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Perspective

Topological Protection of Oxygen Redox in Li-Rich Cathodes

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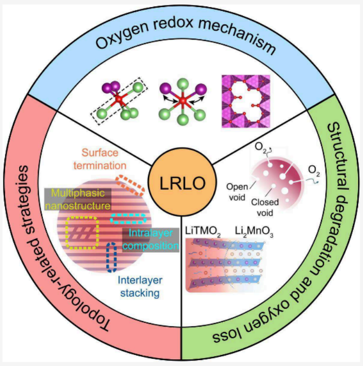
ABSTRACT: Lithium-rich layered oxides (LRLOs) are regarded as promising candidates for next-generation cathode materials because of their high energy density derived from anionic redox activity. Recent years have seen increasing efforts in promoting the cyclability of LRLO cathodes, at the core of which is the suppression of irreversible internal structural evolution during cycling. The present article aims to provide an informative perspective on the materials design strategies related to the issue of oxygen release. Emphasis is placed on the underlying chemistry of oxygen redox in LRLOs and the strategies based on material topology that can mitigate oxygen migration to the cathode surface. We speculate that these insights could guide researchers in developing high-capacity cathodes with intrinsically high reversibility of oxygen redox.



The soaring demand for electrochemical energy storage in today's society, from portable electronic devices and electric vehicles to grid-scale applications, has intensified the efforts to develop next-generation lithium-ion batteries (LIBs) that can achieve both higher energy density and better cycling stability than the currently used ones. To reach this target, one of the biggest bottlenecks lies in the design of new cathode materials with an energy density surpassing that of the state-of-the-art layered $Li(Ni,Mn,Co)O_2$ cathodes.[1] Recently, lithium-rich layered oxide (LRLO) cathodes have sparked broad interest because of their exceptionally high specific capacity (>270 mAh g^{-1}) and favorable operation voltage (>4 V).[2] These advantages are closely related to the anionic redox activity, which can be interpreted in terms of the reversible formation of $(O_2)^{n-}$ species in the crystal lattice.[3] However, compared to cationic redox in traditional cathode materials, such as $LiCoO_2$, $LiFePO_4$, and $LiMn_2O_4$, anionic redox in LRLOs is much more difficult to control and will give rise to two notorious problems: rapid capacity loss and significant voltage decay. Both of them have been documented to be accompanied by severe structural collapse and irreversible oxygen release upon operation of the cell, with their underlying mechanisms still under debate.[4−6] These factors greatly hamper the commercialization of LRLO cathodes, thereby making it a necessity to explore feasible strategies to mitigate the destructive effects of their dynamic structural evolution during cycling.

In the past few years, accumulated evidence from both advanced characterization techniques and theoretical computations has revealed that some specific lattice structures can afford high reversibility upon the anionic redox in LRLOs.[7−10] This can presumably be ascribed to the establishment of an internal kinetic barrier that restricts the migration of the $(O_2)^{n-}$ species and oxygen molecules inside the cathode material. The percolation network of migrating oxygen from the interior region to the cathode surface is thus disconnected, leading to sustained inhibition of the detrimental atomic rearrangements that have frequently been demonstrated in conventional LRLOs during charge/discharge. This kind of structural characteristic can be understood as a topological concept defined by the disrupted connectivity of redox-active oxygen ions to the boundary of the cell. With this backdrop, it is fundamentally important to control the microscale structures with an aim to realize the topological protection of oxygen redox and boost the long-term stability of LRLO cathodes.

Herein, we focus on the strategies of topological design for blocking oxygen migration pathways in LRLO cathodes. This Perspective is structured as follows. The proposed mechanisms of oxygen redox activity in LRLOs will be revisited, followed by recent research on dynamic structural evolution coupled with oxygen loss during cycling. Then, topology-related strategies are summarized in four categories, including surface termination, intralayer composition, interlayer stacking, and multiphasic nanostructure. Lastly, we conclude by providing major challenges and opportunities for modulating the topological structure of LRLO cathodes.

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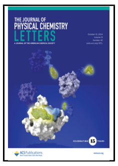

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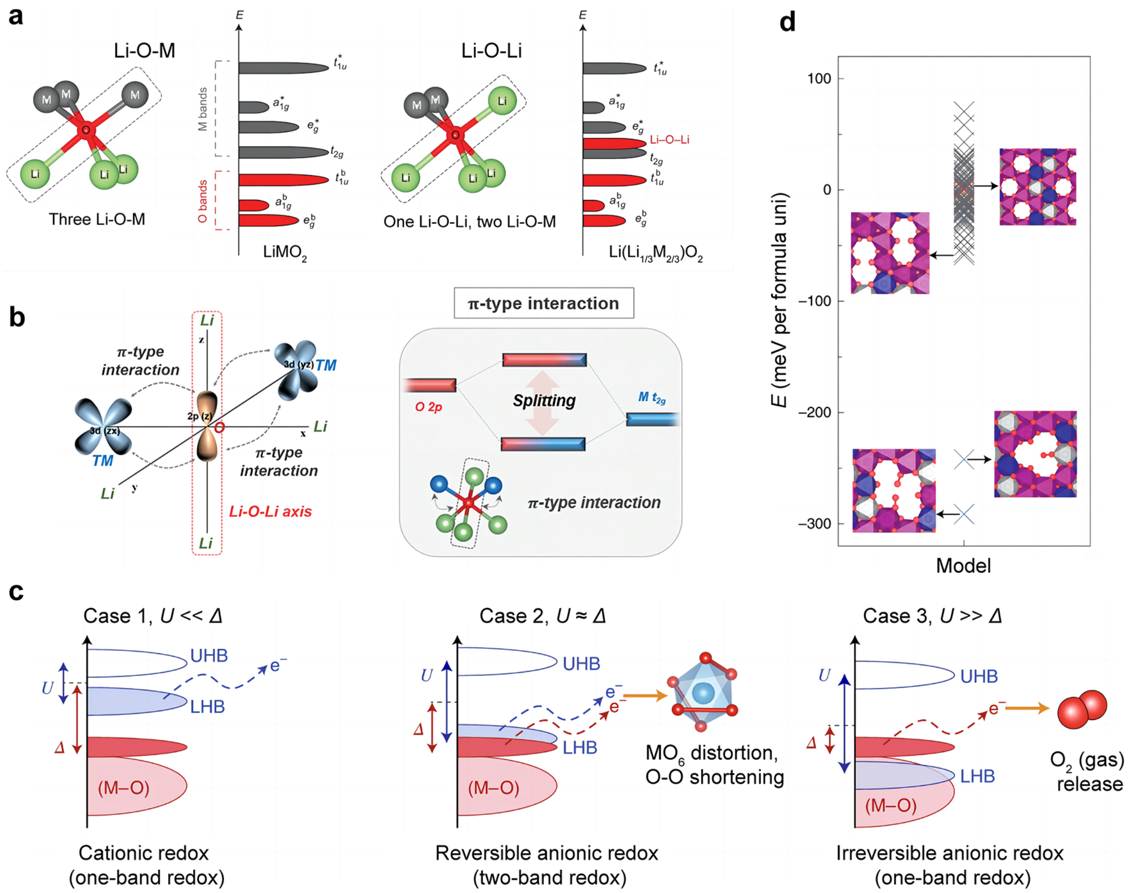

Figure 1. Mechanisms of anionic redox in LRLOs. (a) Different energy levels of the O 2p orbitals between Li−O−Li and Li−O−M configurations. Adapted with permission from ref 12. Copyright 2016 Springer Nature. (b) π-Type interaction between neighboring TM ions and the orphaned O 2p orbitals. Adapted with permission from ref 14. Copyright 2020 John Wiley and Sons. (c) Competition between the Mott−Hubbard Coulomb repulsion term U and the charge-transfer parameter term Δ. Adapted with permission from ref 16. Copyright 2018 Springer Nature. (d) Dimerization of oxygen coupled with migration of TM ions. Adapted with permission from ref 26. Copyright 2020 Springer Nature.

As the prototype of LRLO cathodes, Li_2MnO_3 has been widely studied with an emphasis on its structural and chemical properties. In Li_2MnO_3, one-third of the sites in the transition metal (TM) layers are occupied by Li ions, and Mn^{4+} ions are arranged in a honeycomb configuration with Li ions located at the center of the Mn ring. Each oxygen site in Li_2MnO_3 is 6-fold coordinated with two Mn^{4+} ions and four Li^+ ions, which results in an environment featuring a pair of 180° Li−O−Li configurations and two pairs of Li−O−Mn configurations. Generally, the Mn^{4+} ions in the octahedral sites cannot be further oxidized upon delithiation, and charge neutrality is maintained by the oxidation of lattice oxygen, which manifests as a characteristic first-charge plateau of above 4.4 V. Spectroscopic measurements and theoretical calculations consistently supported that Li removal is charge-compensated by the introduction of localized holes on the oxygen atoms.[11] Detailed analysis of the electronic structure has shown a high charge density along the Li−O−Li configuration, shaped like an isolated O 2p orbital. Ligand field theory suggests that the energy level of the orphaned Li−O−Li state is higher than that of the O 2p orbitals hybridized with Mn 3d orbitals. These O 2p states, located at the top of the O valence band, are the first to oxidize during the delithiation process (Figure 1a).[12] Further research indicated that the orbital along the Li−O−Li axis also has an π-type interaction with the neighboring TM cations. The relative energy levels of the TM-d and the O-p orbitals are crucial for understanding the arrangement of the π-type hybridization, which is closely related to its contribution to the redox process. When the energy level of the unhybridized O-2p orbital is higher than that of the TM-t_{2g} orbital, the bonding π-type hybridization orbitals are predominantly contributed by TM-t_{2g}, while the O-2p orbitals dominate the antibonding π-type hybridization orbitals (Figure 1b). Based on the results of first-principles calculations, the number and types of the neighboring TM cations can directly modulate the Li−O−Li energy level,[13−15] thereby indicating the decisive role of d−p hybridization on the competition between cationic and anionic redox reactions. The unique coordination environment of oxygen in the Li@TM$_6$ structure unit has, therefore, been recognized as the source of additional capacity related to the anionic redox activity.

The Li−O−Li configuration in LRLOs has been found as a prerequisite for the activation of lattice oxygen redox. The relationship between the specific level of the nonbonding O 2p and the antibonding (TM−O)* bands significantly influences the possibility and reversibility of anionic redox in layered cathodes.[13] The Zaanen−Sawatzky−Allen theory was introduced to describe the competitive relation between cations and anions according to the relative values of the Mott−Hubbard Coulomb repulsion term (U) and the charge-transfer parameter term (Δ).[16−19] U refers to the Coulomb and exchange interactions for d−d electrons, while Δ reflects the

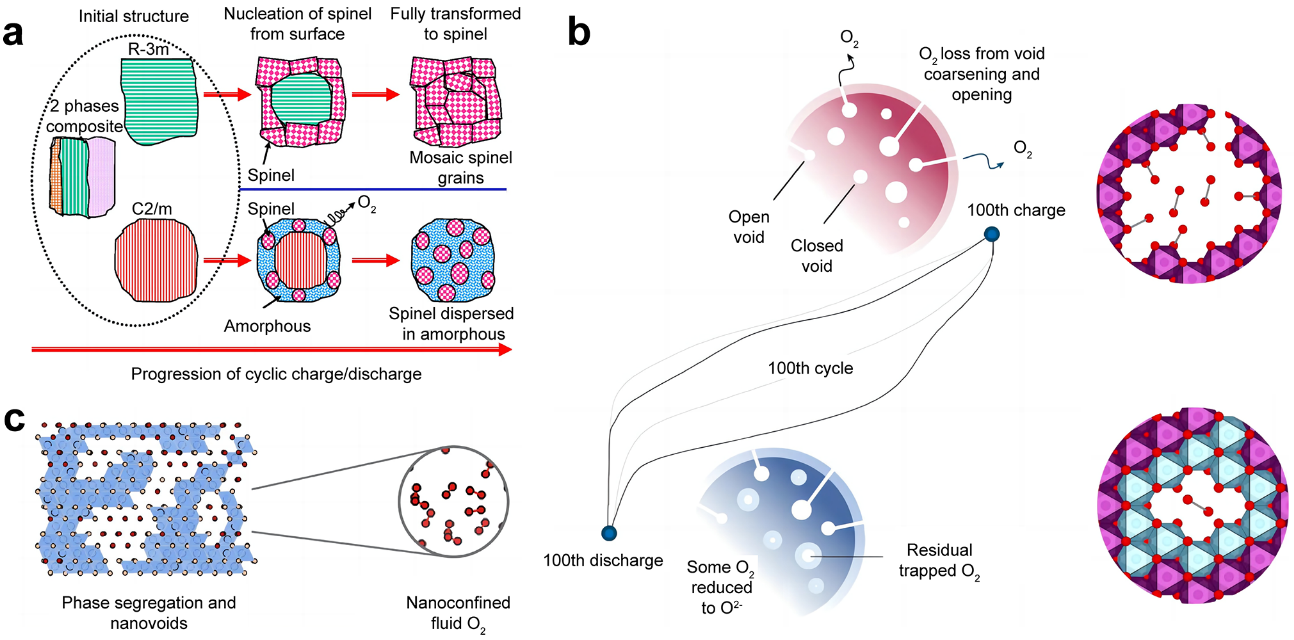

Figure 2. Structural evolution related to oxygen loss. (a) Phase transition from a layered structure to spinel structures. Adapted with permission from ref 29. Copyright 2013 American Chemical Society. (b) Formation and connection of the voids due to TM migration. Adapted with permission from ref 33. Copyright 2024 Springer Nature. (c) Migration of oxygen dimers as a nanoconfined fluid with phase segregation and nanovoid formation. Adapted with permission from ref 36. Copyright 2024 Springer Nature.

covalent character of the metal−ligand bonds, which depends on the electronegativity difference (Figure 1c). U depends strongly on the splitting energy of the TM-d orbitals, with its value increasing for elements from left to right in the periodic table and decreasing from 3d to 5d because of orbital expansion. In the case where $U \ll \Delta$, the Mott−Hubbard regime suggests cationic redox with Li extraction due to the electrons being extracted from the filled lower Hubbard bands (LHB). Conversely, when $U \gg \Delta$, the charge-transfer regime indicates electrons removed from the unhybridized O 2p states located above the LHB, resulting in irreversible anionic redox with serious O_2 release. In the middle condition of $U/2 \approx \Delta$, the overlap of LHB and nonbonding O 2p states leads to adequately positioned bands for triggering reversible anionic redox. In this scenario, the two-band redox process provides extra reversible capacity and is usually accompanied by TMO_6 octahedral distortion, finally leading to short O−O distances, which have been observed in the typical 4d metal-based Li_2TMO_3, such as Li_2RuO_3 and Li_2IrO_3.[16,20−22]

In addition to the localized holes on oxygen for charge compensation, other studies suggested that oxygen dimerization, along with microstructural evolution involving cation disorder, also results in charge compensation. By comparing the structural models of LRLO with and without the cationic antisite defects to simulate the phase stability diagram and voltage curves during cycling, it was found that the defective layered structures with spontaneous formation of oxygen dimers are thermodynamically stable at deep delithiation states,[23−25] which is consistent with experimental observations. X-ray diffraction (XRD) patterns revealed the disappearance of superlattice diffraction peaks and an increase in the fraction of TM ions in the Li layer, indicating disorder of the TM ions. Spectroscopic measurements further confirmed the existence of short O−O bond lengths, similar to those in peroxide, superoxide, or molecular oxygen. The formation of the O−O dimers is closely linked to the disruption of the lattice structure in the form of massive TM migration, which alters the coordination of oxygen ions. This migration causes some oxygen ions to break their original bonds with two TM ions in the ideal Li@TM_6 superstructure, resulting in dangling oxygen ions bonded to only one single TM ion. Further cation migration can lead to oxygen ions bonding to no TM ion at all. These unstable oxygen species tend to combine to form dimers from a thermodynamic perspective (Figure 1d). The formation of oxygen dimers, coupled with TM migration, helps to explain the voltage hysteresis phenomenon in LRLOs. The various structural configurations arising from different TM migration paths create diverse coordination environments for oxygen ions, leading to multiple binding modes for oxygen dimerization, which have been systematically studied through theoretical modeling.[26]

These mechanistic studies have demonstrated that the oxidized oxygen in the crystal lattice can be rationalized through several mechanisms corresponding to the emergence of either a nonstabilized oxygen, a π-stabilized oxygen, or a σ-stabilized oxygen. These states are accompanied by localized holes, delocalized holes by TM−O coupling, and delocalized holes by O−O dimerization, respectively.[27] The redox activity of oxygen is closely related to the formation of oxygen vacancies and the subsequent loss of oxygen from the particles. Understanding these oxidation mechanisms could provide fundamental insights into the electrochemical behavior and structural evolution of LRLO cathodes during cycling.

Oxidized lattice oxygen and the oxygen dimers are prone to being released from the structure via oxygen gas evolution and cathode−electrolyte interfacial side reactions, leaving behind substantial surface oxygen vacancy defects. For layered structures, these surface oxygen vacancy defects destabilize the TM cations due to the reduced coordination number, thus triggering continuous TM migration from the surface to the interior region in a process known as densification.[28−30] During the densification process, the migration of TM ions to

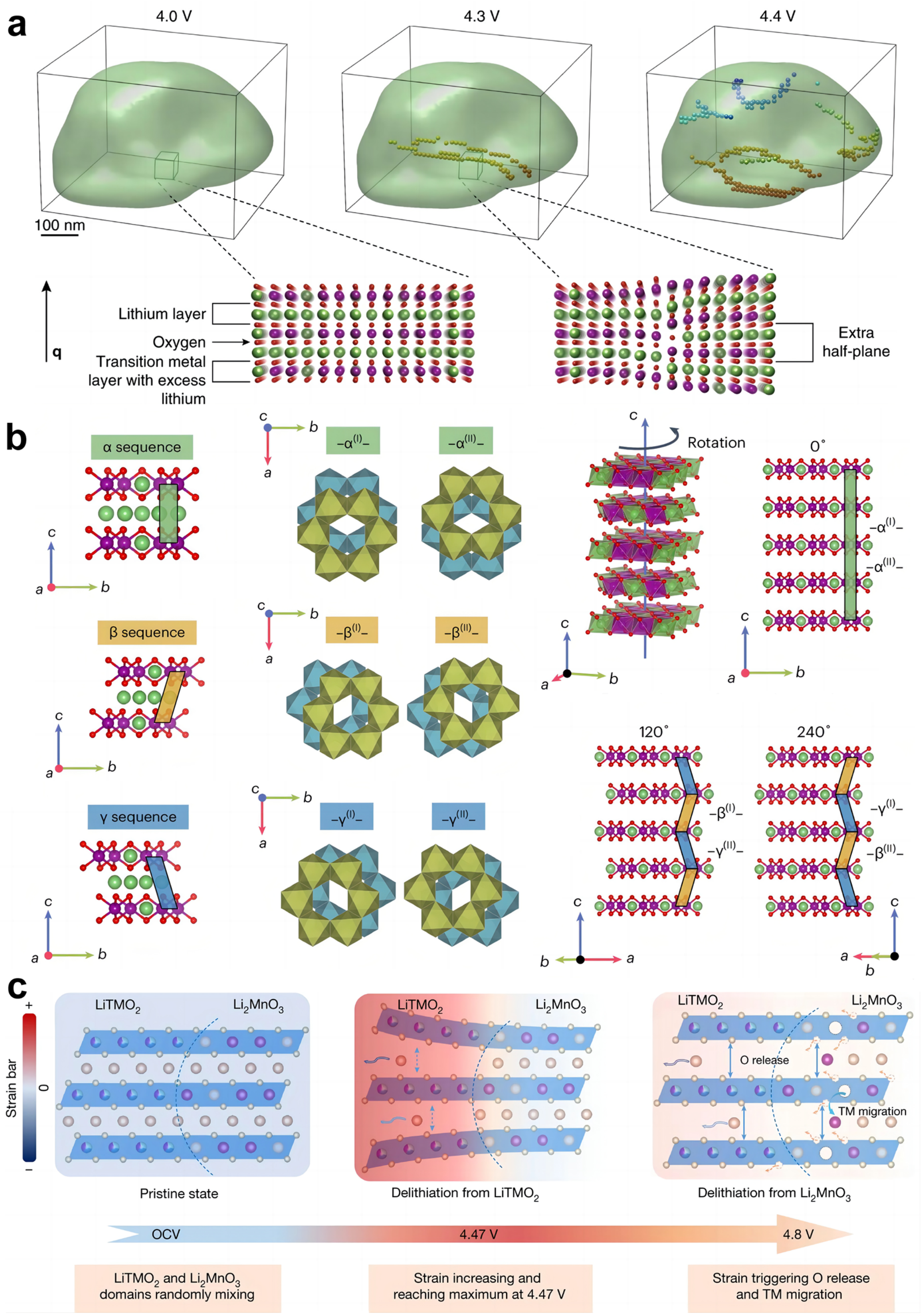

Figure 3. Defects and boundaries affecting oxygen loss. (a) Formation of the dislocation network during charge of LRLO cathodes. Adapted with permission from ref 38. Copyright 2018 Springer Nature. (b) Rotational stacking faults in LRLOs. Adapted with permission from ref 40. Copyright 2024 Springer Nature. (c) Nanoscale lattice distortion at the boundary between $LiTMO_2$ and Li_2MnO_3 domains. Adapted with permission from ref 41. Copyright 2022 Springer Nature.

the Li layer results in the formation of spinel nuclei from the surface, which leads to the transition of the phase structure from layered to spinel. With further cation mixing, the structure ultimately transforms into a rocksalt-like phase. Unlike the case of $LiTMO_2$ domain, the formation of the spinel phase in the Li-rich region is accompanied by the creation of pores. This leads to lattice collapse, which can be attributed to the extensive removal of Li or oxygen during cycling, as shown in Figure 2a.[29]

Unlike the surface oxygen dimers that can easily be released, oxygen ions in the bulk are oxidized to form dimers, along with the disruption of the honeycomb TM superstructure unit and the formation of small vacancy clusters. These isolated small vacancy clusters, which are distributed throughout the particle

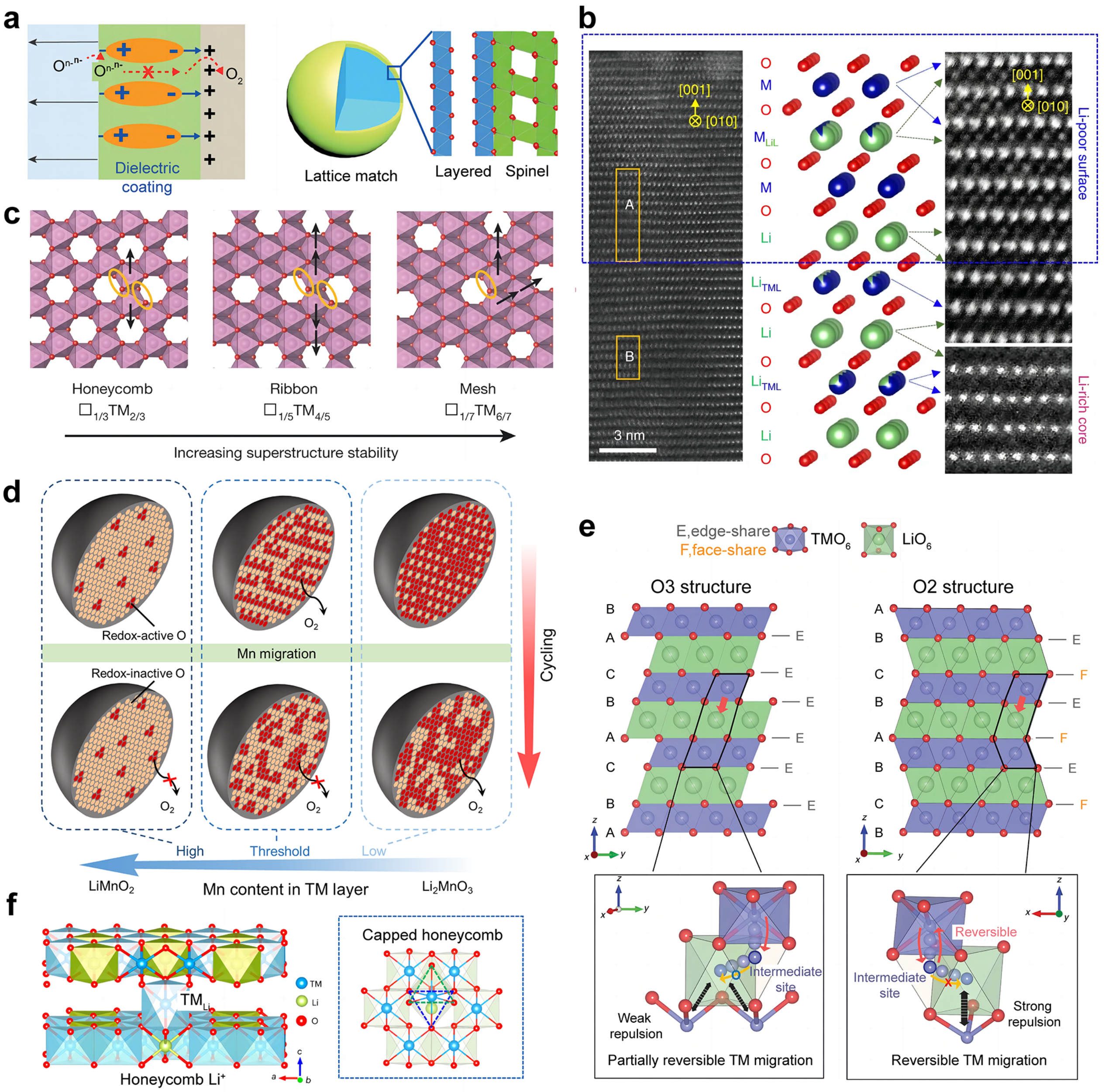

Figure 4. Strategies to suppress oxygen loss. (a) Surface protective coating layers with a spinel structure. Adapted with permission from ref 43. Copyright 2020 John Wiley and Sons. (b) Concentration gradient design to obtain Li-poor surface over a Li-rich core. Adapted with permission from ref 53. Copyright 2019 Springer Nature. (c) Superstructure distribution with increased TM migration steps for oxygen dimer formation. Adapted with permission from ref 31. Copyright 2019 Springer Nature. (d) Prevention of the percolation of redox-active oxygen ions in $Li[Li_{1-x}Mn_x]O_2$ with Li content in the TM layer beneath a threshold value. Adapted with permission from ref 56. Copyright 2024 John Wiley and Sons. (e) Tuning of TM migration mode via changes in interlayer stacking. Adapted with permission from ref 64. Copyright 2020 Springer Nature. (f) Capped-honeycomb local structure with TM ions located next to the honeycomb in the Li layer. Adapted with permission from ref 67. Copyright 2023 Springer Nature.

during the charging process, can trap oxygen dimers in the bulk structure. These trapped oxygen dimers can be reversibly reduced back to O^{2-} upon discharge, contributing to the reversible anionic redox capacity while causing voltage hysteresis.[26,31−33]

The migration of the oxygen vacancies from surface to bulk phase plays a key role in the structural evolution and the electrochemical performance.[34,35] The migration energy barrier for oxidized oxygen O^- (0.9 eV) is much lower than that for O^{2-} (2.3−4.0 eV), suggesting high mobility of lattice oxygen in the charged state.[23] The oxygen vacancy migration will break the anionic framework, thereby leading to nanovoid domains in the bulk. During long-term cycling, further TM migration leads to the aggregation of vacancy clusters and gives rise to large voids in the bulk, which are coupled with lattice reconstruction and mass loss. The kinetic behavior of various oxidized oxygen species depends on the connectivity of these voids (Figure 2b,c). If the voids are linked to the surface, they become open voids, allowing oxygen dimers to move outside as a nanoconfined fluid, which has been illustrated by the combined approach of ab initio molecular dynamics and cluster-expansion-based Monte Carlo simulations.[36] This process potentially facilitates long-range oxygen transport and links bulk O_2 formation to surface O_2 loss. In contrast, the oxygen dimers in the closed voids are still trapped, and some of them may not be reduced to O^{2-} because of the insulating nature of the surrounding Li−O^{2-} region.[33,36]

Besides the particle surface, interfaces also play a vital role in oxygen redox instability and crack formation in the particles. Such interfaces include the grain boundaries in the polycrystalline materials and the domain boundaries inside particles separating layered domains with different orientations.[37−39] The local bonding environment of the oxygen sites near the interfacial region is considered different from that of the regular layered bulk structure, even in the coherent twin boundary. Along the boundary, the oxygen ions could be coordinated with fewer TM ions, which facilitate oxygen oxidation and dimerization. Some theoretical studies suggested that under-coordinated oxygen atoms at the boundary regions would become unstable and have a low energy barrier to migrate to adjacent vacant sites, thereby promoting irreversible oxygen loss similar to the particle surface.[39] Hence, the activation of LRLOs cannot be accomplished within the first cycle, and oxygen is continuously released at the surface and grain boundaries.

For layered-structure cathodes, the existence of stacking faults could significantly impact their structure and properties, as well. When disruption occurs along the direction of the regular stacking sequence, the stacking faults with extra or missing atomic layers will lead to the introduction of dislocations between the layers. As cycling proceeds, these dislocations will cause stress accumulation at specific lattice sites, which results in the propagation and multiplication of intragranular cracks along the layer direction, as shown in Figure 3a.[38] Additionally, the presence of the Li@Mn_6 superstructure in LRLOs is another main factor that necessitates consideration of the stacking relationship between different TM layers. Misalignment of the superstructures between different layers will lead to the emergence of rotational stacking faults (RSFs), as shown in Figure 3b.[40] A recent study has shown that at deep delithiation state, the structure with RSFs can lead to the formation of numerous interlayer oxygen dimers and significant interlayer/intralayer migration of the TM ions.[40] This migration contributes to intragranular cracks, thereby fostering microcrack nucleation and propagation, which could provide the migration expressway for the lattice oxygen to release. These phenomena occur concurrently with cumulative electrochemomechanical degradation during cycling.

Another important driving force for the structural degradation and oxygen loss is the mechanical damage caused by nanoscale lattice distortions due to nonequilibrium dynamics (Figure 3c).[41,42] The nanocomposite LRLOs are regarded as being composed of hexagonal $LiTMO_2$ domains and monoclinic Li_2MnO_3 domains. These two domains share a coherent lattice at the nanoscale but exhibit different electrochemical activities, and the voltage plateau associated with anionic redox is higher than that associated with TM redox. Hence, Li ions are primarily extracted from the $LiTMO_2$ domains, which leads to lattice expansion due to the increase of local electrostatic repulsion between the TM layers. Simultaneously, the lattice parameters of the Li-rich domain are confined without Li extraction. The lattice strain on the two phases caused by the volume differences between high- and low-Li concentrations leads to significant stress accumulation at the boundary, which is considered the source of dislocation formation.[41] The recent investigation of single-crystal cathodes revealed that the spatially asynchronous deintercalation of Li ions also contributes to the lattice rotation, which cannot be recovered by the intercalation of Li ions.[42] The irreversible lattice rotations could promote the accumulation of plastic deformation and mechanical damage with consecutive cycles.

The simplest and most intuitive way to inhibit the escape of oxygen from the cathode material is to construct a surface termination at which the oxygen atoms are much more stable than those in the bulk. If the creation of an oxygen vacancy at this termination will consume a considerable amount of energy, then a relatively low local concentration of oxygen vacancy would be expected, which means that only a limited number of oxygen vacancies can be transferred from the surface to the bulk region. Surface coating and gradient design are the two most common methods. Nonactive layered/spinel oxides, phosphates, fluorides, and organic materials can be employed as the surface coating layers, which have been reported to effectively block the migration of lattice oxygen (Figure 4a).[43−49] Yet, the internal strain due to lattice incompatibility is likely to induce inhomogeneous expansion and contraction at the interface during cycling, which may exacerbate the risk of structural degradation. Compositional gradient design is more favorable in this context. Potential dopants include cations that have strong bonding with oxygen[50] and anions that can either exert pronounced electrostatic interaction to the migrating oxygen (such as F dopant) or form a stable polyanion with the surrounding oxygen.[51,52] For example, S substitution on the surface could lead to the formation of SO_4^{2-}, which can provide charge compensation during the first charge period and stabilize the lattice oxygen in the surface region. The compositional gradient configuration with Li-rich regions in the core and Li-poor regions near the surface is desirable, which can prevent the surface oxygen ions from participating in anion redox (Figure 4b).[53−55] However, this kind of surface modification is rather complicated and is still in the laboratory stage.

Since oxygen loss in LRLO cathodes is closely linked to TM migration, the distribution of Li@Mn_6 superstructure units could play a crucial role in oxygen dimer formation and anionic redox chemistry.[31] It has been recently revealed that TM migration is accompanied by the simultaneous formation of oxygen dimer, and the energy released in the latter process can compensate for the energy consumed in the former, leading to a reduced activation barrier for TM migration.[56] The oxygen dimers tend to distribute near the vacancy clusters formed by TM migration, which could result in TM agglomeration. When Li@Mn_6 structure units are sparse, the increased number of TM migration steps for oxygen dimer formation will significantly hinder the agglomeration process (Figure 4c), thus imposing a higher stability to the structure and avoiding the connection between neighboring vacancy clusters. In contrast, when the Li content in the TM layer is relatively high, fewer TM migration steps would be required for oxygen dimer formation, while the oxygen dimer will, in turn, promote TM migration. This leads to massive atomic rearrangement that establishes a percolating network of redox-active oxygen ions (Figure 4d). Hence, the Li content in the TM layers should not exceed a critical threshold that corresponds to the onset of such percolation.[56] The above conclusion can be substantiated by the results of $Li_2Mn_3O_7$, which exhibits a uniform

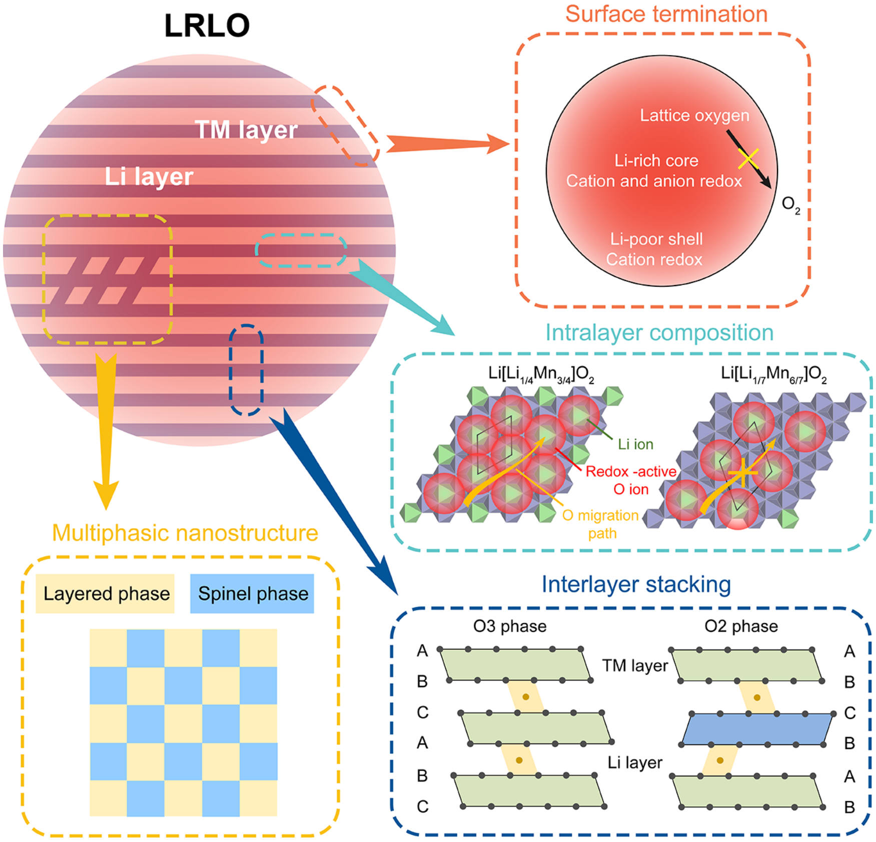

Figure 5. Schematic diagram of topology-related strategies in the design of LRLO cathodes.

delocalized distribution pattern of vacant sites in the Mn layer.[10] This cathode material displays small voltage hysteresis and negligible voltage fade, which indicates the crucial role of the intralayer TM concentration on the reversibility of oxygen redox. By the introduction of doping elements, the interaction between the cations and anions can be enhanced, which could also help suppress the migration of cations. When the doping elements are located in the Li layers acting as pillars, they inhibit layer gliding and interlayer migration of TMs. Furthermore, the increase in configurational entropy caused by doping may to some extent benefit the overall structural stability.[57,58] Multi-ion doping within the lattice could effectively regulate the chemical environment and electronic structure of the lattice oxygen, modulating the overlap between the nonbonding O 2p band and the antibonding (TM−O)* bands, thus facilitating reversible oxygen redox and enhancing the flexibility of the lattice structure, which can suppress oxygen release and transition metal migration. Likewise, the introduction of other superstructure units into LRLOs can also regulate the content and distribution of excess Li in the TM layers.[59−61] For example, the honeycomb structure $Sb@Ni_6$ has been reported as a stabilizing unit in layered cathodes because of the superexchange interaction and the degeneration of electronic orbitals, which makes the atomic-level uniform mixing between $Li@Mn_6$ and $Sb@Ni_6$ a promising route to promote the cycling stability at a high voltage window.[62,63]

Topologically protecting the structure by altering the anion framework stacking mode to enhance the electrochemical performance of LRLOs has also garnered significant attention recently.[64−66] Unlike the "ABCABC" oxygen stacking sequence in the O3-type structures, the O2-type layered structure is considered another viable stacking mode for practical applications where the oxygen stacking sequence along the *c*-axis is "ABCBABCB". The O2-type lithium-rich cathodes were primarily synthesized from P2-phase sodium cathodes through a Li/Na ion exchange strategy. The different layer stacking sequences determine the local environments of the cations related to the TM migration. In O3-phase, all the LiO_6 octahedra in the Li layer are edge-shared with the TMO_6 octahedra in the TM layer. In contrast, the LiO_6 octahedra in the O2-phase are either edge-shared or face-shared with the TMO_6 octahedra in different TM layers (Figure 4e). After interlayer migration, some of the TM ions ultimately occupy the octahedral sites in the Li layer. Compared to the edge-sharing octahedral sites in the O3-phase, the closer distance between face-sharing TM octahedral sites in the O2-phase results in stronger electrostatic repulsion, and therefore, TM ions can reversibly move back from the Li layer to the TM layer during discharge.[64] Unlike the identical oxygen stacking mode between spinel and O3-type structures, the transformation of the O2-type to the spinel structure requires breaking multiple TM−O bonds, which indicates the high stability against the layered-to-spinel phase transition. Although the unique stacking mode in the O2-type could mitigate the irreversible TM migration, the voltage decay problem remains unsolved, which may be related to the progressive structural damage. A recent study has reported that introducing TM ions into the Li layer as pillar ions can further improve the electrochemical performance.[67] Notably, the capped honeycomb structure where TMs partially occupy the interlayer Li sites directly below or above the Li atoms in the TM layer can pin the $Li@Mn_6$ superstructure and achieve negligible voltage fade and the protection of the lattice oxygen (Figure 4f). A similar strategy is also applicable to sodium-ion battery cathodes for the topological protection of lattice oxygen redox.[68]

A recent study has proposed a strain-retardant strategy by introducing a coherent layered perovskite phase into the bulk structure of Ni-rich layered materials.[69] The electrochemically inactive layered perovskite phase has a large phase transition barrier acting like a rivet to maintain the mechanical stability of the overall structure. Through this strategy, the structural distortion or lattice displacement in the layered structure can be significantly suppressed to achieve a pseudozero-strain cathode that enhances the mechanochemical stability and electrochemical properties. This concept of phase complex engineering has already been applied to the modification of LRLOs.[70,71] The spinel structure, composed of a three-dimensional TM framework, possesses higher mechanical stability compared with the layered structure upon delithiation. Moreover, the oxygen ions in the spinel phase do not participate in the redox reactions and, thus, have higher migration barriers. By employing phase complex engineering to construct a coherent biphasic nanostructure with nanoscale mixing of layered and spinel phases, the potential issues associated with surface modifications, such as nonuniform coating and spinel shell peeling, can be mitigated. The nanoscale mixing within the bulk structure effectively reduces the strain accumulation between different phases. Meanwhile, the mutual encapsulation of the spinel phase and the Li-rich phase intrinsically prevents further expansion of the oxygen migration network in the Li-rich phase to realize the topological protection of lattice oxygen redox.

In this Perspective, we focus on the strategies proposed in recent years to achieve topological protection against oxygen loss in LRLO cathodes. Starting from the unique Li@Mn_6 structure unit of LRLOs, the relationship between the local environment and the redox activity of oxygen ions is summarized. Various mechanisms by which oxygen participates in the redox process are also discussed. On this basis, we further analyze the structural evolution processes closely related to oxygen release, including the phase transitions, the presence and growth of various interfaces and cracks, the stacking faults between TM layers, and the accumulation of lattice strain during cycling. These factors collectively lead to continuous degradation of the crystal structure over long-term cycles, thereby providing numerous pathways for oxygen release.

Designing cathode structures to achieve topological protection is a crucial method for inhibiting structural degradation, blocking oxygen release pathways, and enhancing cycling performance. Four major kinds of improvement strategies have been discussed, including modulation of surface termination, design of intralayer composition, control of interlayer stacking, and construction of multiphasic nanostructure (Figure 5). Surface coating treatments and materials design with concentration gradient structures for LRLOs have been widely applied in the past and have demonstrated great success. However, the internal strain could become a problem that impairs cycling performance. Unlike surface modification, the composition and structure design from intralayer and interlayer aspects can uniformly inhibit oxygen migration throughout the bulk phase to reduce the potential migration paths of oxygen ions and prevent the formation of a percolation network of the redox-active oxygen. Taking advantage of special stacking arrangements could be a fruitful research direction that helps exploit cathode materials with inherent capability to topologically obstruct the percolating migration of oxygen to the surface. Synthesizing LRLOs with multiphasic nanostructure is another interesting direction through which two phases may encapsulate each other to achieve the goal of blocking oxygen release. Although integrating all the above methods could probably be irreconcilable, the insights in this Perspective regarding the underlying physics and chemistry of oxygen release and its mitigation will hopefully guide selection of the most appropriate strategies in the research of LRLO cathodes.

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