Configuration-dependent anionic redox in cathode materials

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Abstract
The utilization of anionic redox is one of the most prospective strategies to obtain high specific capacities in addition to the transition metal redox. The specific local environments around the oxygen atoms lead to the transference of the oxygen electrons with different difficulties for the excess capacity of the cathode materials. Nevertheless, the structural and performance degradation is closely related to the irreversible anionic redox, resulting in serious challenges for the commercialization of the cathode materials. Therefore, it is necessary to summarize the correlation between the oxygen configuration for the anionic redox and the resultant structural features to better utilize the anionic redox for the cathode materials with better performances. This review summarizes the latest advances of oxygen redox in the cathode materials in terms of their oxygen configurations. First, the fundamental mechanisms of anionic redox are discussed. On the basis of the local atoms and configurations, the recent strategies are then discussed that are promising to boost the reversibility of the anionic redox and mitigate the side reaction triggered by the oxygen redox. At last, an outlook is presented on the strategies to optimize the reversibility of the anionic redox for achieving the high energy-density cathode materials.

KEYWORDS
anionic redox, cathode materials, configuration, lithium/sodium-ion batteries, oxygen redox
1 | INTRODUCTION

Lithium (Li) ion batteries (LIBs) have found wide applications in portable electronic devices and electric tools since they were commercialized in the early 1990s.\(^1\) Recently, with the rapid development of large-scale energy storage stations and electric vehicles, LIBs with higher energy density and safety, longer lifespan, and lower cost are required. The traditional cathode materials, including LiCoO\(_2\) (theoretical specific capacity 274 mAh g\(^{-1}\)), LiFePO\(_4\) (theoretical specific capacity 170 mAh g\(^{-1}\)), and LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\) (NMC, \(x + y + z = 1\) and \(x < 0.6\)) cannot satisfy the demands in energy density, element abundance, and battery cost.\(^2\) Clearly, it is more efficient to increase the energy density of the cathode material to elevate the energy density of the battery (Figure 1).

The Li-rich layered cathode materials have attracted widespread attention of the society for their extra-high specific capacities (>250 mAh g\(^{-1}\)).\(^3\) Both the transition metal (TM) cation and the oxygen anion (O\(^{2-}\)) participate in the charge compensation during the Li\(^+\) ion extraction. Tarascon et al.\(^4\) reported that the length of the O–O bond is shorter than that of the usual O–O bond (O\(^{2-}\)) at the deep charge state. Therefore, it was believed that the oxygen anion can participate in the charge compensation during cycling, providing extra electrons to compensate for the charges for the cathode materials. As more Li ions can be removed from the lattice, the capacity of the Li-rich cathode materials is higher than that of the traditional layered cathode materials. Ceder et al.\(^5\) demonstrated that the specific local environments around oxygen in the Li-rich manganese-based (LMR; with Li–O–Li configurations) cathode materials create orphaned oxygen states and facilitate its oxidation. Similarly, anionic redox has been observed in many cathode materials for the sodium-ion batteries (SIBs) though their oxygen configurations are different from those in the lithium cathode materials.\(^6\)–\(^8\) SIBs can be an alternative to LIBs in energy storage, considering the high abundance of Na in the earth. Therefore, it is necessary to summarize the relationship between the oxygen redox and the oxygen configurations and structural evolution of the material to have a comprehensive understanding of the impacts of the configurations on the structure and performances of the cathode materials.

LIBs are superior to SIBs in terms of the theoretical energy density due to the high electrochemical potential of Na (~0.3 V higher than that of Li).\(^9\) At present, the energy density of LIBs is over 350 Wh kg\(^{-1}\), while the reported energy density of SIBs is ~180 Wh kg\(^{-1}\).\(^10,11\) The energy density of a battery is mainly determined with its cathode materials. The introduction of elements that have relatively high oxidation potentials, such as Ni and Co, is beneficial for increasing the energy density of the cathode materials.\(^12\) The anionic redox is another important strategy to enhance the energy density of the cathode material as it usually occurs above 4.3 V and provides additional charge compensation for a higher capacity. In addition, the layer spacing of the sodium cathode materials is larger than that of the lithium materials. The Na ions tend to occupy the prismatic sites to form the P\(_2\) and P\(_3\) type structures, which is facile for the diffusion of the Na ions and the rate performance of SIBs.

In this review, a framework is established on the basis of the anionic redox for an overview of the configuration-dependent oxygen redox in the cathode materials. The fundamentals of anionic redox are summarized in Section 2. Different configurations on the cathode materials are discussed in Section 3, and summary and perspective are given in Section 4.

2 | FUNDAMENTALS OF ANIONIC REDOX

2.1 | Overview of anionic redox

The development of the anionic redox is accompanied by the investigation of the LIB and SIB cathode materials (Figure 2). The first record on the anionic redox can be traced back to 1976 when Whittingham reported that TiS\(_2\) can be applied as a cathode material in lithium (metal) batteries.\(^17\) Then, Rouxel et al.\(^18\) proposed the concept of anionic redox and its competition with the cation redox during charging. They believed that the anionic redox involves the \(d\) electrons of the TM cations.
and the electrons in the \( p \) orbitals of the anions. However, not much attention was paid to this concept because the lithium metal batteries that utilized the transition metal sulfides as the cathode soon quitted from the market due to some safety accidents. Later, Goodenough et al.\(^\text{19}\) prepared \( \text{Li}_{x}\text{CoO}_2 \) (0 < \( x \) ≤ 1) as a new cathode material with a higher energy density. Tarascon et al.\(^\text{4,20}\) further found that Co is not tetravalent, and the O–O interlayer distance is reduced at the end of delithiation. The density functional theory (DFT) calculations in 1997 show that both the TM cations and O anions provide charge compensation during Li extraction.\(^\text{13}\)

\( \text{Li}_2\text{MnO}_3 \), a cathode material with 1/3 of its Mn ions replaced with Li, presents a very high lithium de-intercalation capacity.\(^\text{21,22}\) Due to the high oxidization potential (>5.0 V, vs. Li\(^+\)/Li) for the Mn\(^{4+}\)/Mn\(^{5+}\) redox couple, the excess capacity of \( \text{Li}_2\text{MnO}_3 \) can only originate
from the oxygen oxidation. However, there is no evidence for the reversible oxygen redox in Li$_2$MnO$_3$. Dahn et al. and Amine et al. prepared Li[Li$_{1/3}$−$\alpha$ Ni$_{2/3}$Mn$_{2/3}$]O$_2$ by substituting some Ni for Mn in Li$_2$MnO$_3$ and obtained reversible capacities of 230–240 mAh g$^{-1}$ between 2.0 and 4.6 V. Thereafter, the issues about the Li-rich layered oxide materials were widely investigated, such as the charge compensation, structural evolution, and the redox process for the high reversible capacity. Most of the oxygen redox reactions involve excess Li in the TM layer of the Li-rich cathode materials, forming the Li–O–Li configuration.

With the rapid development of large-scale energy storage, the limited abundance of lithium becomes a big bottleneck to LIB applications. As an alternative to LIBs, SIBs are attractive in energy storage. In comparison with the single Li–O–Li configuration in the lithium cathode materials, the sodium-containing layered oxides with P (prismatic)- or O3 (octahedron)-type Na$_x$MO$_2$ ($x \leq 1$) shows more diversified configurations that can facilitate the oxygen redox, enriching the fundamental understandings of the structural effect on the oxygen redox. The discovery of anionic redox opens a new avenue for the TM oxides and propels the energy density of LIB and SIBs to a higher level. The history of the research of anionic redox is accompanied by the development of high-performance cathode materials (Figure 2).

### 2.2 Mechanisms of anionic redox

The mechanisms of the anionic redox can be understood in view of the band structure of the materials. The Fermi level is usually located in the TM$_{3d}$ orbitals before the cathode material is charged. Upon charging, the orbitals below the Fermi level will donate the same quantities of electrons as that of the extracted Li/Na ions. If the TM$_{3d}$ orbitals are completely separated from the O$_{2p}$ orbitals, the TM$_{3d}$ orbitals will be the only donor to provide electrons upon charging, resulting in the totally cationic redox, a case popular in the traditional cathode materials such as LiFePO$_4$.

However, the Fermi level may drop from the 3d orbitals to the top of the O$_{2p}$ orbitals during the Li-ion extraction (as in LiCoO$_2$). The partial overlap of the TM$_{3d}$ orbitals with the O$_{2p}$ orbitals results in the formation of the hybridization of TM–O bonds in the TM$_{3d}$–O$_{2p}$ bond, forming the higher energy orbital $e^*_g$ (antibonding) and lower energy orbital $e_g$ (bonding). As the $t_{2g}$ ($d_{xy}$, $d_{xz}$, $d_{yz}$) orbitals do not overlap with the O$_{2p}$ orbitals, nonbonding states are formed. The $4s$ and $4p$ orbitals of the 3d TMs are hybridized with the O$_{2p}$ orbitals, forming the higher ($a_{1g}$ and $t_{1u}$) and lower ($a_{1g}$ and $t_{1u}$) energy orbitals, respectively.

A qualitative Zaanen–Sawatsky–Allen picture of the Mott–Hubbard (MH) versus charge-transfer (CT) insulators is shown to display an integrated understanding of different redox mechanisms. The electronic structure of Li$_2$MO$_3$ can be inferred from the $U/\Delta$ ratio ($U$ for the on-site TM coulombic repulsion, $\Delta$ for the charge-transfer parameter). In the case of $U \ll \Delta$, the
mechanism is in the MH regime and the O_{2p} orbitals are very low, located at the band bottom, resulting in a pure cationic redox process. In the case of \( U/2 = \Delta \), the (MO\(^+\)) and the O_{2p} states come into the Fermi level, resulting in a mixed cationic and anionic redox. At last, when \( U \gg \Delta \), the O_{2p} states are very close to the Fermi level and the cations cannot be oxidized to a higher valence (TM d\(^0\)), leading to oxygen release and an irreversible anionic redox. A unified picture of the anionic redox between the MH and CT mechanism was reported, and the number of holes per oxygen, \( h^0 \), is critical; it determines the reversibility of the anionic redox.\(^{40}\)

The discovery of oxygen redox opens up a new avenue in boosting the capacity on top of conventional cationic redox. This is especially true for the Li-rich cathode materials with an energy density over 1000 Wh kg\(^{-1}\).\(^{41}\) In contrast, the oxygen redox in most of the cathode materials is accompanied by the loss of the lattice oxygen by way of the electrode/electrolyte reaction and/or oxygen evolution. Therefore, it is critical to suppress the oxygen loss and promote the reversible oxygen redox in utilizing the oxygen redox. However, the oxidation states of the oxygen atoms are dependent on their chemical bondings and local structural environments. The inhomogeneous oxidation is responsible for the irreversible oxygen redox, in Li\(_2\)MnO\(_3\), for example. Coordination is another factor for oxygen release. For example, no O\(_2\) gas release occurs for the P\(_2\)-type Na\(_{0.67}\)(Mg\(_{0.28}\)Mn\(_{0.72}\))O\(_2\) during charging, while the Li-bonded oxygen in Na\(_{0.78}\)(Li\(_{0.25}\)Mn\(_{0.75}\))O\(_2\) are lost.\(^{42}\) Oxygen release is activated at the deep delithiation state upon the Li\(^+\) or Na\(^+\) removal from the structure, leading to the formation of the severely underbonded oxygen (with fewer than three coordinated cations). Tarascon et al.\(^{43}\) proposed the reductive coupling mechanism between TM and O to explain the TM reduction at deep delithiation states. The formation of [Ru\(^{5+}\)+O\(^-\)] rather than the evolution of O\(_2\) from [Ru\(^{6+}\)+O\(^2-\)] accompanying the O–O dimers and restabilizing the oxygen network, can be characterized by X-ray photoelectron spectroscopy (XPS) and electron spin resonance (EPR). In addition, they observed the O–O dimers by STEM.\(^{15}\)

However, Bruce et al.\(^{44}\) believed that the molecular O\(_2\) generated during charging rather than the O\(_2^{2-}\) species in the structure is the key product for the oxygen redox. In fact, the molecular O\(_2\) in the bulk is different from the true O\(_2\) gas generated on the surface. The former is still bonded with the lattice atoms though their O–O distance is close to that of the normal O\(_2\) molecular. The lattice O\(_2\) molecules are reduced to oxygen ions (O\(^2-\)) as the material is discharged to \(-3.75\) V, significantly lower than the anionic oxidation potential. The gap between the oxidation and the reduction potentials is called voltage hysteresis. Therefore, it is significant to clarify the relationship between lattice oxygen redox and irreversible oxygen redox (oxygen release). The reasons for the oxygen release is related to the reduced valence of TM with the structural transition from layered to spinel, and some surface reactions due to the high active species.\(^{45}\)

### 2.3 Advanced characterization techniques for anionic redox

A comprehensive understanding of the physical and electrochemical processes during repeated charge and discharge is the basis for the development and improvement of electrode materials. The anionic redox mechanism is related to the O\(_{2p}\) orbitals, thus the characterization of the electronic structure of the TM and O elements using the spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), resonant inelastic X-ray scattering (RIXS), are of great importance for finding out the charge compensation of the cathode materials involving the anionic redox. The development of the advanced characterization techniques promotes insights into the anionic redox for designing cathode materials with higher energy densities. In this section, we briefly introduce some of the advanced characterization techniques that provide information on the lattice and electronic structures of the cathode materials involving anionic redox.

#### 2.3.1 X-ray photoelectron spectroscopy

XPS is a surface-sensitive technique for measuring the elemental composition, the chemical state of the element, and the electronic state of the material. The general principle of XPS is the Einstein photoelectric law, \( E_{\text{Kinetic}} = h\nu - E_{\text{Binding}} \), where \( E_{\text{Kinetic}} \) is the kinetic energy of the electron expelled from the materials by the photon with energy \( h\nu \), and \( E_{\text{Binding}} \) is the binding energy of the electron in the materials. In addition, the binding energy for the materials is related to the Fermi level.\(^{46}\) The core-level photoemission can provide the atomic fractions of the elemental composition even down to 0.1% sensitivity, and the fixed photon source of about 1 eV resolution is used in conjunction with a hemispherical or cylindrical electron analyzer.\(^{47}\) With the fixed energy, the kinetic energy of the outgoing electrons varies from 10\(^2\) up to 10\(^3\) eV. Therefore, XPS can probe the kinetic energy and the number of electrons escaping from a depth of 0–10 nm of the material. With the hard X-ray from the synchrotron radiation (energy range between 2000 and
15000 eV), the detection depth can reach ~40 nm.\textsuperscript{46} Therefore, XPS can efficiently provide surface information such as the composition of the solid electrolyte interphase (SEI) on the electrode surface.

In the early stage of the anionic redox characterization, this technique was used to characterize the special oxygen species at the charged state of the cathode materials.\textsuperscript{48,49} The Tarascon group investigated the O 1s spectrum in Li$_2$Ru$_{0.5}$Sn$_{0.5}$O$_3$. The new component at ~530.5 eV was attributed to the O$_2$\textsuperscript{2−} species at the charged state or the under-coordinated oxygen atoms.\textsuperscript{43} On the other hand, the limited detection depth of XPS hinders its applications in finding out information in the bulk material. Overall, the XPS technique usually cannot provide information on the oxygen redox in the bulk material due to the severe interference of the oxygen-containing species on the surface.

### 2.3.2 X-ray absorption spectroscopy

The XAS at the TM L/K-edge and the O K-edge is applied to find out the variation of the electronic structure of TM and O at different states not only for the chemical valence but also for the local structural analysis. Depending on the energy ranges of the X-ray, there are soft XAS (sXAS, low energy range 10–15000 eV) and hard XAS (hXAS, high energy range >3000 eV). The XANES region contains information in the near edge energy position, the shape of the XANES spectrum, and the pre-edge features. The near edge energy position is usually used to identify the oxidation state of the atom by using the reference compounds with the known oxidation states.\textsuperscript{50} The shape of the XANES spectra and the pre-edge are sensitive to the local structure around the central atoms, such as the coordination environment. In general, the prepeak intensity with the geometry increases in the order of octahedral < square-pyramidal < tetrahedral.\textsuperscript{50}

The O K-edge is usually characterized by sXAS due to the low binding energy of oxygen at ~530 eV. The detection depth of sXAS varies from a few nanometers in the total electron yield (TEY) mode to a few hundreds of nanometers in the total fluorescence yield (TFY) mode.\textsuperscript{50} Thus, the TEY mode is sensitive to the surface information, while the TFY mode is sensitive to the bulk information. The XAS technique has been applied to characterize the electronic and local structure of the TM ions and oxygen ions.\textsuperscript{51,52} The O K-edge spectra can provide information on the electronic structure of the hybridized TM$_2$O$_{2p}$ bonds. The intensity of the pre-edge peak of the O K-edge area suggests the increasing covalent intensity of the hybridized TM$_2$O$_{2p}$ bonds or the generation of the oxygen holes. The O K-edge XAS spectrum can provide surface and bulk information about the anionic redox in the TEY and TFY modes, superior to the XPS technique. However, as the cathode materials often contain multiple TM elements, such as Ni, Co, and Mn in LMR and the valence variation of each can interfere with the obtained O K-edge spectrum, it is difficult to distinguish the origin for the observed change of the pre-edge peak due to the interference of the TM–O hybridization and the oxygen oxidation. In addition, the O K-edge pre-edge peak of the charged LiFePO$_4$ is strong, making it confusing as LiFePO$_4$ has been identified to be a single Fe redox reaction during cycling.\textsuperscript{53} For the TM L-edge spectra in the TFY mode, many TM L-edge spectra (especially the Mn L-edge) are distorted due to the self-absorption effects, disabling it in further analysis.\textsuperscript{54}

#### 2.3.3 Resonant inelastic X-ray scattering spectroscopy

Reliable detection of the redox reactions of the lattice oxygen requires direct and quantitative characterization of both the cationic (TM) and anionic (O) redox states in the bulk. Such a technical challenge has been solved by the developments of the ultra-highly effective RIXS technique. The crucial achievement through the O-K RIXS is that it can distinguish the lattice oxygen redox feature from the broad TM–O hybridization features around 525 eV emission energy.\textsuperscript{35,55} This energy feature matches the spectroscopic signature of the oxidized oxygen, which originates from the excitations toward the unoccupied O$_{2p}$ states. The RIXS mapping can effectively recognize the unique peak (at emission energy ~524 eV and excitation energy ~531 eV) of the oxygen redox while the pre-edge peak of sXAS is attributed to the TM$_{3d}$O$_{2p}$ bonding. Bruce and coworkers\textsuperscript{44,56} investigated the oxygen oxidation states via the high-resolution RIXS technique. They found the formation of the molecular oxygen (O$_2$) during the charging of some Na–Li–Mn–O and Li-rich cathode materials. In addition, the nondistorted TM L-edge spectra in the inverse partial fluorescence yield (iPFY) mode are utilized to analyze the TM valence in the bulk sample. However, the latter two techniques are far from popular currently.

#### 2.3.4 Neutron powder diffraction (NPD)

The NPD was discovered by James Chadwick in 1932. The neutrons are subatomic particles with no electric charge.\textsuperscript{57} They interact with the atomic nuclei rather than the electrons. Therefore, the NPD technique can obtain the structural information and phase composition of a material.\textsuperscript{58} NPD is sensitive to the light atoms, such as Li, Na, or O, which can characterize the changes of...
O–O bond length and the position of Li or Na in the crystal structure in combination with the neutron pair distribution function (nPDF) analysis. In addition, the heavy atoms with similar atomic numbers (Z number) can have significantly different neutron scattering lengths, for example, 10.3, −3.73, and 2.49 fm (1 fm = 10\(^{-15}\) m) for Ni, Co, and Mn, respectively.\(^{59}\) Different from the X-ray that interacts with the electrons and the scattering intensity of which is proportional to the atomic number, the neutron interacts with the atomic nuclei and its scattering intensity is not monotonously dependent on the atomic number. Therefore, the NPD is especially powerful in determining the position of the light atoms in the lattice (low sensitivity for XRD) and in distinguishing the positions of the elements with similar atomic numbers (difficult to recognize by XRD).

Hu and coworkers investigated the O–O bond length in the highly delithiated LiCoO\(_2\) by NPD in combination with nPDF analysis.\(^{60}\) They found that the O–O pair distance is considerably shortened during charging, indicating the oxygen oxidation of LiCoO\(_2\). Rong et al.\(^{6}\) also observed the decrease of the O–O bond length in the charged P\(_2\)-type Na\(_{0.72}\)[Li\(_{0.22}\)Mn\(_{0.78}\)]O\(_2\). Wang et al.\(^{61}\) unveiled the diffusion behavior of the Li ion in layered cathode materials LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\) by in situ NPD. The concentration of the Li/Ni mixing varies during charging and its dependence on the Li content is like a crater due to the competition between delithiation and magnetic frustration. In addition, the Li ion hops zigzag from one tetrahedral site to the next in the charge process.\(^{61}\)

2.3.5 | Other techniques

EPR is a magnetic resonance technique used to detect the resonance transition between the energy levels of the unpaired electrons in an applied magnetic field. EPR is usually utilized to characterize the electronic state and coordination state of the metal ions, such as V, Co, Ni, Mn, and so on. Tarascon and coworkers\(^{43}\) applied the EPR spectroscopy to investigate the redox of the O and TM ions in Li\(_2\)Ru\(_{0.5}\)Sn\(_{0.5}\)O\(_3\), demonstrating its effectiveness in finding out the electronic structure of oxygen in this material. Recently, Zhao and coworkers observed the coexistence of O\(_2^−\) and the trapped molecular O\(_2\) in the charged P\(_2\)-Na\(_{0.66}\)[Li\(_{0.22}\)Mn\(_{0.78}\)]O\(_2\) by the EPR spectroscopy.\(^{62}\) The Raman spectroscopy can provide detailed information about the chemical structure, phase, crystallinity, and molecular interactions, on the basis of the interactions between the injected light and the chemical bonds within a material. Zhou et al.\(^{63–65}\) developed in situ Raman technique to investigate the formation of the O–O super/peroxo during the charging process.

3 | CONFIGURATION-DEPENDENT ANIONIC REDOX

3.1 | A–O–A’ configurations (A’ for Li or Na in the TM layer)

3.1.1 | Li–O–Li configurations

The specific local structural configurations around the O atoms have been found critically important for anionic redox. Li\(_2\)MnO\(_3\) is the earliest Li-rich layered oxide with unusually high charge capacity (>350 mAh g\(^{-1}\)) but poor cycling performance, low coulombic efficiency (CE, ~60%) and severe structural degradation.\(^{21,23}\) Different mechanisms were proposed to explain its high charge capacity, such as the Li\(^+\)/H\(^+\) ion-exchange mechanism,\(^{23,66–68}\) the redox of the Mn\(^{4+}/\)Mn\(^{7+}\) couple,\(^{22,69}\) and oxygen oxidation.\(^{25,26}\) With the comprehensive studies for more than two decades, scientists have now realized that the oxygen oxidation in Li\(_2\)MnO\(_3\) is not reversible.\(^{25,70}\)

The type of the TM atoms is critical in determining the oxygen activity in other oxide materials due to the TM–O hybridization. To improve the structural stability of Li\(_2\)MnO\(_3\), the LMR analogues were proposed.\(^{71–75}\) However, the origin of the high charge capacity and the reason for the oxygen redox are still unclear. Because of the intrinsic complexity of LMR in composition and structure, Tarascon et al.\(^{43}\) designed iso-structured Li\(_2\)Ru\(_1–x\)Sn\(_x\)O\(_3\) with Ru\(^{4+}/\)Ru\(^{5+}\) as the single cationic redox couple. The Ru and O redox are found reversible during Li\(^+\) insertion/extraction corresponding to a high reversible capacity of 230 mAh g\(^{-1}\), due to the Ru\(_{4d}\)–O\(_{2p}\) orbital hybridization. They then directly visualized the O–O bonding in Li\(_2\)IrO\(_3\) by TEM and neutron diffraction (Figure 4).\(^{15}\) Furthermore, Ceder et al.\(^{5}\) proposed that the specific local environment around the O atoms with the Li–O–Li configuration triggers the oxygen ions to donate electrons and participate in the redox process in Li-rich materials. In addition, the strongly coupled anionic redox and TM migration was revealed in Li\(_{1.17–x}\)Ni\(_{0.21}\)Co\(_{0.08}\)Mn\(_{0.54}\)O\(_2\) by the RIXS and XAS techniques.\(^{70}\) Hong et al.\(^{32}\) explained the connection between the anionic redox and the local structural disordering and voltage hysteresis. The structure–redox coupling originates from the local stabilization of the short M–O bonds (1.8 Å) and the O–O dimers (1.4 Å) via the O-to-TM charge transfer, causing the oxygen de-coordination and the formation of the TM vacancies.
Apart from the Li-rich layered oxides with the Li–O–Li configuration, the cation-disordered (rock salt) materials with the same configuration have attracted great attention for their high capacity in recent years. Many of these materials show high capacities as the Li-rich layered materials by combining cationic and anionic redox. For example, Li$_3$NbO$_4$ shows no electrochemical activity as the Nb d orbitals are empty (d$^0$). Thus, its band gap is large, making it unsuitable for the LIB cathode materials. However, Yabuuchi et al. showed that the Li$_3$NbO$_4$-based rock salt, Li$_{1.3}$NbO$_{3}$M$_{0.4}$O$_2$ (M = Ni, Fe, Co, Mn), delivers a reversible capacity of 250–300 mAh g$^{-1}$ at 50°C. Especially, Li$_{1.3}$Nb$_{0.3}$Mn$_{0.4}$O$_2$ shows the highest reported capacity of ~300 mAh g$^{-1}$. Nevertheless, these compounds exhibit quite large voltage hysteresis in the voltage profiles. As the Mn$^{3+}$/Mn$^{4+}$ redox cannot provide such a large capacity, oxygen can be the only contributor for the charge compensation. The Mn$^{3+}$/Mn$^{4+}$ redox takes place at the low voltages while the oxygen oxidation or oxygen evolution occurs at the high voltages (>4.2 V). Chen et al. proposed that, in single-crystal Li$_{1.2}$TiO$_2$MnO$_{3}$O$_2$, oxygen loss from the structure becomes dominant above 4.5 V and the lattice oxygen oxidation will trigger the irreversible Mn reduction, resulting in voltage decay, structural distortion, and even particle cracking. Moreover, the reduction of Mn, especially on the surface, is associated with the oxygen redox and the densification of the structure from surface to bulk will reduce the three-dimensional (3D) percolation network for the Li-ion diffusion, leading to structural distortion and capacity decay. In terms of the short-range cationic order, the locally inhomogeneous structure (the concentration of the TM channel controls the Li-ion transport, leading to quite different electrochemical profiles between Li$_{1.2}$Mn$_0.4$Ti$_0.4$O$_2$ and Li$_{1.2}$Mn$_0.4$Zr$_0.4$O$_2$). The cation-disordered materials are limited to the random 3D Li-ion transport channel even with the same Li–O–Li configuration. It shows a severer oxygen release during charging. Effective strategies such as increase of the Mn content, cation substitution, anion substitution and surface modification can suppress the oxygen release and improve the cycling performance. Fluorine substitution reduces the extent of the oxygen redox as well as the Jahn–Teller distortion of Mn$^{3+}$, improving the cycling performance.

Since the formation of the O$_2$ molecules was detected by the high-resolution RIXS in Na$_{0.75}$Li$_{0.25}$Mn$_{0.75}$O$_2$, Bruce et al. proposed that the molecular O$_2$, rather than O$_2^{2-}$, is
formed when Li_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2 is charged to above 4.6 V. In addition, the O\textsubscript{2} molecules formed in the bulk are reduced to O\textsuperscript{2−} as the oxide is discharged to 3.75 V, explaining the voltage hysteresis in most of the Li-rich cathode materials. However, the O\textsubscript{2} molecules formed on the surface are lost upon recharge, leaving oxygen vacancies near the surface. The oxygen vacancies penetrate into the lattice structure of the Li-rich oxide, causing severe structural transition.\textsuperscript{89} Peroxides (O\textsubscript{2}\textsuperscript{2−}) and O–O dimers are formed following the TM redox in Li\textsubscript{2}MO\textsubscript{3} (M for 4d and/or 5d TMs).\textsuperscript{15,32,34} In comparison with the 3d TM–O bonding, the stronger 4d/5d TM–O bonding is believed to be key for stabilizing the O–O dimers or the O\textsubscript{2}\textsuperscript{2−} peroxides.\textsuperscript{90,91} With the high-resolution RIXS, they demonstrated the presence of the trapped O\textsubscript{2} molecules in the bulk of the 4d/5d TM oxides (Li\textsubscript{2}RuO\textsubscript{3}, Li\textsubscript{2}Ru\textsubscript{0.5}Sn\textsubscript{0.5}O\textsubscript{3} and Li\textsubscript{2}Ir\textsubscript{0.5}Sn\textsubscript{0.5}O\textsubscript{3}).\textsuperscript{92} However, no molecular O\textsubscript{2} or O–O dimer was observed in Li\textsubscript{2}IrO\textsubscript{3} as the electron holes in the Ir–O orbitals are stable with the reversible redox of Ir\textsuperscript{5+}/Ir\textsuperscript{5.5+}. Thus, the more covalent TM–O bonding in the 4d/5d TM still leads to the formation of molecular O\textsubscript{2}, consistent with the Li-rich 3d TM cathode materials.

The Li-rich materials with the Li–O–Li configurations are currently the most promising cathode materials for the next generation LIBs. Although the oxygen redox can contribute to the high specific capacity in the Li-rich materials, it induces severe issues on the performance of the materials, such as low first-cycle coulombic efficiency, significant voltage hysteresis, and structural degradation. Although the capacity decay has been improved a great deal by the element doping and surface coating, the issues such as the voltage hysteresis and discharge voltage decay remain unaddressed. The oxygen release from the LMR material during cycling results in a coulombic efficiency of less than 85% in the first cycle.\textsuperscript{51,93} Efforts have been conducted to increase the first-cycle coulombic efficiency by suppressing the oxygen loss by surface modification to form a spinel structure to passivate the oxygen activation on the surface, for example (Figure 5).\textsuperscript{51,72,93,94} Different from the TM redox with high and stable reversibility, the oxygen redox that involves the O atoms on the structural framework induces significant structural variation during cycling. Due to the low formation energy on the tetrahedral sites, the TM migration into the tetrahedral Li layers is energetically beneficial and is driven by the generation of Li and/or oxygen vacancies at the deeply charged states, leading to the structural degradation from the layered to spinel.\textsuperscript{95} Voltage hysteresis and continuous voltage decay are closely related to the

**Figure 5** The STEM images of the Nb surface-doped Li\textsubscript{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2 (A and B).\textsuperscript{93} The voltage profiles of LMR and LMR-Nb, inset for the cycling performances (C).\textsuperscript{93} Reproduced with permission.\textsuperscript{93} Copyright 2018, WILEY-VCH. The HAADF (D) and ABF (E) images of Li\textsubscript{1.2}Ti\textsubscript{0.26}Ni\textsubscript{0.18}Co\textsubscript{0.18}Mn\textsubscript{0.18}O\textsubscript{2} (LTR) observed along the [100] zone axis. The cycling performance of LTR between 4.8 and 2.0 V (F).\textsuperscript{51} Reproduced with permission.\textsuperscript{51} Copyright 2019, Wiley-VCH.
Thus, inhibition of the formation of the oxygen vacancies is key in suppressing the structural transition as the formation of the Li vacancies is inevitable during charging (Li-ion extraction). One of the solutions is to increase the amount of the separator ions such as Sn to thermodynamically prevent TM migration. Another strategy is to alter the oxygen stacking sequence from O₃ to O₂ in the Li-rich materials (Figure 6).  

3.1.2 | Na–O–Na configurations

Owing to the large radius of the Na ions, it is difficult for the Na ions to stay in the TM layer to form Na-rich materials. However, some special compounds have been synthesized, such as Na₂RuO₄, Na₃RuO₄, and Na₂IrO₃. The O₃-type Na₂RuO₃ was used as a model material for the oxygen redox due to its Na–O–Na configuration. It is interesting that the Na₂RuO₃ with the honeycomb-ordered [Na₁/₃Ru₂/₃]O₂ slabs shows a capacity of 180 mAh g⁻¹, while the disordered Na₂RuO₃ only exhibits a capacity of 135 mAh g⁻¹. The extra capacity of the ordered Na₂RuO₃ is obtained by forming the ordered O₁-type Na₁RuO₃ when 1 Na⁺ ion is extracted from its lattice. The intermediate O₁-type Na₁RuO₃ facilitates oxygen oxidation, but the oxygen redox reaction cannot be activated in the P₃-type Na₁RuO₃. The DFT calculations identified that the formation of the shortest O–O bond in the O₁-type Na₁RuO₃ elevates the Fermi level of the O–O bond, triggering the oxygen redox. On the contrary, the structure of the P₃-type Na₁RuO₃ is free of any distortion, from which no extra Na-ions can be extracted. The Ru⁵⁺ ions in Na₃RuO₄ can be oxidized to Ru⁶⁺ accompanying with the oxygen oxidation during charging. However, the Ru⁵⁺ ions cannot be further oxidized in Li₃RuO₄. This difference is attributed to the size of the alkali cation according to the DFT calculations.

Similarly, multicrystal Na₂IrO₃ can reversibly cycle with strong oxygen participation and no cationic migration due to the strong overlap of the Ir₅d and O₂p orbitals. The formation of the unstable O₁-type Na₂IrO₃ results in structural distortion when more than 1.5 Na⁺ ions are extracted (Figure 7A). However, only the Ir⁴⁺/Ir⁵⁺ redox is involved in the highly ordered single-crystal Na₂IrO₃. The capacity fading in the single-crystal Na₂IrO₃ is correlated with the Na⁺ ions migration, resulting in the formation of O₃-type Na₂IrO₃ (Figure 7B). Another 3D-structured β-Na₁.₇IrO₃ (space group Fdd) configuration is shown to be more stable and has a higher capacity compared to the single-crystal Na₂IrO₃.
prepared by the Li+/Na+ ion-exchange uptakes 1.3 Na+ per formula unit accompanied with several phase transitions and the redox couples of both the Ir4+/Ir5+ and oxygen.108 Jung and coworkers105 found that the Na-rich Na2MO3 (M = 3d, 4d, and 5d TMs and post-TMs, such as Tc, Ru, Rh, W, Ir, Pt, Mo, and Pd) are stable and significant for the Na-ion batteries. All of these compounds undergo the O3′-O1′ phase transitions to minimize the coulombic interaction (electrostatic repulsion) in cations by forming the cation-vacancy orderings. The most important is that the formation of the O3′- and O1′-type intermediate phases facilitates the oxygen activation and inhibits the oxygen loss upon charging. The low-cost 3d TMs (such as Fe and Mn) tend to form the O–O dimers causing oxygen loss and voltage hysteresis, while the expensive 4d/5d TMs facilitate the structural stabilization and benign electrochemical performances, which is similar to that in the Li-rich materials. Overall, even with the Na–O–Na or Li–O–Li configurations, the local structural arrangement (the ordering of the TM or Li/Na layers) and the type of TMs (3d/4d/5d) are still essential in activating the reversible anionic redox and in stabilizing the structure.

### 3.1.3 | Na–O–Li configurations

In contrast to the Li-rich or Na-rich oxide materials with the anionic redox and therefore high discharge capacities, the Na0.5TMO2 (x ≤ 1) layered materials show more diversified structures (O3′, P2′, and P3′ types). Because of the large ionic radii of the Na+ ions, the Na-deficient layered oxides tend to form the P-type layered structure, while the Li-deficient oxides prefer to form a spinel structure.110 As a typical P-type layered material, Na0.6MnO2 delivers a capacity of 160 mAh g−1 though its cycling performance is not satisfactory due to the presence of the Jahn–Teller active Mn3+ ions.111 Doping of Li-ions in Na0.6MnO2 significantly increases the initial capacity beyond the theoretical capacity by the Mn3+/Mn4+ redox couple.6,35,48,63,112–118 Goodenough et al.48 studied the oxygen redox in these materials (Figure 8A) and pointed out their irreversibility, while Nazar et al.113 found that the energy bands of the oxygen atoms in Na0.6Li0.2Mn0.8O2 are near the Fermi level, suggesting the possible contribution of the oxygen redox. However, these authors failed to provide direct evidence to illustrate the oxygen redox. The direct experimental evidence for the shortened O–O distance (from 2.64 to 2.5 Å) was obtained by the neutron diffraction (ND) and pair distribution function (PDF) techniques to illustrate the oxygen redox (Figure 8B,C).6 Yang et al.35 quantitatively detected both the cationic and anionic redox states in the lattice of Na0.6Li0.2Mn0.8O2 by the RIXS technique and realized a reversibility of 97% for the lattice oxygen redox in the first cycle.

Although the introduction of Li into Na0.6MnO2 successfully activates the oxygen redox with the Na–O–Li configuration, the Li/Mn ratio with the different superstructural orderings determines the reversibility of the oxygen redox in Na0.6Li1−xMn1+xO2. Bruce et al.56 found that the voltage hysteresis in the first cycle is dependent on the Li/Mn ordering in the TM layer by comparing P2′Na0.75Li0.25Mn0.75O2 and P3′Na0.60Li0.2Mn0.80O2. The honeycomb-ordered superstructure of P2′Na0.75Li0.25Mn0.75O2 loses the first charge plateau with large voltage hysteresis upon the first discharging, while the ribbon superstructure in P3′Na0.60Li0.2Mn0.80O2 suppresses the Mn disorder with a small voltage hysteresis. In addition, the O2− oxidation results in oxygen species with stable oxygen electron holes in the ribbon superstructure, while molecular O2 is generated in the honeycomb-ordered superstructure. In spite of the high specific capacity of the Li-substituted P2′Na0.6MnO2,
Na–O–Li configuration also leads to oxygen loss upon charging, as the Li–O–Li configuration does. Both the Li–O–Li and Na–O–Na configurations with the weak ionic A–O bonds, raise the O$_{2p}$ orbitals in energy and activate the partially irreversible oxygen redox. Furthermore, Bruce et al. proposed that both Na$^+$ and Li$^+$ are removed from P$_2$Na$_{0.78}$Li$_{0.25}$Mn$_{0.75}$O$_2$ upon charging, resulting in the underbonded oxygen (fewer than three cations coordinated oxygen) and loss of the surface oxygen while Na$_{0.67}$[Mg$_{0.28}$Mn$_{0.72}$]O$_2$ shows no oxygen loss (Figure 9).
Elemental substitution (such as Mg, Ti, Zn, and Sn) is effective in suppressing the oxygen loss in materials with the Na–O–Li configuration. It weakens the ionic A–O bonds and enhances the covalent M–O bonds by modulating the local charge of Mn and inhibiting the anisotropic Mn–O coupling redox, suppressing the irreversible oxygen redox and enhancing the cycling performance.

3.2 | A–O–M configurations

3.2.1 | Na–O–M configurations

The anionic redox usually occurs due to the existence of the orphaned O2p orbitals with the formation of A–O–A configurations. However, the extra capacity provided by oxygen redox is accompanied by severe oxygen loss. Elemental substitution (Mg, Ni, Cu, Zn, TM vacancies, etc.) in Na0.67MnO2 for the formation of new Na–O–M configurations can activate the oxygen redox and suppress the oxygen loss. Yabuuchi et al. prepared P2-type Na2/3[Mg0.28Mn0.72]O2 that delivers a reversible capacity of 220 mAh g−1 beyond the theoretical capacity of Mn3+/Mn4+ redox couple. They attributed the extra capacity to the contribution of the oxygen redox but provided no evidence. Further investigation on P2-type Na0.67[Mn1−xMgx]O2 with honeycomb-ordering in the TM layer demonstrates that the Na–O–Mg configuration can also activate the oxygen redox without oxygen loss, different from that by the A–O–A configuration (Figure 10). In Na2/3[Mg0.28Mn0.72]O2, the oxygen ion is coordinated by at least three cations and all the O2p electrons can interact with at least one cation. In contrast, the oxygen is under-coordinated with only two or fewer cations in the A–O–A configurations (in LMR or Na0.67Li1−xMnxO2 compounds) since both the Li+ and Na+ ions can be removed from the structure, resulting in severe oxygen evolution.

In addition, the stacking sequence of the oxygen ions in the structure, such as P2, O3, or P3, may induce a variety of local cation coordination environments and different intralayer/interlayer distances, resulting in completely different electrochemical performances, such as the P3-type Na2/3Mg1/3Mn2/3O2 and P2-type Na2/3Mg1/3Mn2/3O2, with the same Na–O–Mg configuration. Tarascon et al. studied the fundamental relationship between the O- or P-type stackings and the reversibility of the oxygen redox in Na2/3Mg1/3Mn2/3O2 by the DFT calculations and revealed that the environment of the oxygen coordination is stabilized via a highly reversible collective distortion in the P2-type structure. In contrast, a disproportionation of the oxygen dimers with voltage hysteresis is shown in the

**Figure 10** The sXRD pattern (A) and voltage profiles at a rate of 10 mA g−1 in the voltage range of 1.5–4.4 V (B) of P2-type Na2/3[Mg0.28Mn0.72]O2. Reproduced with permission. Copyright 2014, Royal Society of Chemistry (RSC). pDOS of O2p, Mn3d, and Co3d orbitals for (C) Na0.67[Mg0.25Mn0.75]O2, (D) Na0.5[Mg0.25Mn0.5Co0.25]O2. Reproduced with permission. Copyright 2019, Wiley-VCH.
O₂-type structure. Unfortunately, the capacity fading and poor rate performance inhibit the development of these materials, even though the capacity originated from the cationic and anionic redox with the Na–O–Mg configuration is considerably high. Cation doping such as Co and Ti was reported to be effective in addressing these issues.

Another interesting strategy is to replace some Mn with cations with high electronegativities, such as Zn or Cu. Anionic redox was observed in P₂-Na₂/₃MnₓZn₁₋ₓO₂ with a new Na–O–Zn configuration, during which no oxygen loss was detected and the structural strain is low as there is no P₂–O₂ phase transition (Figure 11A,B). Later, Zheng et al. and Wang et al. proposed that Cu doping in NaₓMnO₂ for an Na–O–Cu configuration ensures the reversible redox of the lattice oxygen and reduces the voltage hysteresis of the material (Figure 11C). However, the contribution of the oxygen redox by the Na–O–Cu configuration is less than that by the Na–O–Zn, Na–O–Mg, or even Na–O–Li configurations.

Iron (Fe) is an attractive element in the LIB and SIB cathode materials for its high abundance and low cost. Yabuuchi et al. investigated α-NaFeO₂ with the Na–O–Fe configuration. It shows high capacity retention when charged to 3.4 V. However, severe structural deterioration occurs when NaFeO₂ is charged to above 3.5 V. Li et al. found that Fe migration occurs from the TM layer to the Na layer at 4.4 V and results in multiple phase transitions and irreversible structural changes though both the Fe³⁺/Fe⁴⁺ couple and the oxygen redox participate in the charge compensation (Figure 12A–D). The DFT calculations recognized that the Fe migration is thermodynamically spontaneous and is responsible for the poor performance. However, Chung et al. believed that oxygen redox is the only way for the charge compensation and is responsible for the performance fading; they did not observe Fe³⁺/Fe⁴⁺ redox. The oxygen loss at high potential and the resultant formation of Fe₂O₄ species on the surface lead to the surface densification, preventing the diffusion of the Na ions (Figure 12E). Anyway, the oxygen redox triggered with the Na–O–Fe configuration is less reversible than the other configurations, such as Na–O–Li, Na–O–Mg, Na–O–Cu, and Na–O–Zn.

### 3.2.2 Na–O-vacancy configurations

Recently, introduction of vacancies into the TM layer and formation of the Na–O-vacancy (□) configuration were
found effective in triggering the oxygen redox, providing another approach to design high energy-density cathode materials.\textsuperscript{8,12,36,52,139–145,150,151} \textit{Na}_2\textit{Mn}_2\textit{O}_7 (or \textit{Na}_{4/7}[_{\text{Mn}_{6/7}\square_{1/7}}]\textit{O}_2), built up with the edge-sharing \textit{MnO}_6 octahedrons in the \textit{[Mn}_{6/7}\square_{1/7}][\text{O}_2 slab located between the Na ions in the form of \textit{NaO}_6 polyhedrons, has attracted lots of interest. Pralong et al.\textsuperscript{152} investigated the electrochemical performance of \textit{Na}_2\textit{Mn}_2\textit{O}_7 between 3.0 and 1.5 V but ignored its performance at high voltages. Later, Wang et al.\textsuperscript{8} and Yamada et al.\textsuperscript{52} reported the reversible oxygen redox in \textit{Na}_{4/7}[_{\text{Mn}_{6/7}\square_{1/7}}]O_2 with negligible voltage hysteresis (Figure 13). The ordered \square–\textit{Mn} arrangement in the \textit{Mn} layer leads to a \sqrt{7} \times \sqrt{7} superstructure and \textit{Na–O–\square} configuration, generating the orphaned \textit{O}_2p orbitals along the \textit{Na–O–\square} or \square–\textit{O–\square} direction. The existence of the native vacancies enhances the material properties such as high structural flexibility because of the asymmetric \textit{MnO}_6 octahedron and stability and high reversible oxygen redox. Song et al.\textsuperscript{143} demonstrated that the small voltage hysteresis (<50 mV) originates from the well-maintained oxygen stacking without slab gliding or \textit{Mn} migration during cycling (Figure 14A–C). The oxygen around the vacancy with the \textit{Na–O–\square} configurations will generate the nonbonding \textit{O}_2p orbitals, resulting in the reversible oxygen redox. Abate et al.\textsuperscript{140} reported that the coulombic interactions of the \textit{O}^{2−} anions and the interlayer \textit{Na} vacancies in \textit{Na}_{4/7}[_{\text{Mn}_{6/7}\square_{1/7}}]\textit{O}_2 can suppress the rehybridization and stabilize the hole polarons on oxygen (\textit{O}^{−}) at 4.2 V, showing a voltage hysteresis of ~40 mV after some cycles with negligible voltage fade.

To better understand the inducement for the activation and reversibility of the oxygen redox, Yang et al. specifically designed P2-type \textit{Na}_{2/3}[_{\text{Mn}_{7/9}\text{Mg}_{1/9}\square_{1/9}}]\textit{O}_2 that contains equal quantities of vacancies and \textit{Mg}^{2+} ions in its TM layer.\textsuperscript{36} The DFT calculations demonstrate that the \textit{O} atoms close to the vacancies (the \textit{Na–O–\square} configuration) donate more charge than the \textit{O} atoms around the \textit{Mg} atoms (the \textit{Na–O–M} configuration) do during charging. The oxygen in the \textit{Na–O–\square} configuration contributes charge because the vacancies can induce the lone-pair electrons (Figure 14D,E). In addition, the existence of vacancies in the TM layer increases the Jahn–Teller inactive low-spin \textit{Mn}^{3+} ions during discharging by decreasing the \textit{Mn–O} bond length to enhance the structural stability.\textsuperscript{151} By regulating the quantity of the vacancies and introducing \textit{Co} and \textit{Fe} into the TM layer, Li et al.\textsuperscript{13} stabilized the performance of the P2-layered \textit{Na}_{0.7}\textit{Mg}_{0.2}\textit{Fe}_{0.2}\textit{Mn}_{0.6}\square_{0.2}\textit{O}_2 and \textit{Na}_{0.8}\textit{Mg}_{0.1}\textit{Mn}_{0.6}\textit{Co}_{0.2}\square_{0.13}\textit{O}_2. The \textit{Na–O–\square} configuration facilitates the oxygen redox at a lower potential than the \textit{A–O–A} and \textit{A–O–M} configurations.
3.2.3 | Li–O–M configurations

The TM ions are definitely the main contributor of the charge compensation in the conventional electrodes (such as high-voltage materials LiCoO$_2$, NCM, etc.). However, the anions were recently recognized to be another donor for the charge compensation when the traditional cathode materials are charged to higher potentials. $^{60,153-159}$ The anionic redox in LiCoO$_2$ was theoretically expected in 1991, but did not draw much attention of the community because of lack of direct experimental evidence. $^{160}$ Hu et al. $^{60}$ investigated the oxygen redox in highly delithiated LiCoO$_2$ by combining the advanced experimental techniques (such as RIXS, nPDF, etc.) and DFT calculations. Different from the previous beliefs that oxygen loss takes place in the deeply delithiated LiCoO$_2$, the RIXS showed directly that the lattice oxygen redox is reversible and nPDF exhibits the shortened O–O pair distance in the high-potential charged LiCoO$_2$ (Figure 15). It is of great importance to maximize the utilization of the capacity of the cathode materials and stabilization of the oxygen redox at high potentials.

NCM and LiNi$_{0.8}$Co$_{0.2-y}$Al$_y$O$_2$ (NCA) are regarded the most promising cathode materials of LIBs for electric vehicles. Although the Ni and Co redox couples are considered the dominating charge compensators and there are no or only very few Li–O–Li configurations in the pristine material, the oxygen redox can still occur when these materials are charged to high voltages. Piper and coworkers $^{153}$ observed the TM redox (<4.25 V) and oxygen redox (>4.25 V) in LiNi$_{0.8}$Co$_{0.2-y}$Al$_y$O$_2$. Lee et al. $^{158}$ attributed the oxygen redox to the anisotropic structural change in Li$_{1-x}$Ni$_{0.88}$Co$_{0.1}$Al$_{0.2}$O$_2$ because the electron holes generated during oxygen oxidation reduce the coulombic interaction of the O layers. Two types of oxygen involvement have been recognized in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ during cycling. $^{155}$ The RIXS analysis indicates that the TM-O orbitals are hybridized throughout the charge and discharge processes while the oxygen redox at high voltage (~2/3 Li extracted) is 75% reversible in the initial cycling, 63% of which is maintained after 10 cycles (Figure 16). In addition, Hou et al. $^{159}$ found that the high-valence Ni$^{4+}$ generated at high voltage in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ will be reduced to Ni$^{3+}$ as a response to the oxygen release. Therefore, they proposed to stabilize the high-valence Ni$^{4+}$ by doping of inactive cations (such as Ta$^{5+}$) or by surface modification to enhance the cycling performance of, especially, the Ni-rich layered NCM materials at high voltages.

Comprehensive studies have been conducted on the oxygen redox in the Li-rich cathode materials. However, understanding of the oxygen redox mechanism in the conventional cathode materials without the aforementioned oxygen redox in the traditional material is of...
practical importance. Meanwhile, it is also a big chal-
lenge to regulate the oxygen oxidization and suppress the
structural degradation to reach a balance between
structural stability and high energy density. On one
hand, there are inevitably Li vacancies in the charged Ni-
rich cathode materials, inducing the TM migration and
Li/TM mixing in the Li layer. The TM migration will
leave TM vacancies in the TM layer or the TM
vacancies are filled with the Li ions from the Li layer. Therefore, an
Li–O–Li configuration (if the TM vacancies are filled
with the Li-ions) or Li–O–□ configuration (if the TM
vacancies are left unoccupied) will be formed, facilitating
the oxygen redox in the conventional cathode materials.
As the content of the above configuration is lower in the
traditional cathode materials than in the Li-rich cathode
materials, the capacity contribution by the oxygen redox
is much less than in the Li-rich cathode materials.
However, the irreversible TM migration may be accumu-
lated gradually, and this effect become innegligible
after repeated cycling, resulting in severe structural de-
gradation and performance decay.

4 | SUMMARY AND
PERSPECTIVES

In addition to cationic redox, anionic redox is another
effective strategy of charge compensation in boosting the
specific capacities of the cathode materials. The me-
chanism of the anionic redox is complicated and the re-
action involves many factors, such as the types of TM
ions, the local atomic configuration, and the ordering of
the local structure. The reversibility of the anionic redox
is closely related to the configurations of the O atoms.
The ionic bonding in the Li–O–Li, Na–O–Na, or even
Na–O–Li configurations (the type of A–O–A configura-
tion) of the Li-rich and the Na-containing oxide materials
elevates the O$_{2p}$ orbitals on the top of the valence band of
oxygen, facilitating the charge transfer from oxygen. The oxygen redox via such A–O–A configurations can contribute significantly to the specific charge capacities. On the other hand, irreversible anionic redox is often accompanied by TM migration, voltage hysteresis, and even oxygen release. Oxygen loss or generation of the oxygen vacancies on the surface promotes the TM migration and fast performance deterioration, hindering the applications of the anionic redox in improving the energy densities of the Li/Na-rich cathode materials. In light of this, it is critical to balance the extent of the oxygen redox and the structural stability of the cathode materials. This principle should be applicable to the cathode materials with the A–O–A configurations or with other oxygen configurations.

Regulation of the composition or structure of the TM layer to transform the A–O–A configuration to the A–O–M configurations can effectively enhance the reversibility of oxygen redox and the cycling performance of the cathode materials. Although the generation of the A–O–Zn/Cu/Mg configurations can suppress the oxygen loss to some extent, the voltage hysteresis remains an issue to be addressed. Introduction of the TM vacancies can both facilitate the oxygen redox and mitigate the voltage hysteresis. Meanwhile, the structural strain in the Na–O–□ configuration-containing materials is reduced due to the presence of the asymmetric TMO6 octahedrons in these materials. Against these challenges, a compromise can be reached between the high energy density and the cycling performance of the cathode material. It will be an interesting topic whether this idea can be generalized to the cathode materials for LIBs, including the Li-rich and the traditional non-Li-rich layer-structured materials.

The high energy density and high specific capacity of the Li-rich layered materials originate from the oxygen redox reaction, which may lead to the undesired oxygen release, surface reactions, and inevitable Li vacancies in the lattice structure. These side reactions accelerate the structural degradation and performance decay: (1) structural defects such as vacancies on the surface and voids in the bulk, (2) TM migration from the TM layer to the Li layer, (3) irreversible phase transitions from layer to spinel and rocksalt structure and the decay of the

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**FIGURE 15** The ex situ RIXS mapping of LiCoO2 (A).60 The results of the nPDF and O–O bond distance for LiCoO2 (B).60 Reproduced with permission.60 Copyright 2021, Elsevier
specific capacity and operation voltage, (4) increase of the CEI thickness and interfacial resistance. As a matter of fact, the above issues are also as severe in the sodium cathode materials with oxygen redox. Therefore, a combination of the different strategies, from the atomic (lattice doping and the adjustment of O stacking sequence) to microstructural scale (surface structural modification and single/multicrystal structure), is required to control the oxygen redox center (Figure 17). A comprehensive understanding of the associated processes and the reasonable structural design to suppress oxygen loss (or to realize the reversible oxygen redox) are essential to the design of high density-energy cathode materials with improved cycling stability.

FIGURE 16  The O K-edge mRIXS at various states of charge (SOC) of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ in the first cycle and after 10 cycles (A). The O K-edge super partial fluorescence yields (sPFY) was obtained by integrating the intensity within the characteristic emission-energy range from 522.5 to 524.5 eV on the O–K mRIXS (B). Reproduced with permission. Copyright 2020, Wiley-VCH

FIGURE 17  Schematic illustration of configuration-dependent anionic redox
As an extension of the effect of the intrinsic configurations that can trigger the oxygen redox reactions, the acquired configurations and their impacts on the performances of the cathode material are also worth investigating. For example, the extraction of the Li/Na ions from the lattice will lead to Li/Na vacancies and promote the migration of the transition metals into the Li/Na layer. The occurrence of the latter results in the structural variation and generates oxygen configurations beneficial for the oxygen redox reactions. This is not exaggerating and probably happening in the traditional cathode materials such as the Ni-rich layered materials and even in the stable LiCoO₂ when they are charged to high potentials.

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CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

DATA AVAILABILITY STATEMENT
The data presented in this study are available on request from the corresponding authors.

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