

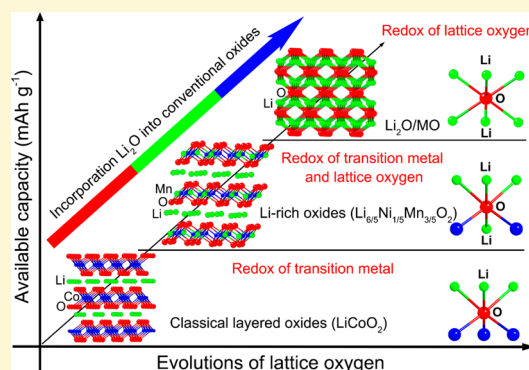
Understanding and Controlling Anionic Electrochemical Activity in High-Capacity Oxides for Next Generation Li-Ion Batteries

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ABSTRACT: Rechargeable Li-ion batteries with higher energy density are in urgent demand to address the global challenge of energy storage. In comparison with anode materials, the relatively low capacity of cathode oxides, which exhibit classical cationic redox activity, has become one of the major bottlenecks to reach higher energy density. Recently, anionic activity, such as oxygen redox reaction, has been discovered in the electrochemical processes, providing extra reversible capacity for certain transition-metal oxides. Consequently, a more complete understanding and precise controlling on anionic electrochemical activity in these high-capacity oxides have become a flourishing, yet challenging subject. This perspective highlights (1) key features of the anionic electrochemical activities; (2) computational and experimental tools to characterize and quantify the anionic activity; and (3) design principles that correlate the chemical and structural compositions with high reversible capacity to accelerate the discovery of novel cathode oxides for next generation Li-ion batteries.



1. INTRODUCTION

In the past four decades, progress has been made steadily to improve the energy density of the various cathode materials. In the 1970s, Whittingham demonstrated that layered TiS_2 could be a cathode material for a lithium rechargeable battery,¹ though the voltage versus a lithium metal anode was only about 2.2 V. In 1980, Goodenough and Mizushima² showed that an open-circuit voltage versus lithium of 4.0 V could be achieved using LiCoO_2 as the cathode material. Although it was not until 1991, that the material and its derivatives $\text{Li}(\text{Co}, \text{Ni})\text{O}_2$ were used in commercial lithium ion batteries enabling the wireless revolution.³ It was soon realized that only half of the lithium could be extracted from LiCoO_2 before a major phase transition occurred, leading to a significant capacity loss and in the extreme case oxygen loss.^{4–6} Many alternatives of LiMO_2 (M is 3+ cation to replace Co which is expensive and toxic) were explored, including LiNiO_2 ^{7–10} and LiMnO_2 ,^{11–13} and all of these materials consist of close-packed planes of oxygen ions with transition metal ions occupying octahedral sites formed by oxygen ions. However, these layered oxides tend to become disordered or transform into a different structure on partial removal of lithium. Transporting the M ions to the lithium layer is thermodynamically driven, causing irreversible phase changes in the materials. Not much progress had been achieved in improving energy density until 2001 when Ohzuku and Makimura synthesized $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$, delivering 20% more energy density than that of LiCoO_2 .^{14,15} The key materials design concept is

that Ni^{2+} is stable in the presence of Mn^{4+} and $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples are both pinned at the top of the oxygen $2p^6$ band, meaning there will be no voltage step while transferring two electrons from Ni^{2+} to Ni^{4+} . This illustrates the recent trend toward multicomponent transition metal oxides, which creates a large number of possible compositional choices. As shown in Figure 1, chemical substitution of Co^{3+} with Ni^{2+} , Mn^{4+} , and Al^{3+} increases the practical capacity limit from 140 mAh g^{-1} to around 200 mAh g^{-1} . Further substitution of the transition metals by Li has been reported as $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Ni}, \text{Mn})\text{O}_2$ (Li-rich material) by Thackeray's group¹⁶ and Dahn's group.^{17,18} This family of materials has shown superior energy density (see Figure 1) almost two times that of LiCoO_2 . Recently, several works have demonstrated that anion (oxygen) redox in these materials is the main reason for the high reversible capacity over 300 mAh g^{-1} at room temperature.^{19,20} Unfortunately these composites suffer from a limited cycle life and poor rate capabilities. High operating voltage (over 4.6 V vs Li^+/Li^0), beyond the electrochemical stability window of most organic electrolytes, is usually required to activate oxygen redox in these materials. The electrolyte oxidation results in the gradual accumulation of a thick solid electrolyte interphase (SEI) layer on the electrode surface, which causes rapid increase of cell impedance. Furthermore, a considerable amount

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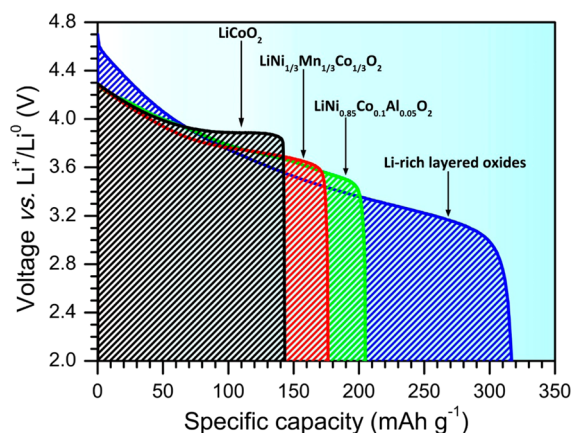


Figure 1. Discharge capacity in different layered oxides. CR2032 coin cells with metallic Li as the counter electrode were assembled to investigate the electrochemical performance. LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$ were cycled between 2.0 and 4.3 V at a current density 20 mA g^{-1} . Li-rich layered oxides were cycled between 2.0 and 4.8 V at a current density 12.5 mA g^{-1} . The loading mass for active material of all layered oxides was around 5.5 mg cm^{-2} .

of lithium ions removal together with oxygen loss from the lattice facilitates cation migration and structural rearrangement. These surface and bulk reactions finally lead to continuous capacity fading and voltage decay during electrochemical cycling, which largely limits the practical deployment of this class of materials in industry. Rate capability refers to how fast an electrochemical system can be charged or discharged, thus determining the power density. It is intuitive to rationalize that smaller particle sizes require shorter diffusion length for full charge/discharge. Nevertheless, the speed of the transport of mobile ions and electrons within the bulk and across the interfaces not only depends on the intrinsic diffusivity and surface chemistry but also on the particle morphology, their size, and their distributions. Often the situation gets more complicated when the reaction in the bulk of the active electrode proceeds with two-phase coexistence, instead of a solid solution. More recent breakthroughs in developing nanoscale LiFePO_4 ,²¹ which has an olivine structure with one-dimensional lithium diffusion channels, successfully demonstrate the importance of controlling size, surface chemistry, and morphology concurrently to the optimization of this novel electrode material reported first by Padhi in 1997.²² It took about 20 years to understand better what are indeed the rate-limiting steps and the relevant dynamic processes in LiFePO_4 .^{23–27} Understanding of the Li-rich layered oxides is still at the infancy stage due to its complex structure, as we will explain below.

The structure of $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Ni}, \text{Mn})\text{O}_2$ differs significantly from that of classical layered oxides such as LiCoO_2 , because additional Li is present in the transition metal (TM) layer inducing cation ordering in the TM layers^{28,29} and symmetry breaking.³⁰ The lithium present in the TM layer leads to formation of a partially ordered honeycomb structure as seen in the end member Li_2MnO_3 , resulting in superlattice peaks between 20° and $26^\circ 2\theta$ (Cu $K\alpha$) in X-ray diffraction (XRD) patterns.^{29,31} Therefore, Li-rich layered oxide is considered either as a solid solution or as a nanocomposite of layered Li_2MnO_3 and $\text{Li}(\text{TM})\text{O}_2$ (TM = Ni, Co, Mn) with excess lithium ions in the transition metal layer. The

discrepancies in Li-rich layered structure determination can originate from the sample variation caused by different synthesis conditions and chemical compositions. Upon lithium extraction, the nickel is oxidized to Ni^{4+} up to 4.4 V. Lithium may continue to be extracted from these materials despite the fact that all the manganese and nickel ions are in their fully charged (+4) oxidation state, which is associated with a plateau region at 4.5 V.^{18,29,32} Significant cation rearrangement occurs upon electrochemical cycling since the superlattice peaks disappear and a secondary phase is detected by synchrotron XRD.³³ Over the past decade, most of the research has been dedicated to explain precisely how the cation migrations occur as a function of the charge/discharge state and the impacts of such dynamic phenomena on electrochemistry. For this purpose, an effective characterization toolset has been established to probe cation migration and rearrangement at both long-range and local length scales, including operando XRD, operando X-ray adsorption spectroscopy (XAS), first-principles calculations, and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). It is not until recently that scientists have focused on the electrochemical activities of oxygen anions in these lithium rich layered oxides.

2. ANIONIC ELECTROCHEMICAL ACTIVITY IN LI-RICH OXIDES

Although there are some discrepancies concerning the structural complexity of Li-rich layered oxide materials, it is generally acknowledged that anionic activity is involved in the electrochemistry besides the cationic redox process, by which extra capacity is obtained. When the material is charged over the transition metal redox reaction region (above 4.4 V for most of the Li-rich materials), the reversible oxygen redox process ($2\text{O}^{2-} \rightarrow \text{O}_2^{n-}$, where $n = 1, 2$, or 3) dominates in the bulk to compensate charge changes during delithiation.³⁴ Oxygen gas has also been detected which results in a large irreversible capacity. At the same time, the lattice oxygen removal in terms of O_2 gas or LiO_2 , Li_2O_2 , or Li_2O solids results in oxygen vacancy formation on the surface and subsurface (5–10 nm range from the surface).³⁴

Meng and co-workers^{35,38–40} systematically studied the effect of oxygen vacancies on structural transformation of Li-rich material during electrochemical cycling. At lower lithium concentration (Figure 2a), the shape of oxygen 2p electron clouds begins to distort, suggesting a potential change of oxygen valence that may promote oxygen vacancies formation.³⁵ As confirmed by scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS) experiments, oxygen vacancies mostly form near the material surfaces and subsurfaces of 5–6 atomic layers.³⁸ A large fraction of the TM ions in these regions therefore are in under-coordinated octahedral sites which are not stable and spontaneously migrate to the fully coordinated octahedral sites nearby in the Li layer. On the other hand, the Li in the TM layer migrates to the shared tetrahedral site in the opposite site, forming a Li–Li dumbbell. The above two migrations cause the spinel-like phase to create on the surface.³⁵ We would like to point out that this surface phase transformation is different from the formation of the rock-salt phase in Ni-rich classical layered oxides such as $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$. And the surface phase transformation from layered to spinel-like is irreversible upon the following cycles, accompanying the increased percentage of microstrain within the particles, and

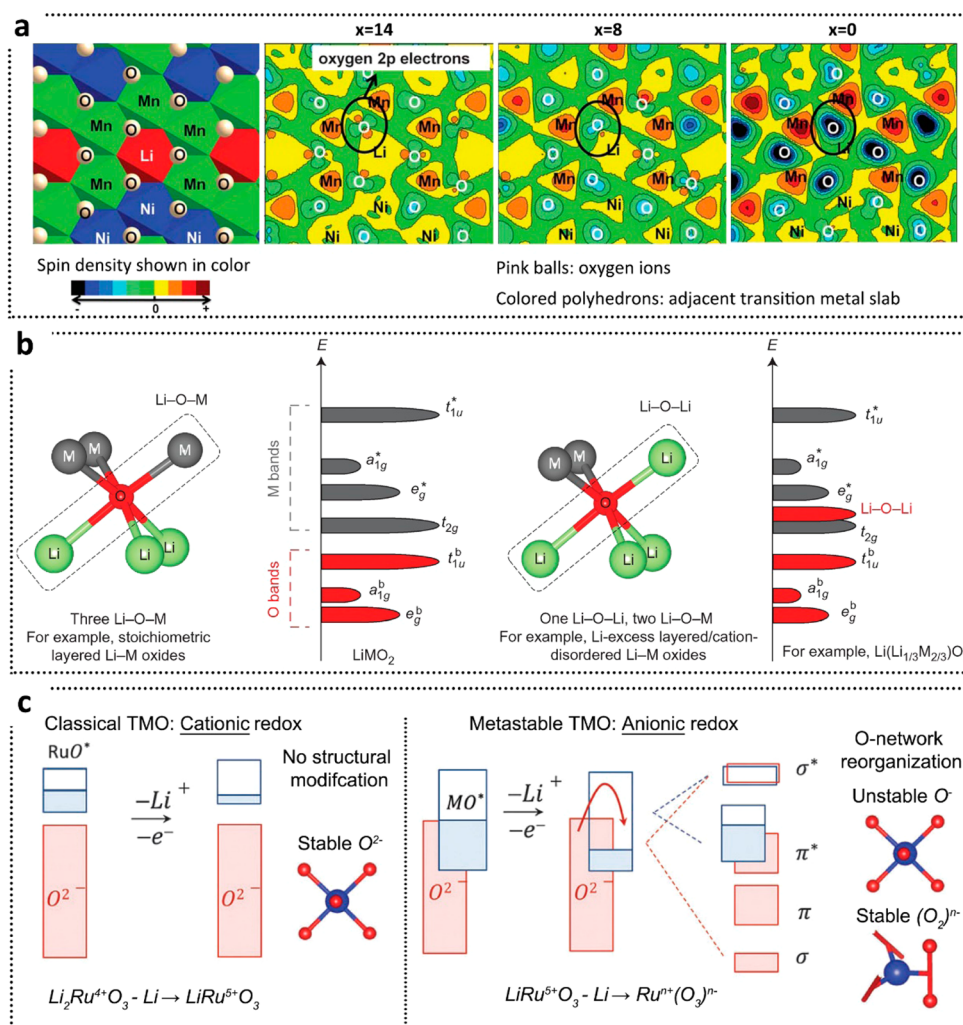


Figure 2. Author: a. Sketch of a partial oxygen layer in $\text{Li}_{x/14}\text{Ni}_{1/4}\text{Mn}_{7/12}\text{O}_2$ and its calculated spin density at different x values. Reprinted with permission from ref 35. Copyright 2011 Royal Society of Chemistry. b. Structural and chemical origin of the preferred oxygen oxidation along the Li-O-Li configuration. Local atomic coordination around the oxygen consisted of three Li-O-TM configurations in the stoichiometric layered Li transition metal oxides (Li-TM oxides). Schematic diagrams of the band structure for the stoichiometric layered Li-TM oxides such as LiCoO_2 . Local atomic coordination around oxygen with one Li-O-Li and two Li-O-TM configurations in the Li-rich layered or cation-disordered Li-TM oxides. Schematic diagram of the band structure for the Li-rich layered Li-TM oxides such as Li_2MnO_3 . The Li-O-Li configurations lead to unhybridized O 2p states (Li-O-Li states) whose energy is higher than that of hybridized O 2p states (Li-O-TM states) and thus more easily oxidized. Reprinted with permission from ref 36. Copyright 2016 Nature Publishing Group. c. Cationic vs anionic redox: qualitative band structure of a structurally stable and metastable transition metal oxide described by strongly covalent TM-O bonds and therefore almost equivalent contributions of TM and O to the redox band. Reprinted with permission from ref 37. Copyright 2016 Royal Society of Chemistry.

finally results in voltage degradation and capacity fading during extended cycles.³⁹ To suppress oxygen gas generation of Li-rich material, one must be able to lower the oxygen partial pressure on the surface of the material. Oxygen vacancies at the subsurface of the as-synthesized Li-rich layered oxides can be introduced through a novel gas-solid interface reaction.⁴¹ Less O_2 gas is released on the surface of the modified Li rich material, which delivers a reversible capacity exceeding 300 mAh g^{-1} at room temperature without an obvious voltage decay.⁴¹

Reversible oxygen redox in the bulk of Li-rich material has been investigated from different aspects. Ceder and co-workers³⁶ apply ab initio calculations to demonstrate that the specific Li-O-Li configurations, which are derived from the excess Li in the transition metal layer, lead to the electrochemically active oxygen states in Li-rich material. As shown in Figure 2b, under these specific configurations, two types of O

2p orbitals are created: (1) hybridized with TM orbitals to form the same hybridized states as in the classical layered oxides and (2) an additional unhybridized orbital in between hybridized O bonding states and the antibonding TM states, making oxygen oxidation and TM oxidation compete with each other to contribute to the extra capacity. O-O bonding (peroxo-like species) resulted from oxygen oxidation tends to form on the condition that TM-O hybridization is not strongly directional. Combining different advanced characterization tools, Bruce and co-workers⁴² prove that, compared with O-($\text{Ni}^{4+}/\text{Co}^{4+}$) interactions, O-($\text{Mn}^{4+}/\text{Li}^+$) interactions possess relatively more ionic and localized O 2p orbitals. Electron transfer can occur from these O 2p orbitals to make the charge be compensated for during excess Li^+ removal, leaving localized electron holes on these less covalent orbitals. On the other hand, Tarascon and co-workers^{43,44} observed O-O bonding formation by the oxidation of O^{2-} to an $(\text{O}_2)^{n-}$ species through

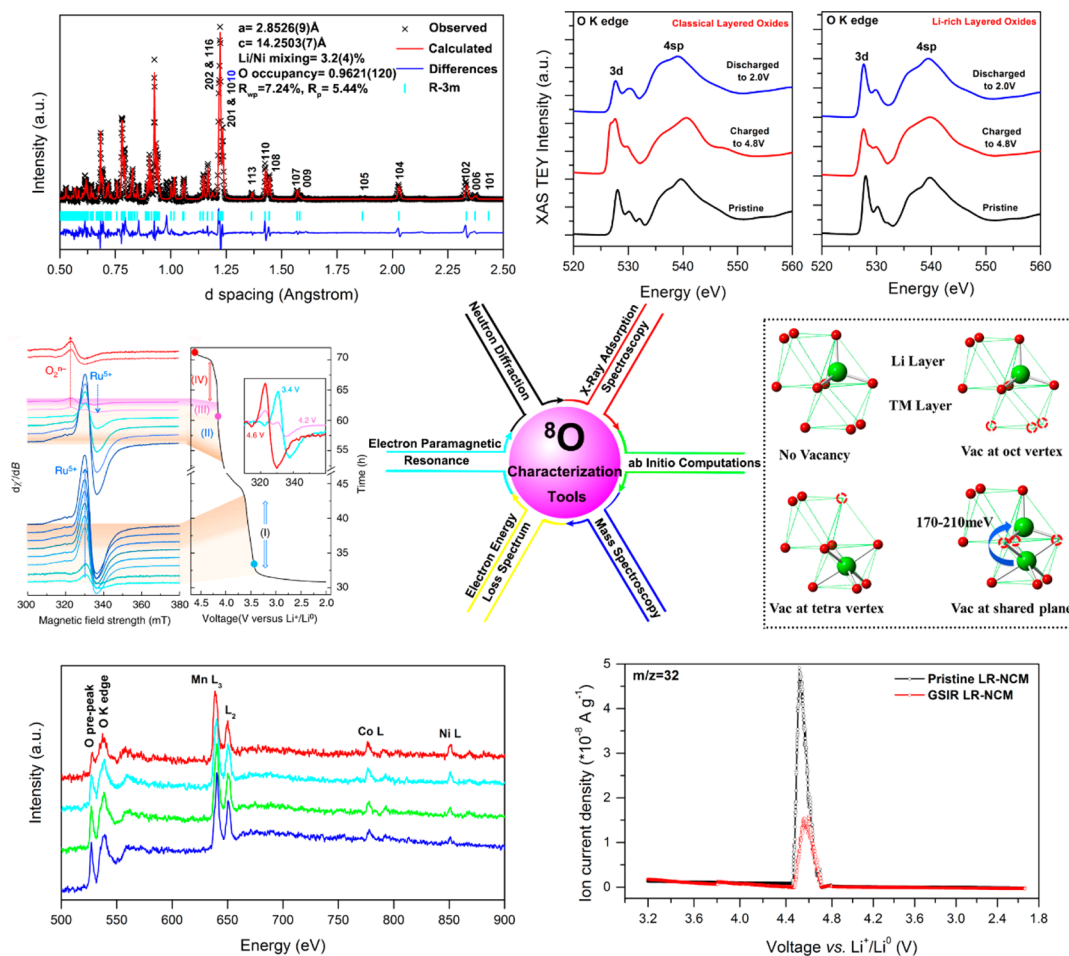


Figure 3. Characterization tools for lattice oxygen in Li-rich layered cathode oxides. The figures for characterizations of neutron diffraction, mass spectroscopy, ab initio computations, and electron energy loss spectrum are from ref 41, and the figure for electron paramagnetic resonance is from the ref 46. Reprinted with permission from refs 41 and 46. Copyright 2015, 2016 Nature Publishing Group.

HAADF-STEM in 4d and 5d TM oxides $\text{Li}_2\text{Ru}_{1-x}\text{Sn}_x\text{O}_3$ and $\text{Li}_2\text{Ir}_{1-x}\text{Sn}_x\text{O}_3$. A pronounced $\text{M}(\text{nd})\text{--O}(\text{np})$ metal–ligand hybridization mechanism is proposed for 4d and 5d TM oxides.³⁷ The ligand orbitals are highly delocalized so they form covalent bonds with the d-metals through $\text{M}(\text{d})\text{--O}_2(\sigma)$ interactions (Figure 2c). The $(\text{O}_2)^{n-}$ species will be then stabilized through their interactions over $\text{Ru}\text{--O}$ as well as $\text{O}\text{--O}$ σ -type bonds, therefore forming $\text{O}\text{--O}$ dimers. Moreover, they investigated the formation of $(\text{O}_2)^{n-}$ species and their recombination into O_2 gas in the Li-rich Li_2TMO_3 family.⁴⁵ Although the exact mechanism is still under exploration, a correlation between the oxidation voltage and possibility of $(\text{O}_2)^{n-}$ recombination into O_2 is proposed that the recombination rate is enhanced at higher voltage than that at relatively lower voltage.

All of the investigations unequivocally demonstrate that oxygen participates in the electrochemical activity of Li-rich layered cathode material at high voltage through either an irreversible oxidation with O_2 gas release and/or a reversible redox process with either O-holes or $\text{O}\text{--O}$ dimer formation. $\text{O}\text{--O}$ bonding tends to form in 4d and 5d TM oxides, while localized electron holes on oxygen can exist in 3d TM systems. Different mechanisms have been proposed based on ab initio calculations to study the role of $\text{M}(\text{4d})$ vs $\text{M}(\text{3d})$ on their electrochemical behavior: (1) the holes in O 2p orbital are localized for 3d TM such as Mn, because partially filled d shells

creates strong directional $\text{TM}\text{--O}$ bonds which prevent the neighboring oxygen from rotating;³⁶ (2) more ionic interactions between $\text{O}\text{--}(\text{Mn}^{4+}/\text{Li}^+)$ place the localized O-holes near the top of the oxygen valence band;⁴² and (3) no empty MO^* -orbitals in the Li_2MnO_3 structure close enough to the top of the O-band leads to a partial decoordination of the $(\text{O}_2)^{n-}$ species and O-holes localization.³⁷ More in situ/operando microscopy/spectroscopy characterizations at various length and time scales are still in need focusing on $\text{O}\text{--O}$ bonding formation/O-holes quantification to fully understand oxygen anion electrochemical activities as well as the role of transition metal species on oxygen redox behavior. It is still unclear how the oxygen participation in electrochemical processes will impact the safety and long-term cyclability of the cathodes.

3. ADVANCED CHARACTERIZATION TOOLS FOR CAPTURING OXYGEN ACTIVITY

Compared to TM cations, oxygen anion electrochemical activity is more challenging to experimentally prove and quantify for the following reasons: First, oxygen participates in the electrochemical activity at highly charged states when the partially delithiated oxides are typically very sensitive to high energy electron beam or X-ray source exposure. Second, peroxy-like species and O-holes resulted from oxygen oxidation are extremely reactive and unstable in air and carbonate based liquid electrolytes, which demands advanced characterization

tools with ultrafast time scale resolution. Third, $M(\text{nd})\text{--O}(\text{np})$ metal–ligand hybridization and rehybridization make it intricate to quantify and differentiate cation and anion contributions to electronic structure changes as well as their contributions to the extra capacity. Based on the above considerations, *ab initio* calculations^{35,36,42,37} are extensively applied to investigate oxygen activity as no external interactions can create an adverse effect on the studied subject. On the other hand, a multimodal experimental approach (Figure 3) must be established.

Despite discrepancies concerning O–O dimer formation vs O-holes formation mechanism, it is commonly predicted that O^{n-} species are unstable and partially released from the lattice, which is confirmed by operando differential electrochemical mass spectrometry (DEMS) measurements.⁴² ^{18}O -labeled Li-rich material is used in DEMS measurements to unequivocally demonstrate that oxygen is extracted from the lattice of the cathode material instead of the electrolyte. Oxygen vacancies formed in the lattice can be accurately quantified through neutron diffraction (ND) since neutron scattering length is not directly related to the atomic number but sensitive to light elements such as oxygen.⁴¹ As for local structure and electronic structure information, angular dark field/bright field ADF/ABF-STEM combined with EELS can be utilized due to sufficient contrast for O columns to be discernible.³⁷ Exceptional care must be taken to exclude beam damage influence. Under a strong beam exposure, neutral O atoms are created on the surface of layered oxides via Knotek–Feibelman mechanism and finally injected into the vacuum, leaving oxygen vacancies as well. Soft XAS and electron paramagnetic resonance (EPR) are useful tools to quantify extra charges that arise from oxygen loss or TM redox.^{42,46} O K-edge of soft XAS can clearly show different redox activity between the classical layered and Li-rich layered oxides after charging to a high voltage of 4.8 V. The increase of the 3d/4sp ratio of classical layered oxide indicates a larger amount of unoccupied 3d orbitals from the transition metal ion oxidation, while the decrease of the 3d/4sp ratio of Li-rich material comes from the dramatic change in the local and electronic structure of oxygen, such as the bond length and oxygen vacancies/oxygen holes formation. Overall, such a multimodal characterization toolset (see Figure 3) has been gradually established by scientists across the world to quantify the electrochemical activities of oxygen anions.

4. MATERIAL DESIGN PRINCIPLES BASED ON OXYGEN ACTIVITY

The knowledge gained from the previous studies on oxygen electrochemical activity guides us to surpass the limits of the transition metal redox in conventional intercalation electrodes for next generation lithium-ion batteries. Figure 4a shows our long-term view in utilizing lattice oxygen activity in oxide cathodes. In the classical layered oxides such as LiCoO_2 , lattice oxygen mostly acts as a pillar (host) to stabilize the structure without contributing much too any extra capacity. When extra lithium is introduced to the transition metal layer, both cationic and anionic redox participate in the electrochemical reaction, which may significantly boost overall energy density. Following this trend, $\text{Li}_2\text{O}/\text{MO}$ nanocompositions⁴⁷ are also proposed, in which lattice oxygen redox is considered as the equally dominating redox center. By carefully examining the local structural changes surrounding the oxygen of these benchmark materials, Li/O ratio is one of the key factors to determine the utilization extent of oxygen electrochemistry activity. Figure 4b

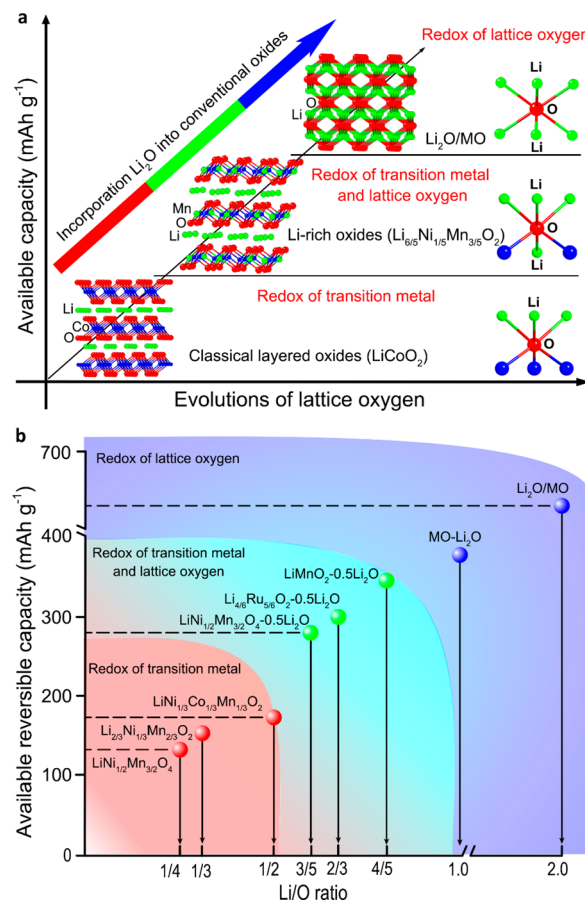


Figure 4. a. Historical utilization of lattice oxygen in benchmark oxides. b. Correlation between available reversible capacity and Li/O ratio in different oxides.

shows the correlation map between theoretically available reversible capacity and Li/O ratio in different oxide cathodes. The entire map is divided into three main sections with three different colors: (1) There is the Li/O ratio between 0 and 0.5 for classical layered and spinel oxides with Li–O–M configuration, where lattice oxygen does not involve in the electrochemical reaction. (2) Next is the Li/O ratio between 0.5 and 1.0 for Li-rich layered oxides with Li–O–Li (M) configuration, where lattice oxygen not only stabilizes the structure but also acts as the redox center which brings in high reversible capacity over 300 mAh g^{-1} . More interestingly, all the compositions in this section can be rewritten as incorporation of $0.5\text{Li}_2\text{O}$ into the classical layered cathode oxides. Recently, a new type of oxide cathodes $\text{Li}_4\text{Mn}_2\text{O}_5$ ($\text{LiMnO}_2\text{--}0.5\text{Li}_2\text{O}$) was prepared with the reversible capacity of 355 mAh g^{-1} , which is ascribed to the redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$, S^{2+} and $\text{O}^{2-}/\text{O}_2^{2-}$ redox couples.⁴⁸ (3) Li/O ratio beyond 1.0 for nanocomposites between Li_2O and metal oxides (MO) with Li–O–Li configuration, where the majority of the reversible capacity is contributed by the oxygen redox, enabling charge/discharge between condensed Li_2O , Li_2O_2 , and LiO_2 without any O_2 gas.⁴⁷ The electrochemical inactive MO can serve as the host to realize oxygen redox activity, and the exact function of MO in these nanocomposites should be further explored. Of course, it is a major challenge to deal with LiO_2 and Li_2O_2 in conventional carbonate based liquid electrolytes. There is an urgent need for novel electrolyte research where solubility and reactivity of these species can be carefully controlled.

5. CONCLUSION

In summary, the recent trend in activating oxygen for reversible electrochemical reactions draws great attention; energy density improvement has been demonstrated though we must be cautious when pursuing further research in this direction. We need to improve the computational and experimental tools to quantify the oxygen activities, quantifying which ones are reversible and which ones are irreversible. Cathode materials and electrolytes should be studied as a whole system as the electrolytes play a critical role for the stability of superoxide and peroxy species. It is also important to study the oxygen electrochemical activities in other layered compounds such as high voltage sodium ion cathode materials. It is expected that the phenomena of oxygen redox behavior can be found in many other electrochemical systems. The oxygen activities can be further tailored by morphology engineering (e.g., nanosizing and shape controlling), compositional optimization (e.g., transition metal species and Li/O or Na/O ratio), and surface modification. It attests to the richness of anionic redox chemistry for novel cathode materials discovery and further inspires the battery community to explore new systems for longer life and higher energy density Li-ion batteries.

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