Review Article

Recent Advances in Electrode Materials with Anion Redox Chemistry for Sodium-Ion Batteries

Natalia Voronina and Seung-Taek Myung

Hybrid Materials Research Center, Department of Nano Technology and Advanced Materials Engineering, Sejong Battery Institute, Sejong University, Seoul 05006, Republic of Korea

Correspondence should be addressed to Seung-Taek Myung; smyung@sejong.ac.kr

Received 30 April 2021; Accepted 3 July 2021; Published 30 July 2021

Copyright © 2021 Natalia Voronina and Seung-Taek Myung. Exclusive Licensee Beijing Institute of Technology Press. Distributed under a Creative Commons Attribution License (CC BY 4.0).

The development of sodium-ion batteries (SIBs), which are promising alternatives to lithium-ion batteries (LIBs), offers new opportunities to address the depletion of Li and Co resources; however, their implementation is hindered by their relatively low capacities and moderate operation voltages and resulting low energy densities. To overcome these limitations, considerable attention has been focused on anionic redox reactions, which proceed at high voltages with extra capacity. This manuscript covers the origin and recent development of anionic redox electrode materials for SIBs, including state-of-the-art P2- and O3-type layered oxides. We sequentially analyze the anion activity–structure–performance relationship in electrode materials. Finally, we discuss remaining challenges and suggest new strategies for future research in anion-redox cathode materials for SIBs.

1. Introduction

Lithium-ion batteries (LIBs) are one of the most efficient energy storage devices to power not only portable electronics but also electric vehicles owing to their high energy density and good cycle life. The electrification of vehicles has confirmed the feasibility of LIBs as medium- or large-scale energy devices; hence, the application of LIBs is being expanded toward grid-scale applications to store electricity generated from renewable applications or power plants. This rising demand directly affects the fluctuation of prices of raw materials such as lithium, cobalt, and nickel resources. Economical and ethical concerns for mining raw materials encourage us to search for alternatives to LIBs. Recently, sodium-ion batteries (SIBs) have reemerged as alternatives to LIBs [1, 2], with emphasis on the merit of the raw material costs; namely, lithium resources are unevenly distributed on the Earth’s crust, whereas sodium is present everywhere. Expensive cobalt and nickel elements are the main redox centers for LIBs, whereas inexpensive manganese-based moieties can provide stable electrochemical activity for SIBs. Because of the difference in the standard electrode potential between Li (−3.04 V versus standard hydrogen electrode (SHE)) and Na (−2.7 V versus SHE), there is evident loss of energy density for SIBs compared to that for LIBs when assuming that both systems deliver the same specific capacity [3]. This fact encourages the rational design of high-capacity cathode materials for SIBs to achieve capacities that are comparable to those for LIBs.

The large sodium ion (1.02 Å) can be stabilized in both prismatic (P) and octahedral (O) environments in layered structures, in which the former has a larger sodium layer than the latter owing to the size of the prismatic environment. The oxygen stacking sequence is combined with the environment of sodium ions in the sodium layer, for example, P2, P3, and O3, as proposed by Delmas et al. [4]. O3 layer compounds are stabilized when the sodium content ranges between 0.9 and 1 in Na_xTMO_2 (TM: metal), where the TM has an average oxidation state of ~3+; however, sodium-deficient Na_xTMO_2 (0.7 ≤ x ≤ 0.4) compounds are crystallized into P2 and P3 structures that show average oxidation states of Me over 3.3+. This affects the first charge capacity; namely, the first discharge capacity is always higher than the charge capacity for P2 and P3 compounds because of the sodium deficiency in the sodium layers. Thus, additional presodiation or the use of additives is needed to increase the first charge capacity and achieve a coulombic efficiency (CE) close to 1 [5, 6]. The large size of sodium ions also induces successive structural changes during the extraction and insertion of sodium ions. The resulting interlayer distance of the O3 layer...
structure is common to see more phase transitions in O3 layered compounds. Therefore, it is generally accepted that P2- and P3-type layered cathode materials typically deliver higher capacity, reaching approximately 200 mAh g\(^{-1}\), with better capacity retention than O3 layered compounds, which usually have capacities of approximately 120 mAh g\(^{-1}\) based on the redox reaction of transition metal elements.

Indeed, the capacity contributed by transition metal elements is limited in those layered compounds. The anionic redox process enables delivery of additional capacity, such that sodium ions can be additionally de/intercalated from/into the structure; namely, the combination of cationic and anionic redox reactions provides more capacity. This type of chemistry has been demonstrated in Li-rich manganese oxide systems (Li\(_2\)MnO\(_3\) [7–9], Li\(_{1.2}\)TM\(_{0.8}\)O\(_2\) [10–12], and their derivatives [13–16]) that have provided capacities to their theoretical limit. These anionic redox can contribute to additional capacity, thereby increasing the specific energy density of the battery. This phenomenon has been observed in overstoichiometric lithium compounds, where lithium partially replaces transition metals (TMs) with typical feature of Li[Li\(_x\)TM\(_{1-x}\)]O\(_2\) (TM: Ni, Co, Fe, Cu, etc.) [12–14] or Li\(_{1-x}\)TM\(_{1-x}\)O\(_2\) (TM: Ru and Ir) [15, 16]. These materials provide a higher capacity than the theoretical value obtained from a redox pair TM. The former compounds based on 3d metal (Mn) are of interest due to their high capacity in excess of 250 mAh (g-oxide)\(^{-1}\). However, they still suffer from voltage drop and irreversible capacity loss associated with migration of cations in the crystal lattice and the release of oxygen during the charging process. The latter compounds based on 4d (Ru) and 5d (Ir) metals have attracted considerable attention from a fundamental and theoretical point of view. It was found that the transition from 3d (Mn) to 4d (Ru) or 5d (Ir) metals can increase the covalence of TM–O and stabilize oxygen-redox reactions. This higher covalence increases the structural rigidity and reduces the stress associated with the removal of lithium ions from the structure. This concept is also applicable to SIBs, which has triggered the intensive investigation of cathode materials from their synthesis to the elucidation of the mechanism of the anionic redox (Figure 1(a)). During deintercalation of charge carriers, the Fermi level lowers to the top of O 2p bands, spontaneously generating excess electrons accompanying deintercalation of charge carriers to prevent structural collapse, and vice versa during intercalation (Figure 1(b)). That is, electron transfer is solely contributed by the oxygen activity, of which the resulting TM–O distance becomes shortened as a result of the oxidation of oxygen. Therefore, additional capacity is delivered along with the contribution by the redox reaction of transition metal elements. Electrochemical oxidation of anions is more facile than the reaction during reduction, and this approach can balance the abnormal CE during the first cycle, potentially obviating the need for presodiation or additives to compensate for the low first charge capacity for P2 and P3 layered compounds.

The selection of elements in transition metal layers is of great importance in improving the reversibility and controlling the operation voltage of the anionic redox reaction, namely, Na\(_x\)[A\(_{-}\)TM\(_{1-x}\)]O\(_2\) (A: Li [17–29], Na [30–45], Mg [46–56], Zn [57–60], Ni [61–68], Cu [67–70], Fe [71, 72] or vacancy [54, 55, 73–81]; TM: Mn [17–29, 46–70, 73–85], Ru [30–42, 85, 86], or Ir [43–45, 87]). There are widely accepted requirements for oxygen-redox reaction, namely, a local Na-O-A coordination medium for the redox activation of oxygen in layered Na\(_x\)[ATM]O\(_2\) for P2, P3, and O3-type layered compounds. The presence of the Na-O-A configuration triggers anionic reactions that depend on structures through the irreversible release of O\(_2\), reversible redox process, and hysteresis process. The migration of these Li and Na in the transition metal layers to the Na layers causes the formation of a lone pair of electrons in the O 2p orbital, so that the high density of state energy for the oxygen allows the oxidation of oxygen although the reaction is kinetically slow. Herein, we review the current status of research and remaining challenges for the anionic reaction and associated mechanisms for different structures and elements of cathode materials for SIBs.

2. Sodium-Deficient Layered Structures

Sodium-deficient layered compounds, Na\(_x\)[A\(_{-}\)TM\(_{1-x}\)]O\(_2\) (A: Li [17–29], Mg [46–56], Zn [57–60], Ni [61–66], or Cu
Theoretically possible because of the difficulty of the oxidation of Mn
to higher valence states in an octahedral environment, in which the
electrolyte does not decompose. In contrast, the divalent Ni and Cu participate in the redox
process, which, in turn, provides additional capacity together with the oxygen redox process. This chapter discusses the effects of those substituents on the operation voltage, capacity, and related oxygen redox mechanism.

2.1 P2-Type Layered Compounds. The P2-type layered structure is stabilized in forms of Na$_{x}$[A$_{1/3}$TM$_{2/3}$]O$_2$ (0.4 ≤ x ≤ 0.8), for which a third of the TM layers can be filled by mono- or divalent elements such as Li [17–29], Mg [46–56], and Zn [57–59] to induce an average oxidation state of Mn of 4+. Hence, the extraction of sodium ions in the structure is not theoretically possible because of the difficulty of the oxidation of Mn$^{4+}$ to higher valence states in an octahedral environment, in which the electrolyte does not decompose. In contrast, the divalent Ni and Cu participate in the redox

2.1.1 P2 Na$_{x}$[Li$_{y}$Mn$_{1-y}$]O$_2$. The presence of the low-valence metal, Li, in the TM layers is intriguing because more sodium can be adopted in the Na layers for charge compensation while maintaining the Mn oxidation state of 4+. The first attempt was made by Yabuuchi and coworkers [17] for P2 Na$_{x}$[Li$_{1/2}$Mn$_{3/2}$]O$_2$ with a valence of Mn$^{3.89+}$ (Figure 2(a)). The large amount of sodium was beneficial for the delivery of a high charge capacity, as P2-type cathode materials always suffer from a small charge capacity compared with the discharge value. The delivered capacity was determined by the oxidation state of Mn, such that the Na$_{x}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ should have delivered a small charge capacity, assuming the oxidation of Mn$^{2+}$ to Mn$^{4+}$. The delivered first charge capacity was intriguingly high (over 170 mAh g$^{-1}$) and accompanied by the partial formation of an O2-like P2 phase with a short interlayer distance, which could not explain the capacity by the cationic redox process because the oxidation of Mn$^{2+}$ to Mn$^{3+}$ does not likely occur in an octahedral environment. The resulting discharge

![Figure 2](image-url)
capacity was also sufficiently high (approximately 200 mAh g\(^{-1}\)) and was retainable with cycling. The authors proposed that partial oxygen loss from the lattice and in-plane rearrangement by partial lithium extraction from the TM layers activates the inactive tetravalent Mn to deliver high capacity. The authors also claimed that the Li in the TM layers is responsible for the increased operation voltage compared with that of Na\(_{0.72}\)MnO\(_2\). Later work by de la Llave and coworkers [21] explored the origins of the good electrode performance of P2 Na\(_{0.66}\)Li\(_{0.22}\)Mn\(_{0.78}\)O\(_2\), which delivered a capacity of \(\sim 190\) mAh g\(^{-1}\). Their thermodynamic investigation demonstrated an energy state of oxygen located close to the Fermi level, which enabled oxidation of oxygen as sodium was extracted from the layered structure (Figure 2(b)). Yabuuchi et al. [17] proposed that lithium from the TM layers migrates toward the sodium layer during the octahedral environment is present at a highly desodiated state such as the O2 or OP4 phase. In this state, the density of states for O 2p was located at a higher energy state than that for Mn\(^{4+}\) 3d [25]; however, the net charge of Mn did not vary during the extraction of sodium ions in the structure (Figure 2(c)). In addition, oxygen was not released from the oxide lattice as the oxidation of oxygen progressed (Figure 2(c)). In addition, oxygen was not released from the oxide lattice as the oxidation of oxygen progressed (Figure 2(c)). In addition, oxygen was not released from the oxide lattice as the oxidation of oxygen progressed (Figure 2(c)). In addition, oxygen was not released from the oxide lattice as the oxidation of oxygen progressed (Figure 2(c)). In addition, oxygen was not released from the oxide lattice as the oxidation of oxygen progressed (Figure 2(c)).

House and coworkers [27] found that the migration of lithium causes in-plane migration of manganese in the structure on charge, such that the lithium in the Na layers moves back to different sites of the TM layers. This disordered arrangement of Li and Mn in the structure is thought to be one of the reasons for the hysteresis in the layered P2 Na\(_{1-x}\)Li\(_{x}\)Mn\(_{1-y}\)O\(_2\) compounds with honeycomb structure (Figure 2(a)). They also compared the hysteresis using superstructured P2 Na\(_{0.66}\)Li\(_{0.22}\)Mn\(_{0.78}\)O\(_2\) (Figure 2(c)). It is worth mentioning that a flat voltage plateau, induced by the O\(^2/3\)-redox pair at ~4.1 V, was observed during charge and discharge for the superstructured P2 Na\(_{0.66}\)Li\(_{0.22}\)Mn\(_{0.78}\)O\(_2\). In this case, Mn migration is suppressed although lithium moves to the Na layers (Figure 2(f)); the improved in-plane ordering is responsible for the reversible flat plateau with high operation voltage on charge and discharge. Notwithstanding, the behavior became less evident as repetitive lithium migration and recovery progressed because of the in-plane disorder in the superstructure.

This series of cathode materials utilize less than 36% oxygen in the lattice, implying that most cases have a high average oxidation state of Mn of higher than 3.5+. Because Jahn–Teller distortion is predominant in Mn\(^{3+}\)O\(_6\) octahedra, it is mainly observed in the deeply discharged state, which usually accompanies the formation of the P2’ structure. However, the aforementioned P2 Na\(_{0.66}\)Li\(_{0.22}\)Mn\(_{0.78}\)O\(_2\) compounds first reduce the oxidized oxygen (O\(^{\sim 2+}\)) to O\(^{2-}\) in the high-voltage region, after which Mn initiates its reduction from Mn\(^{4+}\) to Mn\(^{3+}\) until the end of discharge. Through this process, the average oxidation state of Mn is usually higher than 3.5; therefore, the Jahn–Teller distortion appears less dominant at the end of sodiation, Na\(_{0.66}\)Li\(_{0.22}\)TM\(_{0.78}\)O\(_2\) (0.9 \(\leq \delta \leq 1\), \(\gamma \leq 1/3\)), without notable formation of the P2’ structure, which is affected by the presence of Jahn–Teller distortion.

Cao et al. [29] stabilized the oxygen-redox chemistry in P2 Na\(_{0.66}\)Li\(_{0.22}\)Ru\(_{0.78}\)O\(_2\). Lowering of the transition metal d energy is possible using 4d or 5d elements such as Ru and Ir; hence, the oxygen redox can be active in the nonbonding state of O2. Ru\(^{4+}\) was first oxidized to Ru\(^{5+}\), and further desodiation led to oxidation of oxygen, resulting in additional capacity but no evolution of O2 gas from the crystal structure. The series of reactions resulted in a discharge capacity of \(\sim 160\) mAh g\(^{-1}\). As more covalent character is seen for the elements on the right side of the periodic table, the migration of Li to the Na layers was suppressed even though the oxygen redox was dominant in the Z-phase region, like the O2 or OP4 phase that provides octahedral coordinates, for the highly desodiated state. The suppression of lithium migration and lack of O2 release enabled reversible electrochemical reaction for 500 cycles.

2.1.2. P2 Na\(_{x}\)Mg\(_{y}\)Mn\(_{1-y}\)O\(_2\). The importance of the Na\(^+\)--O(2p)--Li\(^+\) interaction for progression of the oxygen redox in the lattice of P2 Na\(_{x}\)Li\(_{y}\)Mn\(_{1-y}\)O\(_2\) was explained in the previous section. Yabuuchi et al. [46] proposed the highly reversible electrochemical activity of P2 Na\(_{0.62}\)Mg\(_{0.28}\)Mn\(_{0.78}\)O\(_2\), which does not include vacancies in the TM layers and for which Mn has a valence state of \(\sim 3.85\). It was proposed that 0.15e\(^-\) could be used to induce the change of Mn to Mn\(^{3+}\) during charge, which may result in \(\sim 40\) mAh g\(^{-1}\) of capacity assuming a Mn\(^{3+/4+}\) redox. Surprisingly, the compound delivered a charge capacity of \(\sim 150\) mAh with a plateau over 4.1 V undergoing a phase transition from P2 to O2, whereas the recovery on discharge was \(\sim 210\) mAh g\(^{-1}\) even though there was a gradual decay in the capacity with cycling (Figure 3(a)). They reasoned that oxygen-related activity or the partial loss of oxygen was associated with the activity of the compound, although a small portion derived from the oxidation of Mn\(^{3+}\) to Mn\(^{5+}\) (~15%) was available for the first charge capacity. Clement et al. [47] observed structural stability in Na\(_{x}\)Mg\(_{y}\)Mn\(_{1-y}\)O\(_2\) (\(y = 0 - 0.1\), which led to the suppression of the Jahn–Teller distortion by Mn\(^{3+}\) and potential Mn\(^{3+}/Mn^{4+}\) ordering in the structure. Later, Maitra et al. [48] confirmed the availability of the oxygen-redox chemistry in P2 Na\(_{0.23}\)Mg\(_{0.28}\)Mn\(_{0.72}\)O\(_2\), which does not require excess alkali metal such as lithium in the TM layers of the compound. According to their combined studies of O K-edge X-ray absorption (XAS) and resonant inelastic X-ray scattering (RIXS), the voltage plateau above 4.1 V, with the phase transition from P2 to O2 or OP4, can be attributed to the reaction of the electron-
deficient oxide ion (oxygen hole) in the 2p orbital interacting with the Mg$^{2+}$ 3s and Mn$^{3+}$ 3d orbitals. Charge compensation was achieved via this reaction, resulting in the extraction of sodium ions from Na$_{2/3}$[Mg$_{0.28}$Mn$_{0.72}$]O$_2$. It is interesting that the 3s state of Mg$^{2+}$ is higher than the 2p state of oxygen according to the DFT calculation, implying a weak ionic bond of Mg–O that is similar to that of Li–O in Na$_x$[Li$_{1-y}$Mn$_y$]O$_2$ (Section 2.1.1). This finding suggests the placement of the O 2p orbital at the top of the valence band (Figure 3(b)). Mg$^{2+}$ did not migrate, which is different from the Li$^+$ migration in Na$_{0.5}$[Mg$_{0.25}$Mn$_{0.75}$]O$_2$, and O was not released during the electrochemical reaction [48, 53]. House et al. [52] confirmed the origin of oxygen loss through comparison of P2 Na$_{2/3}$[Mg$_{0.28}$Mn$_{0.72}$]O$_2$ and P2 Na$_{0.78}$[Li$_{0.25}$Mn$_{0.75}$]O$_2$. Even when Na$_{2/3}$[Mg$_{0.28}$Mn$_{0.72}$]O$_2$ was charged to 5 V, there was no indication of oxygen evolution or Mg migration. In addition, charging of Na$_{0.78}$[Li$_{0.25}$Mn$_{0.75}$]O$_2$ to over 4.5 V resulted in a clear decrease in the lithium concentration in the structure (Figure 3(c)). Hence, the authors proposed that lithium migration results in oxygen underbonding in the lattice, which triggers oxygen loss together with lithium loss from the surface of Na$_{0.78}$[Li$_{0.25}$Mn$_{0.75}$]O$_2$. This behavior is related to the stronger bond of Mg–O relative to that of Li–O, enabling oxygen-redox activity without excess alkali metal ions in the TM layers. Dai et al. [82] verified the availability of the oxygen redox of Na$_{2/3}$[Mg$_{1/3}$Mn$_{2/3}$]O$_2$ throughout cycling using mRIXS (m: mapping) (Figure 3(d)). The emission energy emerging at 523.7 eV repeatedly appeared at different charge ends, such as the 1st, 10th, 50th, and 100th cycles, whereas the signal was not visible at the end of discharge. This finding indicates that the obtained capacity can be attributed to both cationic and anionic redox processes during cycling.
The presence of vacancies \( \square \) in TM layers also helps accelerate the oxygen-redox reaction by forming Na–O–Mg and Na–O–\( \square \) configurations [54, 55]. Interestingly, the Mg-deficient P2 \( \text{Na}_{0.63}[\text{Mg}_{0.143}\text{Mn}_{0.69}\text{O}_2] \) underwent a single-phase reaction during de-/sodiation, which agrees with the results proposed by Bai et al. [58] and Zheng et al. [59]. Although a strong covalence was expected, the phase transition from P2 to OP4 was inevitable in the high-voltage region. Importantly, the average oxidation Mn was higher than 3.5\(^{\circ}\), which can effectively minimize the cooperative Jahn–Teller effect during cycling. These intrinsic properties resulted in good capacity retention upon cycling (Figure 4(b)); however, further elaboration is required to not only improve the rate capacity but also raise the operation voltage. Konarov et al. [60] circumvented these demerits of \( \text{P2 Na}_0.63[\text{Zn}_{0.25}\text{Mn}_{0.75}\text{O}_2] \) by replacing half of the Zn\(^{2\circ}\) with Ni\(^{2\circ}\). The observed average discharge voltage was approximately 3.5\(^{\circ}\), and their \( \text{Na}_{2/3}[\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Mn}_{0.7}]\text{O}_2 \) was able to deliver a capacity of over 70 mAh g\(^{-1}\) even at a rate of 10C (Figure 4(c)). Such improvement was attributed to the presence of the Ni element, which provided improved electrical conductivity and activity of the Ni\(^{2+/3\circ}\) redox reaction.

2.1.4. \( \text{P2 Na}_{2/3}[\text{A}\text{Mn}_{1/3}\text{O}_2] \) (A: Ni, Cu, and Fe). \( \text{P2 Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2] \) is known to provide a reversible Ni\(^{2+/3\circ}\) redox reaction with three voltage plateaus at 3.2, 3.6, and 4.1\(^{\circ}\), whereas the tetravalent Mn does not participate in the electrochemical reaction. The desodiation leads to the formation of the O2 phase accompanied by a large volume change of approximately 23\% that induces cracking of particles; hence, the material suffers from severe capacity fade during cycling. Recently, this material was revisited to relate the high-voltage reaction occurring over 4.1\(^{\circ}\) to the oxygen-redox reaction [61–72]. Ma et al. [61] investigated \( \text{Na}_{0.78}[\text{Ni}_{0.23}\text{Mn}_{0.09}\text{O}_2] \) with 7\% vacancies in the TM layers. The desodiation induced the oxidation of Ni\(^{2\circ}\) toward Ni\(^{3\circ}\), and the oxidation of oxygen was also confirmed by XAS when Ni was oxidized to 4\(^{\circ}\), which corresponds to the plateau seen over 4.1\(^{\circ}\). Later, Cheng et al. [62] and Dai et al. [67] employed mRIX to confirm the oxygen activity in \( \text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2] \). Similarly, the two-electron reaction was dominant for Ni, whereas the upper voltage plateau over 4.1\(^{\circ}\) was mainly governed by the oxygen-redox reaction. The signature seen at 523\(^{\circ}\) in emission energy was not visible after discharge. Zuo et al. [66] proposed a possible process for the oxygen redox behavior using pDOS data. In the highly desodiated state, the energy of O 2p in the \( \epsilon_{\text{g}} \) (Ni–O) becomes higher than that of Ni 3d, which triggers the oxygen-redox reaction. Zhang et al. [65] observed O2 release from the structure at the highly charge state, which produces a dense Ni2Mn2O7 layer on the outer surface of \( \text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2] \). This, in turn, plays a role in impeding Na\(^{+}\) diffusion, causing irreversible capacity in the first cycle. They circumvented the O2 release by introducing a small amount of \( \text{Fe}^{2\circ}\), \( \text{Ni}_{2/3}[\text{Fe}_{2/9}\text{Ni}_{2/9}\text{Mn}_{5/9}\text{O}_2] \) (Figure 4(d)), such that the first irreversible capacity was dramatically reduced to approximately 4\%. According to their thermodynamic calculation, such improvement was related to the redistribution of electrons in the Fe–O–O configuration, for which the energy of oxygen in the pDOS was above the Fermi energy level after
desodiation. This series of reactions is responsible for the suppression of oxygen release in the highly charged state. Co-doping of Cu/Mg was also effective to retain the oxygen-redox reaction associated with Ni redox in Na$_{0.67}$[Ni$_{0.25}$Mn$_{0.75}$]O$_2$ [64]. Note that a prerequisite for oxygen redox is the unhybridized O 2p orbital that is
provided when ionic bonds are present in TM layers, such as in the Na–O–Li (Mg or Zn) configuration. After oxidation of Ni close to Ni⁴⁺, the density of state energy of O 2p in the e_g*(Ni–O) becomes higher than that of the TMs, such that oxygen can be oxidized. In addition, the TM–O bonds are still hybridized, which induces irreversible capacity as a result of

Figure 5: (a) The first charge and discharge curves of P3-type Na₀.₆[Li₀.₂Mn₀.₈]O₂ tested in a voltage range of 3–4.5 V at 10 mA g⁻¹ (reproduced with permission from Ref. [89], Copyright 2019 The Royal Society of Chemistry); (b) O-K mRIXS of P3-type Na₂/₃[Mg₁/₃Mn₂/₃]O₂ at different electrochemical states, showing that red arrows indicate oxidized feature of oxygen (reprinted with permission from Ref. [90] Copyright 2020 Science Publisher); (c) charge and discharge curves on the first cycle for air-Na₀.₆[Li₀.₂Mn₀.₈]O₂ (black) and oxygen-Na₀.₆[Li₀.₂Mn₀.₈]O₂ (red) with an arrow indicating reversible oxygen redox (reprinted with permission from Ref. [91], Copyright (2020) American Chemical Society); (d) in situ DEMS results of gas evolution rates for O₂ and CO₂ collected during the first and second charging process of P3-type Na₀.₅[Mg₀.₁₅Al₀.₂Mn₀.₆₅]O₂ (reprinted with permission from Ref. [92], Copyright (2020) American Chemical Society).
O$_2$ release. The incorporation of more covalent character into the structure using Fe$^{3+}$ in the TM layers suppressed such unfavorable reactions in highly desodiated states. Abate et al. [71] and Li et al. [72] demonstrated the readiness of the oxygen-redox reaction when Fe$^{3+}$ or Cu$^{2+}$ is placed at the A sites in Na$_x$[A$_{y}$Mn$_{1-y}$]O$_2$ rather than Ni$^{2+}$. They reasoned that although the importance of Na–O–Li (Mg or Zn) for oxygen redox in the desodiated state is recognized, the chemical tunings by introducing such substituents can also play a role in leading to a density of state energy close to the Fermi energy level, enabling active oxygen to deliver additional capacity.

2.2. P3-Type Layered Compounds, Na$_x$[A$_{y}$Mn$_{1-y}$]O$_2$ (A: Li, Mg, Ni, and Co). In general, P3 cathode materials have lower crystallinity than P2-type ones because heating P3-type compounds leads to the formation of the P2 phase at elevated temperature, usually over 900°C. Rong et al. introduced flat charge and discharge voltage plateaus in P3 Na$_{0.67}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$ (Figure 5(a)) [88, 89]. Even though the capacity was limited to approximately 100 mAh g$^{-1}$ in the operation range of 3–4.5 V, it is worth noting that the obtained capacity was activated by the pure O$^{2-}$/O$^{1-}$ redox pair. The associated two-phase reaction was responsible for the flat charge and discharge curves; however, the desodiated new phase was refined as another P3 phase with a smaller interlayer distance. Therefore, the migration of Li and Mn from TM layers to the Na sites was difficult due to the larger trigonal prismatic site than the octahedral one, as revealed using neutron diffraction. This immobile feature, in turn, resulted in suppression of O$_2$ release from the lattice. Wu et al. [90] visualized the activity of oxygen for P3 Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$, which was available for cycling (Figure 5(b)). They also pointed out that the observed nonlattice reaction on charge affected the irreversible capacity.

Therefore, the P3 Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$ was able to present the flat voltage plateau activated by the O$^{2-}$/O$^{1-}$ redox pair, which is similar to the behavior of the superstructured P2 Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$ [27]. They proposed two possible factors for the capacity fade, namely, that structural disorder occurred during cycling and growth of the cathode electrolytic interface (CEI) with accumulation of oxygen-related moieties by the irreversibility on charge.

As the efficacy of Mg was confirmed in P2 Na$_{0.6}$[Mg$_{0.25}$Mn$_{0.75}$]O$_2$ (Figure 3(a)), Kim et al. [91] investigated the availability of oxygen redox in P3 Na$_{0.67}$[Mg$_{0.3}$Mn$_{0.7}$]O$_2$. Compared to the charge capacity obtained in P2 Na$_{0.6}$[Mg$_{0.25}$Mn$_{0.75}$]O$_2$, the observed charge curve was rather sloppy and short (Figure 5(c)). The presence of ionic Mg–O was responsible for the oxygen redox process. Jia et al. [92] incorporated Al into the Mg site in TM layers, P3 Na$_{0.5}$[Mg$_{0.15}$Al$_{0.5}$Mn$_{0.35}$]O$_2$. Their operando XRD results demonstrated the suppression of the phase transition toward the O3 phase, although the original crystallinity was greatly reduced at the end of charge. In addition, the phase was recovered to the P3 phase with broadening during discharge. Surprisingly, O$_2$ evolution was perceived on the voltage plateau over 4.1 V during the first charge (Figure 5(d)) [91], which contrasts with the result shown for P2 Na$_{2/3}$[Mg$_{0.25}$Mn$_{0.72}$]O$_2$, where no evolution of O$_2$ was observed up to 5 V (Figure 3(c)). This irreversible process can cause unexpected growth of the CEI layer on cathodes, as mentioned above for P3 Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$. A similar tendency was also observed in Li[Ni$_{0.8}$Al$_{0.2}$]O$_2$ [93], in which oxygen evolution progressed more when Al$^{3+}$ was present in the compound [92]. Similar to P2 compounds [68], reductive coupling was observed in P3 Na$_{0.67}$[Ni$_{0.2}$Mn$_{0.8}$]O$_2$ [94], and small hysteresis was observed as a result of the electroconductive Co$^{3+}$ in P3 Na$_{0.67}$[Co$_{0.2}$Mn$_{0.8}$]O$_2$ [95]. Investigation of the oxygen-redox reaction of P3 has not progressed as much as that for P2 compounds. The voltage plateaus attributed to the oxygen-redox reaction were generally more sloppy and shorter than those observed in the P2 structure. In addition, the cyclability was inferior to that in P2 compounds. These findings may be related to the low crystallinity of the P3 structure compared with that of the P2 compound. In addition, the irreversible O$_2$ evolution, which may induce the formation of a byproduct like Na$_2$CO$_3$, would result in the growth of CEI layers on the surface of cathodes. The suggested concomitant deterioration of electrodes can be circumvented by surface engineering of the active materials to make the oxygen-redox reaction more sustainable throughout cycling.

2.3. P1-Type Layered Compounds (Na$_2$Mn$_3$O$_7$). An important alternative to improve upon the reversibility of oxygen-redox reactions is the use of vacancy-containing materials, as shown for the P2–□$_{4/3}$Mg material in Section 2.1.2. Herein, another P-type sodium-deficient cathode Na$_2$Mn$_3$O$_7$ (Na$_{4/7}$[□$_{1/7}$Mn$_{6/7}$]O$_2$) with □$_{4/7}$ vacancies is presented [73–81]. The layered structure of Na$_2$Mn$_3$O$_7$ with seven Mn site vacancies (4$\sqrt{3} \times 4$ superstructure) is displayed in Figure 6(a) [74]. Na$_2$Mn$_3$O$_7$, with a valence of Mn$^{4+}$, crystallizes in the triclinic P1 structure, with half of the sodium ions occupying the distorted prism sites (P) and the other half occupying distorted octahedral sites (O). Na$_2$Mn$_3$O$_7$ possesses a notable performance with the smallest voltage hysteresis (~50 mV) among the known P2/P3/O3-type cathode materials with oxygen redox (Figure 6(b)) [74]. Furthermore, multiple reports have shown that the delivered capacity is ~210–220 mAh g$^{-1}$ in the voltage range of 1.5–4.5 V, which is one of the highest attainable capacities for sodium cathodes with simultaneous cationic and anionic redox processes [75–77]. Despite the promising low-voltage hysteresis and high capacity, Na$_2$Mn$_3$O$_7$ still suffers from degradation during cycling. Furthermore, the mechanism of the anion redox reaction with such a small hysteresis is still under debate [78, 79].

Na$_2$Mn$_3$O$_7$ was initially studied by Adamczyk and Pralog in the low-voltage range, and it showed a specific capacity of 160 mAh g$^{-1}$ at ~2 V, based only on the Mn$^{3+}$/Mn$^{4+}$ redox reaction [73]. Later, several groups showed that the desodiation of Na$_2$Mn$_3$O$_7$ at high voltage was governed only by the oxygen-redox reaction [75–77]. Inherent manganese vacancies in the TM layer lead to nonbonding 2p orbitals of oxygen $\delta$$_{Mn}$, giving extra oxygen-redox capacity of ~70–80 mAh g$^{-1}$ at high voltage without making the Mn–O bond labile (Figures 6(c) and 6(d)) [74]. In situ synchrotron XRD revealed negligible structural changes in the high-voltage
range, which differs from the behavior of common P2-O2 or P2-OP4 phase transitions in P2-type materials [75]. The high structural stability of the material at high voltage (100% after 45 cycles) was explained by the presence of intrinsic vacancies, which lead to a MnO6 octahedron with six different Mn–O bond lengths that is more robust to desodiation. Thus, the \([\square_{1/2}\square_{3/2}]_2\)O2 slab can self-regulate its deformation and improve the structural stability of the material. However, at low voltage, which is attributed to the manganese Mn3+/Mn4+ redox reaction, a distorted lattice appeared, leading to the formation of a new phase [77]. This distorted structure was induced by the strong Jahn–Teller effect, associated with the presence of Mn3+ upon additional sodium insertion in the low-voltage region.

In light of the common high-voltage hysteresis of oxygen-redox reactions, the origin of the impressive low-voltage hysteresis in Na2Mn3O7 was studied by Song et al. using ex situ XRD [80]. The authors claimed that the well-maintained oxygen stacking sequence together with the absence of irreversible gliding of the oxygen layers and cation migrations resulted in the highly reversible oxygen redox with a negligible voltage hysteresis between charge and discharge. The authors showed that Na-ion extraction from the octahedral site is an essentially zero-strain process, proceeding through a single-phase reaction. The extraction of sodium ions from the prismatic site occurred through a two-phase reaction (P1 - R3) with the shrinkage/expansion process of the vacant MnO6 octahedron and a larger volume change during charge/discharge (Figure 6(e)). However, the overall stacking sequence of oxygen ions was barely changed during both steps of Na extraction/insertion, which differs from the behavior in P2/P3 cathodes, where extraction/insertion of Na lead to the formation of O–P phases with simultaneous decrease of the interlayer distance.

In a recent work, Tsuchimoto et al. confirmed a unique behavior of O in Na2Mn3O7 using DFT calculations and magnetic and spectroscopic measurements (Figure 6(f)) [78]. The existence of thermodynamically favorable \(\cdot \cdot \cdot O_2\) over the peroxide-like \(O_2^{2-}\) dimers was predicted by computations and showed that hole stabilization occurred through a \((\sigma + \pi)\) multiorbital Mn–O bond. Similar predictions were reported in the work of Kitchaev et al., where a \(\pi\)-bonded Mn-d and O-p orbital network formed a collective delocalized redox center [81]. Therefore, the authors concluded that such a \(\pi\)-network rather than any local bonding environment was responsible for the two-step voltage profile with a low-

---

**Figure 6:** (a) Crystal structure of Na2Mn3O7. O coordinated by two Mn is labeled as O1, whereas O coordinated by three Mn is labeled as O2. Mn vacancies exist in the Mn layers. (b) Potential profile (second cycle) of Na2Mn3O7 upon (de)sodiation between 1.5 and 4.7 V versus Na/Na+. (c) Calculated DOS and spatial electron density at \(-0.4 < E – E_f < 0\) eV of Na2Mn3O7. (d) Calculated DOS and spatial hole density at \(0 < E – E_f < 0.55\) eV of Na2Mn3O7 (reprinted with permission from Ref. [74]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (e) In situ synchrotron XRD and lattice parameter evolution of Na2Mn3O7 during the initial charge/discharge cycle (reprinted with permission from Ref. [80]. Copyright 2019 American Chemical Society). (f) O K-edge RIXS and O K-edge XAS of Na2Mn3O7 for pristine, charged to 4.7 V and discharged to 3 V (reprinted with permission from Ref. [78]. Copyright 2021 Springer Nature).
voltage hysteresis and structural evolution observed in Na₂Mn₃O₇.

### 3. Stoichiometric Sodium Transition-Metal Layer Structures NaₓTMO₂ (x ≈ 1)

Sodium stoichiometric layered compounds, NaₓTMO₂ (x ≈ 1) known as O3 type, typically deliver lower discharge capacities than P2/P3-type sodium cathodes. The diffusion of sodium ions in O3-type compounds occurs from one octahedral site to another through face-shared interstitial tetrahedral sites and is characterized by relatively slow diffusion compared with that in P2/P3 structures. However, sufficient Na content reserved in the alkali layer guarantees a high first charge capacity and high coulombic efficiency, which is an advantage for commercial applications. In this part of the article, we will discuss the O3-type cathodes with anionic redox, in which sodium ions are located only in the alkali layer.

#### 3.1. Mn-Based Compounds

A notable example of a O3-type cathode material with anion redox chemistry is Na[Li₁/₃Mn₂/₃]O₂ [85], the analog of Li[Li₁/₃Mn₂/₃]O₂ (Li₂MnO₃). DFT calculations have predicted the possibility of a thermodynamically stable O3-type Na[Li₁/₃Mn₂/₃]O₂ structure [84]; however, for a long time, a variety of experimental conditions did not result in the formation of the pure O3-type structure. A P2-type component, in addition to other phases, was always obtained. Only recently, Wang et al. synthesized O3-type Na[Li₁/₃Mn₂/₃]O₂ (C 2 m) by carefully adjusting the synthesis conditions and stoichiometry [85]. In Na[Li₁/₃Mn₂/₃]O₂, Na and [Li₁/₃Mn₂/₃]O₂ stack alternatively, and Li⁺ and Mn⁴⁺ form a honeycomb ordering within the [Li₁/₃Mn₂/₃]O₂ slabs. Oxygen is coordinated by two Mn, one Li, and three Na to form an O₉M₃Li₉Na₉ octahedron. Theoretical work by Kim et al. [84] highlighted the possibilities of oxygen redox by oxidizing Na-O(2p)-Li to compensate for the electronic charge during sodium extraction in Na[Li₁/₃Mn₂/₃]O₂. The calculated PDOS and net charges of Mn and O confirmed that Mn remains as 4+ and that the oxidation state of O linearly increases during Na removal (Figures 7(a) and 7(b)). Furthermore, their theoretical calculations were confirmed by the experimental work of Wang et al. [85]. Interestingly, the as-synthesized Na[Li₁/₃Mn₂/₃]O₂ material was not sensitive to moisture, and even after soaking in distilled water, it maintained its structure and crystallinity [85]. The delivered first charge capacity was ∼250 mAh g⁻¹ (0.9 Na⁺ extraction), attributed to the oxygen O²⁻/O¹⁻ redox reaction accompanied by partial Li migration from the TM layer to the tetrahedral Na sites and O₂ release. The resulting discharge capacity was ∼190 mAh g⁻¹ and was maintained during 40 cycles. In situ XRD revealed O3(1)–O3(2)–O3(III) structural transformations with a rapid decrease of the c lattice parameter during the O3(II)–O3(III) phase transition at the first charge. Because of the O₂ release and irreversible Li migration, the pristine state of the structure could not be fully recovered after discharge. In addition, partial Li⁺ migration to the interlayer space (alkali-) sites resulted in the formation of vacancies in the TM layer, which caused the in-plane rearrangement of Mn and loss of the honeycomb ordering in the TM layer. In addition to the in situ XRD analysis, Wang et al. performed Mn K-edge XAS and mRIXS analysis, which experimentally proved that both oxygen O²⁻/O¹⁻ and Mn³⁺/Mn⁴⁺ redox were responsible for the delivered capacity.

#### 3.2. Ru-Based Compounds

The stoichiometric sodium Ru-based compounds O3-type Na[Mg₂/₃Ru₁/₂]O₂ and Na[Mg₂/₃Ru₁/₂]O₂ (R3m) with oxygen-redox participation were studied in the work of Jia et al. [96]. Both materials were crystallized in the R3m space group; however, the oxidation state of Ru was different, namely, Ru⁴⁺ in Na[Mg₂/₃Ru₁/₂]O₂ and Ru⁵⁺ in Na[Mg₂/₃Ru₁/₂]O₂, respectively. On the basis of in situ XRD, Raman, and DEMS analyses, it was shown that during the first charge, Na[Mg₂/₃Ru₁/₂]O₂ underwent a simple O3–O3 phase transition; however, due to the O₂ release at the end of charge, a specific distorted structure was formed. A more complicated sequence of O3–O3–P3 phase transitions was observed for Na[Mg₂/₃Ru₂/₃]O₂, accompanied by sluggish kinetics without O₂ loss. The authors claimed that irreversible lattice oxygen loss in Na[Mg₂/₃Ru₂/₃]O₂ and the formation of a distorted structure sacrificed for a more stable structure with solely Ru⁴⁺/Ru⁵⁺ cationic redox for the subsequent cycling. Instead of using redox-inactive Mg²⁺, Voronina et al. proposed to use redox-active Ni²⁺ to provide additional capacity and achieved reversible capacity of 154 mAh g⁻¹ for Na[Ni₂/₃Ru₂/₃]O₂ material [86]. DFT calculations, operando XRD, and XANES revealed reversible cationic Ni²⁺/Ni³⁺ and anionic O²⁻/O¹⁻ redox reactions with no loss of O₂ in the crystal structure of Na[Ni₂/₃Ru₂/₃]O₂.

#### 3.3. Ir-Based Compounds

In analogy to O3-Na[Li₁/₃Mn₂/₃]O₂, the material Na[Li₁/₃Ir₂/₃]O₂ (C 2 c) was proposed and investigated by Perez et al. [87]. The Li atoms preferred to stay in the center of the Ir honeycombs in the TM layer, whereas Na atoms occupied all the octahedral sites in the interlayer space. Cycling the material in a Na cell resulted in the extraction of 1.5 Na⁺/Li⁺ through a complicated multiphase process and subsequent segregation of Li-rich Li₂IrO₃ and Na-rich NaIrO₂ phases. Because of the absence of calculations and further experimental investigation of the reaction mechanism together with the Na/Li exchange during cycling, the authors were not able to arrive at a clear conclusion on the perspectives of this material. Therefore, substituting Li⁺ with less mobile and smaller Mg²⁺ or Zn²⁺ could be a promising future direction in Ir-based stoichiometric compounds with oxygen redox.

#### 3.4. Cr-Based Compounds with Sulfur Redox

Although cathode materials with oxygen-redox reaction have received more attention to date, some studies have also considered cathode materials with sulfur redox. For example, sulfur redox has been recently investigated in stoichiometric Na sulﬁdes, such as O3-NaCrS₂ and O3-NaCrS₂/CrS₂ [97, 98]. Originally, the sulfur-redox chemistry in chalcogenides can be traced back to the work of Whittingham on TiS₂ in 1976 in Li cells [99], and the reaction mechanism is explained
Figure 7: (a-1) PDOS of Mn 3d orbital electrons (purple) and O 2p orbital electrons (red) from $x = 0$ and (a-2) $x = 0.1$ in Na$_{1-x}$(Li$_{1/3}$Mn$_{2/3}$)O$_2$. (b-1) Calculated net charges, based on Bader charge analysis for O and (b-2) for Mn as a function of Na content (reprinted with permission from Ref. [84]. Copyright (2020) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (c) Voltage profile of first charge and corresponding electrochemical reaction. (d) Operando XRD of NaCr$_{2/3}$Ti$_{1/3}$S$_2$ during the first cycle at a rate of C/5. (e) STEM image of pristine and fully charged NaCr$_{2/3}$Ti$_{1/3}$S$_2$ electrodes (reprinted with permission from Ref. [80]. Copyright (2019) Nature Publishing Group).
in detail by Rouxel in 1996 [100]. However, only recently, attempts have been made to utilize sulfur redox in Cr-based Na cathodes. In the work of Shadike et al., NaCrS₂ underwent Na⁺ extraction/insertion through a solid-solution reaction with the occurrence of Cr/Na vacancy antisite (cation migration to the Na layer) with high-voltage hysteresis and poor reversibility [97]. A similar phenomenon of Cr migration to the Li sites was observed earlier in LiCrO₂ oxide [101]. In LiCrO₂, the oxidation of Cr from 3+ to 4+ on charge resulted in disproportionation and further migration of Cr to tetrahedral sites, forming a rocksalt structure. The authors claimed that in NaCrS₂, the migration of Cr occurred without its oxidation, which triggered sulfur redox. The prerequisite for sulfur redox was an unhybridized S 3p orbital that was provided by Cr migration to the Na layer and changed the configuration symmetry around S, resulting in the formation of the Na–S–O configuration.

In an effort to increase the delivered capacity and decrease the voltage hysteresis, which is associated with TM disorder, the authors spearheaded attempts to stabilize Cr in the TM layer through doping of Ti³⁺ into the NaCrS₂ structure [98]. The capacity of NaCrS₂/Tiₓ/3S₂ was boosted to 186 mAh g⁻¹ due to the synergetic effect of the anion S²⁻/S³⁻ and cation Ti³⁺/Ti⁴⁺ redox reactions without Cr participation (Figure 7(c)). The in situ XRD results showed that the material underwent a sequence of O₃–P₃–O₁' phase transitions with the shortening of the a / b lattice parameter and a large reduction of the c lattice parameter in the region of the P₃–O₁' transition (Figure 7(d)). Doping of Ti³⁺ was unsuccessful in preventing Cr migration from the TM layer to Na vacancies in the P₃–O₁' region. However, the authors claimed that migration of Cr was a highly reversible process and that the main reason for the capacity loss was not migration of Cr but the loss of sulfur (Figure 7(e)). Using experimental and theoretical methods, including K-edge XAS, STEM, XPS, and DFT+U, it was possible to trace the different stages of the compensation mechanism such as the formation of electron holes, anionic dimers, and disulfide-like species as well as the precipitation of sulfur. According to those results, various anionic redox chemistries were proposed as follows:

\[ S^{2-} - (2 - n)e^- \rightarrow S^{n-} \text{(electron holes)} (1.92 < n < 2) \]  

\[ 2S^{1.92-} - (3.84 - 2n)e^- \rightarrow (S_2)n - \text{(dimers)} (3.33 < n < 3.84) \]  

\[ 2S^{2-} - 2e^- \rightarrow (S_2)^2- \text{(disulfides)} \]  

\[ (S_2)^2- - 2e^- \rightarrow (S_2) \text{(sulfur)} \]

Electron holes of S were formed at the top of 3p band, which was accompanied with P₃ phase evolution process (Equation (1)). Further, the formation of (S₂)ᵐ⁻ dimers was occurred, and it was triggered by noncoordinated S 3p states (Equation (2)). The weakening of Cr-S electrostatic repulsion caused Cr migration from TM layer to Na layer, resulting in P₃–O₁' phase transformation. The direct observation of Cr migration was obtained using STEM. The anion defects and formation of (S₂)²⁻ (Equation (3)), followed with irreversible oxidation or disproportionation of disulfides to sulfur (Equation (4)), occurred on the surface of the particles with the subsequent sulfur dissolution in electrolyte. The dissolution of sulfur was proved by measuring XPS spectra of the glass fiber separator before and after 10 and 50 cycles.

In conclusion, despite the TM cation migration and lower operation voltage in sulfides than in oxides, the high reversibility of the sulfur redox pushes further research works on chalcogenide materials for SIBs. For mitigation of cation migration, different doping types can be implemented to improve the cycling stability; furthermore, Cr-based chalcogenides can be expanded to different TM chalcogenides.

3.5. Other Compounds. Besides the above-discussed compounds with anion-redox participation, some more Na-stoichiometric cathodes, such as α-NaFeO₂ and NaVO₃, have been reported. α-NaFeO₂ (R 3 m) is a promising low-cost layered material with a typical O₃ structure. However, it suffers from irreversible capacity with poor cycling performance. The underlying reaction mechanism and such irreversible behavior are still under debate. α-NaFeO₂ material was first reported in 1985 by Kikkawa et al.,[102] followed by a research of Yabuuchi et al.[103], Zhao et al.[104], and Lee et al.[105] groups. α-NaFeO₂ delivered 80–100 mAh g⁻¹ of reversible capacity with a flat voltage plateau at 3.3 V vs. Na (Figure 8(a)). The reversible capacity in the range of Na₁₋ₓFeO₂, x < 0.5, was ascribed to Fe³⁺/Fe⁴⁺ redox reaction and was confirmed by ⁵⁷Fe Mössbauer spectrometry [104]. The electrode performance beyond x > 0.5 was deteriorated and exhibited irreversible structural behavior, which the authors suggest is due to Fe ion migration to neighboring tetrahedral sodium sites and subsequently blocking the diffusion sodium pathways [103]. Lee et al. first showed the nonequilibrium phase transformation during charge/discharge process from hexagonal (R 3 m) to monoclinic (C2/m) phase, accompanied with the evidence of the chemical instability of Fe⁴⁺ species and electrolyte decomposition in the battery cell environment [105].

Recently, Li et al.[106] observed not only the irreversible Fe migration from TM layer to Na layer at the atomic scale by aberration-corrected scanning transmission electron microscop (STEM), but also oxidation of oxygen during desodiation of α-NaFeO₂ using XAS spectra. Moreover, DFT calculations showed that near Fermi level, the Fe 3d and O 2p states are highly overlapping, which means that both Fe and O contribute to charge compensation. In contrast to the Li et al.’s work, Susanto et al.[107] revealed that only oxygen redox responsible for charge compensation from the beginning of charging of α-NaFeO₂. When more than 0.5 Na was extracted, O₂ gas was released together with Fe migration and the formation of FeO₁₂ (cubic spinel Fd 3 m) locally on the surface of the particles (Figure 8(b)). Therefore, reversible charge compensation mechanism through solely oxygen redox was limited up to 0.5 of Na extraction. To address this critical issue, partial substitution of Fe with other TM has been reported previously. However, the participation of oxygen redox has not been shown in sufficient detail, which emphasizes the need for further systematic studies of such materials.
In addition, oxygen-redox participation has also been investigated in stoichiometric layered NaVO₃ material [108, 109]. The material crystallizes into a layered structure with monoclinic C2/c space group, where layers of NaO₆ octahedra and VO₄ tetrahedra alternate (Figure 8(c)). On the basis of in situ synchrotron XRD results, the structure of the material showed insignificant changes during Na⁺ (de-)intercalation with a and b lattice parameter variation only by 0.13 and 0.19%, respectively [109]. A more detailed study on electrochemical process revealed that NaVO₃ undergoes an oxygen-redox reaction during initial charge and cationic V⁴⁺/V⁵⁺ and anionic O₂⁻/O¹⁻ redox during subsequent discharge (Figure 8(d)). Oxygen charge compensation mechanism was proved by DFT calculation showing the domination of O 2p states for partially and fully desodiated structure. The delivered reversible capacity was reached 245 mAh g⁻¹, leading to one of the most highest energy densities (566 Wh kg⁻¹) for SIB materials with anion-redox participation.

4. Sodium-Rich Transition Metal Layer Structures NaₓTM₀₂ (x ≥ 1)

Na-rich materials, Naₓ[NaₓTMₓ/3]O₂, which are analogs of Li-rich materials, are promising materials for high-performance SIBs owing to their high sodium content, offering an opportunity to increase the energy density of SIBs. In sodium-rich materials, sodium ions are located in both alkali and TM layers (octahedral sites), in contrast to full sodium-stoichiometry and deficient materials, in which sodium ions are located only in the alkali layer. The extra Na content may provide extra capacity, delivered by cumulative cationic and anionic redox, potentially exceeding 1 Na⁺ per formula unit.

4.1. Mn-Based Compounds. In contrast to their lithium-ion analogs, where lithium-rich Li₂TM₀₂ (Na[Naₓ/1TM₂/3]O₂)-type oxides (TM: Mn, Mo, Ru, and Ir) have been synthesized and studied for 3d TM (Mn) and 4d/5d TM (Mo, Ru, and Ir), sodium-rich oxides Na₂TM₀₂ have been successfully obtained only for 4d (Ru) and 5d TM (Ir). The reason for that is likely the larger ionic radius mismatch between Na⁺ (1.02 Å) and Mn⁴⁺ (0.53 Å). Therefore, to date, there is no clear evidence of the crystal structure or electrochemical performance of Na₂MnO₃. The material has been discussed only in computer simulations. According to the theoretical work of Gao et al., it is possible to extract 1.75 Na⁺ per formula unit through partial O²⁻/O¹⁻ redox reaction leaving much of the local structure intact [110].

4.2. Ru-Based Compounds. The oxygen-redox chemistry was demonstrated in sodium-rich Ru-based cathodes with good structural stability [30–42]. The first research paper on such materials was published in 2013 by the group of Tamaru et al. on Na₃RuO₃ (R 3 m), in which Ru was stabilized as Ru⁴⁺ [30]. The material delivered a specific capacity of 140 mAh g⁻¹, which exceeded 7%, the theoretical capacity from only Ru⁴⁺/Ru⁵⁺ redox. Sloppy charge/discharge curves were observed with an average potential of 2.8 V vs. Na/Na⁺. It was indicated that the reaction mechanism proceeded through a solid-solution reaction (Na₂–RuO₃, 0 < x < 0.5), followed by a two-phase reaction (0.5 < x < 0.6). Later in 2015, Rozier’s group designed Sn-doped layered Na₂Ru₁₋SnO₃ materials [31]. The voltage profiles of the Sn-doped materials were similar to those of Li-rich materials with two distinct voltage plateaus on charge (2.8 and 3.8 V) and an S-curved shape on discharge. Using XPS analysis, the authors proved that the lower voltage plateau was associated with cationic Ru⁴⁺/Ru⁵⁺ redox and that the higher one was associated with anionic O²⁻/O¹⁻ redox. Similar to De Boisse et al.’s work, a solid-solution–two-phase–solid solution mechanism was observed during Na deintercalation.

In a more recent study, De Boisse et al. synthesized honeycomb ordered O-Na₃RuO₃ (C2/m) and the disordered analog D-Na₃RuO₃ (R 3 m) [32] and investigated the importance of structural order/disorder of alkali and TM ions in the TM layer (Figure 9(a)). The authors claimed that the order in the TM layer is a prerequisite for the activation of oxygen redox, induced by frontier orbital O(2p)–Ru(t₂g) reorganization with the short O–O distances in distorted RuO₆. Because of the in-plane honeycomb ordering, the O-Na₃RuO₃ electrode demonstrated enhanced capacity of 180 mAh g⁻¹ compared with
that of 135 mAh g$^{-1}$ for D-Na$_2$RuO$_3$ (Figure 9(b)). The authors showed that 30% extra capacity was achieved by the spontaneously ordered intermediate ilmenite O1-Na$_1$RuO$_3$ (R 3) phase, which accommodates the cooperative distortion of the RuO$_6$ octahedra. In contrast, in the case of disordered material, the intermediate P3-Na$_1$RuO$_3$ phase exhibited strain frustration, which did not allow activation of the oxygen-redox reaction. Further study of ordered O-Na$_2$RuO$_3$ showed O3–O1–O1’ structural phase transformations during charge with an intermediate O1-Na$_1$RuO$_3$ phase and O1’-Na$_{1/2}$RuO$_3$ (P 3 1 m) phase stabilized in the fully charged state (Figures 9(c) and 9(d)) [33]. The in situ XRD and DFT calculation results showed that the existence of ordered Na vacancies played an essential role in increasing the O 2p electronic population near the Fermi level, which not only stabilized the phase transformations during cycling but also facilitated reversible oxygen-redox reactions (Figure 9(e)) [34].

Moreover, in a later work of Liu et al., the Mn$^{4+}$ substitution strategy was adopted in Na$_2$Ru$_{1-x}$Mn$_x$O$_3$ (x = 0 – 0.3) material [38]. Mn$^{4+}$ doping resulted in an increase of the voltage of the material due to the increase in the M–O band ionicity and charge on O. In addition, Mn$^{4+}$ doping suppressed the O3–P3 phase transition and prevented the formation of the spinel phase in the highly desodiated state and enhanced the robustness against water attack. A surprising super long cycling stability with a capacity retention of 70% was achieved at 5C after 1000 cycles.

Na$_3$RuO$_4$ (Na[Na$_{1/3}$Ru$_{2/3}$]O$_2$) (C2/m) is a further expansion of the Na$_2$RuO$_3$ cathode material toward higher sodium content (O/TM ratio) Ru-based materials with oxygen-redox activity [40–42]. The crystal structure of Na$_3$RuO$_4$ is described as a layered structure with a Ru$^{5+}$ framework forming isolated tetramers of the edge-sharing RuO$_6$ octahedra in the Na$_{1.5}$Ru$_{1.5}$O$_{3.5}$ layer (Figure 10(a)) [41]. The reaction mechanism in Na$_3$RuO$_4$ is currently under debate by several groups [40–42]. The first work of Qiao et al. on the chemical extraction of Na from Na$_3$RuO$_4$ indicated that capacity is delivered by merely O redox reaction through the formation of peroxo-based O–O (de)bonding, which was confirmed by in situ Raman analysis (Figure 10(b)) [40]. On the basis of the XPS and XANES analyses, the authors claimed that Na extraction/insertion proceeded along the inert redox character of Ru$^{4+}$ in the octahedral position. However, Otoyama et al. later revisited this compound and showed that the charge compensation mechanism includes the participation of both Ru and O redox reactions [41]. First, the oxidation of Ru$^{3+}$ to Ru$^{4+}$ occurs, leading to the formation of Na$_{3-x}$Ru$_{1.5}$O$_{3.5}$ (P 2/m), followed by oxygen reduction at the end of charge through a solid-solution process with the formation of amorphous Na$_{3-x}$Ru$_{1.5}$O$_x$ (x = 0 – 1). The presented O-redox reaction proceeded together with the dissolution of the active material, which subsequently led to the irreversible reaction and poor recovery of the Na$_3$RuO$_4$ structure with its initial crystallinity [41]. In the work of Hu et al. [42], similar results were shown, clarifying that both Ru$^{4+}$/Ru$^{3+}$ and O$^{2-}$/O$_2^-$ are active, and it was shown that the oxygen-redox activity decreased with a retention of 36% after 30 cycles, which was the main reason for the large capacity fading and limited reversibility.

To conclude, Na$_3$RuO$_4$ showed electrostatically more unstable behavior upon deep desodiation than Na$_2$RuO$_3$, which could be explained by the higher Na vacancy content.
and only a single-TM-coordinate oxygen ions. This finding highlights the importance of balance upon increasing the number of nonbonding O states for the reversibility of the oxygen-redox reaction and structural stability of the material.

4.3. Ir-Based Compounds. The O3-type Na₂IrO₃ (Na[Na₁₋ₓIrₓ]O₂) (C2/m) compound is another example of a Na-rich composition that displays oxygen-redox activity [43]. In contrast to 3d (Mn) and 4d (Ru) TM compounds, which present drastic evolution of the voltage profile through the first cycle, the 5d (Ir) Na₂IrO₃ material did not show an evolution from a two-plateau to S-shape voltage profile (Figure 11(a)). The enhanced structural rigidity of the compound allowed cycling of the cell reversibly upon high sodium extraction/insertion (1.5 Na⁺ per formula unit, capacity ~130 mAh g⁻¹) with neither oxygen release or cationic migrations to interlayer (alkali-) sites. During extraction of sodium ions, the O3-type layered structure first converted to O1’ (P 1) and further to O1 (C 2m) through gliding of the oxygen close-packed planes (Figure 11(b)). The increased cationic repulsion with charge density loss on the O atom leads to a high covalent TM–O bond, which reduces the possibility of O₂ release and effectively stabilizes the structure. Using DFT calculations, the authors indicated that both the Ir and O bands lay just below the Fermi level, which involve both oxygen O²⁻/O¹⁻ and Ir⁴⁺/Ir⁵⁺ contributions in charge compensation (Figures 11(c) and 11(d)). Interestingly, that oxygen-redox activity was observed in the early stage of the desodiation process, which the author linked to the slightly distorted IrO₆ octahedra in the pristine Na₂IrO₃ material (Figures 11(c) and 11(d)).

To overcome the drawback of the high cost of 5d (Ir) TM, Zhang et al. proposed the partial substitution of Ir by Mn and obtained Na₁₋ₓMnₓIr₀.₄O₂ [44]. The authors reported reasonable reversible capacity of 135 mAh g⁻¹ with 1.5 mol Na⁺ extraction during the first charge. Interestingly, that charge compensation mechanism was attributed to Mn⁷⁺/Mn⁵⁺ cationic redox and O²⁻/O¹⁻ oxygen redox without Ir participation. In situ Raman and XPS analyses were employed to confirm the reversibility of the O₂⁻ formation. Even though Ir did not participate in the electrochemical reaction throughout the entire charge and discharge process, Na₁₋ₓMn₀.₄Ir₀.₄O₂ demonstrated similar to Na₂IrO₃ asymmetric transformation during charge, especially in the O¹’–O₁ phase region. The authors explained this finding with potential stacking faults, which were caused by a systematic shift of TM layers.

A viable alternative for improving the performance of Na₂IrO₃ was proposed by Pearce et al. by synthesizing a fundamentally different crystal structure of β-Na₁₋ₓIrₓO₃ [45]. β-Na₁₋ₓIrₓO₃ was obtained by the electrochemical exchange of Li into Na in β-LiₓIrO₃ material. In the structure of β-Na₁₋ₓIrₓO₃, the Na and Ir layers were shifted relative to each other; instead of a layered structure, the material acquires a Fddd hyperhoneycomb structure with a rigid 3D network (Figures 11(e) and 11(f)). It turned out that such a hyperhoneycomb structure was much more stable, with reversible uptake of nearly 1.3 Na⁺ and good capacity retention of 82% after 100 cycles in a full-cell configuration against hard carbon. Despite the fact that the β-Na₁₋ₓIrₓO₃ material underwent multiple structural phase transitions with different lattice parameters and a large volume change ~26% during sodiation/desodiation, it maintained the same IrO₃ framework (Figure 11(g)). The charge-compensation mechanism revealed that both the anionic (O₂⁻) redox and cationic activity of Ir⁵⁺/Ir⁴⁺ were responsible for the delivered capacity.

In summary, 5d Ir-based compounds exhibit more reversible charge/discharge curves than 4d TM and especially 3d TM compounds, suggesting higher structural integrity due to more diffused orbitals against the irreversible reactions of oxidized oxygen. However, because Ir is one of the rarest metals in the Earth’s crust and because of its high cost, the use of such cathodes is of little practical importance.

5. Biphasic Layered Structures

To achieve better electrode performance, an attractive approach of the combination of P/O phases in one material was recently proposed. The synergetic effect of the
combination of a two-phase composite was observed by Yang et al. in P2/O3 Na0.8Li0.2Fe0.2Mn0.6O2, in which Fe was stabilized as 3+ and Mn as 4+ [111]. The material delivered a reversible capacity of 174 mAh g⁻¹, which was attributed to Fe³⁺/Fe⁴⁺ redox along with partial Mn³⁺/⁴⁺ redox and oxygen contribution. Using NMR Li⁺, it was shown that a portion of lithium migrated from the Na layer and TM layer remained constant during electrochemical cycles. The biphatic O/P nature of the material was nevertheless preserved, and lithium was considered the structure stabilizer.

Hu et al. attempted to further improve the structural stability of this P2/O3 Na0.8Li0.2Fe0.2Mn0.6O2 composite using Ti⁴⁺ doping into Mn⁴⁺ sites [112]. Combining solid-state NMR, EPR, XPS, and HRTEM analyses, the authors demonstrated that Ti⁴⁺ substitution could not only effectively suppress lithium migration from the TM layer to the Na layer but also enhanced the structural stability by alleviating the formation of irreversible surface cracks on particles during cycling.

In conclusion, successful utilization of O/P composites as a cathode material with anion redox to increase the energy density and improve the first coulombic efficiency appears to be a promising strategy, further expanding the variety of potential anion redox materials for SIBs.

6. Cation-Disordered Rocksalt Oxides

Over the last five years, Li-rich cation-disordered rocksalt-type structure oxides with oxygen redox compensation mechanism have emerged as potential high energy density cathodes for LIBs with high reversible capacities ~300 mAh g⁻¹ and extremely high energy densities ~1000 W h kg⁻¹ [113]. Oxygen-redox activity in such systems associated with a highly ionic character of d⁰ charge compensator metal ions, such as Ti⁴⁺/Zr⁴⁺/Nb⁵⁺/Mo⁶⁺.

The concept of Li-rich rocksalt structures was recently applied to Na-rich materials [114, 115]. Sato et al. synthesized a metastable Na-rich cation-disordered rocksalt oxides, which exhibit the oxygen-redox activity. Na1.3Nb0.3Mn0.4O2 [114] and Na1.1Mn0.57Ti0.43O2 [115] have a cubic-close packed (ccp) structure, which presented in XRD with a broad diffraction peaks, indicating the formation of small size and low crystallinity samples, obtained by mechanical milling.
process. The reversible capacity was ~200 mAh g⁻¹ for both materials, despite the different reaction mechanism.

For Na₁.₃Nb₀.₃Mn₀.₄O₂, the detailed investigation of electrochemical process revealed that Mn⁶⁺/Mn⁴⁺ redox prevailed at low voltage, while O₂ oxidation accompanied with O₂ loss dominated at high voltage on first charge. As a result, accumulation of carbonate species and O₂ loss were detected at fully charged state in Na₁.₃Nb₀.₃Mn₀.₄O₂ electrode. Therefore, only reversible two-electron Mn⁵⁺/Mn⁴⁺ redox rather than reversible oxygen redox were observed on the subsequent cycles. By substituting Nb⁵⁺ with Ti⁴⁺, the reversibility of oxygen redox was significantly improved in Na₁.₃Mn₀.₂⁵Ti₀.₂⁵O₂. Reversible cationic Mn⁵⁺/Mn⁴⁺ without reduction to Mn³⁺ and anionic O²⁻/O⁻ redox reactions were responsible for delivered capacity in Na₁.₄⁵Mn₀.₅⁵Ti₀.₂⁵O₂. Moreover, not only the reversibility of anionic redox has been highly improved compared with the former Na₁.₃Nb₀.₃Mn₀.₄O₂ material, but also cycling stability of Na₁.₄⁵Mn₀.₅⁵Ti₀.₂⁵O₂ was greatly increased. Therefore, further research in Na-rich cation-disordered rocksalt cathodes from abundant elements, such as manganese and titanium, with reversible anionic redox is required for the development of high energy density rechargeable SIBs.

7. Conclusions

The use of cathode materials with both anion- and cation-redox reactions represents a promising approach toward important gains in the energy density of SIBs. The estimation of the gravimetric energy density for P₂-type materials with cationic and anionic redox is ~500–600 Wh kg⁻¹ and that for O₃-type materials is ~400 Wh kg⁻¹, which is very promising (Figure 12). To date, considerable progress has been achieved for Na-rich (O₃-type) and Na-deficient (P₂-type) materials. Most of the emphasis on Na-rich materials has been on rare and expensive 4d TM (Ru) and 5d TM (Ir) elements; however, Na-deficient materials rely on the use of low-cost 3d TM (Mn). Therefore, from a practical viewpoint, P₂-type materials have considerable merits such as low cost, high performance, and relatively stable oxygen-redox reactions, making them promising for SIBs with improved energy density. However, recent work of Wang et al. [85] showed that a new Na-stoichiometric compound O₃-Na[Li₁.₃Mn₂/₃]O₂ not only offers an effective possibility of utilizing anionic redox but also does not have the drawback of low coulombic efficiency. Moreover, from this viewpoint, mixed P₂/O₃-type oxides represent an interesting strategy, leading to high-performance materials with enhanced air stability and relatively high sodium content.

From a practical viewpoint, the main drawbacks of materials with anion redox are their severe microstructural and electrochemical instabilities. Therefore, it is critical to understand the origin of these issues and to find ways to mitigate them. Among the microstructural issues, the most significant involve oxygen evolution, cation migration, and surface reconstruction. The principal electrochemical problems in anion redox reactions in SIBs are the sluggish reaction kinetics, high-voltage hysteresis (compared to cationic redox), and voltage fade during cycling, which in turn adversely affect the electrochemical performance. The slow reaction kinetics is mostly caused by drastic rearrangements of bonding configurations; however, high-voltage hysteresis and voltage fade have largely been attributed to the structural cation disordering in plane and out of plane in the material during cycling. Therefore, we would like to provide some important solutions for optimization of the properties of cathode materials with cationic-anionic redox for SIBS.

(1) One of the critical concerns for anion-redox cathodes is the nature of the oxidized species, which needs to be better understood and characterized, especially because it defines the chemical reactivity and solubility of the material. Therefore, the use of a combination of experimental and theoretical techniques, such as O-K mRIXS, in situ XRD/ND, XAS, and Raman methods together with DFT calculations, is critical because these observations and predictions provide a critical benchmark for the detection and determination of the nature of the oxidized species in cathode materials.

(2) The concept of an ordered compositional approach has been successfully realized in P₂-Naₓ[Li₁.₃Mn₂/₃]O₂, O₃-Na₂RuO₃, and Na₂Mn₃O₇ materials and has resulted in beneficial properties with good structural stability, high reversibility of anion redox, and low-voltage hysteresis. However, a nonhysteresis profile has been demonstrated only for Na₂Mn₃O₇. This unique behavior makes it a key compound for understanding the chemical, structural, and electronic properties for engineering materials with truly reversible nonhysteresitic anion redox. Therefore, further theoretical predictions and additional approaches should be expanded to determine the reasons for the nonhysteresitic behavior of Na₂Mn₃O₇ and to identify more compounds with high electrochemically reversible and kinetically easy anion redox processes.

(3) Another factor affecting the stability of cation–anion redox reactions is the surface chemistry of the cathode material. Complex reactions together with
oxygen evolution occur at the electrode/electrolyte boundary at high voltage, leading to a metastable nature of highly charged layered cathode materials. Therefore, the development of surface coatings and commodification strategies, which can overcome the challenges at the electrode/electrolyte boundary and improve the long cycling stability, should be encouraged.

Overall, we are optimistic about cationic–anionic redox cathode materials for SIBs, with significant progress seen in the last 5 years. We hope that this review will shed light on the possibilities to improve such cathodes and increase research interest in the development of Earth-abundant and low-cost SIBs with anion redox activity that are aligned with the requirements for post-LIBs.

Conflicts of Interest
The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgments
This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science, and Technology of Korea (NRF-2015M3D1A1069713, NRF-2019H1D8A2106002, NRF-2020R1A2B5B01095954, and NRF-2020R1A6A1A03043435).

References
[1] N. Yabuuchi, K. Kubota, M. Dahbi, and K. Komaba, “Research development on sodium-ion batteries,” Chemical Reviews, vol. 114, no. 23, pp. 11636–11682, 2014.
[2] V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez, and T. Rojo, “Na-ion batteries: recent advances and present challenges to become low cost energy storage system,” Energy & Environmental Science, vol. 5, no. 3, pp. 5884–5901, 2012.
[3] J.-Y. Hwang, S.-T. Myung, and Y.-K. Sun, “Sodium-ion batteries: present and future,” Chemical Society Review, vol. 46, no. 12, pp. 3529–3614, 2017.
[4] C. Delmas, J.-J. Braconnier, C. Fouassier, and P. Hagenmuller, “Electrochemical intercalation of sodium in Na0.75Co0.25O2 bronzes,” Solid State Ionics, vol. 3-4, pp. 165–169, 1981.
[5] J. H. Jo, J. U. Choi, Y. J. Park, H. Yashiro, and S.-T. Myung, “A new pre-sodiation additive for sodium-ion batteries,” Energy Storage Materials, vol. 33, pp. 281–289, 2020.
[6] C.-H. Jo, J. U. Choi, H. Yashiro, and S.-T. Myung, “Controllable charge capacity using a black additive for high-energy-density sodium-ion batteries,” Journal of Materials Chemistry A, vol. 7, no. 8, pp. 3903–3909, 2019.
[7] A. R. Armstrong and P. G. Bruce, “Electrochemistry beyond Mn\textsuperscript{4+} in Li\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{2},” Electrochemical and Solid-State Letters, vol. 7, no. 1, pp. A1–A4, 2004.
[8] A. R. Armstrong and P. G. Bruce, “Layered Li\textsubscript{1-x}Mn\textsubscript{x}Li\textsubscript{2}O\textsubscript{2} intercalation electrodes: synthesis, structure and electrochemistry,” Journal of Materials Chemistry, vol. 15, no. 1, pp. 218–224, 2005.
[9] N. Guerrini, L. Jin, J. G. Jozano et al., “Charging mechanism of Li2MnO3,” Chemistry of Materials, vol. 32, no. 9, pp. 3733–3740, 2020.
[10] N. Yabuuchi, K. Yoshii, S.-T. Myung, I. Nakai, and S. Komaba, “Detailed studies of a high-capacity electrode material for rechargeable batteries, Li\textsubscript{1-x}Mn\textsubscript{2}O\textsubscript{4}-LiCo\textsubscript{1/3}Ni\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2},” Journal of the American Chemical Society, vol. 133, no. 12, pp. 4404–4419, 2011.
[11] G. Assat and J.-M. Tarascon, “Fundamental understanding and practical challenges of anionic redox activity in Li-ion batteries,” Nature Energy, vol. 3, no. 5, pp. 373–386, 2018.
[12] J. Naylor, E. Makkos, J. Maibach et al., “Depth-dependent oxygen redox activity in lithium-rich layered oxide cathodes,” Journal of Materials Chemistry A, vol. 7, no. 44, pp. 25355–25368, 2019.
[13] Y. Yu, P. Karayaylail, S. H. Nowak et al., “Revealing electronic signatures of lattice oxygen redox in lithium ruthenates and implications for high-energy Li-ion battery material designs,” Chemistry of Materials, vol. 31, no. 19, pp. 7864–7876, 2019.
[14] P. E. Pearce, A. J. Perez, G. Rousse et al., “Evidence for anionic redox activity in a tridimensional-ordered Li-rich positive electrode β-Li2IrO3,” Nature Materials, vol. 16, no. 5, pp. 580–586, 2017.
[15] P. Vanaphuti, J. Bai, L. Ma et al., “Unraveling Na and F coupling effects in stabilizing Li, Mn-rich layered oxide cathodes via local ordering modification,” Energy Storage Materials, vol. 31, pp. 459–469, 2020.
[16] C. Gong, S. D. Pu, X. Gao et al., “Revealing the role of fluoride-rich battery electrode interphase by operando transmission electron microscopy,” Advanced Energy Materials, vol. 10, no. 11, article 2003118, 2021.
[17] N. Yabuuchi, R. Hará, M. Kajiyama et al., “New O2/P2-type Li-excess layered manganese oxides as promising multifunctional electrode materials for rechargeable Li/Na batteries,” Advanced Energy Materials, vol. 4, no. 13, article 1301453, 2014.
[18] M. B. Yahia, J. Vergnet, M. Saubanere, and M. L. Doublet, “Unified picture of anodic redox in Li/Na-ion batteries,” Nature Materials, vol. 18, no. 5, pp. 496–502, 2019.
[19] X. Rong, E. Hu, Y. Lu et al., “Anionic redox reaction-induced high-capacity and low-strain cathode with suppressed phase transition,” Joule, vol. 3, no. 2, pp. 503–517, 2019.
[20] C. Zhao, Q. Yang, F. Geng et al., “Restraining oxygen loss and boosting reversible oxygen redox in a P2-type oxide cathode by trace anion substitution,” ACS Applied Materials & Interfaces, vol. 13, no. 1, pp. 360–369, 2021.
[21] E. de la Llave, E. Talaie, E. Levi et al., “Improving energy density and structural stability of manganese oxide cathodes for Na-ion batteries by structural lithium substitution,” Chemistry of Materials, vol. 28, no. 24, pp. 9064–9076, 2016.
[22] X. Chen, N. Li, E. Kedzie, B. D. McCloskey, H. Tang, and W. Tong, “High-capacity P2-type Na0.75Li0.25Mn0.75O2 cathode enabled by anionic oxygen redox,” Journal of the Electrochemical Society, vol. 166, no. 16, pp. A4136–A4140, 2019.
[23] Y. Zhu, W. Nie, P. Chen, Y. Zhou, and Y. Xu, “Li-doping stabilized P2-Li0.7Na0.3Mn0.5O2 sodium ion cathode with oxygen redox activity,” International Journal of Energy Research, vol. 44, no. 4, pp. 3253–3259, 2020.
[24] C. Li, C. Zhao, B. Hu, W. Tong, M. Shen, and B. Hu, "Unraveling the critical role of Ti substitution in P2-Na$_{2/3}$Mn$_{1-y}$O$_2$ cathodes for highly reversible oxygen redox activity," *Chemistry of Materials*, vol. 32, no. 3, pp. 1054–1063, 2020.

[25] S. M. Kang, D. Kim, K.-S. Lee et al., "Structural and thermodynamic understandings in Mn-based sodium layered oxides during anionic redox," *Advanced Science*, vol. 6, no. 16, article 2001263, 2020.

[26] D. Kim, M. Cho, and K. Cho, "Rational design of Na$_{(1-y)2/3}$Mn$_y$O$_2$ operated by anionic redox reactions from advanced sodium-ion batteries," *Advanced Materials*, vol. 29, no. 33, article 1701788, 2017.

[27] R. A. House, U. Maitra, M. A. Perez-Osorio et al., "Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes," *Nature*, vol. 577, no. 7791, pp. 502–508, 2020.

[28] Q. Liu, Z. Hu, W. Li et al., "Sodium transition metal oxides: the preferred cathode choice for future sodium-ion batteries?", *Energy & Environmental Science*, vol. 14, no. 1, pp. 158–179, 2021.

[29] X. Cao, H. Li, Y. Qiao et al., "Stabilizing reversible oxygen redox chemistry in layered oxides for sodium-ion batteries," *Advanced Energy Materials*, vol. 10, no. 15, article 1903785, 2020.

[30] M. Tamaru, X. Wang, M. Okubo, and A. Yamada, "Layered Na$_x$RuO$_3$ as a cathode material for Na-ion batteries," *Electrochemistry Communications*, vol. 33, pp. 23–26, 2013.

[31] P. Rozier, M. Sathiya, A. R. Paulraj et al., "Anionic redox chemistry in Na-rich Na$_x$Ru$_{6-y}$Sn$_y$O$_{12}$ positive electrode material for Na-ion batteries," *Electrochemistry Communications*, vol. 53, pp. 29–32, 2015.

[32] B. Mortemard De Boisse, G. Liu, J. Ma et al., "Intermediate honeycomb ordering to trigger oxygen redox chemistry in layered battery electrode," *Nature Communications*, vol. 7, pp. 1–9, 2016.

[33] B. Mortemard de Boisse, M. Reynaud, J. Ma et al., "Coulombic self-ordering upon charging a large-capacity layered cathode material for rechargeable batteries," *Nature Communications*, vol. 10, no. 1, article 2185, 2019.

[34] G. Choi, J. Lee, and D. Kim, "Uncovering the structural evolution in Na-excess layered cathodes for rational use of an anionic redox reaction," *ACS Applied Materials and Interfaces*, vol. 12, no. 26, pp. 29203–29211, 2020.

[35] M. H. N. Assadi, M. Okubo, A. Yamada, and Y. Tateyama, "Oxygen redox promoted by Na excess and covalency in hexagonal and monoclinic Na$_x$RuO$_3$ polymorphs," *Journal of the Electrochemical Society*, vol. 166, no. 3, pp. A5343–A5348, 2019.

[36] M. H. N. Assadi, M. Okubo, A. Yamada, and Y. Tateyama, "Oxygen redox in hexagonal layered Na$_x$TMO$_3$ (TM = 4d elements) for high capacity Na ion batteries," *Journal of Materials Chemistry A*, vol. 6, no. 8, pp. 3747–3753, 2018.

[37] J. Do, I. Kim, H. Kim, and Y. Jung, "Towards stable Na-rich layered transition metal oxides for high energy density sodium-ion batteries," *Energy Storage Materials*, vol. 25, pp. 62–69, 2020.

[38] S. Liu, F. Lu, H. Li et al., "Na$_{x}$Ru$_{6-y}$Mn$_y$O$_{12}$: a novel cathode material for ultrafast sodium ion battery with large capacity and superlong cycle life," *Journal of Power Sources*, vol. 421, pp. 14–22, 2019.

[39] S. Song, M. Kotobuki, F. Zheng et al., "Na-rich layered Na$_x$Ru$_{0.95}$Zr$_{0.05}$O$_3$ cathode material for Na-ion batteries," *Journal of Power Sources*, vol. 342, pp. 685–689, 2017.

[40] Y. Qiao, S. Guo, K. Zhu et al., "Reversible anionic redox activity in Na$_x$RuO$_3$ cathodes: a prototype Na-rich layered oxide," *Energy and Environmental Science*, vol. 11, no. 2, pp. 299–305, 2018.

[41] M. Otoyama, Q. Jacquet, A. Iadecola, M. Saubanère, G. Rousse, and J. M. Tarascon, "Synthesis and electrochemical activity of some Na(Li)-rich ruthenium oxides with the feasibility to stabilize Ru$^{6+}$," *Advanced Energy Materials*, vol. 9, no. 15, pp. 1–12, 2019.

[42] Y. Hu, T. Liu, C. Cheng et al., "Quantification of anionic redox chemistry in a prototype Na-rich layered oxide," *ACS Applied Materials and Interfaces*, vol. 12, no. 3, pp. 3617–3623, 2020.

[43] A. J. Perez, D. Batuk, M. Saubanère et al., "Strong oxygen participation in the redox governing the structural and electrochemical properties of Na-rich layered oxide Na$_x$IrO$_3$," *Chemistry of Materials*, vol. 28, no. 22, pp. 8278–8288, 2016.

[44] X. Zhang, Y. Qiao, S. Guo et al., "Manganese-based Na-rich materials boost anodic redox in high-performance layered cathodes for sodium-ion batteries," *Advanced Materials*, vol. 31, no. 27, pp. 1–9, 2019.

[45] P. E. Pearce, G. Rousse, O. M. Karakulina et al., "β-Na$_x$IrO$_3$: a tridimensional Na-insertion material with a redox active oxygen network," *Chemistry of Materials*, vol. 30, no. 10, pp. 3285–3293, 2018.

[46] N. Yabuuchi, R. Hara, K. Kubota, J. Paulsen, S. Kumakura, and S. Komaba, "A new electrode materials for rechargeable sodium batteries: P2-type Na$_{2/3}$(Mn$_{0.72}$Ir$_{0.28}$)O$_2$," *Journal of Materials Chemistry A*, vol. 2, no. 40, pp. 16851–16855, 2014.

[47] R. J. Clement, J. Billaud, A. R. Armstrong et al., "Structurally stable Mg-doped P2-Na$_{2/3}$Mn$_{0.5}$Mg$_{0.5}$O$_2$ sodium-ion battery cathodes with high rate performance: insights from electrochemical, NMR and diffraction studies," *Energy & Environmental Science*, vol. 9, no. 10, pp. 3240–3251, 2016.

[48] U. Maitra, R. A. House, J. W. Somervelle et al., "Oxygen redox chemistry without excess alkali-metal ions in Na$_{2/3}$[Mg$_{0.28}$Mn$_{0.72}$]O$_2$," *Nature Chemistry*, vol. 10, no. 3, pp. 288–295, 2018.

[49] N. Tapia-Ruiz, W. M. Dose, N. Sharma et al., "High voltage structural evolution and enhanced Na-ion diffusion in P2-Na$_{2/3}$Ni$_{0.5}$Mg$_{0.5}$O$_2$ (0 ≤ x ≤ 0.2) cathodes fromdiffraction, electrochemical and ab initio studies," *Energy & Environmental Science*, vol. 11, no. 6, pp. 1470–1479, 2018.

[50] Q.-C. Wang, J.-K. Meng, X.-Y. Yue et al., "Tuning P2-structured cathode material by Na-site Mg substitution for Na-ion batteries," *Journal of the American Chemical Society*, vol. 141, no. 2, pp. 840–848, 2019.

[51] H. J. Kim, A. Konarov, J. H. Jo et al., "Controlled oxygen redox for excellent power capability in layered sodium-based compounds," *Advanced Energy Materials*, vol. 9, no. 32, article 1901181, 2019.

[52] R. A. House, U. Maitra, L. Jin et al., "What triggers oxygen loss in oxygen redox cathode materials?", *Chemistry of Materials*, vol. 31, no. 9, pp. 3293–3300, 2019.

[53] J. Vergnet, M. Saubanere, M.-L. Doublet, and J.-M. Tarascon, "The structural stability of P2-layered Na-based electrodes during anodic redox," * Joule*, vol. 4, no. 2, pp. 1–15, 2020.

[54] L. Yang, Z. Liium, S. Liu et al., "Superiority of native vacancies in activating anionic redox in P2-type Na$_{2/3}$[Mn$_{0.79}$Mg$_{0.21}$]O$_2$," *Nano Energy*, vol. 78, article 105172, 2020.
[55] X. Bai, A. Iadecola, J.-M. Tarascon, and P. Rozier, “Decoupling the effect of vacancies and electropositive cations on the anionic redox processes in Na based P2-type layered oxides,” *Energy Storage Materials*, vol. 31, pp. 146–155, 2020.

[56] C. Cheng, M. Ding, T. Yan et al., “Exploring the charge compensation mechanism of P2-type Na0.6Mn0.3Mn0.1O2 cathode materials for advanced sodium-ion batteries,” *Energies*, vol. 13, no. 21, p. 5729, 2020.

[57] A. Konarov, J. H. Jo, J. U. Choi et al., “Exceptionally highly stable cycling performance and facile oxygen-redox of manganese-based cathode materials for rechargeable sodium batteries,” *NANO Energy*, vol. 59, pp. 197–206, 2019.

[58] X. Bai, M. Sathiya, B. Mondoza-sanchex et al., “Anionic redox activity in a newly Zn-doped sodium layered oxide P2-Na3M1−yZnyO2 (0 < y < 0.23),” *Advanced Energy Materials*, vol. 8, no. 32, article 1802379, 2018.

[59] W. Zheng, Q. Liu, Z. Wang et al., “Stabilizing the oxygen lattice and reversible oxygen redox in Na-deficient cathode oxides,” *Journal of Power Sources*, vol. 43, p. 227086, 2019.

[60] A. Konarov, H. J. Kim, J.-H. Jo et al., “High-voltage oxides-redox-based cathode for rechargeable sodium-ion batteries,” *Advanced Energy Materials*, vol. 10, no. 24, article 2001111, 2020.

[61] C. Ma, J. Alvarado, J. Xu et al., “Exploring oxygen activity in the high energy P2-type Na0.36Ni0.33Mn0.3O2 cathode material for Na-ion batteries,” *Journal of the American Chemical Society*, vol. 139, no. 13, pp. 4835–4845, 2017.

[62] C. Cheng, S. Li, T. Liu et al., “Elucidation of anionic and cationic redox reactions in a prototype sodium-layered oxide cathode,” *ACS Applied Materials & Interfaces*, vol. 11, no. 44, pp. 41304–41312, 2019.

[63] W. Kong, W. Yang, D. Ning et al., “Tuning anionic/cationic redox chemistry in a P2-type Na0.67Mn0.3Fe2O4 cathode material via a synergic strategy,” *Science China Materials*, vol. 63, no. 9, pp. 1703–1718, 2020.

[64] W. Kong, R. Gao, Q. Li et al., “Simultaneously tuning cationic and anionic redox in a P2-Na0.6Mn0.3Fe2O4 cathode material through synergic Cu/Mg co-doping,” *Journal of Materials Chemistry* A, vol. 7, no. 15, pp. 9099–9109, 2019.

[65] Y. Zhang, M. Wu, J. Ma et al., “Revisiting the Na0.3Ni1/3Mn2/3O2 cathode: oxygen redox chemistry and oxygen release suppression,” *ACS Central Science*, vol. 6, no. 2, pp. 232–240, 2020.

[66] W. Zuo, F. Ren, Q. Li et al., “Insights of the anionic redox in P2-Na0.67Ni0.33Mn0.5O2,” *Nano Energy*, vol. 78, p. 105285, 2020.

[67] K. Dai, J. Mao, Z. Zhuo et al., “Negligible voltage hysteresis with strong anionic redox in conventional battery electrode,” *Nano Energy*, vol. 74, p. 104831, 2020.

[68] C. Hakim, N. Sabi, L. A. Ma et al., “Understanding the redox process upon electrochemical cycling of the P2-Na0.78Co1/3Mn2/3Ni1/6O2 electrode material for sodium-ion batteries,” *Communications Chemistry*, vol. 3, no. 1, p. 9, 2020.

[69] P.-F. Wang, Y. Xiao, N. Piao et al., “Both cationic and anionic redox chemistry in a P2-type sodium layered oxide,” *Nano Energy*, vol. 69, p. 104474, 2020.

[70] W. Zheng, Q. Liu, Z. Wang et al., “Oxygen redox activity with small voltage hysteresis in Na0.67Co0.26Mn0.7O2 for sodium-ion batteries,” *Energy Storage Materials*, vol. 28, pp. 300–306, 2020.
[87] A. J. Perez, G. Rousse, and J. M. Tarascon, “Structural instability driven by Li/Na competition in Na[(Li1/2H1/2)O2] cathode material for Li- and Na-ion batteries,” Inorganic Chemistry, vol. 58, no. 22, pp. 15644–15651, 2019.

[88] X. Rong, J. Liu, E. Hu et al., “Structure-induced reversible anionic redox activity in Na layered oxide cathode,” Joule, vol. 2, no. 1, pp. 125–140, 2018.

[89] H. Xu, S. Guo, and H. Zhou, “Review on anionic redox in sodium-ion batteries,” Journal of Materials Chemistry A, vol. 7, no. 41, pp. 23662–23678, 2019.

[90] J. Wu, Z. Zhuo, X. Rong et al., “Dissociate lattice oxygen redox reactions from capacity and voltage drops of battery electrode,” Science Advances, vol. 6, no. 6, article eaaw3871, 2020.

[91] E. J. Kim, L. A. Ma, D. M. Pickup et al., “Vacancy-enhanced oxygen redox reversibility in P3-type magnesium-doped sodium manganese oxide $\text{Na}_{0.67}\text{Mg}_{0.3}\text{Mn}_{1.4}\text{O}_2$, ” ACS Applied Energy Materials, vol. 3, no. 11, pp. 10423–10434, 2020.

[92] J. Min, H. Li, Y. Qiao et al., “Elucidating anionic redox chemistry in P3 layered cathode for Na-ion batteries,” ACS Applied Materials & Interfaces, vol. 12, no. 34, pp. 38249–38255, 2020.

[93] N. Li, S. Sallis, J. K. Papp, M. C. BD, W. Yang, and W. Tong, “Correlating the phase evolution and anionic redox in Co-free Ni-Rich layered oxide cathodes,” Nano Energy, vol. 78, article 105365, 2020.

[94] E. J. Kim, L. A. Ma, L. C. Duan et al., “Oxygen redox activity through a reducing coupling mechanism in the P3-type nickel-doped sodium manganese oxide,” ACS Applied Materials & Interfaces, vol. 3, no. 1, pp. 184–191, 2020.

[95] E. J. Kim, K. Mofredj, D. M. Pickup, A. V. Chadwick, J. T. S. Irvine, and A. R. Armstrong, “Activation of anion redox in P3 structure cobalt-doped sodium manganese oxide via introduction of transition metal vacancies,” Journal of Power Sources, vol. 481, p. 2299010, 2021.

[96] M. Jia, Y. Qiao, X. Li, K. Jiang, and H. Zhou, “Unraveling the anionic oxygen loss and related structural evolution within O3-type Na layered oxide cathodes,” Journal of Materials Chemistry A, vol. 7, no. 35, pp. 20405–20413, 2019.

[97] Z. Shadike, Y. N. Zhou, L. L. Chen et al., “Antisite occupation induced single anionic redox chemistry and structural stabilization of layered sodium chromium sulfide,” Nature Communications, vol. 8, no. 1, pp. 1–9, 2017.

[98] T. Wang, G. X. Ren, Z. Shadike et al., “Anionic redox reaction in layered NaCr$_{2/3}$Ti$_{1/3}$S$_2$ through electron holes formation and dimerization of S–S,” Nature Communications, vol. 10, no. 1, p. 4458, 2019.

[99] M. S. Whittingham, “Electrical energy storage and intercalation chemistry,” Science, vol. 192, no. 4244, pp. 1126–1127, 1976.

[100] J. Rouxel, “Anion-cation redox competition and the formation of new compounds in highly covalent systems,” Angewandte Chemie - International Edition in English, vol. 35, no. 17, pp. 1053–1059, 1996.

[101] Y. Lyu, L. Ben, Y. Sun et al., “Atomic insight into electrochemical inactivity of lithium chromate (LiCrO$_2$): irreversible migration of chromium into lithium layers in surface regions,” Journal of Power Sources, vol. 273, pp. 1218–1225, 2015.

[102] S. Kikkawa, S. Miyazaki, and M. Koizumi, “Sodium deintercalation from $\alpha$-NaFeO$_2$, ” Materials Research Bulletin, vol. 20, no. 4, pp. 373–377, 1985.

[103] N. Yabuuchi, H. Yoshida, and S. Komaba, “Crystal structures and electrode performance of alpha-NaFeO$_2$ for rechargeable sodium batteries,” Electrochemistry, vol. 80, no. 10, pp. 716–719, 2012.

[104] J. Zhao, L. Zhao, N. Dimov, S. Okada, and T. Nishida, “Electrochemical and thermal properties of $\alpha$-NaFeO$_2$ cathode for Na-ion batteries,” Journal of The Electrochemical Society, vol. 160, no. 5, pp. A3077–A3081, 2013.

[105] E. Lee, D. E. Brown, E. E. Alp et al., “New insights into the performance degradation of Fe-based layered oxides in sodium-ion batteries: instability of Fe$^{2+}$/Fe$^{3+}$ redox in $\alpha$-NaFeO$_2$, ” Chemistry of Materials, vol. 27, no. 19, pp. 6755–6764, 2015.

[106] Y. Li, Y. Gao, X. Wang et al., “Iron migration and oxygen oxidation during sodium extraction from NaFeO$_2$, ” Nano Energy, vol. 47, pp. 519–526, 2018.

[107] D. Susanto, M. K. Cho, G. Ali et al., “Anionic redox activity as a key factor in the performance degradation of NaFeO$_2$ cathodes for sodium ion batteries,” Chemistry of Materials, vol. 31, no. 10, pp. 3644–3651, 2019.

[108] J. Zhang, B. Su, A. Kitajou et al., “Activating abnormal capacity in stoichiometric NaVO$_3$ as cathode material for sodium-ion battery,” Journal of Power Sources, vol. 400, pp. 377–382, 2018.

[109] B. Su, S. Wu, H. Liang et al., “High-performance NaVO$_3$ with mixed cationic and anionic redox reactions for Na-ion battery applications,” Chemical Materials, vol. 32, no. 20, pp. 8836–8844, 2020.

[110] X. Gao, D. Wang, R. Lian et al., “Electronic properties, phase transformation, and anionic redox of monoclinic Na$_2$MnO$_3$ cathode material for sodium-ion batteries: first-principle calculations,” ChemElectroChem, vol. 6, no. 15, pp. 3987–3993, 2019.

[111] L. Yang, J. M. L. del Amo, Z. Shadike et al., “A Co- and Ni-free P2/O3 biphasic lithium stabilized layered oxide for sodium-ion batteries and its cycling behavior,” Advanced Functional Materials, vol. 30, no. 42, pp. 1–11, 2020.

[112] B. Hu, F. Geng, C. Zhao et al., “Deciphering the origin of high electrochemical performance in a novel Ti-substituted P2/O3 biphasic cathode for sodium-ion batteries,” ACS Applied Materials & Interfaces, vol. 12, no. 37, pp. 41485–41494, 2020.

[113] R. J. Clément, Z. Lun, and G. Ceder, “Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes,” Energy & Environmental Science, vol. 13, no. 2, pp. 345–373, 2020.

[114] K. Sato, M. Nakayama, A. M. Glushenkov et al., “Na-excess cation-disordered rocksalt oxide: Na$_{3}$Ni$_{2/3}$Mn$_{1/3}$O$_2$, ” Chemistry of Materials, vol. 29, no. 12, pp. 5043–5047, 2017.

[115] T. Kubayashi, W. Zhao, H. B. Rajendra, K. Yamanaka, T. Ohta, and N. Yabuuchi, “Nanosize cation-disordered rocksalt oxides: Na$_{3}$TiO$_2$–NaMnO$_2$ binary system,” Small, vol. 16, no. 12, pp. 1–6, 2020.