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Authors

Huang, Weiyuan

Zhuo, Zengqing

Dai, Alvin

et al.

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Low-nickel cathode chemistry for sustainable and high-energy lithium-ion batteries

Weiyuan Huang¹, Zengqing Zhuo², Alvin Dai¹, Jinghao Huang³, Jing Wang¹, Tao Zhou³, Xiao-Min Lin³, Xianghui Xiao⁴, Lu Ma⁴, Rachid Amine⁵, Gihan Kwon⁴, Xiaojing Huang⁴, Tianyi Li⁶, Hari Adhikari³, Jinghua Guo², Steve Trask¹, Jianguo Wen³, Khalil Amine^{1*}, Tongchao Liu^{1*}

¹Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439, USA

⁴National Synchrotron Light source II, Brookhaven National Laboratory, Upton, NY 11973, USA

⁵Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA.

⁶X-ray Science Division, Advanced Photon Sources, Argonne National Laboratory, Lemont, IL 60439, USA

*Corresponding author: liut@anl.gov (T. L.); amine@anl.gov (K. A.).

Abstract

The pursuit of high-energy-density cathodes for lithium-ion batteries has primarily relied on increasing the nickel (Ni) content, raising concerns over supply chain constraints, soaring prices and long-term sustainability. More critically, Ni-rich cathodes suffer from rapid electrochemical degradation driven by inherent structural and mechanical failure, and an insurmountable trade-off between capacity and cycle stability, which remains unresolved for decades. Here we introduce a low-Ni chemistry cathode (LNC) with a radial phase integration design to overcome these limitations, enabling a remarkable Ni usage reduction (Ni<0.6) while demonstrating higher capacity and significantly improved cyclability compared to high-Ni cathodes (Ni=0.8), a breakthrough not previously reported. Advanced X-ray techniques and electron microscopy reveal that the designed cathode exhibits a highly reversible oxygen anionic redox, benefiting from a structurally stable surface and minimizing irreversible phase transitions. Moreover, the integrated structure substantially mitigates lattice strain and improves mechanical stability even under harsh conditions. Consequently, the LNC achieves a high practical capacity of 215 mAh g⁻¹ with enhanced cycling performance. This advance offers a promising pathway toward sustainable, high-performance cathodes with reduced reliance on critical raw materials.

Opening Bold Paragraph

Electric vehicles rely on lithium ion batteries that deliver high energy density and long lifespan, yet most current cathodes rely heavily on nickel (Ni), a costly metal with supply risks and environmental impacts. Reducing Ni dependence while maintaining high energy performance remains a major challenge. Here we propose a low Ni chemistry cathode with a radial phase integration structure that enables reversible anionic redox reactions, suppresses destructive phase transformation, and enhances mechanical integrity. This design not only dramatically reduces Ni usage but also delivers higher practical capacity and significantly longer cycle life compared to mainstream high-Ni cathodes. By balancing energy density, durability, and resource use, our cathode offers a scalable, eco friendly solution for clean-energy storage. It holds strong promise for advancing next-generation electric vehicles and grid-scale storage systems.

Main text

Electric vehicles (EVs) have experienced a significant surge in market share in recent years, largely driven by advancements in battery technologies¹⁻³. The commercialization of lithium-ion batteries for modern EVs hinges on cathode materials that balance high capacity, long cycle life and sustainability^{4,5}. Among these, layered oxide cathodes $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) with high Ni content have solidified as the primary options due to their potential for achieving high energy density and superior electrochemical properties^{6,7}. Ni has become a critical resource for modern technologies, with over 10% of global production used in lithium-ion batteries and more than 50% consumed by the stainless-steel industry. Although global reserves exceed 100 million tons, and identified resources are three times higher, the rapidly growing demand in battery raises serious sustainability issues^{8,9}. Geopolitical risks further threaten the supply chain stability, as the majority of Ni production is concentrated in Indonesia and the Philippines¹⁰. Additionally, nickel mining and processing have significant environmental impacts, contributing to deforestation, water and air pollution, and extensive carbon emissions¹¹. With battery-grade nickel prices soaring to levels comparable to cobalt, the reliance on Ni-rich cathodes becomes increasingly questionable in terms of cost, ethics, and environmental sustainability¹².

Another challenge facing Ni-rich cathodes is their rapid electrochemical decay, primarily driven by surface parasitic reactions and structural/mechanical degradation^{13,14}. The former is closely linked to reactive Ni^{4+} species formed during high-voltage charging react with electrolytes, triggering oxygen release and irreversible phase transitions^{15,16}. The latter, manifesting as particle cracking, arises from significant anisotropic lattice variations^{17,18}, particularly pronounced during the H2-H3 transitions¹⁹. These mechanical failures further accelerate surface-to-bulk degradation and exacerbate capacity fade^{20,21}. While elemental doping^{22,23}, surface coating^{24,25}, and Ni concentration gradient designs²⁶⁻²⁸ have been explored to improve stability, these approaches still fail to address the fundamental issues of the intrinsic structural instability and the high dependence on costly nickel for capacity. Even the partial incorporation of a Li_2MnO_3 -like phase improves structural robustness, but at the cost

of lower reversible capacity, illustrating the persistent trade-off^{29,30}. Therefore, the major share of global cathode production remains stuck in reduced-Ni cathodes due to a reluctant compromise of cost, stability, and performance^{12,31}.

Low-Ni cathodes, particularly Li- and Mn-rich layered oxides, have attracted significant attention due to their high theoretical capacity and abundance of Mn. However, their rapid voltage decay substantially reduces their cycle life and complicates battery management, limiting their potential for large-scale practical deployment^{32,33}. An alternative promising approach involves a complex concentrated doping strategy, which significantly improves the structural and electrochemical stability of low-Ni cathodes¹², but the limited Ni content still restricts reversible capacity. Moreover, the persistent issue of voltage decay under high charge voltage operation remains unresolved. These limitations highlight the need for a new cathode design paradigm that breaks the constraints of Ni-dependent capacity while achieving both high performance and sustainability.

In this work, we propose a sustainable low-Ni chemistry cathode featuring a radial phase integration structure that achieves both high capacity and long-term cycling stability. This transformative design introduces a multistage manganese concentration gradient and reduced overall Ni content ($\text{Ni} < 0.6$), distinct from previous work in this field. Benefiting from its unique structural features, the LNC cathode demonstrates significantly reduced lattice strain, mitigated irreversible local structure variations and detrimental phase transformations, thereby improving mechanical integrity during repeated cycling. The epitaxially grown Li percolation rock-salt surface is electrochemically active while maintaining ultra-high structural stability, effectively preventing continuous surface-to-bulk structural degradation, even under harsh operational voltages. As a result, the designed cathode achieves highly reversible anionic redox chemistry, overcoming the practical capacity limitations of conventional low-Ni cathodes. It demonstrates a high capacity of 215 mAh g^{-1} , surpassing even high-Ni cathodes (e.g., $\text{Ni} = 0.8$), while maintaining exceptional capacity and voltage stability, outperforming mainstream NMC series cathodes. This study confirms the feasibility of achieving high energy density and extended cyclability in sustainable low-Ni chemistry through optimized structural configurations.

Results

Radial phase integration structure design

The LNC cathode material was synthesized using a modified co-precipitation method followed by high-temperature calcination (see Methods). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) revealed the composition as $\text{Li}(\text{Li}_{0.05}\text{Ni}_{0.57}\text{Mn}_{0.31}\text{Co}_{0.07})\text{O}_2$ (Supplementary Table 1). High energy X-ray diffraction (HEXRD) and Rietveld refinement confirmed a typical layered structure with R-3m symmetry (Fig. 1a), with additional diffraction peaks between $2.1\text{-}2.4^\circ$ indicating Li/Mn superlattice ordering in transition metal (TM) layers, characteristic of a Li-rich phase³⁴. The refined c-axis lattice parameter was determined to be $14.21319 \pm 0.00018 \text{ \AA}$, and the $\text{Li}^+/\text{Ni}^{2+}$ cation mixing was approximately 3%. The particle morphology was

further measured by scanning electron microscopy (SEM). **Fig. 1b** shows that LNC has a spherical secondary particle morphology with a size of 15-20 μm . For comparison, four prevalent commercial cathode materials, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (N60), $\text{LiNi}_{0.7}\text{Mn}_{0.15}\text{Co}_{0.15}\text{O}_2$ (N70), $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (N80) and $\text{LiNi}_{0.9}\text{Mn}_{0.06}\text{Co}_{0.04}\text{O}_2$ (N90) were selected. These materials exhibit similar R-3m structures (**Supplementary Fig. 1**) and spherical morphology with a size of around 10 μm (**Supplementary Fig. 2**). Compared to conventional Ni-rich cathodes, the increased (003)/(104) intensity ratio observed in the XRD pattern of LNC can be ascribed to enhanced lattice ordering induced by the incorporation of Li into the TM layers. Pair distribution function (PDF) analysis shows reduced peak intensities for both intra-layered TM-TM_I and inter-layered TM-TM_{II} distances in LNC, consistent with the presence of Li in the TM layer (**Supplementary Fig. 3** and **4**). This result was corroborated by Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra, particularly around Mn, further confirming the existence of Li/Mn superlattice ordering (**Supplementary Fig. 5**). To analyze the composition variations within a secondary particle, we performed three-dimensional (3D) X-ray fluorescence (XRF), a powerful and high-sensitive technique for capturing spatial elemental concentrations, on the LNC sample. Cross-sectional reconstructions (**Fig. 1c**) and quantitative line profiles (**Fig. 1d**) revealed a multistage composition gradient: a steep Mn-rich outer layer, a compositionally stable transition region, and a gentle Ni-rich gradient in the core. Within the outmost 2 μm , Mn decreases from 61% to 31%, while Ni increases from 35% to 61% and Co from 4% to 8%. In the intermediate region, the composition remains nearly constant at 61% Ni, 31% Mn and 8% Co. In the core, Mn further decreases to 20%, with Ni and Co increasing to 70% and 10%, respectively. These gradient features were further validated by energy-dispersive X-ray spectroscopy (EDS) conducted on cross-sectioned particles (**Supplementary Fig. 6**). Such a multistage architecture is expected to facilitate smooth phase transition and improve internal structural compatibility.

The corresponding microstructures were directly visualized using atomic-resolution aberration-corrected scanning transmission electron microscopy (STEM). As shown in **Fig. 1e** and **Supplementary Fig. 7**, the outmost region of the particle exhibits a Li-rich layered structure with an epitaxially grown rock-salt matrix. Notably, numerous Li-rich atomic columns (indicated by arrows) are observed within the rock-salt matrix, forming a Li percolation feature (**Fig. 1f**). This structure is expected to be electrochemically active, providing effective Li^+ diffusion paths, in contrast to conventional TM dense rock-salt surface in Ni-rich cathodes that potential obstruct efficient Li^+ diffusion. The Li-rich layered structure presents a dumbbell-like TM atom configuration, corresponding to Li_2MnO_3 -type superlattice ordering (**Fig. 1g**). Intensity profiles (**Supplementary Fig. 8**) along the TM slabs (highlighted by a dashed rectangle in **Fig. 1g**) show signals between dumbbell peaks, reflecting a delocalized Li/Mn superlattice. Compared to the in-plane localized honeycomb arrangement, the delocalized Li/Mn superlattice ordering in LNC more effectively mitigates oxygen dimerization at high charge states, thereby stabilizing lattice oxygen and supporting reversible anionic redox^{35,36}. The central bulk region consists of a typical Ni-rich layered structure with some degree $\text{Li}^+/\text{Ni}^{2+}$ cation mixing (**Fig. 1h**). These findings confirm that the prepared LNC

cathode demonstrates a new multistage compositional characteristic and a unique radial phase integration structure, which is expected to enhance capacity and high voltage electrochemical stability.

Enhanced electrochemical performance with minimal voltage decay

Given the desired radial phase integration characteristics of the LNC cathode, it was highly significant to explore its impacts on electrochemical performance. As shown in [Supplementary Fig. 9a](#), LNC exhibits a distinct voltage plateau above 4.4 V in the first charge cycle, contributing over 40 mAh g⁻¹ of capacity, attributed to the activation of the Li-rich phase involving oxygen redox reactions^{37,38}. Correspondingly, the dQ/dV curves display a broad slope above 4.4 V ([Supplementary Fig. 9b](#)), distinguishing LNC from the Ni-rich NMCs and confirming the activation of anionic redox during the first charge process. After activation, the strong coupling between anionic and cationic redox leads to overlapping signals across multiple transitions, obscuring distinct dQ/dV peaks in subsequent cycles³⁹. [Fig. 2a](#) shows the comparison of galvanostatic charge-discharge profiles for LNC, N60, N70, N80 and N90 at C/10 rate within 2.5-4.5 V (vs. Li/Li⁺). LNC delivers a discharge capacity of 215 mAh g⁻¹, outperforming N60 (199 mAh g⁻¹), N70 (203 mAh g⁻¹), and N80 (213 mAh g⁻¹), while slightly lower than N90 (224 mAh g⁻¹). [Fig. 2b-d](#) present the cyclability in terms of capacity, energy density and average voltage at C/3 rate after three formation cycles at C/10 rate. LNC demonstrates a much improve capacity retention of 92%, compared to 76% for N60, 67% for N70, 61% for N80 and 58% for N90 ([Fig. 2b](#)). [Supplementary Fig. 10](#) provides the corresponding charge-discharge profiles from the 5th to 200th cycle. LNC also shows improved energy density retention of 90%, much higher than 73%, 62%, 56% and 52% observed for N60, N70, N80 and N90, respectively ([Fig. 2c](#)). Despite the activation of anionic redox, LNC shows a negligible average voltage decay of only 0.46 mV per cycle, substantially lower than that of 0.77 mV, 1.56 mV, 1.57 mV, 1.87 mV per cycle for N60 to N90 ([Fig. 2d](#)). Unlike conventional Li-rich cathodes, which suffer from serious average voltage decay of 2-4 mV per cycle^{40,41}, LNC exhibits significantly improved voltage stability, even surpassing Ni-rich NMCs. Voltage decay in Ni-rich cathodes, particularly under high voltages, stems from irreversible phase transformations and lattice oxygen instability^{42,43}, which trigger interfacial parasitic reactions and surface structural degradation, further accelerating performance deterioration¹⁹. Their phase reversibility during repeated cycles were further analyzed through dQ/dV measurements. As shown in [Fig. 2e](#), the dQ/dV profiles from the 5th to the 200th cycle, ranging from N60 to N90, reveal a progressive fading and negative shifts in reduction peaks at around 4.2 V (H3 to H2), 4.0 V (H2 to M), and 3.7 V (M to H1), reflecting continuous irreversible structural degradation. In sharp contrast, negligible peak changes are visualized in LNC, further confirming its enhanced structural and electrochemical stability. Further comparison of electrochemical stability performance in full cell shows that LNC cathode exhibits a remarkably high capacity retention of 90% after 500 cycles at C/2

rate within 2.4-4.4 V (vs. graphite), whereas N60, N70, N80 and N90 experience a rapid capacity degradation, retaining only 73%, 71%, 67% and 60% capacity retention, respectively (**Fig. 2f** and **Supplementary Fig. 11**). In pouch full cells, LNC demonstrates exceptional cycling stability, achieving ~97% capacity retention over 400 cycles at 1C rate with an upper cutoff voltage of 4.3 V (vs. graphite), significantly outperforming the N80 (**Fig. 2g**, the capacity fluctuations arise from environmental temperature variations). Additionally, the comparison of rate capability in **Supplementary Fig. 12** shows that LNC delivers discharge capacities of 196 mAh g⁻¹ and 142 mAh g⁻¹ at C/2 and 5 C rates, respectively, exceeding N60 to N90. These experimental results clearly demonstrate that LNC offers comprehensive electrochemical advantages, surpassing Ni-rich NMC cathode materials (N60 to N90) in terms of both capacity and voltage stability.

Minimized lattice variations during cycling

To quantitatively assess the degree of phase transitions and lattice variations, and correlate these to the electrochemical properties, in situ HEXRD experiments on N60, N80, and LNC were performed during the initial charge-discharge process. As shown in **Fig. 3a** and **Supplementary Fig. 13**, N60 shows a gradual shift of the (003) Bragg peak to lower 2 θ values, indicating interlayer spacing expansion due to increased electrostatic repulsion between adjacent TM layers as Li⁺ extraction. Upon further charging, an abrupt peak position change occurs (marked by dashed circles), corresponding to a phase transition from H1 to M. This is accompanied by shifts in (101), (018), (110) and (113) peaks. After reaching the lowest 2 θ value, the (003) peak shifts markedly to the higher side, indicating a phase transition from H2 to H3 with a rapid interlayer spacing contraction at highly delithiated states. Such substantial lattice changes ($\Delta 2\theta_{003}=0.046^\circ$) could potentially induce mechanical damage to the particles. The discharge process follows the reverse phase transition sequence. For N80, a similar phase transition process was observed but with more pronounced lattice variations ($\Delta 2\theta_{003}=0.091^\circ$), including a sudden peak jump at 3.7 V and an abrupt contraction above 4.2 V (**Fig. 3b** and **Supplementary Fig. 14**). In contrast, LNC cathode shows smooth and consecutive phase transitions, with much reduced lattice variations ($\Delta 2\theta_{003}=0.028^\circ$) throughout the whole charge and discharge process (**Fig. 3c** and **Supplementary Fig. 15**). **Fig. 3d-f** show the Rietveld-refined lattice parameter evolution. For the c parameter, N60 shows gradual increase from 14.1893 Å to 14.2552 Å, followed by an abruptly increasing associated with H1 to M phase transition. After reaching a maximum of 14.4777 Å, it gradually decreases to 14.1564 Å at 4.5 V, with a maximum lattice variation of 2.22% (**Fig. 3d**). N80 exhibits an obvious two-phase transition with a c lattice separation of 14.1747 Å and 14.3258 Å, then gradually increases to a maximum of 14.4414 Å before sharply decreasing to 13.8005 Å at 4.5 V, with a maximum lattice parameter variation of 4.44%. In contrast, LNC exhibits a smooth increase in c parameter from 14.1970 Å to 14.4020 Å and slowly decrease to 14.2010 Å, with a maximum lattice variation of only 1.42%. For the a parameter and unit cell volume, N60 shows variations of 1.84% and 3.82%, N80 shows 2.09% and

6.63%, and LNC exhibits the smallest values at 1.73% and 3.40%, respectively.

To evaluate structural reversibility over extended cycling, *ex situ* HEXRD measurements were performed on N60, N80, and LNC electrodes after 10, 50, and 100 cycles. As shown in [Supplementary Fig. 16](#), LNC exhibits the smallest lattice variations, in sharp contrast to N60 and N80, indicating enhanced structural reversibility. These results are consistent with the dQ/dV analysis shown in [Fig. 2e](#). In general, the low-Ni chemistry structure design can significantly suppress sharp and huge lattice parameter variations and phase separation, contributing positive effect on structural stability.

Anionic redox and local coordination structure stability

In conventional Li-rich layered cathodes, oxygen anionic redox reactions are typically accompanied by irreversible lattice oxygen loss and structural reconstructions, leading to severe capacity and voltage decay that hinder their practical application^{44,45}. To understand capacity and voltage stability of LNC cathode at high operation voltages, it is crucial to investigate the chemical states and electronic structure evolutions, particularly the anionic redox reactions upon cycling. The O K-edge mapping of the resonant inelastic X-ray scattering (mRIXS) technique, with a probe depth of 100-200 nm, is a powerful technique for distinguishing intrinsic oxidized oxygen signals from TM contributions and probing lattice anionic redox activity⁴⁶. The outermost 500 nm region of the particle features a Li- and Mn-rich layered structure with a 5 nm epitaxially grown rock-salt matrix ([Fig. 1](#)), making the observed O signal primarily attributable to the Li-rich structure. mRIXS measures the lattice oxidized oxygen through two characteristic features: an excitation at 531 eV and an emission at 524 eV, along with a low energy loss feature close to elastic line at the same excitation energy. As shown in [Fig. 4a](#), pristine LNC shows a broad feature at around 526 eV emission energy from strong TM-O hybridization. When charged to 4.5 V, a new fingerprint feature appears at around 531 eV excitation and 523.5 eV emission energies (red arrows), accompanied with an intensified elastic peak (white arrows). These features serve as an indicator for oxidized lattice oxygen formation, although the exact species involved remain under debate⁴⁷. When discharged to 2.5 V, these oxidized oxygen features diminish, signifying a reversible oxygen anionic redox reaction in LNC cathode. Notably, the strong signal for lattice oxidized oxygen is well maintain after 2 and even 100 cycles. The intensity variation of the characteristic O K-edge mRIXS features can be used to track the reversibility and retention of lattice anionic redox upon electrochemical cycling. As shown in [Fig. 4b](#), the mRIXS intensity cut at 531 eV excitation energy reveals a characteristic peak at 524 eV that emerges upon charging to 4.5 V and remains nearly unchanged even after 100 cycles, implying the reversible oxygen anionic redox in the LNC cathodes. In contrast, no obvious oxidized O signal is detected in N60, suggesting very limited contribution to reversible capacity ([Supplementary Fig. 17](#)). These findings highlight the critical effect of low-Ni chemistry structure design in enabling highly reversible lattice oxygen anionic redox over extended cycling.

In situ X-ray absorption spectroscopy (XAS) was further employed to investigate the chemical state evolution of LNC cathodes during the initial charge and discharge

processes. As shown in **Fig. 4c** and **Supplementary Fig. 18a**, the Ni K-edge shifts to higher energies during charge, indicating Ni oxidation, and returns to lower energy upon discharge, confirming its reversibility. For Mn and Co, changes in edge features were related to the local coordination environment variations (**Supplementary Figs. 18b,c and 19**). The corresponding FT-EXAFS spectroscopy demonstrates the TM-O and TM-TM distance variations of Ni, Mn and Co (**Supplementary Fig. 20**). Ex situ XANES profiles (**Fig. 4d**) show that all samples (LNC, N60, N80) exhibit Ni oxidation up to 4.4 V, followed by a slight valence decrease at 4.5 V, consistent with a ligand-to-metal charge transfer process ($\text{Ni}^{4+}\text{-O}^{2-} \rightarrow \text{Ni}^{3+}\text{-O}^{\text{n-}}$). Additionally, the slightly lower valence state of Ni in the LNC cathode compared to N60 and N80 at high charge voltages can be attributed to the higher degree of anionic redox reactions participation. The ex situ XANES profiles of Mn and Co, as well as the FT-EXAFS of Ni, Mn and Co, are displayed in **Supplementary Figs. 21 to 26**. It can be observed that LNC shows reduced changes in the local coordination environment around TM atoms compared with N60 and N80. After 100 cycles, N60 and N80 show pronounced positive shifts in the Ni, Mn, and Co K-edges (**Fig. 4e-g**), indicating irreversible structural degradation and elevated TM valence states due to poor Li^+ reinsertion. As Ni is oxidized to higher valence states, the increased bond strength shortens the Ni-O coordination distance, and the more symmetric oxygen coordination around Ni contributes to the increased Ni-O peak intensity (**Fig. 4h**)⁴⁸. Strikingly, the XANES and EXAFS profiles of LNC after 100 cycles nearly overlap with those after 1 cycle, indicating remarkable structural stability and reversible Li^+ intercalation behavior (**Fig. 4h-j**). These results suggest that the LNC cathode with low-Ni chemistry radial phase integration design provides immunity against local coordination variations and structural degradation, potentially beneficial for stabilizing lattice oxygen for reversible anionic redox reactions, which collectively yield enhanced capacity and longer cycle life compared to conventional Ni-rich layered cathodes.

Mechanical and atomic structural stability

Beyond macroscopic observation, we further investigate the mechanochemical structural changes from the particle to atomic level to gain a deeper understanding of the effectiveness of the proposed concept on electrochemical properties. Specifically, full-field transmission X-ray microscopy (TXM) coupled with 3D XANES was used to track the three-dimensional chemical mapping of the particles. The Ni K-edge white-line position, fitted via fourth-order polynomial at each pixel, was mapped to reflect valence changes. **Fig. 5a-c** shows the 3D renderings and 2D cross-sections of N60, N80 and LNC particles. In the pristine state, all particles exhibit a uniform blue-green color. When charged to 4.5 V, the color of both surface and bulk in N60 and N80 turns red, indicating an increase in Ni valence states due to Li^+ extraction. However, the surface color of LNC changes to green, suggesting that the Li percolation rock-salt matrix exhibits limited electrochemical activity, which is beneficial for suppressing surface side reactions and structural reconstruction induced by highly oxidized Ni^{4+} and oxidized oxygen anionic species, while enabling efficient Li^+ diffusion. Inside the bulk, the yellow-red color suggests a moderated Ni oxidation state, attributed to the higher

involvement of oxygen anionic redox, as also supported by ex situ XAS (Fig. 4d). After 100 cycles, both N60 and N80 exhibit a green color, while LNC almost returns to its original blue-green color, illustrating the highly reversible and stable chemical structure in LNC. Correspondingly, statistical pixel counts analysis of the white line peak position confirms a much remarkable positive shift of white line energy in N60 and N80 than in LNC (Fig. 5d). Furthermore, TXM imaging reveals intergranular microcracks in cycled N60 and N80, while LNC maintains an intact morphology, reflecting the benefits of reduced lattice strain and surface structural stability.

The intragranular morphology and local structure changes of cycled N80 and LNC cathodes were further investigated using high-angle annular dark field STEM (HAADF-STEM). For N80 after 100 cycles, numerous microcracks can be observed inside the particles (marked by arrows) as shown in Fig. 5e and Supplementary Fig. 27. At the atomic level, the surface layered structure mostly transforms into inactive rock-salt structure, as evidenced by the fast Fourier transform (FFT) images of the selected area in Fig. 5f. The dark high contrasted dotted regions (marked by dashed lines) represent nanovoids formed inside the lattice, a phenomenon commonly observed in cycled layered oxides and often associated with irreversible lattice oxygen release^{15,44,49}. In Supplementary Fig. 28, electron energy loss spectroscopy (EELS) of N80 exhibits a depressed O pre-edge peak compared with LNC, indicating a more pronounced rock-salt structural signature⁴². Such structural evolution from a layered (Li_xTMO_2) to a rock-salt (NiO-type) phase is frequently correlated with irreversible lattice oxygen loss over repeated cycling^{49,50}. Moreover, inside the bulk, severe atomic disordering defects can be visualized near the cracking region (Fig. 5g). For LNC, the particle retains its morphology, and the epitaxially grown Li percolation rock-salt surface structure remains intact with a thickness comparable to that of pristine state (Fig. 5h and Supplementary Fig. 29). This ultra-stable rock-salt surface can serve as an effective barrier prevents progressive structural degradation and mechanical damage. Inside is a stable Li-rich feature region, confirmed by the selected area FFT image with additional spotted-streaks along the c direction (marked by arrows). The two-atoms dumbbell feature of Li_2MnO_3 -like structure outer layer and a LiTMO_2 -type layered structure central bulk can also be clearly visualized in Figs. 5i and 5j. All these results prove that low-Ni chemistry structure design can significantly enhance the morphological and structural stability, leading to high practical capacity and prolong cyclability even under harsh operation voltages with highly reversible oxygen anionic redox reaction.

Discussion

Moving towards lower Ni cathodes in EVs batteries represents a strategic shift toward improved performance and sustainability. This work presents a new low-Ni chemistry cathode ($\text{Ni}<0.6$) featuring multistage compositional concentration distribution and radial phase integration to decouple capacity reliance from Ni content, addressing the longstanding challenge in cathode development. The designed structure significantly reduces lattice strain and phase transitions, forming an ultra-stable host that resists mechanical degradation under high-voltage cycling. A Li-rich framework with delocalized superlattice units further stabilizes the structure and mitigates irreversible

oxygen redox. The epitaxially grown Li-percolation rock-salt matrix, which is both electrochemically active and structurally stable, enhances surface oxygen stability and prevents continuous surface to the bulk structural degradation. Consequently, the LNC cathode demonstrates highly reversible oxygen anionic redox activity, delivers ultrahigh capacity, and maintains long-term cycling stability, surpassing state-of-the-art high-Ni cathodes. We anticipate this perspective will inspire the design and development of a new wave of high-capacity and stable intercalation cathodes that suitable for advanced battery systems.

Methods

Material synthesis: The precursor of LNC was synthesized via a co-precipitation method. Specifically, stoichiometric amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99\%$) and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99\%$) were dissolved in DI water to prepare a 2 M solution with a molar ratio of 8:1:1 and stored in the first container. Another solution with Ni, Mn and Co in a molar ratio of 4:5.5:0.5 was prepared and stored in a second container. The solution from the first container was then pumped into the reactor under N_2 atmosphere along with a 4 M NaOH and a 5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution as chelating agent. Simultaneously, the solution from the second container solution pumped into the first container. The pH value was controlled to 10.5-11, the temperature was kept at 60 °C, and the stirring speed was kept at 1000 rpm. The precursor powders were collected after washing, filtering and vacuum drying in an oven at 60 °C overnight. The precursors were then thoroughly mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ (Li: TM= 1.15: 1) and sintering at 850 °C for 12 h at a heating rate of 5 °C min^{-1} to obtain the final products. For comparison, Ni-rich series cathodes were prepared by thoroughly mixing the corresponding precursors (Zhejiang Power New Energy Co. Ltd.) with $\text{LiOH} \cdot \text{H}_2\text{O}$ (Li: TM= 1.03: 1), followed by calcination at various temperatures for 12 h under an oxygen atmosphere: 850 °C for $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, 800 °C for $\text{LiNi}_{0.7}\text{Mn}_{0.15}\text{Co}_{0.15}\text{O}_2$, 750 °C for $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and 730 °C for $\text{LiNi}_{0.9}\text{Mn}_{0.06}\text{Co}_{0.04}\text{O}_2$.

Characterization: The chemical composition was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Scanning electron microscope (SEM) was performed using a JEOL JSM-7100F. High energy X-ray diffraction (HEXRD) data were collected at 28-ID-1 beamline of National Synchrotron Light Source II (NSLS-II) of Brookhaven National Laboratory, using a beam with a wavelength of 0.1665 Å, and at the 11-ID-C beamline of the Advanced Photon Source (APS), using a wavelength of 0.11595 Å. Rietveld refinements were carried out using GSAS-II software. Atomic pair distribution function (PDF) data were collected in the transmission mode at 28-ID-1 beamline of NSLS-II, with fitting performed using the PDFgui software. X-ray absorption spectroscopy (XAS) experiments were conducted at 7-BM-B beamline of NSLS-II. For extracting the FT-EXAFS spectrum of the Ni K-edge, the k-range was set to 3.0-13.8, while for Co and Mn, it was 3.0-11.5, using a Hanning window. For TEM analysis, thin-section specimens were prepared using a commercial Gatan Precision Ion Polishing System (PIPS). High resolution transmission

electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) was performed on an Argonne Chromatic Aberration-Corrected TEM (ACAT) with an accelerating voltage of 200 kV. The energy resolution of the EELS measurements is 0.25 eV.

Electrochemical test: To prepare electrode, active materials were mixed with carbon black (C45 Conductive Carbon Black, TIMCAL) and polyvinylidene fluoride binder (PVDF, Solvay® 5130 PVDF dissolved in n-methyl-2-pyrrolidone (NMP)) at a mass ratio of 8:1:1. The mixture was ground in a mortar at 2000 rpm, and the resulting slurry was cast onto Al foil for the cathode electrode and Cu foil for the anode. The 2032 type coin half-cells used Li metal foil as anode, Celgard 2325 separators, and 1.2 M LiPF₆ in EC/EMC (3: 7) electrolyte. The mass loading of cathode materials was ~4 mg cm⁻². For the full cell, a graphite electrode was used as anode with a capacity ratio of negative electrode capacity to positive electrode capacity (N/P ratio) of 1.1-1.2:1. The galvanostatic charge-discharge performance was evaluated using a NEWARE battery test system. For the pouch full cell, the cathode material mass loading was ~10 mg cm⁻². The electrolyte consisted of 1.2 M LiPF₆ in EC/EMC (3:7) with a 2% VC additive. Galvanostatic charge-discharge performance was evaluated using a MACCOR testing system.

3D X-ray fluorescence microscopy (XRF): 3D synchrotron XRF mapping was conducted at the 3-ID hard X-ray nanoprobe beamline of the NSLS-II at Brookhaven National Laboratory. Sample particles were drop-cast on a 10 µm thick Si sample holder, which featured patterned fiducial lines (Cr) for sample location, focusing, and rotation alignment. Tomography measurements involved collecting projections from -90° to 90° with 2° intervals. The tomographic reconstruction was performed using the algebraic reconstruction technique. The spatial resolution of the 3D XRF imaging is 50 nm.

In-situ high energy X-ray diffraction (HEXRD): In-situ HEXRD characterization was performed during the charge-discharge process at the 28-ID beamline of NSLS-II ($\lambda=0.1665$ Å). The tested 2032-type coin cells were assembled with two holes of 3 mm on both the cathode and anode caps. The galvanostatic charge-discharge tests were conducted using a Bio-Logic battery system.

Mapping of resonant inelastic X-ray scattering (mRIXS): mRIXS measurements were performed at iRIXS end station on Beamline 8.0.1 of the Advanced Light Source (ALS). The resolution of the excitation energy and emission energy was approximately 0.35 eV and 0.25 eV, respectively. An excitation energy step size of 0.2 eV was chosen for all maps and the mRIXS data were collected at each excitation energy. The final 2D images were obtained through a data processing method that involved normalization to the beam flux and collection time, integration, and combination.

Full-field transmission X-ray microscopy (TXM) imaging: TXM imaging was conducted at 18-ID FXI beamline of NSLS-II of Brookhaven National Laboratory,

generating 3D nano-XANES datasets. Projection images were captured from 0 to 180° for each energy, and 3D tomography was reconstructed from these images. The voxel resolution of the resulting X-ray microscopy imaging was 40 nm.

Data availability

All data are available in the main text or Supplementary Information, which can also be available from the corresponding author upon request.

Correspondence and requests for materials should be addressed to Tongchao Liu and Khalil Amine.

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Author contributions

W.H, T.Liu. and K.A. conceived the idea and designed the experiments. W.H synthesized all the materials. W.H., A.D., R.A. and S.T. conducted electrochemical measurements. Z.Z. and J.G. conducted the mRIXS. J.H., T.Z., H.A., and J.Wen. carried out the TEM results. X.L. carried out the ICP-OES. W.H., J.Wang, G.K. and T.Li. performed synchrotron HEXRD and PDF. W.H. and L.M. performed XAS. W.H. and X.X. conducted the TXM. X.H. conducted the XRF. W.H., T.Liu and K.A. wrote the manuscript and all authors edited the manuscript.

Competing interests

The authors declare no competing interests.

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Figure legends

Fig. 1 | Structure and composition characterization of LNC cathode. **a.** HEXRD pattern and Rietveld refinement of LNC. Inset highlights the superlattice peaks. **b.** SEM image of LNC particles with an inset showing the cross-sectional view of a particle. **c.** 3D tomography reconstruction from XRF imaging, showing the spatial element distributions of Ni, Mn and Co. Element content is indicated by color bars, with blue to red color representing low to high content. **d.** Central line scanning plots of LNC illustrating compositional variations. **e.** Atomic resolution HAADF-STEM images reveal a Li-rich layered structure with an epitaxially grown rock-salt phase. **f-h.** High-resolution images highlight the surface (**f**), outer layer (**g**), and bulk (**h**) regions. In **f**, arrows indicate the Li percolation regions. In **g**, a dashed rectangle marks the region with two TM atom dumbbell configuration, while arrows in **h** indicate Li/TM disordering.

Fig. 2 | Electrochemical measurements of LNC and Ni-rich NMC series cathodes. **a.** The 3rd cycled charge-discharge profiles of LNC and Ni-rich NMC series cathodes at C/10 rate in the voltage range of 2.5-4.5 V in half cells. **b-d.** Specific capacity (**b**), energy density (**c**) and average voltage (**d**) stability of LNC and Ni-rich NMC series cathodes at C/3 rate. **e.** dQ/dV profiles of LNC and Ni-rich NMC series cathodes in the 5th, 10th, 20th, 50th, 100th and 200th cycles at C/3 rate. **f.** Long-term cycling performance of LNC and Ni-rich NMC series cathodes at C/2 rate in the voltage of 2.4-4.4 V in full cells. **g.** Long-term cycling performance of LNC and N80 cathodes at 1C rate with an upper cutoff voltage of 4.3 V in pouch full cells.

Fig. 3 | Structural evolution during charge and discharge process. **a-c.** Two-dimensional contour patterns of in situ HEXRD ($\lambda=0.1665$ Å) for N60 (**a**), N80 (**b**) and LNC (**c**) cathodes during the initial charge and discharge process. Impurities are marked with white arrows. **d-f.** Comparison of the variation in lattice parameter *c* (**d**), lattice parameter *a* (**e**) and unit cell volume (**f**) for N60, N80 and LNC cathodes obtained from Rietveld refinements.

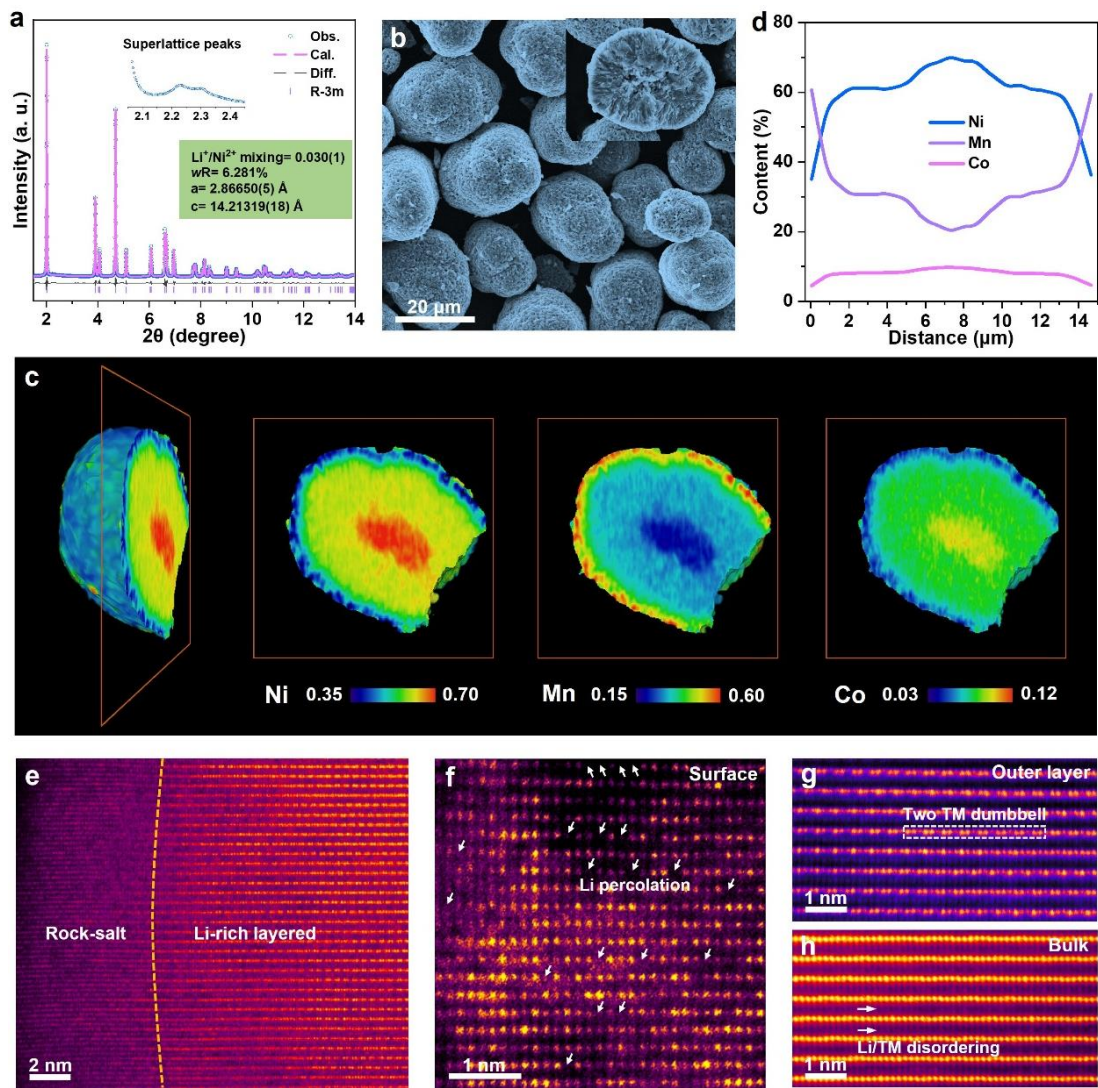
Fig. 4 | Chemical state change during cycling. **a.** O-K mRIXS images of LNC cathode at various states: OCV, 1st charge to 4.5 V, 1st discharge to 2.5 V, 2nd charge to 4.5 V, and 100th charge to 4.5 V. **b.** mRIXS intensity cut at 531 eV excitation energy of LNC cathodes at OCV, charged to 4.5 V at the 1st, 2nd and 100th cycles. **c.** Two-dimensional contour patterns of in situ XAS showing the Ni-K edge XANES variations of LNC cathode during the initial charge and discharge process. **d.** Ni-K edge XANES spectra of N60, N80 and LNC cathodes at OCV, 1st charged to 4.4 V and 4.5 V. **e-g.** XANES spectra of Ni- (**e**), Mn- (**f**) and Co-K edge (**g**) in the 1st and 100th cycled N60, N80 and LNC cathodes. **h-j.** FT-EXAFS results of Ni (**h**), Mn (**i**) and Co (**j**) in the 1st and 100th cycled N60, N80 and LNC cathodes.

Fig. 5 | Morphological and structural stability after long-term cycling. **a-c.** 3D

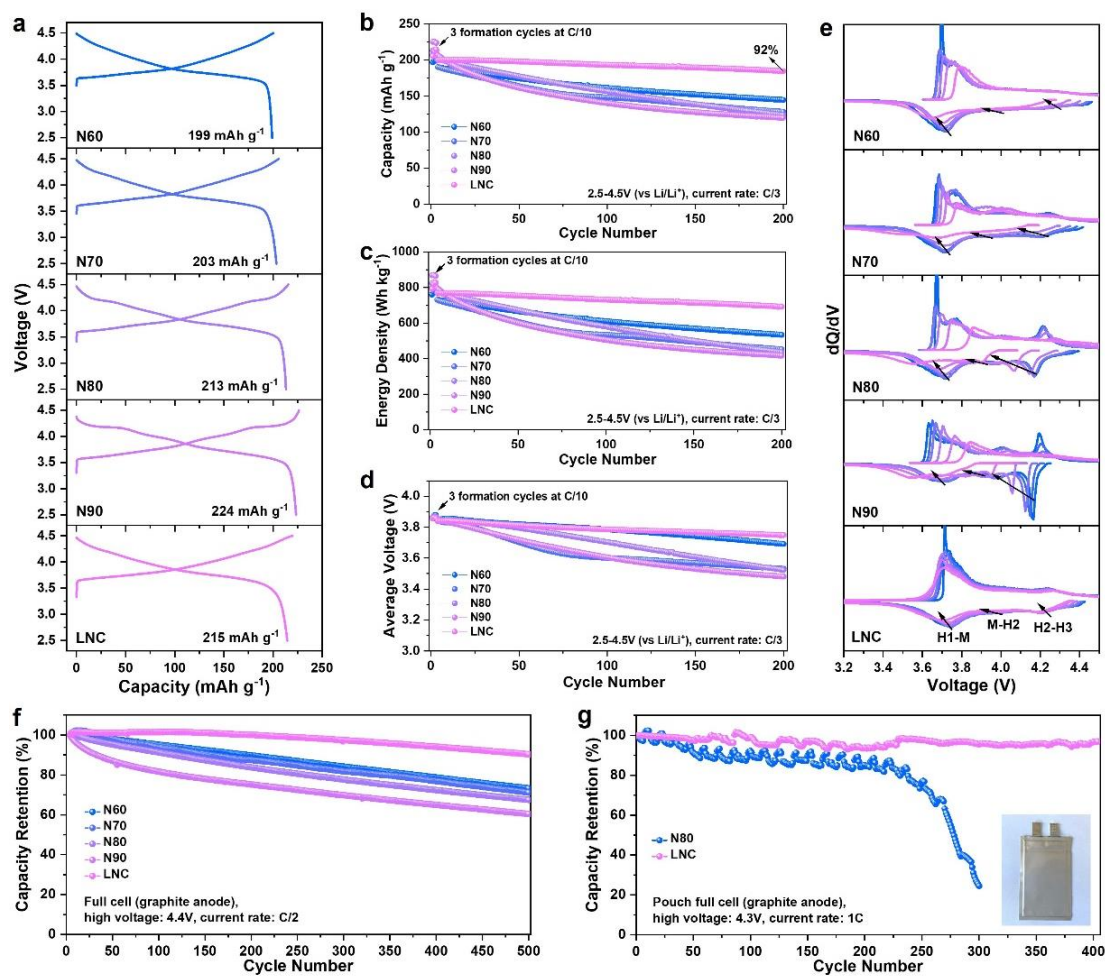
rendering and cross section views of N60 (**a**), N80 (**b**) and LNC (**c**) cathodes at OCV, charge to 4.5 V and in the 100th cycle. **d**. The corresponding statistical white line peak position energy distribution for N60, N80 and LNC cathodes at OCV, charge to 4.5 V and in the 100th cycle. **e-g**. HAADF-STEM images of the 100th cycled N80 showing intragranular cracks (**e**), surface (**f**) and bulk (**g**) structure. The right panel shows the FFT images of the selected area in **f**. **h-j**. HAADF-STEM images of the 100th cycled LNC showing the surface (**h**), outer layer (**i**) and bulk (**j**) structure. The right panel shows the FFT images of the selected area in **h**, and the superlattice diffraction fringes are indicated by arrows.

Figures

Fig. 1



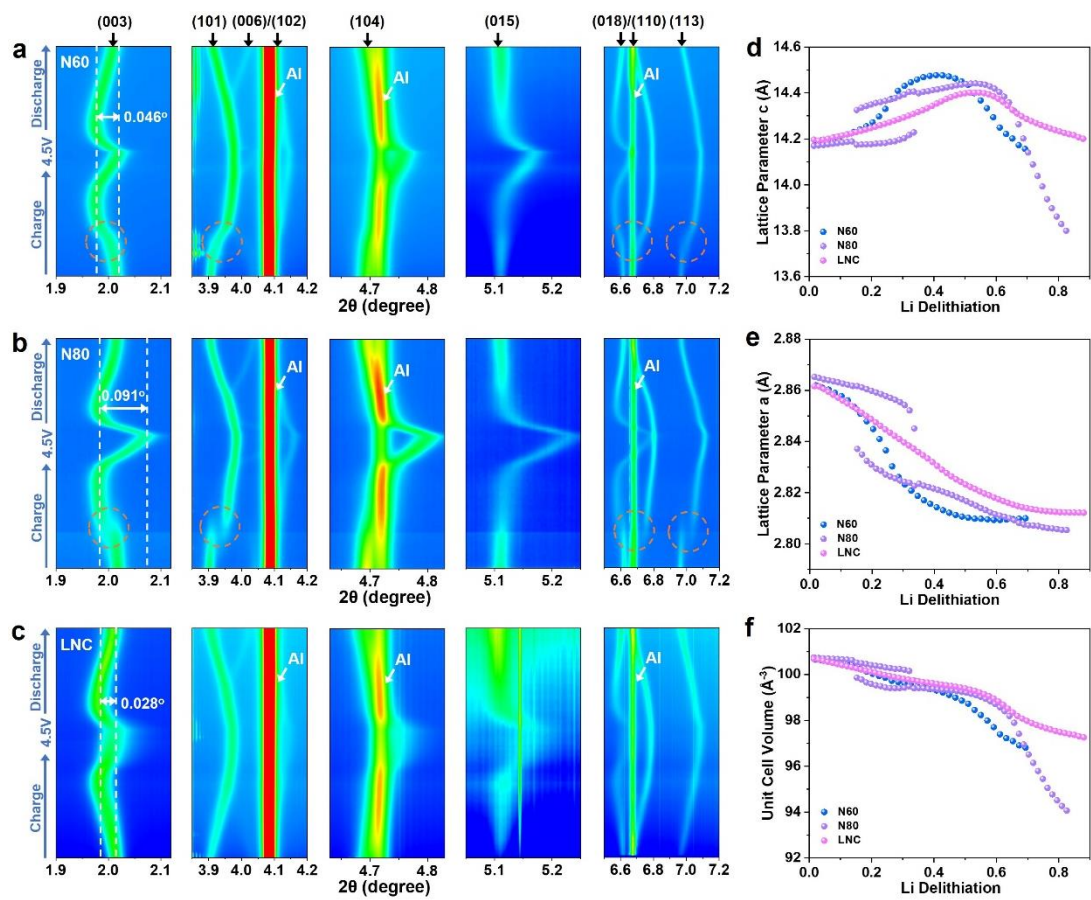
678 **Fig. 2**



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681 **Fig. 3**



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