

A Quasi-Ordered Mn-Rich Cathode with Highly Reversible Oxygen Anion Redox Chemistry

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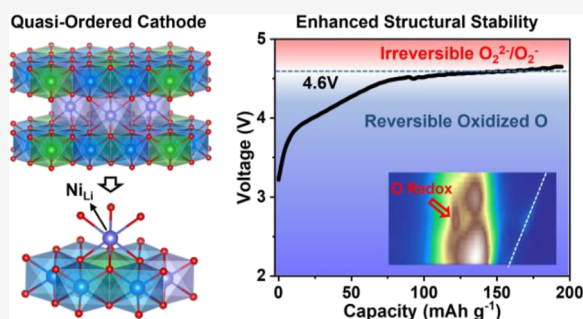


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ABSTRACT: Anionic oxygen redox chemistry in Li-rich Mn-based layer oxide cathodes represents a transformative approach for boosting the energy density of next-generation lithium-ion batteries. However, conventional oxygen redox reactions often induce oxygen dimerization at high voltages, leading to irreversible lattice oxygen loss and a rapid voltage fade. Herein, we achieve highly reversible oxygen redox chemistry through a new quasi-ordered structural design that incorporates both intra- and interlayer cation disorder configurations. This unique structure significantly enhances lattice oxygen stability, effectively stabilizes oxidized oxygen, and inhibits the formation of peroxo- or superoxolike species, thereby enabling anionic redox reactions to proceed reversibly even at deep delithiation states. The quasi-ordered design mitigates irreversible phase transitions and preserves the structural integrity throughout extended cycling. Consequently, the proposed cathode demonstrates exceptional cyclability with negligible capacity and voltage fade, retaining 99% capacity and 98% average voltage after long-term cycling. This work provides fresh insights into addressing issues related to lattice oxygen instabilities and reforming strategies for developing long-life, high-energy-density anionic redox cathode materials for advanced batteries.



INTRODUCTION

The limited capacity of conventional cathodes poses a significant bottleneck in the development of high-energy-density Li-ion batteries, which are essential for long-range electric vehicle technologies.¹ Achieving high reversible capacity requires a delicate balance of substantial redox center activity and sufficient Li⁺ storage active sites to facilitate reversible Li⁺ insertion and extraction within the structural framework.² Compared to conventional layered oxide cathodes that mainly relies on transition metal (TM) redox for capacity, Li-rich Mn-based cathodes incorporate cationic and anionic redox reactions with Li⁺ storing in both the Li and TM slabs simultaneously.^{3,4} The Li–O–Li special configurations (nonbonding O) in Li-rich cathodes position the O 2p states near the top of the valence band, making oxygen oxidation thermodynamically accessible and enabling substantial capacity contributions from oxygen redox during cycling.^{5,6} However, these extra capacities from oxygen redox reactions often come at the expense of voltage stability and capacity retention,⁷ which not only shorten cycle life but also complicates battery management, hindering their large-scale practical deployment.

The instability of oxygen redox chemistry is primarily associated with Li-rich ordered configuration, where abundant and spatially proximate nonbonding O atoms increase susceptibility to oxygen loss and irreversible TM migration

toward TM dense phases.⁸ Specifically, in Li-rich domains with localized LiMn₆ honeycomb superstructure ordering, TM migration is thermodynamically favorable during delithiation, creating intralayer vacancies and initiating the formation of low-coordination oxidized oxygen species.^{9,10} Locally enriched oxidized O species often aggregate and dimerize, forming peroxo- and superoxo-like species and even oxygen molecules,^{4,11} which subsequently escapes from the lattice, leading to irreversible structural degradation and nanovoid formation.¹² Efforts to mitigate lattice oxygen instability during cycling have included strategies such as increasing the TM migration barrier through modified interlayer stacking^{13,14} or constructing ordered TM ribbon or mesh structures within the TM layers to spatially separate oxidized oxygen.^{10,15} Specifically, in O₂-type Li-rich cathodes, structural stability originates from the specific lattice stacking sequence, where intralayer TM migration is thermodynamically suppressed due to strong repulsion between face-sharing cations.^{13,16} This suppression

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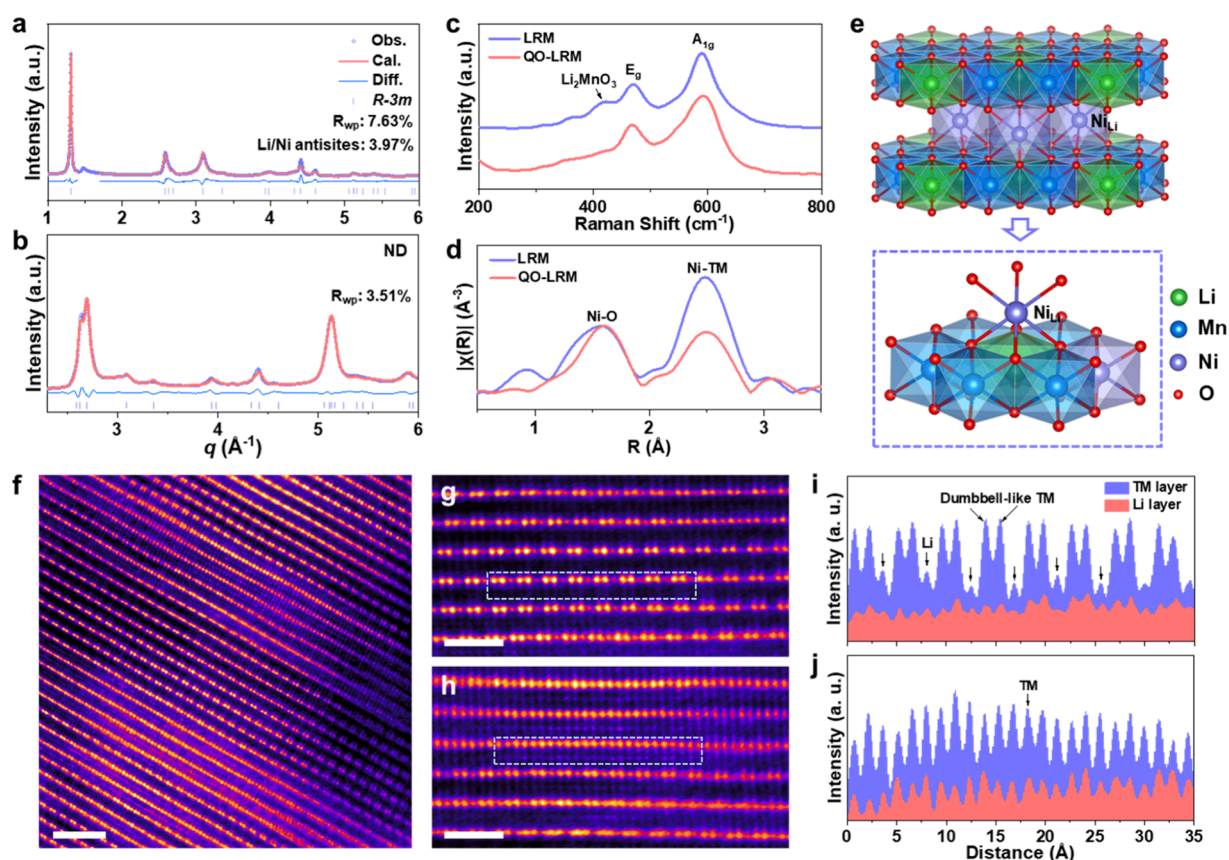


Figure 1. Structural characterization of the QO-LRM cathode. Combined Rietveld refinement of X-ray diffraction (a) and neutron diffraction (b) patterns for QO-LRM. (c) Raman spectra of QO-LRM and LRM. (d) FT-EXAFS at the Ni K-edge, illustrating local structural environments in QO-LRM and LRM. (e) Schematic diagram of the quasi-ordered structure configuration. (f) HAADF-STEM images showing the atomic arrangement of QO-LRM. Scale bar: 1 nm. Enlarged views highlighting the Li-rich (g) and LiTMO₂ (h) structures. Scale bars: 0.5 nm. (i, j) Atomic intensity distribution along the selected columns marked by dashed rectangles in (g) and (h), respectively.

facilitates reversible TM migration and enhances the structural robustness during cycling. While these approaches improve electrochemical performance to some extent, they have not yet prevented structural instability during prolonged cycling. Another concept like disordered rock-salt cathodes can disrupt TM/Li ordering and maintain substantial oxygen redox for ultrahigh capacity. However, these materials still experience significant oxygen loss and irreversible cation rearrangement, which damages Li diffusion percolation paths and leads to rapid capacity and voltage fade.¹⁷ Therefore, the state-of-the-art material paradigm fails to overcome the intrinsic instability of lattice oxygen redox, necessitating the leverage of new material science principles to create a stable local lattice oxygen binding environment.

Beyond typical Li-rich cathodes, we introduce a new Co-free Li-rich Mn-based quasi-ordered layered structure cathode (QO-LRM) in this work, featuring both intra- and interlayer cation disorder configurations to address the long-standing challenge of lattice oxygen instability-induced electrochemical decay. The unique structural design, featuring a short-range, partially Ni-substituted intralayer LiMn₆ honeycomb superstructure and a high degree of interlayer cation disorder, effectively mitigates the formation of peroxo- or superoxol-like species and facilitates reversible anionic redox. This innovation extends the upper voltage and utilization limit for reversible lattice oxygen reactions, delivering over three times the reversible oxygen anion redox capacity of conventional Li-

rich cathodes while maintaining exceptional lattice oxygen stability and structural integrity over long-term cycling. Consequently, the designed QO-LRM cathode demonstrates a high capacity of 262 mAh g⁻¹ with ultrastable O redox chemistry, showing negligible capacity and voltage decay, with a capacity retention of 99% and a voltage retention of 98% after 100 cycles. This work establishes a promising framework for rational structure design to achieve high-performance anionic redox cathodes for next-generation batteries.

RESULTS AND DISCUSSION

Characterization of the Quasi-Ordered Structure Design. The QO-LRM material was prepared by coprecipitation followed by a molten salt procedure (see Experimental section in the [Supporting Information](#)). The chemical composition was determined to be Li_{0.88}Mn_{0.72}Ni_{0.13}O₂ by inductively coupled plasma-optical emission spectroscopy (ICP-OES, [Table S1](#)). Powder X-ray diffraction (XRD) and neutron diffraction (ND) were employed to characterize the lattice structure of the QO-LRM cathode. [Figure 1a,b](#) shows characteristic Bragg diffraction peaks indicative of a well-defined layered structure of the *R*-3*m* space group, with additional superlattice peaks at around $q = 1.5 \text{ \AA}^{-1}$ corresponding to the honeycomb LiMn₆ superstructure units in the TM layers. The combined refinement results of XRD and ND reveal that QO-LRM contains 3.97% of the Li/TM disorder ([Tables S2 and S3](#)), which is significantly higher than that of

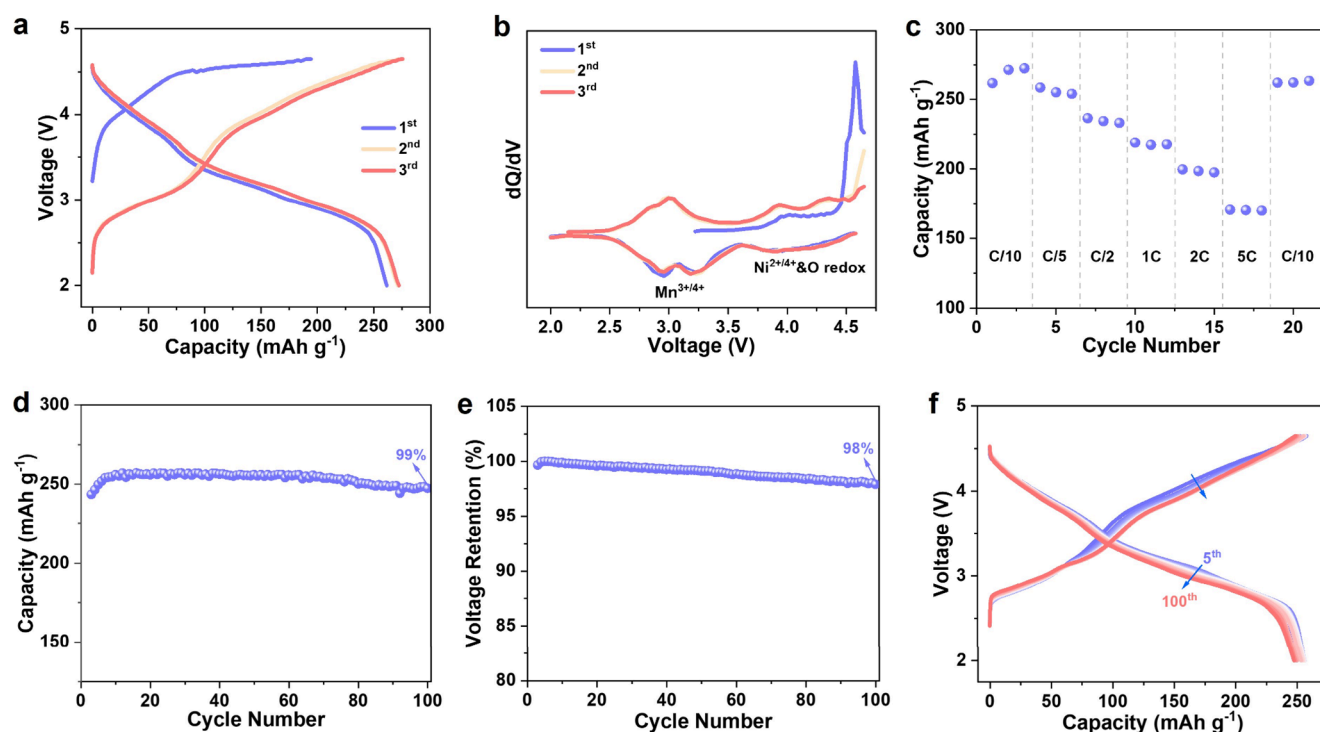


Figure 2. Electrochemical performance of the QO-LRM cathode. (a) Charge–discharge curves of QO-LRM for the first three cycles at a current rate of 0.1C within the voltage range of 2.0–4.65 V. (b) Corresponding dQ/dV profiles for QO-LRM. (c) Rate performance of the QO-LRM cathode. Capacity stability (d) and average voltage stability (e) of QO-LRM at 0.2C. (f) Charge–discharge profiles of QO-LRM from the 5th to the 100th cycle at a current rate of 0.2C.

0.89% in $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ (denoted as LRM, Figure S1 and Tables S4 and S5), a typical Co-free Li-rich Mn-based cathode, demonstrating a pronounced interlayer disordered arrangement of cations. Additionally, the QO-LRM cathode exhibits a broadened superstructure peak with reduced peak intensity compared to that of the LRM cathode (Figure S2), which is attributed to superlattice structure distortion and stacking faults. Raman spectroscopy was performed to further investigate the local structural characteristics (Figure 1c). Specifically, two peaks around 470 and 590 cm^{-1} represent the E_g and A_{1g} vibrations of the LiTMO_2 -type layered structure, respectively.¹⁸ The peak around 416 cm^{-1} in the spectrum of LRM is identified as the fingerprint of the Li_2MnO_3 -like phase,^{18,19} which significantly decreases in QO-LRM, aligning with the XRD and ND results and confirming the intralayer disorder structure with substantial decrease in long-range order of honeycomb superlattice within the QO-LRM cathode. Fourier transform extended X-ray absorption fine structures (FT-EXAFS) further examined the local structure configurations of QO-LRM and LRM (Figure 1d). No significant differences were observed in the Mn–O and Mn–TM peak intensities (Figure S3), while QO-LRM exhibited a much lower intensity in the Ni–TM peak compared to LRM, indicating the intralayer Ni replacement of Mn in LiMnO_6 superstructure units. Density functional theory (DFT) calculations suggest that Ni substitution in the LiMnO_6 superstructure increases the oxygen vacancy formation energy at deep delithiated states (Figure S4 and Table S6).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted to visualize the lattice structure at the atomic scale. Figure 1f presents the atomic arrangement of the QO-LRM, with enlarged views of Li-rich and LiTMO_2 structures displayed in Figure 1g and

Figure 1h, respectively. The QO-LRM shows a discretely distributed dumbbell atomic arrangement, separated by long-range bright spot columns, with additional bright spot columns observed between adjacent two-atom dumbbells. Intensity profiles along selected atomic regions (highlighted in Figure 1g) reveal a clear atomic intensity signal between dumbbell atoms in the QO-LRM (Figure 1i). Moreover, obvious Li/TM disordering was observed in QO-LRM, as some atomic intensities appear within the Li layers of both Li-rich and LiTMO_2 structures (Figure 1i,j). Similar phenomena were also observed along the [010] direction (Figure S5). High-resolution energy dispersive spectrometry (EDS) analysis revealed a greater Ni distribution in the interlayer disordering regions (Figure S6), suggesting that the lattice disorder is linked to the Ni distribution. In contrast, LRM exhibited an ordered layered structure with a long-range two-atom dumbbell arrangement, signifying the existence of localized LiMnO_6 superstructure domains in the TM layers (Figure S7). No obvious interlayered disordering was observed in LRM. In general, the comprehensive characterizations reveal that the QO-LRM cathode exhibits a quasi-ordered layered structure with intra- and interlayer cation redistribution (Figure 1e), which is anticipated to reconfigure lattice oxygen environment and ultimately enhances oxygen redox stability.

Enhanced Electrochemical Performance. Electrochemical tests of LRM and QO-LRM cathodes were performed galvanostatically within the voltage range of 2–4.65 V. As shown in Figure 2a, QO-LRM exhibits an initial charge capacity of 194 mAh g^{-1} and a much higher discharge capacity of 262 mAh g^{-1} at 0.1C ($1\text{C} = 250 \text{ mAh g}^{-1}$), attributing to its Li-deficient nature. Figure 2b presents the results of dQ/dV plots during the first three cycles, which provide insights into the redox mechanism. A high-intensity peak during the first

charge can be assigned to the initial activation process of the Li-rich structure. A broad reductive hump at 3.6–4.5 V is observed, which results from the partial overlap of cationic $\text{Ni}^{2+/4+}$ and anionic oxygen redox. In comparison, the LRM delivers a lower discharge capacity of 213 mAh g^{-1} (Figure S8a). The rate capability was further evaluated from 0.1 to 5C. QO-LRM exhibits higher capacities of 237 mAh g^{-1} at 0.5C and 171 mAh g^{-1} at 5C (Figure 2c), compared to 207 and 113 mAh g^{-1} for LRM (Figure S8b). Regarding long-term cycling performance, QO-LRM demonstrates superior capacity and average voltage stability, as expected, achieving 99% capacity retention and 98% voltage retention (voltage decay of 0.46 mV per cycle) after 100 cycles at 0.2C (Figure 2d,e and Figure S9). This performance is notably superior to that of LRM, which shows 80% capacity retention and 90% voltage retention (voltage decay of 3.71 mV per cycle, Figure S10a–c). These results are confirmed by the corresponding charge–discharge profiles and dQ/dV curves of the QO-LRM (Figure 2f and Figure S11) and LRM cathodes (Figure S10d,e). Overall, QO-LRM shows superior electrochemical stability and rate capability compared to prevalence Li-rich cathodes, Co-free LRM, and Co-containing $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ (LRM-NMC, Figures S12 and S13), owing to the enhanced oxygen redox stability arising from the designed quasi-ordered structure.

Quasi-Ordered Design Enables Reversible Structural Evolution and Oxygen Redox Reactions. To unveil the lattice structure evolution of QO-LRM upon cycling, in situ XRD measurements were performed during the initial two cycles. As shown in Figure 3a, the (003) peak of QO-LRM continuously shifts to higher angles during the first charge and to lower angles during discharge, corresponding to lattice

shrinkage upon charging and lattice expansion during discharge along the c -axis, while the changes along the a -axis demonstrate an opposite trend. These abnormal structural changes are associated with the hybridized cationic–anionic redox behaviors in the quasi-ordered structure. Remarkably, QO-LRM maintains its original lattice structure after the initial activation, exhibiting a similar structural evolution in the second cycle as in the first cycle, which highlights its exceptional stability in both lattice structure and chemistry. This is distinguishing from conventional Li-rich cathodes, which show inverse lattice parameter changes during the initial charge process and remain nearly unchanged beyond 4.5 V with the participation of oxygen oxidation (Figure S14). Additionally, the LRM presents significantly different peak shifts in subsequent cycles compared to the first cycle, indicating that the original LRM transforms into a new structure after initial activation and undergoes continuous lattice degradation during further cycling.

To elucidate the charge compensation mechanisms in the QO-LRM cathode, in situ X-ray absorption near edge spectroscopy (XANES) was used to track the chemical state variations of TMs during the charge and discharge processes. As shown in Figure 3b, QO-LRM shows a positive shift of the Ni K-edge, implying Ni oxidation as Li^+ extraction. No significant Ni K-edge shift is observed upon charging above 4.1 V, indicating that oxygen redox participation occurs. After discharging below 3.3 V, the negligible shift in the Ni K-edge suggests that the low voltage capacity in QO-LRM predominantly arises from $\text{Mn}^{4+/3+}$ redox reactions during discharge. For LRM, the Ni edge shift becomes much slower when charged above 4.5 V, which can be ascribed to the involvement of oxygen oxidation reactions in charge compensation at this stage (Figure S15). Regarding Mn, slight edge changes are detected due to local structural variations, as Mn is nearly in the +4 valence state in the pristine state and cannot be further oxidized.

Given the critical role of oxygen redox reactions in the charge compensation mechanism, mapping of resonant inelastic X-ray scattering (mRIXS) was employed as a sensitive and reliable method to probe oxygen oxidation states and investigate oxygen chemistry. As presented in Figure 4a and Figure S16, the broad feature around 525.5 eV in emission energy corresponds to O^{2-} states in the pristine LRM. Upon charging to 4.5 and 4.6 V, new features emerge at excitation and emission energies around 531 and 524 eV, as well as the features near the elastic line at 531 eV excitation energy in LRM (indicated by arrows). These features indicate the formation of O_2 dimers,²⁰ reflecting the oxidation of lattice oxygen from the -2 state to a higher valence state. Here, we use the term ‘oxidized O’ to specifically refer to lattice oxygen that has undergone oxidation, without implying a defined molecular structure or bonding configuration. In QO-LRM, the oxidized O signal is observed at both 4.4 and 4.6 V (Figure 4b), confirming that oxygen redox is activated at lower voltages and is coupled with cationic redox processes, facilitated by the special quasi-ordered structural configurations. Figure 4c,e presents the soft X-ray absorption spectroscopy (sXAS) spectra of O K-edge in the total fluorescence yield (TFY) mode for LRM and QO-LRM cathodes at various charge states. The pre-edge peaks below 534 eV correspond to the transitions from occupied O 1s orbitals to unoccupied hybridized TM 3d and O 2p orbitals, while the broad peaks above 534 eV are attributed to the transitions to hybridized states TM 4sp and O 2p

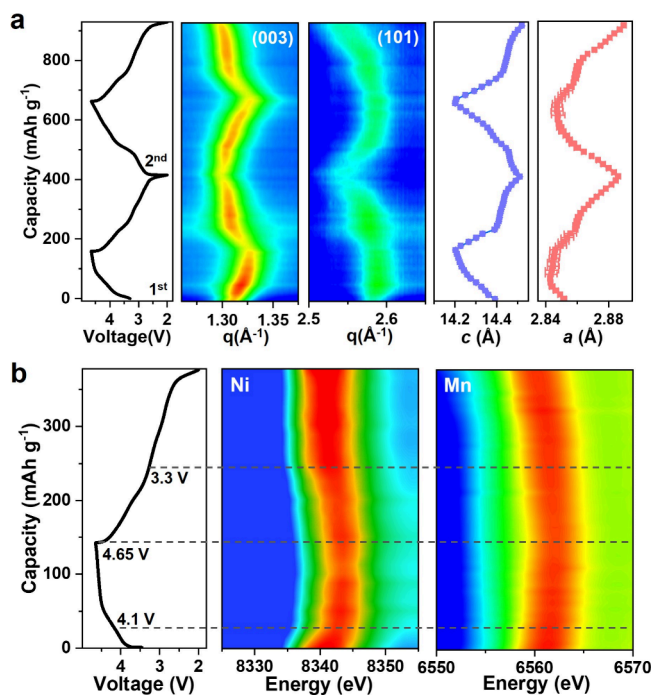


Figure 3. Structural and chemical state evolution of QO-LRM during cycling. (a) In situ XRD patterns showing variations in the (003) and (101) Bragg peaks, along with the refined lattice parameter changes for the QO-LRM cathode during the first two cycles. (b) In situ XANES spectra of Ni K and Mn K-edges for QO-LRM.

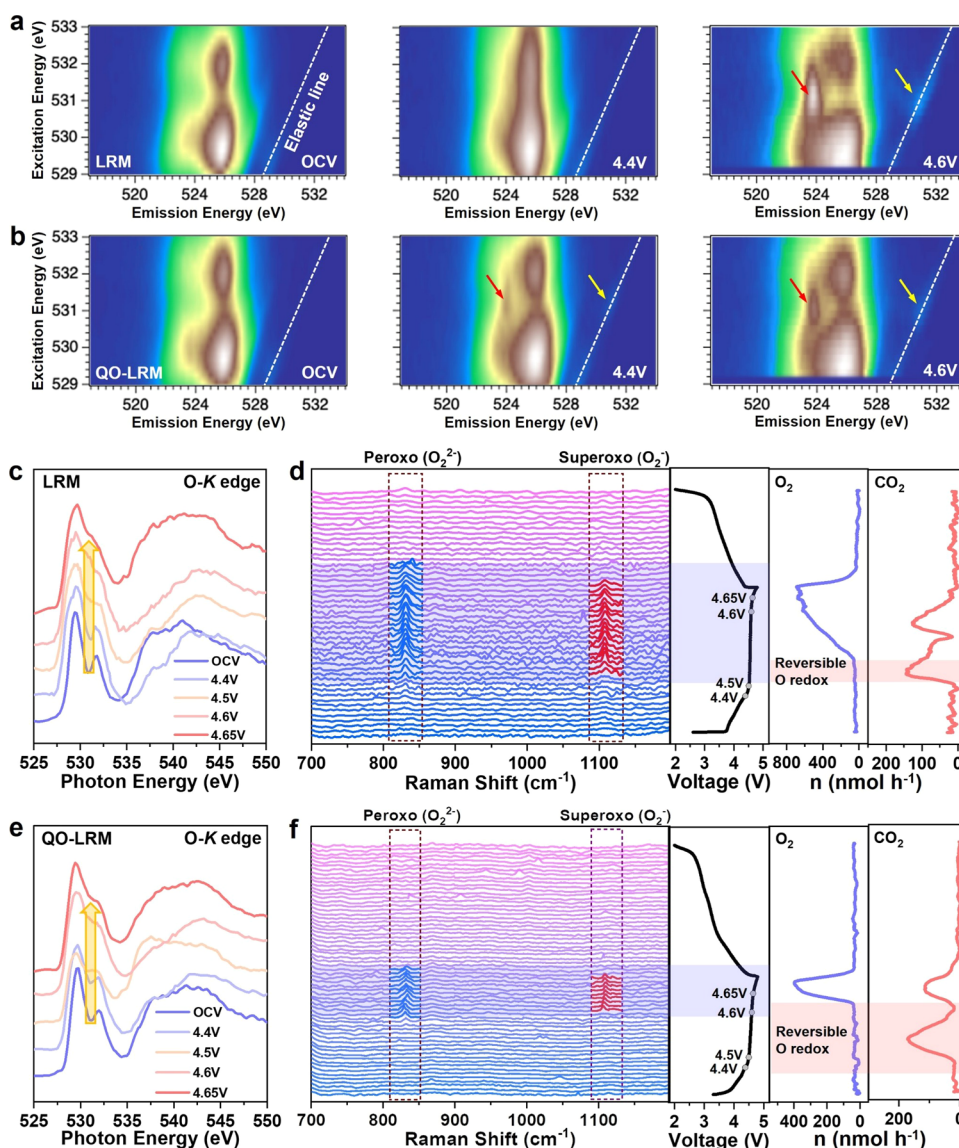


Figure 4. Oxygen anion redox behavior of QO-LRM. O–K mRIXS images of LRM (a) and QO-LRM (b) at OCV, 4.4 V, and 4.6 V, with arrows highlighting features associated with O_2 dimer formation, reflecting the oxidation of lattice oxygen. O–K sXAS spectra of LRM (c) and QO-LRM (e) at OCV, 4.4 V, 4.5 V, 4.6 V, and 4.65 V. The arrows highlight the increase in integrated intensity of the sXAS profiles. In situ Raman and DEMS measurements for LRM (d) and QO-LRM (f).

orbitals. In QO-LRM, the integrated intensity of the pre-edge peaks increases progressively from OCV to 4.4, 4.5, 4.6, and 4.65 V, corresponding to an increasing density of the oxidized O states.^{5,21}

To further investigate the real-time lattice oxygen evolution, we conducted in situ shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINES). In Figure 4d, new peaks at around 830 and 1120 cm^{-1} appear in LRM when charged to approximately 4.5 V, indicating the formation of peroxo (O_2^{2-})- and superoxo (O_2^-)-like species with an extended O–O distance.²² In contrast, no detectable signals of either an O_2^{2-} or an O_2^- -like species are observed in QO-LRM until the charging voltage exceeds 4.6 V (Figure 4f). This delayed appearance, despite clear oxidized O signals in mRIXS at 4.4 V, signifies that O^{2-} is initially oxidized without the immediate formation of $\text{O}_2^{2-}/\text{O}_2^-$ -like species, while the subsequent generation of $\text{O}_2^{2-}/\text{O}_2^-$ -like species is significantly delayed by the quasi-ordered design. The unstable lattice oxygen oxidized products, such as O_2^{2-} - and O_2^- -like species, are prone to

transform into O_2 gas. In situ differential electrochemical mass spectrometry (DEMS) was performed to detect the gas evolution during cycling. The O_2 release can be related to the lattice oxygen loss, while CO_2 is primarily attributed to the decomposition of the carbonated electrolyte. We refer to the region starting from the oxygen redox activation before O_2 gas release as the reversible O redox band, as highlighted in Figure 4d,f. It is observed that the release of the O_2 signal is significantly delayed in QO-LRM and is released in a smaller amount compared to LRM, further confirming the inhibition of irreversible lattice oxygen loss. The capacity contribution from reversible redox in QO-LRM is more than three times higher than that in conventional LRM. This elevation of the oxidation state limit provides vast potential for fully utilizing the reversible anionic redox reactions, benefiting from the unique quasi-ordered structural design, which effectively optimizes the configuration of lattice oxygen, thereby preventing its undesired transformation into unstable $\text{O}_2^{2-}/\text{O}_2^-$ -like species and greatly improving structural stability.

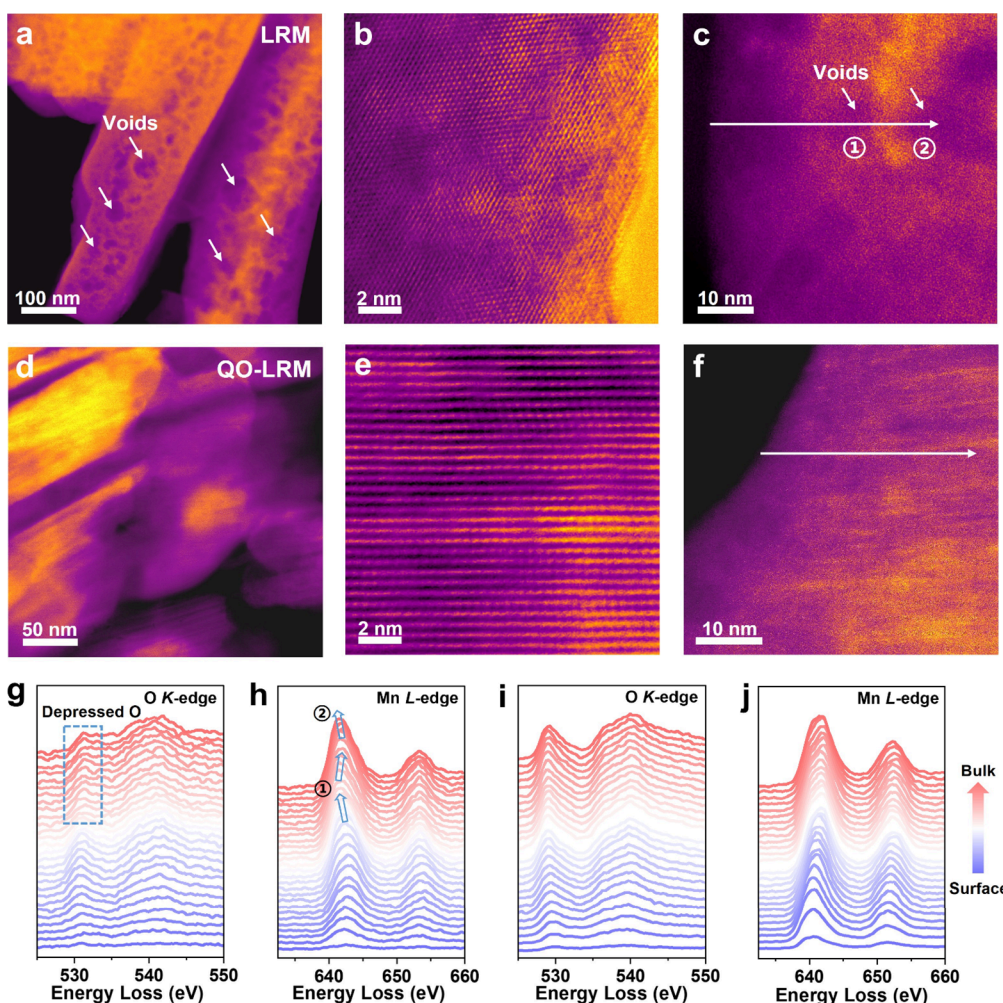


Figure 5. Enhanced structural stability of QO-LRM. HAADF-STEM images showing the morphology of LRM (a) and QO-LRM (d) cathodes after 100 cycles, with nanovoids indicated by arrows in (a). Atomic-resolution HAADF-STEM images revealing the presence of the retained layered structure with dumbbell-like TM configurations in QO-LRM (e), compared to LRM with a rock-salt structure (b). EELS line scans from the surface to bulk are indicated by arrows in LRM (c) and QO-LRM (f). O K-edge and Mn L-edge EELS spectra of LRM (g, h) and QO-LRM (i, j) cathodes. The reduced O K-edge intensity is highlighted in (g) and the lower Mn L-edge peak energy in nanovoid regions of LRM is shown in (h).

Enhanced Structural Stability. To explore the intricate connection between oxygen redox chemistry and structural stability, the HAADF-STEM technique was adopted to conduct structural examination at nano and atomic scales after 100 cycles. Figure 5a presents the nanovoid formation across the entire particles in the cycled LRM cathode. Atomic-resolution STEM imaging further verifies a transformation of the surface structure into a rock-salt phase (Figure 5b). By coupling HAADF-STEM imaging with electron energy loss spectroscopy (EELS) analysis, we confirm that the nanovoids arise due to irreversible lattice oxygen loss, as evidenced by the depressed oxygen peak and Mn reduction in both the surface and bulk nanovoid regions (Figure 5c,g,h). These irreversible oxygen losses and phase transitions greatly contribute to the capacity and voltage decay in LRM cathodes. In contrast, the cycled QO-LRM cathode maintains its morphological integrity, showing no noticeable nanovoid formation (Figure 5d). Remarkably, clear layered lattice fringes with intralayer dumbbell configurations are still visible in the bulk, even after extended cycling (Figure 5e), indicating minimal TM migration and negligible irreversible structural degradation. EELS results reveal a relatively uniform distribution of the

polarized O and Mn chemical states in the bulk (Figure 5f,i,j), with lower polarized O intensity and Mn valence states at the surface attributed to the inevitable interfacial side reactions. These findings demonstrate that the unique quasi-ordered structure design of QO-LRM provides an exceptionally stable lattice framework, which correlates with highly reversible oxygen redox chemistry and contributes to the impressive cycling performance.

CONCLUSIONS

The introduction of anionic redox reactions endows Li-rich cathode systems with ultrahigh capacity, but this comes at the cost of rapid structural degradation and electrochemical decay due to lattice oxygen instability. This has reinforced the long-standing belief that oxidized lattice oxygen is thermodynamically unstable and inherently correlates with poor electrochemical reversibility, blocking the utilization of oxygen redox chemistry. Excitedly, in this work, we reveal that the reversibility of oxygen redox is not directly related to the extent of lattice oxygen oxidation; instead, it is highly associated with lattice configurations. By developing a quasi-ordered structural design strategy, we effectively stabilize lattice

oxidized O species and inhibit the formation of $\text{O}_2^{2-}/\text{O}_2^-$ -like species that trigger irreversible lattice O loss. This strategy significantly elevates the upper utilization limit of reversible oxygen redox, enabling the simultaneous achievement of high capacity with virtually no voltage decay—demonstrated by 98% average voltage retention over 100 cycles with only 0.46 mV voltage decay per cycle, which is approximately an order of magnitude lower than that observed in conventional Li-rich cathodes. These findings represent a breakthrough in understanding and enhancing the stability of anionic redox chemistry, paving the way for the development of cathodes with higher energy density and long lifespan.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c03271>.

Experimental procedures and additional data include XRD patterns, ND patterns, HAADF-STEM images, EDS mappings, XANES spectra, EXAFS spectra, mRIXS intensity cut patterns, and electrochemical performance data (PDF)

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Notes

The authors declare no competing financial interest.

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