free cathode materials in lithium-ion batteries (LIBs), driven by cobalt's scarcity, high cost, and supply chain vulnerabilities. One promising class consists of lithium-rich cobalt-free layered oxides $[x\text{LiMO}_2 \cdot (1-x)\text{Li}_2\text{MO}_3]$ ($M = \text{Mn, Ni, etc.}$), combining rhombohedral and monoclinic crystal phases. Their cationic and anionic redox activity yields high theoretical capacities ($\sim 250 \text{ mAh g}^{-1}$), while their high manganese and reduced nickel content offer enhanced thermal stability and cost-effectiveness. Despite these advantages, significant challenges persist, most notably voltage decay during cycling, associated with a layered-to-disordered spinel-type phase transition. Research efforts have focused on mitigating this voltage fade, for instance through dopant incorporation to stabilize the crystal structure. However, post-mortem analyses in such studies typically provide only qualitative insight into the stabilizing effect of dopants like Al, as the disordered nature of the degradation phases hinders quantification. In this study, we employ a comprehensive set of post-mortem characterization methods combined with a statistical spectroscopic approach to quantitatively assess the impact of Al doping on the electrochemical stability of $\text{Li}_{1.26}\text{Ni}_{0.15}\text{Mn}_{0.61}\text{O}_2$, specifically the suppression of disordered spinel phase formation along particle edges.

Lithium-rich, cobalt-free layered oxides were produced through the spray pyrolysis of an aqueous precursor solution, succeeded by a calcination process. The undoped material can be described as having a monoclinic crystal structure, but it has an increased rhombohedral character when doped with Al. According to TEM analysis, the rhombohedral phase is present as a shell around a monoclinic core in the doped materials. Doping effectively mitigates voltage fade and improves capacity retention from 46% to 67% (250 cycles, 0.2 C). During electrochemical operation, the anionic redox reactions within the monoclinic structure result in the creation of oxygen vacancies on the particle surface of the undoped material. This leads to the generation of Mn^{3+} , triggering the formation of a disordered spinel phase at the particle surface. In contrast, the monoclinic phase in the doped material is predominantly situated in the bulk, reducing susceptibility to irreversible oxygen redox and structural degradation. Additionally, the rhombohedral shell is less susceptible to degradation into a disordered spinel. Consequently, it forms a stabilizing interphase and minimizes structural degradation in the doped sample. Instead, the rhombohedral content of the material increases during cycling, resulting in an overall enhancement in electrochemical stability.

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References:

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