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Resolving atomic-scale phase transformation and oxygen loss mechanism in ultrahigh-nickel layered cathodes for cobalt-free lithium-ion batteries



By using *in situ* and 3D electron microscopy, we decipher the chemomechanical degradation pathway of LiNiO₂-based ultrahigh-nickel layered cathodes for lithium-ion batteries. We reveal that the O1 phase acts as a preferential nucleation site for rock-salt transformation via a two-step pathway involving cation mixing and shear along the (003) plane. Two types of cracks initiating from both the particle surface and interior as well as concurrent rock-salt phase transformation are uncovered. Our results provide deep understanding of the degradation mechanism of LiNiO₂-derived cathodes.



Understanding

Dependency and conditional studies on material behavior Chunyang Wang, Lili Han, Rui Zhang, ..., Penghui Cao, Feng Lin, Huolin L. Xin

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Highlights

O1 phase acts as a preferential nucleation site for rock-salt transformation

O1 → rock-salt transformation involves cation mixing and shear along (003) planes

Cracks initiating from both particle surface and interior are identified in 3D

Concurrent rock-salt transformation is identified in both open and internal cracks

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Resolving atomic-scale phase transformation and oxygen loss mechanism in ultrahigh-nickel layered cathodes for cobalt-free lithium-ion batteries

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SUMMARY

Doped LiNiO₂ has recently become one of the most promising cathode materials for its high specific energy, long cycle life, and reduced cobalt content. Despite this, the degradation mechanism of LiNiO₂ and its derivatives still remains elusive. Here, by combining in situ electron microscopy and first-principles calculations, we elucidate the atomic-level chemomechanical degradation pathway of LiNiO₂-derived cathodes. We uncover that the O1 phase formed at high voltages acts as a preferential site for rock-salt transformation via a two-step pathway involving cation mixing and shear along (003) planes. Moreover, electron tomography reveals that planar cracks nucleated simultaneously from particle interior and surface propagate along the [100] direction on (003) planes, accompanied by concurrent structural degradation in a discrete manner. Our results provide an in-depth understanding of the degradation mechanism of LiNiO₂-derived cathodes, pointing out the concept that suppressing the O1 phase and oxygen loss is key to stabilizing LiNiO₂ for developing next-generation high-energy cathode materials.

INTRODUCTION

Efforts to develop next-generation battery cells and modules that reduce battery cost, increase battery life, and improve its performance and safety are essential to deploying lithium-ion batteries (LIBs) in vehicles and grid power systems. Even though nickel-rich compounds, such as $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) and Li- $Ni_{1-x-v}Co_xAl_vO_2$ (NCA) materials, have now dominated the cathode materials market for battery electric vehicles, ¹⁻³ the high volatility of the cobalt price and the fact that cobalt is sourced from a single geopolitical region has made the elimination of cobalt from cathode chemistry a pressing need for the automotive industry. Therefore, high-Ni and low-Co or completely Co-free layered cathodes have become the focus of intense research in the battery community.^{4–8} Particularly, with the discovery of effective dopants that can inhibit oxygen loss in deep charged states, doped lithium nickelate (LiNiO2; LNO) has recently become one of the most promising high-energy cathode materials for LIBs because of their high specific energy, long cycle life, and reduced cobalt content.9-12 Despite extensive electrochemical studies on this system in the 1990s¹³⁻¹⁵ and recent renewed interest,^{7,16-18} the intrinsic cycling instability which involves complex degradation behaviors of this material has plaqued its commercialization. For example, the extraction of Li from LNO causes a detrimental phase transformation that involves considerable volume shrinkage and thereby deteriorated capacity retention and structural stability.^{16,19}

Progress and potential

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High-Ni and low-Co or Co-free layered cathode materials have resurfaced as the subject of intensive research within the battery community, as a result of the tripled cost and a speculated worldwide shortage of cobalt-a main component within the cathodes of lithium-ion batteries (LIBs). Despite improved capacity and lower costs, LiNiO₂ and LiNiO₂-based high-Ni cathodes still suffer from a complex chemomechanical degradation that has eluded researchers so far. Here, we resolve the atomic-scale phase transition and cracking pathways in LiNiO₂ and doped LiNiO₂ using in situ microscopy, electron tomography, and firstprinciples calculations. Our results will have a significant impact on the basic understanding of the chemomechanical degradation of ultrahigh-nickel layered cathodes in general, as well as provide useful guidance for optimizing LiNiO₂-derived materials for practical applications.







Moreover, the poor thermal stability of delithiated high-Ni-content cathode, especially at high states of charge, also poses a threat to the safety of LIBs.²⁰ Various strategies such as surface coating or bulk doping have been adopted to alleviate the intrinsic cycling instability of LNO as well as layered cathodes with high Ni content.^{5,21-26} Although Ni is partially substituted by different doping elements, the doped LNO still has many structural stability problems inherited from the parent LNO compound, such as phase transformation from the layered H1 (or O3) phase to the H2 and H3 phases during delithiation. More severely, when LNO and Nirich cathodes are deeply charged to higher voltage, a phase transformation from H3 to O1 was observed.^{16,27–29} During this transformation, the stacking sequence of oxygen changes from cubic close packing (ABCABC) in the layered structure to hexagonal close packing (ABAB) in the O1 phase when almost all Li ions are extracted from the Li layer. Yet atomic-scale insights on how these O1 phases form and how they contribute to the chemomechanical degradation of deeply charged LNO and Ni-rich cathodes still remains unclear. Aside from this, it has also recently been demonstrated that accompanying phase transformations, the complex degradation process also involves cation mixing, oxygen loss, defects formation, and cracking.^{16,30–34} These processes are believed to be highly correlated at the atomic scale and collectively contribute to the breakdown of cathode materials. However, for LNO and high-Ni layered cathodes derived from LNO, a clear understanding of the thermal stability and atomic-scale degradation mechanisms involving phase transformation, cation mixing, oxygen loss, and cracking is still lacking. Here, by coupling in situ high-resolution transmission electron microscopy (HRTEM), electron tomography, in situ synchrotron X-ray diffraction (XRD), and first-principle calculations, we uncover the complex and concurrent structural and chemomechanical degradation mechanism in LNO and LNO-derived layered cathodes.

RESULTS

LNO and a newly developed Ti/Mg codoped LNO⁷ (hereafter referred to as doped LNO) layered cathodes were chosen as model materials, and both were charged to 4.4 V (versus Li/Li⁺) at 1.5 cycles (a fully charged state at the second cycle) for the study. Detailed characterization of the microstructures and compositions of both types of cathodes are provided in Figures S1 and S2. In situ heating was performed in TEM to exponentially accelerate the oxygen release and phase transformation so that we could observe chemomechanical breakdown of cathode particles within a reasonable time frame. Figure 1A shows the atomic models of pristine layered structure (O3 phase, space group R-3m), O3 phase with partially transited O1 phase, and pure O1 phase, which form at different charged states. Electrochemical performances (Figure 1B) show that the doped LNO has evidently smoother charge/ discharge profiles compared with that of LNO, in particular within the 3.5-3.7 V and 4.0–4.4 V ranges, indicating that the two-phase transitions (H2 \rightarrow H3 and H3 \rightarrow O1)²⁷ are mitigated to some extent. Figure 1C shows a representative electron diffraction pattern (EDP) and an HRTEM image of a delithiated LNO particle. The unidirectional streaking of the Bragg reflections along the [003] direction in the EDP is present due to the formation of two-dimensional (2D) planar type defects parallel to the (003) planes. In LNO, they are indicative that there are considerable amounts of randomly distributed O1 stacking faults (SFs) in the O3 lattice. The extra Bragg spots (marked by magenta arrows) indicate alternating stacks of O1 and O3 phases. The HRTEM image in Figure 1C also shows that in contrast to the perfect layered structure of pristine LNO (Figure S3A), a distorted layered structure with O1 SFs is formed in local regions of delithiated LNO. Besides, cation mixing was observed to occur in delithiated LNO according to the Bragg spots indicated by

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Figure 1. Structural degradation of delithiated LNO and doped LNO

(A) Atomic models of O3 phase (space group R-3m), O3 phase with partially transited O1 phase, and pure O1 phase. Li, Ni, and O are denoted by green, gray, and red symbols, respectively.

(B) Electrochemical performances of LNO and doped LNO.

(C) Electron diffraction pattern (EDP) and high-resolution transmission electron microscopy (HRTEM) image of LNO charged to 4.4 V (versus Li/Li⁺) at 1.5 cycles. Streakings and Bragg spots originating from O1 stacking faults (SFs) are indicated by arrows. Bragg spots produced by transition metal (TM) cation mixing in Li layer is also identified.





Figure 1. Continued

(D) EDP and HRTEM image of doped LNO charged to 4.4 V (versus Li/Li⁺) at 1.5 cycles. The delithiated doped LNO shows a nearly perfect layered structure.

(E and F) Ab initio MD simulation (T = 300 K) showing the transition from O3 to O1 in fully delithiated LNO. (G and H) In situ synchrotron X-ray diffractions of delithiated doped LNO (G) and LNO with increase of oxygen loss (H).

the magenta arrow in Figure 1C. The representative EDP and HRTEM image in Figure 1D show that, in contrast to LNO, doped LNO preserves a nearly uniform layered structure as that of the pristine one (Figure S3B), with significantly reduced cation mixing and O1 SFs after delithiation. In agreement with the experimental observations, ab initio molecular dynamics (MD) simulations (Figures 1E and 1F) confirm that O1 SFs are readily formed in fully delithiated LNO (see simulation details in Video S1 and experimental procedures). Moreover, in situ synchrotron XRD experiments were carried out to obtain an overall understanding of the structural evolution induced by oxygen loss under thermal-abuse conditions. During the in situ experiment, as the temperature increases, rapid oxygen release is activated (see details in Figure S4). Both delithiated LNO and doped LNO show a similar oxygen-lossinduced structural transformation pathway from layered \rightarrow disordered spinel \rightarrow rock-salt (RS) during oxygen loss (Figures 1G and 1H). Bragg peaks corresponding to the O1 phase were identified in the XRD patterns of both LNO and doped LNO cathodes (Figure S5). Moreover, we tracked the evolution of the layered matrix and O1 phase by plotting the c axis of the O1 phase and d(003) plane of the layered matrix in Figure S6. The c axes of the O1 phases before heating are indicated by the solid lines in both plots. Upon heating, the caxes of the O1 phases in both LNO and doped LNO basically remain stable from room temperature all the way up to 200°C. This implies that O1 phase is relatively stable at lower temperatures and the transition from O1 to the spinel or RS structure only takes place abruptly at a critical temperature around 200°C, which is also verified by the onset of shrinkage of the c axis or d(003) of the layered structure at around 200°C. Notably, owing to the doping effect, the disordered spinel \rightarrow RS transformation is clearly mitigated. That is, owing to the doping of Ti and Mg, the degradation process of doped LNO is remarkably delayed compared with LNO. From the above results, the benefit of doping is twofold: reduction of O1 SF formation and enhancement of oxygen retention (delaying the structural degradation of layered structure).

Figure 2A illustrates the TEM experimental setup of *in situ* thermal-abuse experiments. Figures 2B and 2C show time-resolved EDPs and HRTEM images of delithiated LNO and doped LNO during in situ heating at different temperatures. For delithiated LNO, reflections indicative of the O1 phase (similar to that shown in Figure 1C) vanished rapidly at the very beginning of oxygen loss (210°C); meanwhile, cation mixing significantly increased and immediately resulted in the formation of disordered spinel and RS (230°C). With a further increase of oxygen loss (300°C), the whole particle finally transformed from a disordered spinel to RS phase. For delithiated doped LNO, although the amount of O1 phase is significantly reduced compared with that in delithiated LNO, the structural transformation pathway is similar, but the disordered spinel \rightarrow RS transformation is delayed substantially (Figure 2C). Figures 2D-2F present timeresolved HRTEM images, showing layered \rightarrow disordered spinel \rightarrow RS transformation induced by oxygen loss in delithiated LNO. A higher-resolution HRTEM image of the O1 phase embedded in the O3 matrix is provided in Figure S7. Interestingly, the O1 phase was directly observed to preferentially transform into RS upon oxygen loss. Atomic-scale in situ dynamics (Figures 3A and 3B and unmarked images in Figure S8) show a two-step transformation from the O1 phase (vellow symbols) to RS (orange symbols), i.e., cation mixing followed by a shear displacement along the (003) planes. In the meantime, the region with a perfect O3 layered structure remains stable, although with





Figure 2. *In situ* structural evolution of delithiated LNO and doped LNO induced by oxygen loss (A) Schematic illustration of the *in situ* heating TEM experimental setup.

(B and C) Time-resolved EDPs of LNO (B) and doped LNO (C) during in situ heating at different temperatures.

(D–F) Time-resolved HRTEM images showing structural transformations of delithiated LNO from layered structure (O3) with O1 phases (D) to disordered spinel (E) and then to rock-salt (RS) structure (F) induced by oxygen loss during *in situ* heating. The lower panels show corresponding fast Fourier transforms and enlarged images of local regions. O3 and O1 phases are indicated by white and yellow lines, respectively.

small amounts of cation mixing. A similar transformation from the O1 phase to RS (Figure S9) was also observed in doped LNO particles. To understand the rationale behind the new transformation pathway, we carried out first-principles calculations to compare the kinetic barriers of a Ni ion migrating from the oxygen-surrounding octahedral site in the transition metal (TM) layer to the nearest octahedral site in the Li layer of the O1 and O3 phases, respectively (see the migration paths of the Ni ion in O1 and O3 in Figure S10). In agreement with the experimental observations (Figure 2), the nudged elastic band (NEB) calculations (see experimental procedures for details) reveal that the barrier







Figure 3. Preferential transformation from O1 phase to RS

(A) *In situ* HRTEM images showing the transformation from O1 phase to RS. O1 phase and RS are denoted by yellow and orange symbols, respectively. During the transformation, the region on the right side with perfect layered structure (white symbols) remains stable.

(B) Schematic illustration of the two-step transformation pathway.

(C) The minimum energy path calculation of moving Ni from TM layer to Li site in O3 and O1 phase, respectively.

for the Ni ion migrating into the Li layer is lower in the O1-faulted phase (Figure 3C). This means it is kinetically faster for cation mixing to happen in the O1-faulted phase. This again, from a theoretical point of view, confirms that SFs and the O1 phase provide a highway for the structural degradation of LNO and its derivatives, including all high-Ni-content materials.

Apart from chemodegradation, mechanical breakdown is an equally important failure mode to monitor. In the *in situ* heating experiment, with a further increase of temperature to trigger oxygen loss, cracks were observed to form both in the delithiated LNO and doped LNO primary particles (Figure S11). To accurately determine the threedimensional (3D) configuration of these cracks, we performed electron tomography experiments on the primary particles based on a tilt series of high-angle annular dark-field imaging scanning TEM (HAADF-STEM) images (experimental procedures). Figure 4A shows the 3D reconstructed cracks in a delithiated LNO particle before and after *in situ* heating. According to the indexes of the facets, the cracks are precisely determined as lying parallel to the (003) planes. Furthermore, by singling out the cracks through 3D segmentation, two types of cracks are directly identified in 3D for the first time. Figures 4B–4E and Video S2 show that apart from cracks extending from grain surface to interior (open cracks, blue colored), a large fraction of the cracks is found embedded (internal





Figure 4. Crack formation accompanying structural transformation

(A) Three-dimensional (3D) structure of the delithiated LNO at room temperature and after heating at 500°C obtained by electron tomography. Facets of the particle are indicated.

(B-D) 3D configurations of open (blue colored) and internal (yellow colored) cracks in LNO in (A).

(E) 3D view from another direction showing the planar distribution of both types of cracks along the [100] direction on the (003) plane.

(F) HRTEM image of a crack formed in the doped LNO after severe oxygen loss. Alternating arrangement of RS and cracks formed during oxygen loss are indicated by orange and cyan circles, respectively.

cracks, yellow colored) in the grain interior. Interestingly, both types of cracks were found to distribute discontinuously along the (003) planes with a preferential propagating orientation along the [100] direction. 3D reconstruction of the cracks in doped LNO (Figure S12) shows that although open cracks are also formed at the surface, further propagation of the surface-initiated cracks toward the interior seems to be evidently mitigated due to the doping effects. In the meantime, only a small amount of internal cracks is observed. In general, the results confirm that Ti/Mg dopants effectively suppress the formation of internal cracks as well as the propagation of surface-initiated cracks toward the interior of doped LNO particles.

Figure 4F shows an HRTEM image of a delithiated doped LNO particle after severe oxygen loss. In good agreement with the 3D tomographic reconstruction, alternating RS







Figure 5. Generation of dislocations during chemomechanical degradation

(A) HRTEM image showing dislocation configurations around crack tips. The Burgers vectors of these dislocations are determined as 1/2 [110], corresponding perfect dislocations in RS with space group of Fm-3m.

(B) Schematic illustration of the degraded layered cathode with cracks corresponding to (A).

(C) Schematic of the configuration and stress state at the crack tip.

(D) Stress state at a crack tip determined by geometrical phase analysis.

patches and cracks (regions containing cracks are brighter in contrast due to loss of mass) connected in stripes were observed. In contrast to the RS in the planar cracks, regions around the crack remain as disordered spinel, due to less cation mixing. It is highly suspected that the stripe-like features originate from the O1 SFs and also act as sinks for oxygen vacancies generated in nearby regions, which thereby promote the spinel \rightarrow RS transformation in LNO and doped LNO. The HRTEM in combination with the electron tomography results suggest that discrete planar cracks and RS transformation nucleate heterogeneously via concurrent aggregation of vacancies and TM ions along the (003) planes. In fact, as the nucleation of RS originates from the aggregation of TM atoms in delithiated Li layers, substantial defects arise, e.g., vacancies and dislocations form in the RS nuclei; atomic-scale dynamics (Figure S13) show that these defects provide extra channels for migration of TM atoms from the disordered spinel to RS phase during oxygen loss. Moreover, due to the formation of cracks, large amounts of dislocations with Burges vectors of 1/2(110) (Figure S14) are formed around the crack tips (Figures 5A and 5B). It is worth noting that most of these dislocations exist in the form of dislocation dipoles at the interface between RS and cracks. Geometrical phase analysis (GPA)³⁵ was performed on HRTEM images to understand the strain state at the crack tip. Interestingly, as shown in Figures 5C and 5D, a compressive strain field is introduced to the crack tip due to the formation of a dislocation. Because the introduced compressive stress field could suppress crack growth by counteracting the tensile stress at the crack tip, it could alleviate the chemomechanical degradation of the cathode to some extent. This observation implies that line defects, which are usually considered detrimental, could be possibly utilized to improve the chemomechanical stability of cathode materials. The crack formation and propagation are discussed in detail below.





DISCUSSION

Accurate identification of where the cracks originate is of crucial importance to understanding the mechanical failure mechanism of primary particles. Due to the limitation of conventional 2D projection imaging on 3D objects, ^{36–38} in most cases it is impossible to distinguish whether a crack is connected to the particle surface or not from a single projection image (only in exceptional circumstances, we might be able to see cracks already connected to the particle surface in a projection image).³⁰ In more general cases, when we see a crack in a projection with its two ends within the particle, it is still unclear whether it is connected to the surface or not. In this work, for the first time, by using 3D electron tomography and a segmentation analysis, we successfully determined two types of planar intragranular cracks, i.e., open and internal cracks in degraded LNO-based cathodes. As both types of cracks occurred in the particles, it can be concluded that the cracks originating from both the particle surface and interior collectively contribute to the mechanical failure of LNO-based layered cathodes. Yet it is worth noting that due to the introduction of the dopants, the cracking in doped LNO is evidently alleviated and the cracking mode is slightly modified compared with LNO (Figure S12). In doped LNO, Mg is uniformly distributed in the primary particle while Ti segregates to the particle surface to form a hierarchical distribution. Due to the strong bonding between dopant Ti and oxygen, surface segregation of Ti inclines to stabilize the surface of doped LNO particle and thereby prevent surface-initiated cracks propagating toward the interior of the particle. In addition, as there are also considerable uniformly distributed Ti and Mg dopants in the particle interior, the amount of cracks initiating from the particle interior is also reduced.

The propagation of cracks is closely related to the stress state at crack tips. Due to the formation of considerable amounts of internal cracks, the oxygen gas released from the thermal decomposition³⁹ will be trapped in the internal cracks and exerts pressure on the crack surfaces, likely becoming one of the driving forces for crack propagation. In the meantime, more oxygen will be released from the crack surfaces and, hence, a gradient of oxygen vacancies inclines to form from the crack surface (higher density) toward the interior (lower density). The gradient of oxygen vacancy induces a field of mismatch strain³² which will also contribute to the propagation of these cracks. It is noteworthy that due to the formation of edge dislocations at crack tips, a compressive strain field originating from the dislocation could be generated at the crack tip (as observed in Figure 5D), which therefore will accommodate the aforementioned tensile stress at the crack tip to some extent and thereby delay the mechanical degradation.

The chemomechanical degradation mechanism of LNO-derived layered cathodes under thermal-abuse conditions is summarized as follows. With Li deintercalated from the cathodes at high cutoff voltages, O1 phases are inclined to form due to the introduction of considerable amounts of SFs. Upon oxygen loss, O1 phases preferentially transform into RS via cation mixing and shear along the (003) plane. Meanwhile, other regions (O3 lattice) gradually transform into disordered spinel via cation mixing. As the Li vacancies in the disordered spinel are still not fully occupied by TM atoms, with oxygen loss increasing the TM ions in disordered spinel aggregate locally to transform toward RS, and the Li vacancies and oxygen vacancies aggregate to form crack embryos. Once these cracks nucleate, they may propagate along the basal plane driven by the tensile stress as well as the internal pressure of the oxygen gas released from the disordered spinel \rightarrow RS transformation. Finally, with more severe oxygen loss, the concurrent structural and mechanical degradation eventually lead to a complete breakdown of the cathode particle.





Long-term electrochemical tests were performed on both LNO and doped LNO. The post-cycled cathodes were statistically characterized and compared with the cathodes degraded under thermal-abuse conditions by in situ heating. In general, the long-term post-cycled cathodes show some characteristics similar to those that degraded under thermal-abuse conditions during in situ heating. For example, similar cracks on the (003) planes were observed in post-cycled LNO (Figure S15A). Yet it should be noted that, due to the fact that the oxygen loss during long-term cycling is more gentle and much slower than that promoted by in situ heating, cracks are not universally observed in the long-term post-cycled LNO cathodes and barely observed in long-term post-cycled doped LNO (Figure S16). Also, for the same reason, the RS transformation in post-cycled LNO and doped LNO mainly localizes on the particle surface or around cracks, not as severe as that forms during in situ heating. Aside from this, much more O1 phase is formed in long-term post-cycled samples (Figures S15C, S15D, S16C, and S16D) than in the secondly charged cathodes used as the start point for in situ heating, indicating that O1 phase accumulates with cycling, and with long enough cycles the O1 phase starts to transform toward RS, firstly at the particle surface or around cracks. From the above comparison, despite the distinct oxygen loss severity and rates for long-term cycling and in situ heating, it can be concluded that the degradation pathways are similar to a large extent. They both imply the importance of mitigating the formation of the detrimental O1 phase and cracks, which could be more severe during violent oxygen loss conditions such as fast charge-discharge or thermal-abuse conditions.

Several useful guidelines could be gained from the above findings. First, the O1 phase, which forms in deep delithiation state, should be suppressed to mitigate the subsequent oxygen loss and RS transformation. To achieve this, strategies capable of improving the shear resistance between neighboring TM layers on the (003) planes could be helpful to increase the energy barriers for O1-phase or stacking-fault formation, thereby improving the structural stability of LNO-based cathodes. Second, in contrast to the conventional wisdom that oxygen loss initiates from surfaces, we found that considerable oxygen release and concurrent chemomechanical degradation could initiate from inside cathode particles. This implies that efforts on protecting only the surface of primary particles will not be sufficient to improve the mechanical stability of primary particles in regard of prohibiting crack formation and propagation. To achieve this, both surface and bulk of primary particles need to be protected, e.g., by concurrent 3D bulk and surface doping as demonstrated in Ti/Mg codoped LNO.⁷ Third, as cracks prefer to propagate along the [100] direction on the (003) plane in LNO-based cathodes, it can be conjectured that if specifically oriented long-/shortrange ordering and strengthening effects can be introduced into the TM layers, e.g., through preferentially oriented substitution of TM atoms by dopants or superlattice formation, the crack nucleation/propagation resistance along the [100] direction on the (003) plane could possibly be increased. In this way, the oxygen loss and RS formation that originate from cracking could be considerably suppressed.

Conclusion

In conclusion, by combining *in situ* observations, electron tomography, and first-principles calculations, our work provides a deep understanding of the concurrent structural and mechanical degradation mechanism of LNO and LNO-derived layered cathodes. In particular, a new degradation pathway, i.e., the preferential structural transformation from the O1 phase to RS, is uncovered for the first time. Moreover, we reveal that preferentially oriented planar cracks initiating both in the interior and on the surface of primary particles collectively contribute to the mechanical breakdown of the cathodes. Our findings provide new insights into the degradation mechanism of ultrahigh-Ni-content



layered cathodes and point toward new directions in designing more robust high-Nicontent layered cathodes for next-generation high-energy-density LIBs.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Huolin L. Xin (huolinx@uci.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The data that support the plots within this paper, and other findings of this study, are available from the corresponding authors upon reasonable request.

Materials synthesis and preparation

LiNiO₂ or doped LiNiO₂ was prepared by a coprecipitation method followed by calcination. During precipitation, metal solution (0.096 M NiSO₄·6H₂O, 0.002 M MgSO₄·7H₂O, and 0.002 M TiOSO₄ dissolved in aqueous solution) and base solution (NaOH and NH₃·H₂O aqueous solution with a molar ratio NaOH/NH₃ = 1.2) were pumped into a starting solution (NaOH and NH₃·H₂O aqueous solution with a molar ratio NaOH/NH₃ = 1.2, pH value adjusted to 11.0) simultaneously at 55°C under N₂ protection. The precipitate was collected, washed, and filtered with deionized water and dried in a vacuum oven overnight at 105°C. The hydroxide precursor was mixed with LiOH and calcined under oxygen flow at 460°C for 2 h and then at 700°C for 6 h to obtain the final LiNiO₂ or doped LiNiO₂ powder.

In situ TEM experiments

For preparation of the TEM samples, LNO or doped LNO electrodes from disassembled charged coin cells were first sonicated and dispersed in ethanol and then loaded on a Wildfire *In Situ* Heating Nano-Chip (DENS Solutions) with silicon nitride window. The heating chip was subsequently loaded on a double-tilt *in situ* MEMS heating holder. The particles were then heated by a local Joule heating element integrated on the heating chip. All *in situ* electron diffraction patterns, HRTEM images, and HAADF-STEM images were collected on an FEI Talos F200X transmission electron microscope with an X-FEG field emission source operated at 200 keV. The dose rate of HRTEM imaging is ~350 e/Å²s, which is relatively low to avoid beam damage to the samples. In addition, to exclude the beam irradiation effects, we also performed *ex situ* experiments in which the samples were only imaged after being heated to different stages with beam blanked. The results are consistent with the *in situ* results. In addition, as the *in situ* diffraction experiments performed at low magnification are consistent with the HRTEM results, this also confirms that the beam effects are negligible during our HRTEM imaging conditions and time scale.

3D electron tomography experiments

The electron tomography experiments were carried out on an FEI Talos F200X electron microscope using a single-tilt *in situ* heating holder. Tilt series of HAADF-STEM images of delithiated particles for electron tomography were acquired before and after *in situ* heating. The images were acquired from -70° to $+70^{\circ}$ with 2° tilt intervals. The tomograms were reconstructed using a custom-written MATLAB script implementing the multiplicative simultaneous iterative reconstruction technique. The 3D reconstructions were visualized by Avizo.





Calculation method

In the present work, we perform the first-principle calculations using the density functional theory implemented in the QE⁴⁰ (the Quantum Espresso package). The generalized gradient approximation in Perdew-Burke-Ernzerhof form and Ultrasoft pseudopotentials with spin-orbital approximation are employed. The kinetic energy cutoff for the plane wave and charge density are set to 50 Ry and 450 Ry, respectively. The migration pathway of the Ni ions and the energy barrier to migration are determined by finding the minimum energy path from one lattice site to an adjacent site using a climbing-NEB method⁴¹ as implemented in QE. The initial configurations are determined by optimizing the structure, including the cells, until the forces become smaller than 0.01 eV/Å. The final configurations are set to Ni ions on the octahedral site in the Li plane. A group of images generated by linear interpolation between the two endpoint configurations are optimized until the norm of the force orthogonal to the migration path is less than 0.05 eV/Å In the MD calculations, a 2 × 2 × 1 supercell containing 9 $Li_x NiO_2$ (x = 0) units initiated with O3 phase was constructed. To investigate the thermal dynamic properties of fully delithiated $Li_x NiO_2$ (x = 0) system, we carry out ab initio MD calculation using the Born-Oppenheimer MD method implemented in the QE package. The local spin density approximation and a 2 \times 2 \times 1 Monkhorst-Pack k-point mesh are employed. The equations of motion are integrated using the Verlet algorithm, and the integration time step Δt is set to 5 fs. First, the model system was equilibrated in the local relaxation process, followed by an MD-producing run of 1 ps whereby the temperature was set to T = 300 K and controlled by an Andersen thermostat.

SUPPLEMENTAL INFORMATION

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AUTHOR CONTRIBUTIONS

H.L.X. conceived and directed the project. C.W. performed *in situ* TEM experiments and tomographic analysis. L.H. performed electrochemical experiments and electron tomography experiments. K.K. performed TEM sample preparation. R.Z. and Y.R. performed *in situ* synchrotron XRD experiments and analysis. H.C., H.L.X., and P.C. carried out computational simulations. P.Z. performed TGA-MS



experiments. L.M. and F.L. synthesized and electrochemically tested the cathode materials. C.W. and H.L.X. wrote the paper with help from all authors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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