

Review of: "Elucidating and Mitigating High-Voltage Degradation Cascades in Cobalt-Free LiNiO₂ Lithium-Ion Battery Cathodes (Adv. Mater. 3/2022)"

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In this study, the authors found that lattice oxygen loss and the O1 stacking transition are the main reasons for the irreversible capacity loss of LNO when charged to the high-voltage region. And the appearance of Li⁺/Ni²⁺ mixing in the O1 structure diminishes the reversibility of oxygen gliding, resulting in irreversible stacking faults. These stacking structural changes then accelerate mechanical degradation, such as creep, cracking, and even bending of the layered structure due to incoherency of the oxygen framework, causing rapid capacity fade. And the graphene-coated modified LNO materials prepared by the authors exhibited improved capacity retention due to its encapsulation effect on lattice oxygen, which confirmed the above theory from the aspect of specific material modification. This study has very high reference significance for understanding the failure mechanism of high-voltage high-nickel layered cathode materials and subsequent targeted material modification. However, there are still some issues that deserve attention and consideration.

1. Lattice oxygen loss is undoubtedly the most fundamental serious problem faced by layered oxide cathode materials, which causes layered structure collapse and thermal runaway. Then it is crucial to understand the factors that induce the loss of lattice oxygen, including: oxidative decomposition of the electrolyte, unstable Ni⁴⁺ spontaneously captures the electrons of lattice oxygen and transforms into stable Ni²⁺ (resulting in O²⁻ becoming active O atoms), Co element The electron energy level of the overlap with O element, etc. In this study, the author did not clarify the cause of oxygen loss in detail, but only introduced oxygen loss caused by high voltage, which is worth thinking about.
2. The formation of O1 structure is responsible for the failure of layered materials. The author introduces that the formation of O1 structure is mainly related to two aspects: (1) the loss of local lattice oxygen causes phase structure transformation; (2) The c-axis depth shrinkage caused by the high voltage (i.e. the deep H2 to H3 phase transition) causes the stacking of the electron cloud of the adjacent oxygen atomic layer to promote the phase transition. These two reasons contain both chemical and physical influence mechanisms, and they are also interrelated, which has important guiding significance for the subsequent material modification.
3. Li⁺/Ni²⁺ mixing in LiNiO₂ materials deserves attention. The formation of Li⁺/Ni²⁺ mixing includes both material lithiation and roasting process and charge-discharge cycle process. A moderate amount of

$\text{Li}^+/\text{Ni}^{2+}$ mixing helps to maintain the stability of the layered structure, while severe $\text{Li}^+/\text{Ni}^{2+}$ mixing results in lower output capacity and lithium diffusion kinetics. The authors introduce that the formation of $\text{Li}^+/\text{Ni}^{2+}$ intermixing will be induced after the formation of O1 structure, which will hinder the reversible recovery of O1 to O3 structure, resulting in irreversible loss of capacity. However, it has been reported in many literatures that the $\text{Li}^+/\text{Ni}^{2+}$ mixing formed during cycling can cause local lattice distortion, which in turn can lead to the generation of intra-lattice cracks and material failure, especially in high-Ni cathodes. So how does this failure effect compare to what the authors describe?

4. LiNiO_2 material has the dual advantages of high capacity and low cost due to its high nickel content and no Co element, but its cycle stability problem is particularly serious. Then the role of Co and Mn should be paid attention and discussed. As reported in the literature: Co can suppress the disordered mixing of cations through its own electronic structure (suppressing in-plane magnetoresistance and 180° superexchange between planes); And produce more stable Ni^{2+} , thereby reducing the highly active Ni^{3+} . In conclusion, their role in maintaining the stability of the layered structure should be introduced.
5. The graphene-coated cathode materials introduced by the authors have an unconvincing effect of suppressing oxygen loss. How does graphene coating affect the loss of lattice oxygen that directly affects it? Even though its encapsulation effect inhibits the overflow of the formed O_2 , it is difficult to directly affect the behavior of oxygen atoms in the lattice. Could it be the partial pressure of oxygen acting as a physical shield? Of course, this study also inspires us to focus on the stable modification of lattice oxygen.