Structural elucidation of the degradation mechanism of nickel-rich layered cathodes during high-voltage cycling†

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Phase transition occurring during cycling plays a fundamentally important role in the cycling performance of nickel-rich cathodes. Here, splitting of two O3 phases, rather than the often observed O1 phases in the conventional LiCoO2 electrode, was discovered in LiNi0.85Co0.10Mn0.05O2 at a high-voltage region (> 4.6 V). Such degradation could be mitigated via Al doping.

Lithium ion batteries (LIBs) are considered one of the most promising energy storage devices for battery electric vehicles (BEVs). Among the available cathode materials for LIBs, nickel-rich layered LiNiCoM1-xO2 (x ≥ 0.8, M = Mn, Al, Fe, Mg, etc.) oxides are the ideal choice due to their higher capacity, lower cost and less environmental impact. However, nickel-rich layered oxide materials usually suffer from increasingly severe capacity fading, with increasing nickel content. Severe electrochemical performance degradation largely originates from sharp phase transitions, causing heterogeneous lattice expansion and contraction during electrochemical cycling. H2–H3 phase transition, in a deeply delithiated state, plays a key role in determining the structural stability of a nickel-rich layered cathode, as the transformation leads to detrimentally anisotropic volume change and aggravating capacity fading.

Up to now, it remains an open question whether the degradation mechanism of Ni-rich layered cathodes is a phase transition process or a solid-solution reaction during high-voltage cycling. For example, Manthiram et al. reported the formation of a solid solution phase in LiNi0.95Co0.025Mn0.025O2 electrodes during cycling, while Biasi et al. demonstrated that the LiNiO2 cathode suffers from the phase transformation from a layered hexagonal H1 phase to a layered H2/H3 phase during the de-lithiation process. Recently, Sun’s group reported that three phase transitions, i.e. H1 → H2, H2 → H3 and H3 → O1, are detected in LiNi0.85Co0.025Mn0.025O2, which means that the stacking sequence of oxygen atoms changes from cubic close-packing (ABCABC) in the H1/H2/H3 phase to hexagonal close-packing (ABAB) in the O1 phase when almost all Li-ions are extracted from the Li layer in the layered structure.

Here, in situ high-resolution synchrotron radiation diffraction (SRD) is used to investigate the structural evolution of a LiNi0.85Co0.10Mn0.05O2 cathode material (N85CM). Interestingly, new phase transitions were observed, which are different from those published in the literature. Two layered phases, i.e. H3a and H3b phases, with the same oxygen stacking (O3 structure) but different lattice parameters are generated after charging to above 4.6 V. To mitigate the degradation of N85CM during high-voltage cycling, small-dose of Al (2 mol%) for Mn in LiNi0.85Co0.10Mn0.05Al0.02O2 (N85CMA) is adopted. The in situ SRD results suggest that N85CMA experienced a solid-solution reaction within a wide voltage window (2.7–4.8 V vs. Li/Li+) and Sr-doping significantly suppresses the split hexagonal phase, proposed to mitigate the structural and functional fatigue of layered Ni-rich cathode materials during high-voltage cycling.

N85CM and N85CMA are synthesized by a sol–gel method followed by a conventional high-temperature solid-state method. For comparison, the traditional LiCoO2 cathode was also prepared. High-resolution synchrotron radiation diffraction (SRD) was performed (Fig. S1 in the ESI†) to investigate the structures of N85CM, LiCoO2 and N85CMA. All the diffraction reflections of the three samples can be indexed to a hexagonal 3R-FeO2 layered structure with a space group R̅3m. No obvious impurities can be observed. The electrochemical properties of the selected samples were tested at a cut-off voltage of 4.8 V, and the initial charge–discharge curves of the electrodes are shown in Fig. 1 and Fig. S4 (ESI†). Both N85CM and N85CMA electrodes are found to exhibit similar monotonous charge/discharge features.

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To illuminate the structural evolution of N85CM during high-voltage cycling, in situ high-resolution SRD was performed in the voltage range of 2.7–4.8 V. The contour plots of intensity and positions for several reflections, i.e. 003, 101, 018 and 110, are exhibited in Fig. 1a. The original SRD patterns of the 003 peak during the first cycle from 2.7–4.8 V of N85CM are exhibited in Fig. 1b, and the corresponding voltage profile of the first cycle between 2.7 and 4.8 V. H and O indicate the hexagonal layered phase with an O3 structure and the trigonal layered phase with an O1 structure, respectively.

Residual lithium on the surface of the materials,

which may result from the incomplete insertion of lithium ions into the layered structure.

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Fig. 1 In situ SRD of (a) N85CM, (c) LiCoO2 and (e) N85CMA electrodes: Contour plot of reflection evolution of 003, 101, 006, 018 and 110 during the first charging and discharging process. The original SRD patterns of 003 reflection of (b) N85CM, (d) LiCoO2 and (f) N85CMA during the first cycle between 2.7 and 4.8 V. H and O indicate the hexagonal layered phase with an O3 structure and the trigonal layered phase with an O1 structure, respectively.
In order to clarify whether O3 oxygen stacking in the new layered H3 phase is maintained, in situ SRD was performed on the traditional LiCoO2 cathode during high-voltage cycling (shown in Fig. 1(c and d)). At a highly delithiated state (4.5–4.8 V), a set of reflections such as 001 and 100 indexing to trigonal O1-type Li₁₋ₓCoO₂ (x > 0.8) is clearly probed. The observed O1a and O1b phases are in good agreement with the previous in situ XRD results of LiCoO2 reported in the literature, which are different with the phase transition mechanisms in N85CM. The evolution of the lattice parameters of the LiCoO2 cathode as a function of reaction time obtained from Rietveld refinement is shown in Fig. 2b, showing massive structural collapse in the c-axis upon high-voltage cycling.

In order to alleviate the severe structural deterioration of the N85CM material, we adopted a simple method of aluminum doping to synthesize N85CMA. Fig. 1c and Fig. S4b (ESI†) show the charge–discharge curve of N85CMA during the first cycle. The voltage of N85CMA increases steeply up to about 3.68 V and then reaches a plateau. No pronounced increase in the voltage polarization is found in N85CMA, which matches well with those observed in the literature. Within a wide voltage window (2.7–4.8 V vs. Li/Li⁺) and at 1.0C rate, N85CM delivers a discharge capacity of 165.8 mA h g⁻¹ and 57.2% capacity retention after 70 cycles, while N85CMA delivers a discharge capacity of 182.2 mA h g⁻¹ and 73.1% capacity retention after 70 cycles (Fig. S4c, ESI†). After cycles, compared with N85CMA, the surface of N85CM particles suffered from severe pulverization, demonstrated in Fig. S6 (ESI†). Therefore, the substitution of Al could remarkably enhance the long-term structural and chemical stability of Ni-rich layered materials, thus favoring an improved capacity of N85CMA during high-voltage cycling.

In situ high-resolution SRD measurements were performed in the voltage range of 2.7–4.8 V to study the structural evolution of N85CMA, as shown in Fig. 1e. The characteristic reflections 003, 101, 018 and 110 shift to lower angles firstly and then to higher angles with further de-lithiation. Besides, there is no clear reflection splitting during charging from 2.7 V to 4.8 V, indicating no pronounced biphasic region. The continuous and steady evolution of reflections of N85CMA indicates no clear structural phase transition with cycling, suggesting that N85CMA is solid solution with the homogeneous reaction in the process of charging and discharging. Furthermore, the
profiles of the corresponding lattice parameters of N85CM are shown in Fig. 2c. The curves of lattice parameters a and c are smooth and there is no new branch of stacking axis constants. A solid solution reaction process alleviates the mechanical and structural degradation, thus resulting in a superior electrochemical performance (see Fig. S4, ES†), as also demonstrated in previous research.26–31

In summary, the structural evolution of layered Ni-rich cathode materials is investigated by high-resolution SRD. According to the results of in situ SRD, the N85CM cathode experiences complex phase transformations and a dramatically new phase transformation (H2–H3 transition). The phase transformation causes a severe change in mechanical stress among various phases, triggering off the irreversible structural degradation and functional fatigue. It is found that the substitution of Al could effectively suppress the H2–H3 phase transformation, beneficial to the improvement of the electrochemical performance of Ni-rich cathode materials. With this new exploration and effective modification, more nickel rich cathode materials with excellent structural stability and electrochemical performance could be expected in the near future.

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Conflicts of interest
There are no conflicts to declare.

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