Review Article

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

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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 $\sim 3+$; however, sodium-deficient Na_xTMO_2 ($0.7 \leq x \leq 0.4$) 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

FIGURE 1: (a) Recent trend of cathode material for SIBs dealing anionic redox chemistry and (b) schematic pDOS diagram for oxygen redox reaction.

structure is smaller than those of P2 and P3, such that it 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_2MnO_3 [7–9], $\text{Li}_{1.2}\text{TM}_{0.8}\text{O}_2$ [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 $\text{Li}[\text{Li}_x\text{TM}_{1-x}]\text{O}_2$ (TM: Ni, Co, Fe, Cu, etc.) [12–14] or $\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$ (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 $250 \text{ mAh (g-oxide)}^{-1}$. 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, $\text{Na}_x[\text{A}_y\text{TM}_{1-y}]\text{O}_2$ (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 $\text{Na}_x[\text{ATM}]\text{O}_2$ 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, $\text{Na}_x[\text{A}_y\text{TM}_{1-y}]\text{O}_2$ (A: Li [17–29], Mg [46–56], Zn [57–60], Ni [61–66], or Cu

FIGURE 2: (a) Initial charge and discharge curves of P2-type Na_{5/6}[Li_{1/4}Mn_{3/4}]O₂ cycled at a rate of 10 mA g⁻¹ in a voltage range of 2–4.8 V in a Na cell (reprinted with permission from ref. [17], Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim), (b) schematic projected density of state of P2-type Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ (reprinted with permission from ref. [21], Copyright 2016 American Chemical Society), (c) average net charges obtained from the Bader charge calculation for Mn and its fitted values as a function of inverse Na content (x) in P2-type Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ (reprinted with permission from ref. [25], Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim), (d) gas evolution from P2-type Na_{0.67}[Li_{0.22}Mn_{0.78}]O₂ for the first cycle at C/20 (reprinted with permission from ref. [21], Copyright 2016 American Chemical Society), (e) the first charge and discharge profile of ordered superstructure P2-type Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂, and (f) dependence of oxygen redox stability on superstructure (reproduced with permission from ref. [28], Copyright 2020 The Royal Society of Chemistry).

[67–70], $0.4 \leq x \leq 0.8$, $y \leq 1/3$), known as P2 and P3 types, typically deliver high discharge capacities of 160–220 mAh g⁻¹. The prismatic environment for sodium ions enables maintenance of the large interlayer distances during de/sodiation, which is beneficial for facile diffusion of sodium ions and smooth phase transitions. However, in addition to the aforementioned merits, the sodium deficiency in the compounds results in small charge capacities (80–150 mAh g⁻¹), thereby resulting in an abnormal CE in the first cycle that should be circumvented for their adoption in practical applications. This concern can be resolved through the additional charge capacity derived by oxidation of lattice oxygen in the structure of layered P2 and P3 compounds.

2.1. P2-Type Layered Compounds. The P2-type layered structure is stabilized in forms of Na _{x} [A _{y} TM_{1- y}]O₂ ($0.4 \leq x \leq 0.8$), 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 Mn⁴⁺ 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.

2.1.1. P2 Na _{x} [Li _{y} Mn_{1- y}]O₂. 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_{5/6}[Li_{1/4}Mn_{3/4}]O₂ 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_{5/6}[Li_{1/4}Mn_{3/4}]O₂ should have delivered a small charge capacity, assuming the oxidation of Mn³⁺ to Mn⁴⁺. 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 Mn⁴⁺ to Mn⁵⁺ does not likely occur in an octahedral environment. The resulting discharge

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 $\text{Na}_{2/3}\text{MnO}_2$. Later work by de la Llave and coworkers [21] explored the origins of the good electrode performance of $\text{P2 Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, which delivered a capacity of $\sim 190 \text{ mAh g}^{-1}$. 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 when 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(d)). The continuous reduction of the *a*-axis parameter was also indicative of the gradual oxidation from O^{2-} to O^{n-} ($n < 2$) during charge, compensating for the charge imbalance occurring in Mn^{4+} . Li et al. [24] observed the migration of lithium using NMR in $\text{Na}_{0.72}[\text{Li}_{0.24}\text{Mn}_{0.76}]\text{O}_2$; however, the movement of lithium was suppressed by the reinforced bond in the structure provided by Ti^{4+}O_2 in Ti-substituted $\text{Na}_{0.72}[\text{Li}_{0.24}\text{Ti}_{0.10}\text{Mn}_{0.66}]\text{O}_2$. The improved structural stability enabled the retention of high capacity for cycling. A similar effect was observed in a F-doped system, $\text{P2 Na}_{0.65}[\text{Li}_{0.22}\text{Mn}_{0.78}\text{F}_{0.01}]\text{O}_2$ [20]. However, the aforementioned $\text{P2 Na}_x[\text{Li}_y\text{Mn}_{1-y}]\text{O}_2$ compounds exhibited hysteresis between charge and discharge, as evident in Figure 2(a).

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 $\text{P2 Na}_x[\text{Li}_y\text{Mn}_{1-y}]\text{O}_2$ compounds with honeycomb structure (Figure 2(a)). They also compared the hysteresis using superstructured $\text{P2 Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ (Figure 2(e)). It is worth mentioning that a flat voltage plateau, induced by the $\text{O}^{2-/n-}$ redox pair at $\sim 4.1 \text{ V}$, was observed during charge and discharge for the superstructured $\text{P2 Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. 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 $\text{P2 Na}_x[\text{Li}_y\text{Mn}_{1-y}]\text{O}_2$ compounds first reduce the oxidized oxygen (O^{n-}) 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, $\text{Na}_x[\text{Li}_y\text{TM}_{1-y}]\text{O}_2$ ($0.9 \leq x \leq 1$, $y \leq 1/3$), 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 $\text{P2 Na}_{0.66}[\text{Li}_{0.22}\text{Ru}_{0.78}]\text{O}_2$. Lowering of the transition metal *d* energy is possible using 4*d* or 5*d* elements such as Ru and Ir; hence, the oxygen redox can be active in the nonbonding state of O *2p*. Ru^{4+} was first oxidized to Ru^{5+} , and further desodiation led to oxidation of oxygen, resulting in additional capacity but no evolution of O_2 gas from the crystal structure. The series of reactions resulted in a discharge capacity of $\sim 160 \text{ mAh g}^{-1}$. 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 O_2 release enabled reversible electrochemical reaction for 500 cycles.

2.1.2. $\text{P2 Na}_x[\text{Mg}_y\text{Mn}_{1-y}]\text{O}_2$. The importance of the $\text{Na}^+ - \text{O}(2p) - \text{Li}^+$ interaction for progression of the oxygen redox in the lattice of $\text{P2 Na}_x[\text{Li}_y\text{Mn}_{1-y}]\text{O}_2$ was explained in the previous section. Yabuuchi et al. [46] proposed the highly reversible electrochemical activity of $\text{P2 Na}_{2/3}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, 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^{4+} during charge, which may result in $\sim 40 \text{ mAh g}^{-1}$ of capacity assuming a $\text{Mn}^{3+/4+}$ redox. Surprisingly, the compound delivered a charge capacity of $\sim 150 \text{ mAh}$ with a plateau over 4.1 V undergoing a phase transition from P2 to O2, whereas the recovery on discharge was $\sim 210 \text{ mAh g}^{-1}$ 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^{4+} ($\sim 15\%$) was available for the first charge capacity. Clement et al. [47] observed structural stability in $\text{Na}_x[\text{Mg}_y\text{Mn}_{1-y}]\text{O}_2$ ($y = 0 - 0.1$), which led to the suppression of the Jahn–Teller distortion by Mn^{3+} and potential $\text{Mn}^{3+}/\text{Mn}^{4+}$ ordering in the structure. Later, Maitra et al. [48] confirmed the availability of the oxygen-redox chemistry in $\text{P2 Na}_{2/3}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, 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–

FIGURE 3: (a) Initial charge and discharge profiles of P2-type Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂ tested at 10 mA g⁻¹ (reproduced with permission from Ref. [29], Copyright 2014 The Royal Society of Chemistry); (b) projected density of state showing oxygen states at the Fermi level for P2-type Na_{0.5}[Mg_{0.25}Mn_{0.75}]O₂ (reprinted with permission from Ref. [51] Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (c) the concentration profiles of alkali ions Li, Na, and Mg within P2-type Na_{0.78}[Li_{0.25}Mn_{0.75}]O₂ (top) and P2-type Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ (bottom) electrode particles at 5 V charging condition (reprinted with permission from Ref. [52], Copyright (2016) American Chemical Society); (d) O-K mRIXS images charged (top) and discharged (bottom) P2-type Na_{2/3}[Mg_{1/3}Mn_{2/3}]O₂ electrodes after the 1st, 10th, 50th, and 100th cycles (red arrow: oxidized oxygen features in charged states) (reprinted with permission from Ref. [83] Copyright 2020 Frontiers Media S.A.); (e) projected density of state of charged P2-type Na_{0.5}[Mg_{0.25}Mn_{0.5}Co_{0.25}]O₂ (reprinted with permission from Ref. [35] Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

deficient oxide ion (oxygen hole) in the 2p orbital interacting with the Mg²⁺ 3s and Mn⁴⁺ 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}]O₂. It is interesting that the 3s state of Mg²⁺ 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_{1-y}]O₂ (Section 2.1.1). This finding suggests the placement of the O 2p orbital at the top of the valence band (Figure 3(b)). Mg²⁺ did not migrate, which is different from the Li⁺ migration in Na_x[Li_{1-y}Mn_{1-y}]O₂, 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}]O₂ and P2 Na_{0.78}[Li_{0.25}Mn_{0.75}]O₂. Even when Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂ was charged to 5 V, there was no indication of oxygen evolution nor Mg migration. In addition, charging of

Na_{0.78}[Li_{0.25}Mn_{0.75}]O₂ 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}]O₂. 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}]O₂ 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– $\square_{\text{Mg}}$ configurations [54, 55]. Interestingly, the Mg-deficient P2 $\text{Na}_{0.63}[\text{Mg}_{0.143}\text{Mn}_{0.820}\square_{\text{Mg}0.036}]\text{O}_2$ underwent a single-phase reaction during de-/sodiation [55], without showing a phase transition to the O2 or OP4 phase. The vacancy in $\text{Na}_{0.63}[\text{Mg}_{0.143}\text{Mn}_{0.820}\square_{\text{Mg}0.036}]\text{O}_2$ slightly lowered the average oxidation state of Mn compared with that of the vacancy-free $\text{Na}_{0.72}[\text{Mg}_{0.31}\text{Mn}_{0.69}]\text{O}_2$. In addition, it is interesting to see the additional voltage plateau over 4 V induced by the oxidation of oxygen in the lattice, even though the P2 phase was dominant in the plateau region. Their operando XRD study confirmed that the variation in the *a*-axis observed for $\text{Na}_{0.63}[\text{Mg}_{0.143}\text{Mn}_{0.820}\square_{\text{Mg}0.036}]\text{O}_2$ occurred after the reaction associated with the oxidation of Mn^{3+} to Mn^{4+} . The same effect was observed in $\text{Na}_{2/3}[\text{Mg}_{1/9}\text{Mn}_{7/9}\square_{\text{Mg}1/9}]\text{O}_2$, with not only the absence of the phase transition but a higher capacity than that of the vacancy-free compound [55]. DFT calculation indicated that the oxygen close to the vacancies (Na–O– $\square_{\text{Mg}}$) provides more charge than the oxygen coordinated with Mg (Na–O–Mg) on charge, resulting in more charge compensation with the presence of vacancies that induce the lower-level voltage plateau for the oxygen reaction. Therefore, these properties were responsible for the increased capacity with improved reversibility in these vacancy-containing compounds [51].

Efforts have been made to improve the sluggish oxygen-redox reaction in terms of the operation voltage, capacity retention, and rate capability by introducing transition metals (Ni [51] and Co [51]). Tapia-Ruiz et al. [49] demonstrated that increased operation voltage was achieved with partial substitution of Mg^{2+} by Ni^{2+} , $\text{Na}_{2/3}[\text{Mg}_{1/3-x}\text{Ni}_x\text{Mn}_{2/3}]\text{O}_2$ ($0 \leq x \leq 0.2$), with the added Ni resulting in the suppression of the P2 to O2 phase transition. Kim et al. [51] utilized the nature of the overlapping of density of states between cobalt 3*d* and oxygen 2*p* observed in LiCoO_2 , facilitating electron transfer. The effect of Co in $\text{Na}_{0.6}[\text{Mg}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ resulted in not only a high discharge capacity, 214 mAh g^{−1}, including the capacity provided by the oxygen redox, but also good capacity retention for 1000 cycles at a rate of 5C (1.82 A g^{−1}). Their pDOS demonstrated the effect of Co, which sufficiently lowered the bandgap energy to 0.61 from 2.65 eV, and the high DOS energy of oxygen relative to that of Mn and Co (Figure 3(e)). However, further investigation of these compounds is suggested to minimize the polarization during the oxygen redox process observed in the OP4-phase region.

2.1.3. P2 $\text{Na}_x[\text{Zn}_y\text{Mn}_{1-y}]\text{O}_2$. The potential use of Zn is also of interest because of its high Pauling electronegativity, 1.65, which is higher than that of Mg (1.33) that has no *d* orbital. Konarov et al. [57] compared the pDOS O 2*p* orbitals for $\text{Na}_{0.5}\text{MnO}_2$ and $\text{Na}_{0.5}[\text{Zn}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, with the latter having a large charge density between −1 and 0 eV for oxygen owing to the existence of the Na–O–Zn configuration. The desodiated state of $\text{Na}_0[\text{Zn}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ contained an unoccupied state of the O 2*p* orbital above the Fermi energy (Figure 4(a)). Unlike Li–O and Mg–O bonding, which are ionic, the high electronegativity in Na–O–Zn bonding is

likely to induce covalence in the structure. Zn migration or oxygen loss was not observed during de/sodiation, which may result in an increase in the Na–O–Zn bonding, resulting in an unpaired electron that can trigger $\text{O}^{2-/1-}$ redox, 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⁺, 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 P2 $\text{Na}_x[\text{Zn}_y\text{Mn}_{1-y}]\text{O}_2$ by replacing half of the Zn^{2+} with Ni^{2+} . The observed average discharge voltage was approximately 3.5 V, and their $\text{Na}_{2/3}[(\text{Ni}_{0.5}\text{Zn}_{0.5})_{0.3}\text{Mn}_{0.7}]\text{O}_2$ 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 $\text{Ni}^{2+/4+}$ redox reaction.

2.1.4. P2 $\text{Na}_x[\text{A}_y\text{Mn}_{1-y}]\text{O}_2$ (A: Ni, Cu, and Fe). P2 $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ is known to provide a reversible $\text{Ni}^{2+}/4+$ redox reaction with three voltage plateaus at 3.2, 3.6, and 4.1 V, 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 V to the oxygen-redox reaction [61–72]. Ma et al. [61] investigated $\text{Na}_{0.78}[\text{Ni}_{0.23}\text{Mn}_{0.69}]\text{O}_2$ with 7% vacancies in the *TM* layers. The desodiation induced the oxidation of Ni^{2+} toward Ni^{4+} , and the oxidation of oxygen was also confirmed by XAS when Ni was oxidized to 4⁺, which corresponds to the plateau seen over 4.1 V. 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 V was mainly governed by the oxygen-redox reaction. The signature seen at 523 eV 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 2*p* in the e_g^* (Ni–O) becomes higher than that of Ni3*d*, which triggers the oxygen-redox reaction. Zhang et al. [65] observed O_2 release from the structure at the highly charge state, which produces a dense $\text{Ni}_2\text{Mn}_2\text{O}_7$ layer on the outer surface of $\text{Na}_{2/3-x}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$. This, in turn, plays a role in impeding Na^+ diffusion, causing irreversible capacity in the first cycle. They circumvented the O_2 release by introducing a small amount of Fe^{3+} , $\text{Na}_{2/3}[\text{Fe}_{2/9}\text{Ni}_{2/9}\text{Mn}_{5/9}]\text{O}_2$ (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

FIGURE 4: (a) Projected density of state for fully desodiated P2-type $\text{Na}_0[\text{Zn}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and spatial hole density (yellow) for $0 \text{ eV} < E < 1 \text{ eV}$ and (b) cyclability of P2-type $\text{Na}_{2/3}[\text{Zn}_x\text{Mn}_{1-x}]\text{O}_2$ ($x = 0-0.3$) (reprinted with permission from Ref. [57], Copyright 2019 Elsevier); (c) voltage profile and reaction mechanism of high voltage P2-type $\text{Na}_{2/3}[\text{Zn}_{0.125}\text{Ni}_{0.125}\text{Mn}_{0.7}]\text{O}_2$ (reprinted with permission from Ref. [60], Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (d) DEMS analysis of oxygen evolution during the first charge for $\text{Na}_{2/3}[\text{Fe}_{2/9}\text{Ni}_{2/9}\text{Mn}_{5/9}]\text{O}_2$ cathode (reprinted with permission from Ref. [65], Copyright (2020) American Chemical Society).

desodiation. This series of reactions is responsible for the suppression of oxygen release in the structure in the highly charged state. Co-doping of Cu/Mg was also effective to

retain the oxygen-redox reaction associated with Ni redox in $\text{Na}_{0.67}[\text{Ni}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ [64]. Note that a prerequisite for oxygen redox is the unhybridized O 2p orbital that is

FIGURE 5: (a) The first charge and discharge curves of P3-type $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ 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 $\text{Na}_{2/3}[\text{Mg}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ 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- $\text{Na}_{0.67}[\text{Mg}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ (black) and oxygen- $\text{Na}_{0.67}[\text{Mg}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ (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 O_2 and CO_2 collected during the first and second charging process of P3-type $\text{Na}_{0.5}[\text{Mg}_{0.15}\text{Al}_{0.2}\text{Mn}_{0.65}]\text{O}_2$ (reprinted with permission from Ref. [92], Copyright (2020) American Chemical Society).

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 Ni^{4+} , 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

O₂ release. The incorporation of more covalent character into the structure using Fe³⁺ 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 Fe³⁺ or Cu²⁺ is placed at the *A* sites in Na_x[A_yMn_{1-y}]O₂ rather than Ni²⁺. 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_yMn_{1-y}]O₂ (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_{0.6}[Li_{0.2}Mn_{0.8}]O₂ (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-/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 O₂ release from the lattice. Wu et al. [90] visualized the activity of oxygen for P3 Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂, 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}]O₂ was able to present the flat voltage plateau activated by the O^{2-/n-} redox pair, which is similar to the behavior of the superstructured P2 Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ [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_x[Mg_yMn_{1-y}]O₂ (Figure 3(a)), Kim et al. [91] investigated the availability of oxygen redox in P3 Na_{0.67}[Mg_{0.2}Mn_{0.8}]O₂. Compared to the charge capacity obtained in P2 Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂, 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_{0.2}Mn_{0.65}]O₂. 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, O₂ 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_{0.28}Mn_{0.72}]O₂, where no evolution of

O₂ 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}]O₂. A similar tendency was also observed in Li[Ni_{0.8}Al_{0.2}]O₂ [93], in which oxygen evolution progressed more when Al³⁺ 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}]O₂ [94], and small hysteresis was observed as a result of the electroconductive Co³⁺ in P3 Na_{0.67}[Co_{0.2}Mn_{0.8}]O₂ [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 O₂ evolution, which may induce the formation of a byproduct like Na₂CO₃, 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 through-out cycling.

2.3. P1-Type Layered Compounds (Na₂Mn₃O₇). An important alternative to improve upon the reversibility of oxygen-redox reactions is the use of vacancy-containing materials, as shown for the P2-□_{Mg} material in Section 2.1.2. Herein, another P-type sodium-deficient cathode Na₂Mn₃O₇ (Na_{4/7}[□_{1/7}Mn_{6/7}]O₂) with □_{Mn} vacancies is presented [73–81]. The layered structure of Na₂Mn₃O₇ with every seven Mn site vacancies ($\sqrt{7} \times \sqrt{7}$ superstructure) is displayed in Figure 6(a) [74]. Na₂Mn₃O₇, with a valence of Mn⁴⁺, 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). Na₂Mn₃O₇ 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, Na₂Mn₃O₇ 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].

Na₂Mn₃O₇ 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+/4+} redox reaction [73]. Later, several groups showed that the desodiation of Na₂Mn₃O₇ 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 □_{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

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 NaMn₃O₇ (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).

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 [□_{1/7}Mn_{6/7}]₂O₂ 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/in situ* paramagnetic resonance and 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 (*P* $\bar{1}$ -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 O[•] over the peroxide-like O₂²⁻ 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 π -bonded Mn-d and O-p orbital network formed a collective delocalized redox center [81]. Therefore, the authors concluded that such a π -network rather than any local bonding environment was responsible for the two-step voltage profile with a low-

voltage hysteresis and structural evolution observed in $\text{Na}_2\text{Mn}_3\text{O}_7$.

3. Stoichiometric Sodium Transition-Metal Layer Structures Na_xTMO_2 ($x \sim 1$)

Sodium stoichiometric layered compounds, Na_xTMO_2 ($x \sim 1$) 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 $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ [85], the analog of $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (Li_2MnO_3). DFT calculations have predicted the possibility of a thermodynamically stable O3-type $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ 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 $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($C\bar{2}m$) by carefully adjusting the synthetic conditions and stoichiometry [85]. In $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, Na and $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ stack alternatively, and Li^+ and Mn^{4+} form a honeycomb ordering within the $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ slabs. Oxygen is coordinated by two Mn, one Li, and three Na to form an $\text{OMn}_2\text{LiNa}_3$ octahedron. Theoretical work by Kim et al. [84] highlighted the possibilities of oxygen redox by oxidizing $\text{Na}-\text{O}(2p)-\text{Li}$ to compensate for the electronic charge during sodium extraction in $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$. 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 $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ 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 $\sim 250 \text{ mAh g}^{-1}$ (0.9 Na^+ extraction), attributed to the oxygen $\text{O}^{2-}/\text{O}^{1-}$ redox reaction accompanied by partial Li migration from the *TM* layer to the tetrahedral Na sites and O_2 release. The resulting discharge capacity was $\sim 190 \text{ mAh g}^{-1}$ and was maintained during 40 cycles. *In situ* XRD revealed O3(I)–O3(II)–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 O_2 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 vacan-

cies 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 $\text{O}^{2-}/\text{O}^{1-}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox were responsible for the delivered capacity.

3.2. Ru-Based Compounds. The stoichiometric sodium Ru-based compounds O3-type $\text{Na}[\text{Mg}_{2/3}\text{Ru}_{1/3}]\text{O}_2$ and $\text{Na}[\text{Mg}_{1/2}\text{Ru}_{1/2}]\text{O}_2$ ($R\bar{3}m$) with oxygen-redox participation were studied in the work of Jia et al. [96]. Both materials were crystallized in the $R\bar{3}m$ space group; however, the oxidation state of Ru was different, namely, Ru^{4+} in $\text{Na}[\text{Mg}_{1/2}\text{Ru}_{1/2}]\text{O}_2$ and Ru^{5+} in $\text{Na}[\text{Mg}_{2/3}\text{Ru}_{1/3}]\text{O}_2$, respectively. On the basis of *in situ* XRD, Raman, and DEMS analyses, it was shown that during the first charge, $\text{Na}[\text{Mg}_{2/3}\text{Ru}_{1/3}]\text{O}_2$ underwent a simple O3–O'3 transition; however, due to the O_2 release at the end of charge, a specific distorted structure was formed. A more complicated sequence of O3–O'3–P3 phase transitions was observed for $\text{Na}[\text{Mg}_{1/2}\text{Ru}_{1/2}]\text{O}_2$, accompanied by sluggish kinetics without O_2 loss. The authors claimed that irreversible lattice oxygen loss in $\text{Na}[\text{Mg}_{2/3}\text{Ru}_{1/3}]\text{O}_2$ and the formation of a distorted structure sacrificed for a more stable structure with solely $\text{Ru}^{4+}/\text{Ru}^{5+}$ cationic redox for the subsequent cycling. Instead of using redox-inactive Mg^{2+} , Voronina et al. proposed to use redox-active Ni^{2+} to provide additional capacity and achieved reversible capacity of 154 mAh g^{-1} for $\text{Na}[\text{Ni}_{2/3}\text{Ru}_{1/3}]\text{O}_2$ material [86]. DTF calculations, operando XRD, and XANES revealed reversible cationic $\text{Ni}^{2+}/\text{Ni}^{3+}$ and anionic $\text{O}^{2-}/\text{O}^{1-}$ redox reactions with no loss of O_2 in the crystal structure of $\text{Na}[\text{Ni}_{2/3}\text{Ru}_{1/3}]\text{O}_2$.

3.3. Ir-Based Compounds. In analogy to O3- $\text{Na}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, the material $\text{Na}[\text{Li}_{1/3}\text{Ir}_{2/3}]\text{O}_2$ ($C\bar{2}c$) 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 $1.5 \text{ Na}^+/\text{Li}^+$ through a complicated multiphase process and subsequent segregation of Li-rich Li_xIrO_2 and Na-rich Na_xIrO_2 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 Mg^{2+} or Zn^{2+} 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- NaCrS_2 and O3- $\text{NaCr}_{2/3}\text{Ti}_{1/3}\text{S}_2$ [97, 98]. Originally, the sulfur-redox chemistry in chalcogenides can be traced back to the work of Whittingham on TiS_2 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 $\text{Na}_{1-x}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$. (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 $\text{NaCr}_{2/3}\text{Ti}_{1/3}\text{S}_2$ during the first cycle at a rate of C/5. (e) STEM image of pristine and fully charged $\text{NaCr}_{2/3}\text{Ti}_{1/3}\text{S}_2$ 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 Shadiké 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-□ 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 NaCr_{2/3}Ti_{1/3}S₂ was boosted to 186 mAh g⁻¹ due to the synergetic effect of the anion S²⁻/S¹⁻ 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:

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)ⁿ⁻ 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* $\bar{3}$ *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 Na_{1-x}FeO₂, *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* $\bar{3}$ *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 microscopic (STEM), but also oxidation of oxygen during desodiation of α-NaFeO₂ using XAS spectra. Moreover, DFT calculations showed that near Fermi level, the Fe 3*d* and O 2*p* 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 Fe₃O₄ (cubic spinel *Fd* $\bar{3}$ *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.

FIGURE 8: (a) Charge-discharge profiles of α -NaFeO₂ (reprinted with permission from Ref. [104]. Copyright (2012) The Electrochemical Society of Japan). (b) Schematic illustration of irreversible Na⁺ intercalation. Formation of Fe₃O₄ on the surface of α -NaFeO₂. Reprinted with permission from Ref. [107]. Copyright (2019) American Chemical Society. (c) Crystal structure of NaVO₃. (d) Charge-discharge curve of NaVO₃ (reprinted with permission from Ref. [109]. Copyright (2020) American Chemical Society).

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 2*p* 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 Na_xTMO₂ (*x* > 1)

Na-rich materials, Na₁[Na_{*x*}TM_{1-*x*}]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 Li₂TMO₃ (Na[Na_{1/3}TM_{2/3}]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 Na₂TMO₃ 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 Na₂RuO₃ (*R* $\bar{3}$ *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 (Na_{2-*x*}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 Na₂Ru_{1-*y*}Sn_{*y*}O₃ 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⁻/O^{*n-*} 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-Na₂RuO₃ (*C2/m*) and the disordered analog D-Na₂RuO₃ (*R* $\bar{3}$ *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(2*p*)–Ru(*t_g*) reorganization with the short O–O distances in distorted RuO₆. Because of the in-plane honeycomb ordering, the O-Na₂RuO₃ electrode demonstrated enhanced capacity of 180 mAh g⁻¹ compared with

FIGURE 9: (a) Structure of ordered and disordered Na₂RuO₃. (b) Electrochemical properties of disordered and ordered Na₂RuO₃ (reprinted with permission from Ref. [32]. Copyright (2016) Nature Publishing Group). (c) In situ XRD pattern during the first cycle of Na₂RuO₃ with the corresponding cycling curve. (d) Crystal structures of O3-Na₂RuO₃, O1-Na₁RuO₃, and O1'-Na_{1/2}RuO₃ phases (reprinted with permission from Ref. [33]. Copyright (2019) Nature Publishing Group). (e) Combined partial density of state (PDOS) profiles of Ru 4d and O 2p electrons in Na_{1/3}[Na_{0.67}Ru_{0.33}]O₂ (reprinted with permission from Ref. [34]. Copyright (2020) American Chemical Society).

that of 135 mAh g⁻¹ for D-Na₂RuO₃ (Figure 9(b)). The authors showed that 30% extra capacity was achieved by the spontaneously ordered intermediate ilmenite O1-Na₁RuO₃ ($R\bar{3}$) phase, which accommodates the cooperative distortion of the RuO₆ octahedra. In contrast, in the case of disordered material, the intermediate P3-Na₁RuO₃ phase exhibited strain frustration, which did not allow activation of the oxygen-redox reaction. Further study of ordered O-Na₂RuO₃ showed O3–O1–O1' structural phase transformations during charge with an intermediate O1-Na₁RuO₃ phase and O1'-Na_{1/2}RuO₃ ($P\bar{3}1m$) 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 Mn⁴⁺-substitution strategy was adopted in Na₂Ru_{1-x}Mn_xO₃ ($x = 0 - 0.3$) material [38]. Mn⁴⁺ 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, Mn⁴⁺ 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.

Na₃RuO₄ (Na[Na_{1/2}Ru_{1/2}]O₂) ($C2/m$) is a further expansion of the Na₂RuO₃ cathode material toward higher sodium content (O/TM ratio) Ru-based materials with oxygen-redox

activity [40–42]. The crystal structure of Na₃RuO₄ is described as a layered structure with a Ru⁵⁺ framework forming isolated tetramers of the edge-sharing RuO₆ octahedra in the Na_{1/2}Ru_{1/2}O₂ layer (Figure 10(a)) [41]. The reaction mechanism in Na₃RuO₄ is currently under debate by several groups [40–42]. The first work of Qiao et al. on the chemical extraction of Na from Na₃RuO₄ 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 Ru⁵⁺ 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 Ru⁵⁺ to Ru⁶⁺ occurs, leading to the formation of Na₂RuO₄ ($P2_1/c$), followed by oxygen reduction at the end of charge through a solid-solution process with the formation of amorphous Na_xRuO₄ ($x = 0 - 1$). 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 Na₃RuO₄ structure with its initial crystallinity [41]. In the work of Hu et al. [42], similar results were shown, clarifying that both Ru⁵⁺/Ru⁶⁺ and O²⁻/O¹⁻ 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, Na₃RuO₄ showed electrostatically more unstable behavior upon deep desodiation than Na₂RuO₃, which could be explained by the higher Na vacancy content

FIGURE 10: (a) Crystal structure of Na_3RuO_4 (reprinted with permission from Ref. [41]. Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (b) Voltage profile of first cycle and capacity dependent in situ Raman spectral contour plot (reprinted with permission from ref [40]. Copyright (2018) The Royal Society of Chemistry).

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 Na_2IrO_3 ($\text{Na}[\text{Na}_{1/3}\text{Ir}_{2/3}]\text{O}_2$) ($C2/m$) 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) Na_2IrO_3 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 $\sim 130 \text{ mAh g}^{-1}$) with neither oxygen release or cationic migrations to interlayer (alkali-) sites. During extraction of sodium ions, the O3-type layered structure first converted to $\text{O1}'$ ($P\bar{1}$) and further to O1 ($C\bar{2}m$) 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 O_2 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 $\text{O}^{2-}/\text{O}^{1-}$ and $\text{Ir}^{4+}/\text{Ir}^{5+}$ 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 IrO_6 octahedra in the pristine Na_2IrO_3 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 $\text{Na}_{1.2}\text{Mn}_{0.4}\text{Ir}_{0.4}\text{O}_2$ [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 $\text{Mn}^{3+}/\text{Mn}^{4+}$ cationic redox and $\text{O}^{2-}/\text{O}^{1-}$ oxygen redox without Ir participation. *In situ* Raman and XPS analyses were employed to confirm the reversibility of the O_2^{2-} formation. Even though

Ir did not participate in the electrochemical reaction throughout the entire charge and discharge process, $\text{Na}_{1.2}\text{Mn}_{0.4}\text{Ir}_{0.4}\text{O}_2$ demonstrated similar to Na_2IrO_3 asymmetric transformation during charge, especially in the $\text{O}'1\text{-O}1$ 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 Na_2IrO_3 was proposed by Pearce et al. by synthesizing a fundamentally different crystal structure of $\beta\text{-Na}_{1.7}\text{IrO}_3$ [45]. $\beta\text{-Na}_{1.7}\text{IrO}_3$ was obtained by the electrochemical exchange of Li into Na in $\beta\text{-Li}_2\text{IrO}_3$ material. In the structure of $\beta\text{-Na}_{1.7}\text{IrO}_3$, 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 $\beta\text{-Na}_{1.7}\text{IrO}_3$ material underwent multiple structural phase transitions with different lattice parameters and a large volume change $\sim 26\%$ during sodiation/desodiation, it maintained the same IrO_3 framework (Figure 11(g)). The charge-compensation mechanism revealed that both the anionic $(\text{O}_2)^{n-}$ redox and cationic activity of $\text{Ir}^{5+}/\text{Ir}^{4+}$ 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

FIGURE 11: (a) First and second galvanostatic cycles of O3-Na₂IrO₃ vs. Na. (b) Refinement of neutron diffraction patterns for the O3-Na₂IrO₃ and O1-Na_{0.5}IrO₃ structures. (c) Projected DOS and O-O crystal orbital overlap population (COOP) of Na₂IrO₃. (d) Respected presentation of electron density differences (reprinted with permission from Ref. [43]. Copyright (2016) American Chemical Society). (e) Structure of β-Na_{1.7}IrO₃. (f) ABE-STEM simulation of the β-Na_{1.7}IrO₃. (g) Synchrotron operando XRD patterns of β-IrO₃ charged vs. Na^{+/Na} and subsequent charge together with the corresponding charge profile (reprinted with permission from Ref. [45]. Copyright (2018) American Chemical Society).

combination of a two-phase composite was observed by Yang et al. in P2/O3 Na_{0.8}Li_{0.2}Fe_{0.2}Mn_{0.6}O₂, 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 Fe^{3+/4+} redox along with partial Mn^{3+/4+} redox and oxygen contribution. Using NMR Li⁷, it was shown that a portion of lithium migrated from the *TM* layer to the alkali layer during the first charge. However, further distribution of lithium between the Na layer and *TM* layer remained constant during electrochemical cycles. The biphasic 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 Na_{0.8}Li_{0.2}Fe_{0.2}Mn_{0.6}O₂ 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 Wh 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. Na_{1.3}Nb_{0.3}Mn_{0.4}O₂ [114] and Na_{1.14}Mn_{0.57}Ti_{0.29}O₂ [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

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.

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