Exploring the Anionic Redox Chemistry in Cathode Materials for High-Energy-Density Sodium-Ion Batteries

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ABSTRACT: Improving the energy and power densities of sodium-ion batteries is a prime challenge to establish this energy storage technology to be on par with state-of-the-art lithium-ion batteries. The energy density of the sodium-ion batteries is limited due to the lower redox potential of their electrode materials compared to that of the corresponding Li analogues; however, it can be overcome by triggering the anionic redox. Although anionic redox has received significant research interest, a clear understanding of the underlying mechanism for delivery of high capacity by utilizing anionic redox is still lacking. Formidable challenges associated with the utilization of anionic redox such as rapid material degradation, voltage fade, and oxygen release hinder its practical applications. Given the great potential of anionic redox chemistry for developing high-energy batteries, in this mini-review, the recent mechanistic understanding, electrode material degradation pathways including oxygen release, and strategies to trigger anionic redox are discussed. An overview of the existing potential and future research directions of sodium-ion batteries involving anionic reaction is provided at the end.

1. INTRODUCTION

The emission of greenhouse gases due to the burning of fossil fuels and other factors is affecting our climate and resulting in global warming. Climate change is a major driving force for the energy paradigm shift from traditional to renewable sources. However, most of the renewable energy sources require energy storage for smooth operation of the electricity grid. Another key area where utilization of energy storage is thriving is the transportation sector. Vehicles on roads burning fossil fuels contribute a significant amount of greenhouse gases to our environment. Emissions from on-road vehicles can be minimized by using electric vehicles (EVs). At present, the energy storage market is mainly dominated by lithium-ion batteries; however, cost and limited lithium reserves are the bottleneck for energy-demanding storage applications such as grid-scale batteries and long-haul transportation vehicles. This limitation has opened the doors for research on other battery technologies, of which sodium-ion battery technology is at the forefront. There are certain drawbacks associated with sodium-ion batteries, including a larger ionic radius (1.02 Å for Na⁺ and 0.76 Å for Li⁺), a higher atomic mass (23 g/mol for Na and 7 g/mol for Li), and a higher redox potential (~2.71 V for sodium and ~3.04 V for lithium against the standard hydrogen electrode), leading to a decrease in the theoretical energy density. However, unlike lithium, the remarkably high abundance of sodium in the Earth’s crust and seawater potentially makes it a sustainable source for energy storage, which is reflected in the growing number of research publications and patents on this technology in recent years, as shown in Figure 1. Despite the aforementioned merits, sodium-ion batteries are struggling in the current commercial market in order to compete with lithium-ion batteries.

Figure 1. Number of research publications and patents on sodium-ion batteries in recent years (data fetched from Scopus and World Intellectual Property Organization on May 6, 2022).

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The main reason for the slow adoption of sodium-ion battery technology is the lower practical capacity of its cathode materials. To date, several classes of sodium cathode materials have been introduced. These materials include sodium metal phosphates, fluorophosphates, Prussian blue analogues, and layered metal oxides. Layered type cathode materials are of greater interest for sodium-ion batteries because of their higher energy densities due to possible utilization of anionic redox and feasible synthesis methods. Figure 2 classifies different cathode materials with respect to their volumetric capacity and average potential and separates them into following different regions: phosphates and fluorophosphates cathode materials for sodium-ion batteries (orange), layered type cathode materials for sodium-ion batteries (green), and cathode material for lithium-ion batteries (blue). It can be observed that, despite the lower average potential, layered type cathode materials for sodium-ion batteries that are capable of anionic redox can deliver volumetric energy densities (600–800 Ah/L or 2000–2800 Wh/kg) on par with the energy densities of cathode materials for lithium-ion battery, making these materials promising to meet the growing future energy storage requirements. Anionic redox in layered cathode materials for sodium-ion batteries can be triggered by a variety of different techniques; therefore, a concise summary of the anionic redox mechanism is critical for a better understanding and design of high-energy cathode materials for batteries.

In this mini-review, we summarize the recent dominant mechanistic views on anionic redox and introduce the major classes of anionic redox-active cathode materials for sodium-ion batteries by classifying them as 3d, 4d, and 5d metal oxides by the recent examples from the selected scientific literature. Challenges for anionic redox and an outlook for sodium-ion batteries are discussed thereafter.

2. ANIONIC REDOX MECHANISM

Inspired by the discovery of high-energy layered lithium-rich cathode materials for lithium-ion batteries utilizing cationic as well as anionic redox, a great deal of effort has been devoted to design cathode materials for sodium-ion batteries that can exhibit anionic redox. The layered cathode materials for sodium-ion batteries are usually classified into P2, P3, O2, O3′, and O3 types, where P represents the trigonal-prismatic coordination and O represents the octahedral coordination between sodium and oxygen. The numbers 2 and 3 represent the numbers of transition-metal layers with different types of oxygen stacking modes in the structure: for example, ABBA and ABCABC. O3-type cathode materials offer higher capacity compared to P2-type due to the presence of a higher amount of sodium (0.88 to 1 in O3) in the structure; however, the prismatic sodium diffusion path in P2-type cathodes is wider, which results in a lower diffusion barrier and a higher rate capability. Moreover, a phase transition in P2-type cathode materials requires a π/3 rotation of the MO6 octahedron; thus, the structure of P2-type cathodes is more stable and undergoes fewer phase transitions during electrochemical sodium extraction and insertion. Despite several merits, typical P2, P3, and O3 cathode materials relying on cationic redox cannot deliver capacity high enough to compete with lithium-ion batteries. Moreover, a variety of different crystal structures exists in case of cathode materials for sodium-ion batteries that makes it difficult to adopt a unified strategy to trigger anionic redox in sodium-ion batteries. Therefore, several different techniques have been successfully deployed to develop anionic redox capable high-energy cathode materials.

### 2.1. Structural Requirements of Anionic Redox

In lithium-ion batteries, anionic redox is usually triggered by the introduction of excess lithium in the transition-metal layer that generates nonbonding 2p states of oxygen. However, it is difficult to implement this strategy in cathode materials for sodium-ion batteries, as practically P2- and P3-type cathode materials have significantly less than a stoichiometric amount of sodium in the structure. The typical sodium content and crystal structures of P2-, P3-, O3-, and O3′-type cathode materials along with their synthesis temperature are summarized in Figure 3. Additionally, a mismatch between sodium-ion size and 3d transition-metal size makes it difficult to stabilize sodium in the transition-metal layer. To deal with this difficulty, researchers have inserted alkali metals with a smaller ionic radius such as lithium in the transition-metal layer to form an alkali-rich cathode material or sodium-rich cathode materials with larger and highly covalent 4d and 5d transition metals such as Sn, Ru, and Ir.

![Figure 3](https://doi.org/10.1021/acsomega.2c03883)
sodium. It is clear that increasing the energy density of cathode materials is challenging and anionic redox is a feasible way to go.

The removal of alkali metal from cathode materials during the charge process oxidizes the transition metal and shortens the transition-metal–oxygen bond length resulting in stronger TM(d)–O(2p) hybridization. At this point, further charging at high voltage results in the formation of holes in these hybridization states, followed by oxygen release. Oxygen release from lithium-rich cathode materials at high voltage has been considered to be irreversible; however, recent studies show that the evolution of oxygen gas is not entirely irreversible. With a rational structural manipulation, it is possible to remarkably tune the reversibility and activity of anionic redox, particularly in cathode materials for sodium-ion batteries, without synthesizing a sodium excess cathode material. This phenomenon opened new opportunities for designing high-energy cathode materials for sodium-ion batteries that are not seen in lithium-ion batteries.

2.2. Reversibility of the Anionic Redox. Anionic redox-capable cathode materials can deliver high capacity; however, to date stabilization of anionic redox is a challenge. In recent theoretical studies, it was explained that the presence of O(2p) lone pairs plays a critical role in triggering and deciding the reversibility of anionic redox. The number of these O(2p) lone pairs is bound to the ratio of oxygen to the transition metal (O/M ratio) in the structure. This ratio is 2 in AMO₂ type cathode materials, 3 in A₂MO₃ type cathode materials, and 6 in A₃MO₆ type cathode materials. The average numbers of O(2p) lone pairs are zero, one, and two in materials with O/M ratios of 2, 3, and 6, respectively. These lone pairs are formed as the amount of oxygen increases compared to that of the transition metal, where all the O(2p) states cannot be hybridized to metal d states. Hybridization of O(2p) with alkali-metal s states is not feasible due to the larger energy difference. These lone pairs are not present in stoichiometric AMO₂ type cathode materials, as shown in Figure 4a. Lone pairs exist in case of A₂MO₃ and A₃MO₆ type cathode materials, and the energy level of lone pairs (or nonbonded O(2p) states) lies above the hybridized O states but lower than the transition-metal antibonding states, as shown in Figure 4b. These lone pairs are regarded as Na–O–Li states in some of the literature. Motivated by this concept, several alkali-metal-rich cathode materials were synthesized to attain a higher number of nonbonded O(2p) states by different methods. Interestingly, for sodium-ion batteries, sodium-deficient class P2- and P3-type cathode materials can also demonstrate anionic redox. P2-type cathodes have garnered interest recently due to the low sodium diffusion barrier and appropriate phase stability; however, this material is still plagued with several challenges such as Mn⁴⁺ and Jahn–Teller distortion owing to the t₂g electronic configuration. Anionic redox in this class of cathode material can be activated by substitution of an alkali metal in the transition-metal layer.

Theoretical investigations suggest that Coulombic interactions U and charge transfer term Δ also play a role in the degree of anionic redox in the cathode materials. The charge transfer term Δ is the energy difference between (M−O) bonding and (M−O) antibonding states, and it relies on the electronegativity difference between the transition metal and oxygen, whereas U represents the d–d Coulombic interactions that can further split the (M−O)⁰ bands resulting in empty upper and filled lower Hubbard bands. Based on the values of U and Δ, three scenarios can be obtained: cationic redox will occur when U ≪ Δ, (irreversible) anionic redox will occur when U ≫ Δ, and cationic and (reversible) anionic redox may exist together for U/2 ≈ Δ, as the energies of the lower Hubbard band of the metal and O(2p) band almost overlap in this case, as shown in Figure 4c–e. When the energy values of two states are close, electron transfer can lead to structural disorder, resulting in reduced O−O distance and formation of M−(O₂)⁰ interactions. This phenomenon is known as the reductive coupling mechanism that lowers the overall energy of the system but results in distortion of the octahedron. In this case, M−O₂ covalency is usually the deciding factor for the reversibility of the anionic redox. M−O₂ covalency can be tuned by the selective use of 3d, 4d, or 5d transition metals. Strategies to trigger anionic redox by designing novel layered cathode materials for sodium-ion batteries are discussed below.

3. LAYERED CATHODES WITH ANIONIC REDOX

3.1. 3d Transition-Metal-Based Cathode Materials. Na₈[AₓMn₁₋ₓ]O₄-type cathode materials have been extensively studied as future materials for commercial sodium-ion batteries due to their low cost and abundant materials. Nobel laureate J. B. Goodenough’s group reported a P3-type Na₉-xLiₓMn₀.₈O₄ cathode material that delivered a high capacity of 150 mAh/g with a high voltage plateau at 4.2 V in the first charge. This high voltage plateau is usually representative of anionic redox, and they further confirmed it by using XPS that indicated the formation of holes in O(2p) states. da la Llave et al. further investigated this material by using a combination of theoretical and experimental techniques; by calculating the density of states (DOS) they attested that unpaired oxygen bands reside closer to the Fermi level than Mn bands, making it possible for oxygen to reversibly contribute to the redox process, a phenomenon similar to that depicted in Figure 4b. These findings were later confirmed by multiple experimental techniques such as the neutron pair distribution function and total X-ray scattering, where the formation of O–O peroxo-like species was directly observed in this material. The stable high capacity of this material is shown in Figure 5a. House et al. demonstrated that, upon charging this material beyond 5 V, oxygen gas is released from the surface of this electrode, as shown in Figure 5f.
In Na$_{y}$[Li$_{x}$Mn$_{3/2}$]O$_{2}$, Mn resides as Mn$^{4+}$, and it is difficult to oxidize it further in an octahedral geometry; as a result, there is a minimal contribution of cationic redox and the risk of gas evolution at high voltage, as shown in Figure 5b. To offset this issue and include the cationic redox, several different variants of this material, including Na$_{0.72}$[Li$_{0.24}$Mn$_{0.76}$]O$_{2}$ and Na$_{0.66}$[Li$_{0.22}$Ti$_{0.15}$Mn$_{0.63}$]O$_{2}$ with some portion of Mn$^{3+}$ along with Mn$^{4+}$ were synthesized; these materials delivered capacities beyond 200 mAh/g due to incorporation of cationic as well as anionic redox. It is interesting to note that anionic redox can be triggered by adding alkaline ions in the transition-metal layer without synthesizing sodium-rich materials. It was later shown that anionic redox is not only limited to the addition of alkali metals; the addition of alkaline-earth metals such as Mg can also trigger this phenomenon in P2-type cathode materials.

The Yabuuchi group demonstrated anionic redox in Na$_{0.66}$[Mn$_{0.23}$Mn$_{0.77}$]O$_{2}$ without having excess alkali metal. This material demonstrated an anomalous high capacity of 220 mAh/g beyond its theoretical capacity by incorporating Mn$^{3+}$/Mn$^{4+}$ cationic and anionic redox. This material introduced a new concept in anionic redox that this phenomenon is not limited to alkali-metal-rich cathode materials. Maitra et al. further investigated this material by using a variety of different experimental as well as theoretical techniques and ruled out the possibility of oxygen release by using operando differential electrochemical mass spectrometry. A DOS calculation showed that, like alkali metal, the presence of an alkaline-earth metal, Mg, also promotes the formation of unpaired oxygen that contributes to the anionic redox. Several other studies were conducted on this material using state of the art synchrotron-based characterization techniques such as mapping of resonant inelastic scattering (mRIXS) and neutron diffraction. Interestingly, diffraction studies show that no significant structural changes take place during the high-voltage plateau in this material; XPS studies confirmed the compensation of charge by unpaired lattice oxygen at high voltage, as shown in Figure 5c. These studies confirmed highly reversible anionic redox during extended cycling of this material with a drawback of a P3–O3 phase transition during initial cycles that compromised its energy efficiency. Anionic redox in this type of cathode material was also demonstrated by the formation of vacancies in the transition-metal layer and doping of other transition metals with a full d-shell such as Cu and Zn.

The capacity in the Na$_{x}$[A$_{y}$Mn$_{3−}$]O$_{2}$ materials is dominated by anionic redox, since Mn delivers little to no capacity in these cathode materials. To overcome this limitation, Meng’s group added nickel in the transition-metal layer, since nickel is a popular electrochemically active transition metal for layered battery cathode materials. They were able to successfully synthesize O3-type Na$_{0.76}$[Ni$_{0.24}$Co$_{0.2}$Mn$_{0.6}$]O$_{2}$ that delivered a high capacity of $\sim$180 mAh/g during the first charge. The contribution of Ni in cationic redox was confirmed by measuring Ni K-edge XANES spectra, as shown in Figure 5d,e. However, this material suffered a noticeable capacity loss due to irreversible oxygen release. Another novel P2-type Na$_{0.76}$[Ni$_{0.24}$Co$_{0.2}$Mn$_{0.6}$]O$_{2}$ with vacancies in the transition-metal layer was reported by the same group. Vacancies in transition-metal layers also contribute toward the formation of non-bonding oxygen and activation of oxygen redox. These materials demonstrated the typical cationic redox region of Ni$^{2+}$/Ni$^{3+}$ below 4.1 V and anodic redox above 4.1 V. Several other attempts to incorporate the benefits of nickel were made: for example, by synthesizing P2-type Na$_{0.66}$[Ni$_{0.33}$Mn$_{0.66}$]O$_{2}$ and Na$_{0.66}$[Fe$_{0.22}$Ni$_{0.22}$Mn$_{0.56}$]O$_{2}$. The presence of a nickel-based example, by synthesizing P2-type Na$_{0.66}$[Ni$_{0.33}$Mn$_{0.66}$]O$_{2}$ and Na$_{0.66}$[Fe$_{0.22}$Ni$_{0.22}$Mn$_{0.56}$]O$_{2}$.
redox pair enhances the cationic redox, but stability and capacity retention still remain a challenge in these materials.

3.2. 4d and 5d Transition-Metal-Based Cathode Materials. A stronger covalent bond exists between 4d and 5d transition metals and oxygen that limits the gaseous oxygen release and promotes the reversibility of anionic redox. Moreover, it is possible to synthesize sodium-rich cathode materials using 4d and 5d transition metals. Motivated by this concept, Tamaru et al. demonstrated the first successful synthesis of monoclinic Na$_2$RuO$_3$ by a solid-state synthesis method. This material delivered a moderate capacity of $\sim$ 40 mAh/g, limited by the Ru$^{4+}$/Ru$^{5+}$ redox pair. They further confirmed that more than one electron could be extracted from this material if honeycomb ordering in the transition-metal layer is achieved by obtaining the following Na[$\text{Na}_{1/3}$Ru$_{2/3}$]O$_2$ structure. Formation of the honeycomb structure was confirmed by the superlattice peaks in the XRD pattern, as shown in Figure 6a. Honeycomb ordering in the transition-metal layer raised the energy level of the $\sigma^*$ antibonding orbital and thus triggered the anionic redox, as shown in schematic representation in Figure 6d,e.12 Thus, honeycomb ordering in the transition-metal layer is considered a requirement for anionic redox in O3-type layered sodium-rich cathode materials. The Tarascon group modified this material by Sn substitution and synthesized a Na$_2$Ru$_{1-x}$Sn$_x$O$_3$ series.11 This material exhibited both cationic Ru$^{4+}$/Ru$^{5+}$ as well as anionic O$^{2-}$/O$^{2-}$ redox. The contribution of anionic redox increases and that of cationic redox decreases by increasing the Sn content in this material, as shown in Figure 6b,c. As a result of the inclusion of anionic redox, the capacity of this material improved, but the stability decreased. Following the success of the Ru-based sodium-rich cathode material, several different compositions and phases were reported. Qiao et al. reported the formation of a Na$_2$RuO$_3$ phase, and by using in situ Raman spectroscopy, they were able to show that 2.7 Na per unit cell can be extracted by charging to 4 V purely based on anionic redox.57 Reversibility was poor in this material, and it was believed that Ru stays in the 5+ state without any change in the oxidation state. However, Otoyama et al. later utilized XAS and UV–vis and demonstrated that Ru could be oxidized from 5+ to 6+.46 Novel prototype materials such as Na$_2$ZrO$_2$ and Na$_2$IrO$_3$ were synthesized and investigated,10,49 and these studies had a scientific impact; however, from a commercial standpoint, sodium-rich cathode materials based on 4d and 5d transition metals are not beneficial because of their higher cost and less availability. In pursuit of low-cost and meaningful sodium-rich cathode materials, 3d transition metals are incorporated along with 4d and 5d transition metals and several compositions such as Na$_2$Ru$_{1-x}$Sn$_x$O$_3$, Na$_2$Ru$_{1/3}$Mg$_{2/3}$O$_3$, and Na$_2$Ir$_{1/3}$Mn$_{2/3}$O$_3$ have been reported.

Figure 6. (a) XRD pattern showing a honeycomb ordering in a Na$_2$RuO$_3$ sodium-rich layered cathode material. (b, c) Control of anionic redox by changing the Sn content in Na$_2$Ru$_{1-x}$Sn$_x$O$_3$ and (d) structural and (e) electronic changes during charging of Na$_2$RuO$_3$. (a), (d), and (e) Adapted with permission from ref 12. Copyright 2016 Springer Nature Limited. (b) and (c) Reprinted with permission from ref 11. Copyright 2015 Elsevier.

Figure 7 summarizes different metals that have been doped in layered cathode materials for sodium-ion batteries. Element highlighted in red are substituted in 3d transition-metal-based layered cathode materials and elements highlighted in blue are used in 4d/5d transition-metal-based layered cathode materials, whereas elementd highlighted in red are substituted in 3d transition-metal-based layered cathode materials. Element highlighted in green are utilized in both 3d and 4d/5d transition-metal-based layered cathode materials. The research efforts on achieving a stable anionic O$^{2-}$/O$^{2-}$ redox. The roles of most of these substituted metals have been described in this mini-review. Despite significant research efforts, in terms of electrochemical stability, capacity, and cost, these materials have a long way to go before penetration into commercial markets. It can be conveniently anticipated that the growing energy storage demand and lack of abundant feasible lithium reserves will further push the research efforts on sodium-ion batteries in the forward direction.

### CONCLUSIONS AND OUTLOOK

The global energy landscape is transitioning rapidly from conventional fossil-fuel-based energy sources to renewable energy sources. To meet these changing needs, stable, sustainable, and low-cost energy conversion and storage media...
are required. Anionic redox can play a critical role in the design of high-energy cathode materials for sodium-ion batteries to make them viable in commercial markets. Despite significant research efforts, a clear understanding of anionic redox is still lacking and there are several factors that can affect the reversibility and capacity delivered by anodic redox in cathode materials. From the unbounded oxygen, covalency to vacancies, there are multiple ways in different materials to activate anionic redox that provide several opportunities and challenges at the same time. Oxygen loss, voltage hysteresis, transition-metal migration, and irreversible phase transition are some of the challenges that need to be addressed to mitigate the rapid degradation associated with anionic redox. There is no single mechanism or strategy to address these challenges. Therefore, a multifold approach from the atomic scale to the particle level will be required to harness the power of anionic redox.

In terms of future outlook, further mainstream applied research is required for a better understanding of the structural changes and overcoming the sluggish kinetics associated with the anodic redox. However, we are optimistic that utilization of cationic as well as anionic redox is the way to go for high-energy sodium-ion batteries. As discussed in this mini-review, anionic redox can be triggered by creating vacancies, adding additional alkali metals, and designing a Na-rich structure, so that no significant extra cost is required to harness the high energy from anodic redox. However, until now there no commercially viable cathode materials with significant anodic redox activity, but with the advancement of modern characterization and modeling techniques, we are optimistic that a better understanding of this phenomenon will prevail in the coming years and high-energy cathode materials will be innovated utilizing the anodic redox.

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