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Recent Advances in Mn-Rich Layered Materials for Sodium-Ion Batteries

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Branded with low cost and a high degree of safety, with an ambitious aim of substituting lithium-ion batteries in many fields, sodium-ion batteries have received fervid attention in recent years after being dormant for decades. Layered materials are a major focus of study owing to the extensive experience already gained in lithium-ion batteries, and the pursuit of a Mn-rich composition is critical to reduce the cost while retaining the performance. This review provides a timely update of the recent progress of Mn-rich layered materials for sodium-ion batteries based on the understandings of the phase forming principles, structure transformation upon cycling and charge compensation mechanisms and discusses potential ambiguities in the pursuit of high-performance materials.

1. Introduction

The recent global lithium price soaring to an all-time-high has led to a serious motivation to replace lithium-ion batteries (LIBs) in certain fields, which has driven the unprecedented surging attention on sodium-ion batteries (SIBs) lately from the market, policy makers, manufacturers, and researchers. The abundance of sodium in the earth crust compared with lithium has always been a key factor when considering the advantages of developing SIBs. As the SIBs technique matures, these advantages have also been extended to properties such as low-temperature performance, safety, transportation difficulty, cell design and so forth. Therefore, SIBs have become the major technique aimed at substituting LIBs in low-speed electric vehicles, grid-scale energy storage, 5G station energy storage. Many countries, such as China, have developed national strategies in promoting SIBs to achieve de-carbonization targets.

Despite being invented almost at the same time as LIBs, SIBs did not attract tremendous attention until recently when the cost of LIBs became an issue. One of the main reasons is that SIBs intrinsically hold lower energy density than LIBs. Studies have been rigorously pursuing high density at the lowest possible cost, yet the elements that supply high energy density are normally pricey. In the meantime, exploitation of the energy density under extreme conditions puts the material structure at risk. These three factors form a “triangle paradox” as shown in Figure 1. The ultimate goal is to find a point where the main factors of cost, energy density and structural stability are concurrently balanced. Tracing back to the materials developed previously or being developed currently, one can easily find examples of how efforts were made to find such balance. In LiMPO₄ (M = Fe, Mn, Ni, Co, or the mixtures of such) families, despite enjoying the merit of rather low cost, LiFePO₄ does not have very high energy density. Therefore, attempts were made to substitute the Fe with Mn/Ni/Co partially or fully so as to elevate the average voltage. However, these elements are either too expensive or prone to dissolution, thus reducing the cycle life. In layered lithium cathode materials, increasing the Ni amount has been the major approach to elevate the energy density, but it would inevitably introduce side effects such as Li-Ni ion exchange, phase transition and so forth that lead to cycle life concerns. As a matter of fact, the position of the balance point also depends on the target market. When deployed in electric vehicles/ scooters, energy density is considered as a more important factor, which leads to research directions that elevate energy density at the risk of sacrificing the cycle life. The order follows “energy density > safety ≥ cycle ≥ cost”. When deployed in grid storage applications, however, cycle life (>10000 times) becomes a more important factor, and energy density does not stand out as the priority. The order follows “cycle ≥ safety ≥ cost > energy density”. However, it remains elusive whether there is a way to achieve the longest cycle life, highest possible energy density and the lowest cost simultaneously.

The cost breakdown of a sodium-ion battery pack has been estimated by various resources. Cathode materials share ≈1/3 of the overall cost and contribute to the energy density significantly. Therefore, the development of a sodium-ion battery, under most circumstances, is determined by the cathode material development.
Through the past years, three major categories of cathode materials have been investigated, including layered materials, polyanionic materials and Prussian blue analogues.[5–9] Figure 2 shows a radar map that compares the capacity, voltage, rate, cyclability, cost efficiency, safety, processability, air stability, and material density of each material. Each type of material has its advantages and disadvantages that determines its field of potential application. In general, mobile products require higher energy density and lower cost, hence materials in the layered metal oxides category and Prussian blue analogues category are found to be more ideal candidates. Within these two families of materials, layered metal oxides have already been extensively studied and used in LIBs, they are supposed to be the one yet to be industrialized at the quickest pace. The major hassles that need to be addressed are material cost, structure stability, as well as energy density improvement. Prussian blue analogues have shown impressive energy density at very low cost thanks to the use of cheap elements like Fe, Mn, C, N etc. However, the structure can be easily damaged by water molecule in ambient atmosphere, making it very difficult for industrial processing. In addition, concerns have been raised that cyanides might release from the material in case of heating, which is extremely dangerous when collision or fire accidents happen. On the other hand, the utilization of SIBs in stationary grid storage requires high safety, long cycle life and cost more, which has promoted the use of polyanionic compounds such as iron-based pyro phosphates among startup companies.[7,10,11]

While both LIBs and SIBs chiefly adopt layered materials as the cathode materials, different pathways are being taken to achieve the ideal cathode material. In LIBs, the process follows a bottom-up triangle. It did not take too long to come to a consensus that Ni, Co, Mn and occasionally Al should be used as the building blocks, with the major composition evolving from LiNi1/3Mn1/3Co1/3O2 (NMC333) to LiNi0.8Mn0.1Co0.1O2 (NMC442), LiNi0.3Mn0.3Co0.4O2 (NMC532), LiNi0.6Mn0.2Co0.2O2 (NMC622), LiNi0.8Mn0.1Co0.1O2 (NMC811), LiNi0.85Co0.1Al0.05O2 (NCA851005), and recently LiNi0.9Mn0.05Co0.05O2 (NMC900505) etc.[12] The simple structure stacking sequence follows an O3-type with the lithium-ions residing at the octahedral sites. More work was done on revealing the phase transition behaviors, charge compensation mechanisms with a correlation to its electrochemical behaviors. In practice, the evolution from low-Ni to high-Ni composition has been mostly slowed down by material production in the 2010s. Optimization of the physical properties like tap density, secondary particle morphologies, conductivities through co-precipitation technique, adjusting the sintering process and slurry processing etc. has been the major challenge addressed in layered lithium cathode materials in recent years. For SIBs, however, the process is anticipated to happen in reverse. Unlike LIBs that adopt Ni, Co, Mn and Al only, layered sodium materials have been searching for a combination of different elements since the beginning. A handful of elements such as Mn, Fe, Cu, Ti, Ni, Mg, Al, and Cr have all been used to build the material.[13] To date, Mn, Ni, Fe, Cu, Mg, and Li (in descending order of the amount) have been used by start-up companies such as HINA, Natrium, and Faradion. Each element was identified to play critical roles in determining the stacking sequences, phase transitions and so forth. The cost of specific elements is also a critical concern since SIBs need to be cost-efficient. Once these problems are addressed, it is anticipated that tailoring the physical properties and material processing.
processing by borrowing from the experience gained in the LIB industry will speed up the commercialization of SIBs.

The above discussions imply that a breakthrough in optimizing the composition of a layered material with low cost, high performance, and long cycle life is critical to the development of SIBs. Cost-wise, Ni-rich layered cathode materials are excluded since the price of Ni is very high due to the extensive usage in LIBs, even though the capacity can be very impressive. Performance-wise, Ti-rich layered materials cannot operate at an acceptable voltage range for cathode materials and thus are eliminated. Cycle-wise, Fe-rich layered materials are found to experience severe electrolyte oxidation decomposition due to the parasitic reactions with Fe\(^{4+}\), and the migration of Fe\(^{4+}\) to the sodium layer, which makes it an inferior choice. The only candidate that has the potential to fulfill these requirements is layered Mn-rich materials, which is not surprising since layered lithium cathode materials also started with Mn-rich compositions. As a matter of fact, the development of Mn-rich lithium cathode materials did not prosper eventually, this is mostly due to 1) the aggressive demand for high capacity; 2) Mn dissolution at high operating voltage; 3) Mn migration to the lithium layer; 4) structural distortion caused by the Jahn–Teller effect of Mn\(^{4+}\); 5) oxygen release. These factors can be circumvented in layered Mn-rich materials, therefore, it is necessary to update the progress in a timely manner. In this regard, this review paper is aimed at summarizing recent advances in the development of layered Mn-rich cathode materials, spanning from the structure-forming principles to phase transitions and different charge compensation behaviors. Insightful discussions on several ambiguous topics will also be carried out.

2. Layered Mn-Rich Sodium Materials

Mn has been an indispensable element in most Li-ion battery cathode materials. In layered LiNi\(_x\)Mn\(_{2-x}\)O\(_2\) (NMC) and spinel LiNi\(_x\)Mg\(_{1-x}\)O\(_2\) (LMO), Mn serves as a stabilizing agent that prevents the material from collapsing. In other materials, such as spinel LiMn\(_2\)O\(_4\) (LMO), LiMnPO\(_4\) (LMP), and LiFe\(_{x}\)Mn\(_{1-x}\)PO\(_4\) (LFMP), Mn serves as a redox center that supplies capacity to the battery. Layered materials of SIBs differ from their lithium counterparts in that the stacking sequence can be largely impacted by both the transition metal types and composition, as well as the amount of sodium in the alkaline layer.

According to Delmas’s notations, layered SIBs cathode materials can be categorized as O and P-types. In O-type materials, the sodium-ions reside at the octahedral sites in the alkaline layer. In P-type materials, the sodium-ions reside at the trigonal prismatic sites. Figure 3 shows the schematics of these two structures as well as their sodium occupation sites. The O3 notation stands for the occupation of Na-ions in the octahedral sites with 2 layers per repeating sequence. The P2 notation stands for the occupation of Na-ions in the trigonal prismatic sites with 3 layers per repeating sequence. Under most circumstances, O3 structure is converted into P3 structure and P2 structure turns into O2 structure during charging, and the reverse process happens during discharge. These two processes are accompanied with large volume expansion and contraction respectively, thus significantly affecting the structural integrity of the materials. This section primarily focuses on the formation principles of different types of structures and their features. The actual phase transitions during operation can be much more complex when other factors such as vacancy ordering, oxygen evolution, as well as cation migration are involved. These will be discussed in Section 3.

2.1. Formation Principles of Mn-Rich Layered Materials

The structures of layered sodium cathode material are largely dictated by the composition, namely Na\(_x\)M\(_y\)O\(_z\), where M refers to one or a combination of multiple metallic elements. Layered lithium cathode materials LiMO\(_2\) mostly stabilize in the form of O3 structures, and a slight deficiency in the Li value would lead to the formation of species like spinel phases. Layered sodium cathode materials tend to form both O and P structures. Tremendous efforts have been devoted to predicting the structure based on the composition. Early on, the structure was determined by measuring the TM–O distances (Figure 4a). Using the ratio between the interlayer distances of d(O–Na–O) and d(O–TM–O) as an indicator, it is possible to predict whether the material will stabilize in P2 or O3 phases, distinguished by a ratio of \(\approx 1.62\). However, the accuracy of this measurement has been rather rough. This problem was not further resolved until recently when the concept of cationic potential was introduced. According to the analysis, the cationic potential can be defined as the sum of the TM’s weighted average ionic potentials multiplied by the Na weighted average ionic potentials normalized to the ionic potential of the anion, as in Equation 1 below:

\[
Φ_{\text{cation}} = \frac{Φ_{\text{TM}} Φ_{\text{Na}}}{Φ_{\text{O}}} \tag{1}
\]

Using the cationic potential as a tool, the authors have successfully designed several materials with specific structures. By plotting the \(Φ_A\) against the \(Φ_{\text{cation}}\) of given compositions, they came up with Figure 4b, which shows the boundary of O3 and
P2 phases. While Mn and Ni are the major elements that constitute layered sodium materials, there is a lack of studies on the composition-phase correlation. In light of this, Xiao et al. did a thorough survey study on the composition of Na\textsubscript{x}Mn\textsubscript{y}Ni\textsubscript{1-y}O\textsubscript{2} and its corresponding structures. The results are shown in Figure 4c. When 0.66 ≤ x ≤ 1 and 0 ≤ y ≤ 1, the resulting materials demonstrate an evident trend of different phase regions. Apparently, when the amount of Mn is >60%, there is a good chance that the material would demonstrate a P2 phase, or at least a P2-dominant phase, regardless of the Na amount. When the amount of Mn is between 40% and 60% with an appropriate x number, the resulting material shows a mixture of P2 and O3 phases. With y ≤ 40%, NiO becomes a universal impurity phase. Using the composition of Na\textsubscript{0.85}Mn\textsubscript{0.6}Ni\textsubscript{0.4}O\textsubscript{2} as a model, the authors substituted 0.1Mn with other transition metals and demonstrated that the resulting ratio of P2 phase follows the trend of the corresponding cationic potential rather well. The surveyed elements, in the ascending order of P2-promoting capability, follows the trend of Ti < Co < Fe < Cu < Ni < Mn. Such a result indicates that Mn greatly promotes formation of the P2-phase, whereas Ti is a very O3-phase promoting element. The conclusion is in agreement with other studies that demonstrate the possibility of constructing Na-rich P2 phase with Mn and Na-poor O3 phase with Ti. This synthesis phase diagram (Figure 4c), despite only showing the case with 900 °C synthesis temperature, shows that there is a good likelihood that cationic potential can play a pivotal role in screening layered sodium cathode material structures and facilitate the progress. However, there are two scenarios that were overlooked in the definition of cationic potential concept. The
first one is synthesis temperature. Many studies have shown that even the same composition can lead to different stackings when sintered at different temperatures. An example is the progression of the P3-P2 phase transition upon increasing temperature, which will be discussed later. The second factor that needs to be further considered are vacancies. An example is the use of de-lithiated Li1.2Mn0.54Ni0.13Co0.13O2 for sodiation as reported by Xiao et al.\textsuperscript{[33]} Li1.2Mn0.54Ni0.13Co0.13O2 is a type of Li-rich layered cathode material that has 20% of the transition metal layer being occupied by lithium. It is synthesized by mixing the precursor Mn0.68Ni0.16Co0.16(OH)2 with an appropriate amount of lithium source followed by calcination. When de-lithiated to 4.6 V, these lithium ions are extracted, leaving vacancies in the transition metal layer.\textsuperscript{[34]} Using this structure as a host for Na intercalation, the authors found that the fully sodiated phase belongs to an O3 structure (Figure 4e) and the sodiation process follows a solid solution manner. However, when directly mixed with a sodium source followed by calcination, the composition of Na[Li0.2Mn0.54Ni0.13Co0.13]O2 both fall into the P2-structure category. This study reveals that the prediction of the layered material structure using cationic potential also needs further refinement with a full consideration of the effect of vacancies.

2.2. Na-Rich P2-Type Layered Materials

Since Mn is a very P2-phase promoting element, high amounts of Mn in the structure have a strong tendency of driving the structure toward P2 formation. P2 structure is excellent in terms of cost and fast ion diffusion, yet the amount of sodium in the composition is quite low, which is disadvantageous for full-cell performance. Even though sodium compensation agents, pre-sodiation treatments and other strategies have been proposed to counterbalance the low amount of sodium, there is still a great need to search for Na-rich P2 materials.\textsuperscript{[35]} Figure 5 shows a summary of the range of x in NaMn1-yMyO2 where stable P2 phase can form.\textsuperscript{[36]} It can be seen that the structure remains a layered framework within a wide range of x, this differs significantly from its lithium counterpart, where little deviation from x = 1 can lead to the structure transformation to a spinel phase. With a basic composition of NaMnO2, the structure falls into the P2 category when 0.6 ≤ x ≤ 0.7, and O3' α-NaMnO2, β-NaMnO2 when x = 1. The incorporation of different elements into the composition can alter the range of x while maintaining P2 structures. For instance, when M is Ni, the range turns into 0.6 ≤ x ≤ 0.7. When M is Li, the range turns into 0.66 ≤ x ≤ 0.8. When M is Mg, the range turns into 0.28 ≤ x ≤ 0.67. Only when M is both Ni and Li, the upper limit of x can be extended to 0.83, which is close to practical applications without the need for pre-sodiation. However, from the perspective of phase stability, the maximum x value that can form a P2 phase is 0.9, thus there is great interest in searching for a composition that approaches this limit. Experimentally, Na-rich P2 materials have been obtained following the Li/Ni combination. Meng et al. synthesized a P2-Na0.83[Li0.07Ni0.31Mn0.62]O2 material.\textsuperscript{[37]} It demonstrates a reversible capacity of 145 mAh g\textsuperscript{-1} in the voltage range of 2.0–4.4 V. Since there is always sufficient Na-ions remaining in the layers upon de-sodiation, the layered structure can be well preserved. However, the migration of Li-ions from the transition metal layer to the alkaline ion layer or within the transition metal layer to lower coordination site presents a concern of Li loss during cycling, which can be circumvented by restricting the charging voltage.

![Figure 5](https://www.afm-journal.de/)

**Figure 5.** Ranges of x in NaMn1-yMyO2 with different final structures. Adapted with permission.\textsuperscript{[38]} Copyright 2015, IOP.
Another example is the synthesis of a high Na-content P2-type Na$_{65/54}$Li$_{7/54}$Ni$_{4/54}$Mn$_{34/54}$O$_2$. With such a high amount of Na in the structure, it is possible to promote the oxidation of Ni$^{2+}$ to Ni$^{4+}$ at a relatively low cutoff voltage of 2–4 V without losing the structural integrity. The material displays a capacity of over 100 mAh g$^{-1}$ as well as a cycle life of up to 3000 times.[32] The presence of vacancies in the TM layer might also drive the sodium upper limit to a Na-rich stoichiometry. Meng et al. synthesized a P2-structured Na$_{0.78}$Ni$_{0.22}$Mn$_{0.99}$O$_2$ without the use of Li.[33] The material stoichiometry shows 8% vacancy rate in the transition metal layer, which enables a 0.78 Na ratio under such a Mn-rich environment. Detailed analysis also reveals oxygen reactivity under high voltage, which is not surprising since the vacancy sites are coordinated by unhybridized oxygen.

2.3. Mn-Rich O3-Type Layered Materials

When there is a large amount of Mn in the structure, there is a high chance that it will turn into a P2 phase, or at least a combination of P2 and O3 phases. To form an O3 structure while having high amounts of Mn, substitution of other elements is necessary, which mostly includes Fe, Ti and Li.[34] When using Fe and Ti as the substitution element, it is possible to retain a full O3 phase with 50% Mn in the structure.[31,39] When using Li, however, the ratio of Mn can be substantially increased to 66% with a NaMn$_{2/3}$Li$_{1/3}$O$_2$ composition. A pure O3 structure with this composition, however, can only be attained by using Na$_3$O$_2$, Li$_2$O, Mn$_3$O$_4$ with precisely adjusted synthesis conditions.[16] Vacancies, which were discussed in the previous section, might also promote O3 phase with a Mn-rich composition.

2.4. Mixed P2 and O3 Materials

According to the definition of cationic potential, a given composition should result in a fixed structure, but there are many cases where mixed P2/O3 phases are reported despite having a designed Mn-rich composition. A typical example is the material designed and commercialized by Faradion (UK) with a composition of Na$_{x}$Ni$_{1-y-z}$MnxMgyTizO$_2$, which shows rather high performance with a mixed P2/O3 composition.[40] The benefit of this mixed phase is that the advantages of both phases are gained. In the meantime, these two phases undergo phase changes, hence resulting in layer gliding at different voltages: both phases could act as a stabilizer that interlocks the other when such gliding happens.[41–43] Figure 6a–c shows the atomic structures of Na$_{0.85}$Ni$_{0.5}$Mn$_{0.4}$Ti$_{0.1}$O$_2$ (Na0.85NMT) and Na$_{0.85}$Ni$_{0.5}$Mn$_{0.4}$Fe$_{0.1}$O$_2$ (Na0.85NMF) and their selected area electron diffraction (SAED) patterns. These two compositions differ only in the substitution of 10% Ti and Fe, yet the structure turned out to be drastically distinct. Na0.85NMT shows a pure O3 phase with unique layer spacing values, but Na0.85NMF shows an obvious intermixture of O3 and P2 phases that appear periodically. SAED patterns also corroborate that these two phases are spread out in a single particle. This leads to a speculation on whether these two nano-domains share the same compositions or not. Very few of the relevant works have discussed this topic, as this could involve multiple factors that need advanced characterization techniques to be deciphered. Several possible scenarios could result in this phenomenon. First, if the composition of the TM layer is the same, there is a chance that the accompanying amount of Na-ion in the adjacent layer is not. This could lead to the formation of different stacking sequences but remains hard to prove. The second possibility is that the TM composition does show differences in different layers, which should unambiguously result in different phases. The cationic potential concept is not overthrown in neither case. A unifying explanation is that there is inhomogeneity in the local composition, which needs to be further resolved by utilizing in situ heating XRD or XAS techniques that can track the phase development process. Tracing the separate phase evolution behaviors of the mixed phase is rather important. As shown in Figure 6d,e, with a pure O3 phase, the O3-P3 phase transition happens at 2.9–3.0 V, and reversibly returns to an O3 phase when discharged at 3.0 V. However, when there is some P2 phase in the particle, the O3-P3 phase transition voltage is obviously delayed to ~3.3 V during charging and 2.5 V during discharging. Since the charging voltage is restricted to 4.0 V, no P2-O2 phase transition is expected. This phenomenon indicates that the presence of a P2 phase next to an O3 phase elevates the energy required for layer gliding, thus showing a higher phase transition voltage.

2.5. Mixed P2 and P3 Materials

One of the common P-type Mn-rich oxide structures is the P3-type that is prone to be generated at lower temperature during the synthesis process. Shacklette et al.[46] originally synthesized and reported a P3-type Na$_{0.67}$CoO$_2$, which is capable of delivering a reversible capacity of 140 mAh g$^{-1}$ in the voltage range of 2.0–3.7 V. P3-type oxides are attributed to the R3m space group, where Na-sites are face-sharing with MO$_2$ octahedra on one side and edge-sharing with MO$_2$ octahedra on the other side. The transition to P2 or O2 during the electrochemical process is difficult since the breaking of TM–O bonds are needed. Therefore, the structure transformation and reversibility of the P3-type are different compared to P2-type during the charging and discharging processes. Du et al.[47] proposed a P3-type Na$_{0.6}$Li$_{0.4}$MnO$_2$ with anionic redox behavior, which possessed a pair of plateaus at 4.2 and 4.1 V during the initial charge and discharge processes. However, such reversible behavior does not appear in the P2-type material. Guo et al.[48] performed a detailed comparison of the electrochemical behavior of the P2- and P3-structured materials. For P2-Na$_{0.6}$Ti$_{0.2}$Cr$_{0.6}$O$_2$ and P3-Na$_{0.6}$Ti$_{0.3}$Co$_{0.6}$O$_2$ materials with approximate compositions, the P2-type material possessed better reactivity and cycling stability compared to the P3 phase and showed a lower Na diffusion barrier when multiple Na vacancies were available, which indicated that the P2 phase has better rate capability. During the synthesis process, the structure transition from P3-type to P2-type can be achieved by increasing the sintering temperature. Lei et al.[49] have constructed a phase diagram of Na$_2$CoO$_2$ in the range of 450–750 °C. The P3 phase was present at the synthesis conditions with lower Na content and lower temperature, while the P2-type was more inclined to appear at higher temperature conditions. Paulsen et al.[50] suggested that...
in the system of Na$_{2/3}$Mn$_{1-x}$Ni$_x$O$_2$. Ni contributed to the generation of P2-type structure, as the Ni content decreases, pure P2 structures were generated at higher sintering temperatures. Sathiya et al.\cite{51} proposed that using sodium carbonate as a precursor facilitates the transition from P3 to P2 at lower temperatures. Pfeiffer et al.\cite{44} investigated the phase transition behavior of Na$_{2/3}$Mn$_{3/4}$Ni$_{1/4}$O$_2$ during sintering by utilizing in situ XRD, and the phase diagram of O3-P2-P3 has been obtained (Figure 7a). The P3 phase crystallized at 450 °C, and the structure transition to the P2 phase did not proceed until 825 °C and was completed at 875 °C.

The phase diagram reveals that the mixed phases of P2-type and P3-type materials can be conveniently obtained by controlling the Na content and sintering temperature interval.\cite{44,49,51} Hence the construction of the mixed materials of P2-type and P3-type by a simple synthesis method has also been preferred as a method to improve the electrochemical performance of the Mn-rich sodium-ion cathode material. The strategy of building composite structures to improve the reversible structure transition of P2/P3-P2/OP4 during the electrochemical process was proposed by Zhou et al.\cite{52} P2/P3-Na$_{0.7}$Li$_{0.06}$Mg$_{0.06}$Ni$_{0.22}$Mn$_{0.67}$O$_2$ was obtained by annealing the precursors at 800 °C for 12 h, and a high initial coulombic efficiency of 94.8% was attributed to the stabilizing effect of the two-phase composite on the structure. On the basis of the composition for P2 and P3, Huang et al.\cite{45} introduced Li-doped P3/P2/O$_3$-$\text{Na}_{0.62}\text{Li}_{0.18}\text{Mn}_{0.66}\text{Ni}_{0.17}\text{Co}_{0.17}\text{O}_2$, and AC-STEM was used to explicitly observe the intergrowth of the different phases at the atomic scale (Figure 7b). The nanoscale composition between different phases promotes structural stability during electrochemical processes and consequently improves the cycling stability. More recently, a method to realize the P2/P3/O3 ternary composite by adjusting the
2.6. Performance of Mn-Rich Layered Materials

Figure 8a summarizes the capacity versus voltage performance of Mn-rich layered materials that were reported recently. Under most circumstances, Mn-rich layered materials stabilize as P2 phases. The performance chart shows that P2 material performances range from low capacity/high voltage to high capacity/low voltage.[2] Within a narrow voltage window, for example, 2.0–4.0 V, the material shows rather low capacity ≈90–100 mAh g⁻¹, but the discharge voltage can be elevated to up to 3.4 V. Expanding the voltage range to 1.5–4.4 V can boost the capacity to beyond 180–200 mAh g⁻¹, but the average voltage drops. This is because Mn can participate in the redox process between 1.5 and 2 V, although the increased capacity at such low voltage inevitably leads to a drop in average voltage. Therefore, it should be considered whether there is a more efficient way of increasing the capacity and voltage simultaneously, in other words, developing materials on the upper right corner of the chart.

Approaches adopted to increase the energy density of layered sodium cathode materials are summarized in Figure 8b. The blue solid line represents a regular case where the capacity and voltage are both moderate. The first approach (yellow dashed line) is to elevate the charge cut-off voltage for higher capacity. Like the case of layered lithium nickel manganese cobalt oxides that de-lithiate in the manner of a solid-solution reaction, increasing the charging voltage leads to an increase in charging capacity. However, this method incurs side reactions, including the decomposition of electrolyte under high voltage, extra phase transitions (such as the O3-H1 transition in Ni-rich layered cathode), as well as gassing issues, all of which shorten the cycle life. This issue becomes even more severe in the case of layered sodium materials. First, the voltage of SIBs is intrinsically lower than LIBs, which means that operating an SIB at 4.0 V is almost equivalent to 4.3 V in LIB, thus placing the electrolyte at decomposition risk, and leaving little room for voltage tuning. Second, the phase changes in layered sodium cathode materials are notoriously detrimental to the performance, this includes phase transitions caused by layer gliding and vacancy ordering. In many of the layered sodium cathode materials, phase transitions such as O3-P3-O1, P2-O2-OP4 could manifest themselves as high voltage plateaus, accompanied with sudden volume change, thus resulting in structure decay. It is also reported that oxygen participation in the charge compensation process is a more regular case in layered sodium cathode materials, therefore increasing the voltage would cause more gassing. This is the approach adopted by Faradion Inc., who charges the cell to a high voltage of 4.35 V and obtained an energy density of 155 Wh kg⁻¹. Despite delaying structure decay through the construction of a P2/O3 hybrid phase using Mg, Ti co-doping, the cycle life is still rather limited.

The second scenario (red dashed line) represents the case of increasing the energy density by exploiting the discharge capacity. This approach is rather acceptable since most of the materials can demonstrate different levels of capacity elevation through electronic structure modifications, so that the redox reactions can be triggered at a relatively lower or narrower potential region. However, for layered materials that are built up through stacking different layers of transition metals and sintering temperature and atmosphere has been attempted by Li et al. A mixed P3/P2/O3-Na0.374Ni0.319Mn0.590O2 (NNMO) was synthesized under ambient air at 1000 °C.[3] The disordered arrangement of the three phases in the same particle greatly suppressed irreversible phase transitions in the electrochemical process and thus improved the cycle stability. Interestingly though, the authors adjusted the phase composition by changing the sintering atmosphere, which was rarely discussed before. The results showed that NNMO with mixed phases of P3 and P2 was obtained by sintering in air atmosphere, while the NNMO with mixed phases of P2 and O3 was synthesized under an oxygen atmosphere, even at the same temperature of 900 °C. Hence, it enlightens the thought about the influence of the oxygen partial pressure or TM valence state on the determination of the final phase composition, and the investigation of the synthesis mechanism urgently demands clarification with the aid of these singular phenomena. In addition, the presence of the P3 phase at sintering temperatures of 900 °C and even 1000 °C is slightly different from the results of previous studies.
Na-ions, removing Na-ions from the structure leads to a loose layer that lacks support. Therefore, in order to retain the structure stability, it is necessary to keep some of the Na-ions in the layer to serve as “pillars”. In this regard, increasing the energy density at the cost of relentless extraction of Na-ions needs to be reconsidered.

The third scenario (green dashed line) represents the approach to improving the energy density by elevating the average voltage instead of the capacity. This approach requires the use of elements that are active at relatively high voltage, or specific structures that demonstrate reactivity at a higher voltage. A good example is P2-type materials, as shown in Figure 8a. While most of the regular O3 materials show an average voltage of 2.9–3.1 V (versus Na/Na⁺), some of the P2 materials demonstrate an average voltage of 3.3–3.5 V (vs Na/Na⁺). Such an improvement indicates that despite having lower capacity, P2 materials can reach equivalent energy density to O3 materials when properly designed. A second approach to elevate the voltage is to tune the elemental composition of layered materials. A good example is the use of Sn in Na₀.₇Ni₀.₃₅Sn₀.₆₅O₂, which has demonstrated over 3.7 V average voltage with a cutoff voltage of 4.0 V, far exceeding the regularly reported value of layered materials. A recent study by Xiao et al. has also discovered that Li doping can substantially improve the average voltage of P₂-Na₀.₆₆Mn₀.₇₅Ni₀.₂₅O₂ (NNMO). Ex situ X-ray absorption spectroscopy and theoretical calculations revealed that the substituted Li prefers to overtake the site surrounding Mn, thus modifying the electrochemical behavior of both Mn and Ni. In pristine NNMO, the charge compensation is mainly attributed to the redox of Mn³⁺/Mn⁴⁺ at
low voltage, Ni²⁺/Ni⁺ and lattice oxygen redox at high voltage. With Li in the transition metal layer, the amount of Mn³⁺/Mn⁴⁺ redox has been suppressed and Ni²⁺/Ni⁺ redox has been elevated, thus showing an elevated voltage by over 0.3 V.[56]

In the above discussion, it has been made clear that these approaches adopted to increase the energy density of layered materials are all viable under certain circumstances, but one would need to consider the cycling stability and material cost at the same time for better output. However, for Mn-rich materials, the third approach turns out to be a more realistic one since 1) Mn is an element with strong P2-promoting capability, 2) Mn does not always participate in the charge compensation process under regular conditions (2.0–4.0 V), thus the capacity is rather limited and 3) P2 phase transition to O2 or OP4 happens at well >4.0 V, whereas O3 to P3 phase transition happens at ≈ 3.0 V, which makes it possible to circumvent the P2 to O2 phase transition by simply restricting the upper voltage limit and is otherwise not possible in O3 materials.

3. Degradation Modes of Mn-Rich Layered Materials

Removing sodium-ions from the layers leads to an increase of the repulsion force of lattice oxygen, hence causing layer gliding. In layered lithium cathode materials, the gliding of layers is only observed in Ni-rich materials at high de-lithiation voltage.[57] However, due to the large interlayer spacing of layered sodium cathode materials, layer gliding may happen throughout the charge/discharge process, accompanied by phase transition and large volume change.[58] Additionally, sodium vacancy ordering may also take place during the process that exacerbates the performance.[59] The collective effects of these phenomena make the phase transition of layered sodium cathode materials very complicated, in addition to the cation migration behaviors commonly seen in layered materials.[58,60]

3.1. Phase Transitions of NaMnO₂

NaMnO₂ can be stabilized in two polymorphs, namely monoclinic O3'-type α-NaMnO₂ and orthorhombic zigzag-type layered high temperature β-NaMnO₂ (Figure 9a). α-NaMnO₂ is still composed of planar layers of MnO₆ octahedra and turns into an O3/P2/P3 structure through the alteration of the stacking sequence. The zigzag β-NaMnO₂, however, has edge-sharing MnO₆ octahedra that has Na-ions residing in the intermediate sites. The charge/discharge curves of these two types of materials are shown in Figure 9b. α-NaMnO₂ displays a capacity of 180 mAh g⁻¹ with multiple phase transitions in the voltage range of 2–3.8 V, yet the stability deteriorates during cycling and only 58% of the original capacity is retained after 50 cycles.[62]

Li et al. carried out an in situ SXRD test and found that the structure and superstructure evolution experiences multiple critical phase changes during cycling associated with the sodium amount in the structure as shown in Figure 9c. Several strong ordering phases of 5/8, 1/2, and 1/3 Na compositions are observed as superstructure orderings. Upon charging, the structure gradually evolves from O3’ strong ordering to O3’ weak ordering, followed by the emergence of O1 phase with remarkably high interlayer spacing when charged >3.6 V. The phase separation phenomenon was ascribed to the Mn⁴⁺ and Mn⁵⁺ charge separation, which creates periodical ordering of Jahn–Teller active Mn⁴⁺/Na-rich layer and Jahn–Teller inactive Mn⁵⁺/Na-deficient layers. Such a super-ordering structure allows for the remaining Na-ions to reside at the Mn⁺⁺ layers as pillars and stabilize in the form of O1 phase with high interlayer spacing. The good reversibility of this process ensures even better cycling stability with higher cutoff voltage, which is rather abnormal. β-NaMnO₂ demonstrates more stable performance than α-NaMnO₂, which is able to cycle for 100 times with 70% retention. This capacity fade is mainly attributed to the increase of stacking faults during cycling, resulting in the loss of crystallinity. The prevention of the Mn³⁺/Mn⁴⁺ charge separation can be achieved by introducing elements that break the separation. Ni was the first element adopted for such a purpose. NaNi₀.₅Mn₀.₅O₂ has been widely used as a standard cathode material in the early ages of sodium-ion batteries.[64] However, simply incorporating Ni into the structure does not necessarily prevent other phase transitions such as charge-vacancy ordering and O3-P3 transformation processes. This problem has been extensively investigated by incorporating multiple elements such as Ti, Mg, Fe etc.[59,62–66]

3.2. Phase Transitions in Mn-Rich P2 Layered Cathode

The Na-ions in the P2 layered cathode occupy trigonal prismatic sites between neighboring oxygen planes. The MO₂ sheets glide in the a–b plane to avoid close oxygen-oxygen contact along different directions during the Na extraction process. This process results in different oxygen arrangements with an imperfect O2-type layered structure that contains stacking faults.[69–71] Taking Na₂/₃[Ni₁/₆Mn₁/₂Fe₁/₃]O₂ as an example, when it is charged >4.1 V, O2-type stacking faults start to appear due to the gliding of the oxygen layers. Further extraction of Na leads to the coexistence of the P2 and O2 phase, which results in the plane spacing decreasing from ~5.6 to 4.4 Å and a total unit cell volume contraction of 23%. Such a huge strain presents a concern to the structure instability.[72]

In addition to the O2 phase, the P2 structure may also turn into an OP4 phase during the charging process. Based on the ex situ X-ray diffraction results, the OP4-type structure is confirmed in the P2-Na₂/₃[Fe₁/₂Mn₁/₂]O₂ charged to 4.2 V.[73] During its charging process, sodium is uniformly extracted from all layers initially. At higher voltage states, they are selectively extracted from one layer in every two adjacent layers, resulting in the P2–OP4 phase transition. It can reduce the damage induced by the gliding of the TMO₂ layers and the unit cell contraction, resulting in better structural stability. Other researchers suggest that the high voltage phase is a “Z” phase instead. By combining ex situ and operando X-ray diffraction with scanning transmission electron microscopy and simulated diffraction patterns, Na₂/₃[Ni₁/₆Mn₁/₂Fe₁/₃]O₂ layered cathode was found to form a ““Z” phase when charged >4.1 V.[74] The
STEM-HAADF image shows that Na$_{2/3}$[Ni$_{1/6}$Mn$_{1/2}$Fe$_{1/3}$]O$_2$ cathode has a typical P2 layered structure (AAAA stacking sequence). When charged to 4.5 V, the lattice image shows some adjacent layers retaining an AA stacking sequence, while others glide to form an AB sequence, and the plane spacing decreases. The STEM-HAADF analysis is consistent with the simultaneous presence of P-type and O-type layers in the “Z”-phase. So the “Z” phase in Na$_{2/3}$[Ni$_{1/6}$Mn$_{1/2}$Fe$_{1/3}$]O$_2$ is not a solid solution during charging process, but an evolving intergrowth structure (Figure 10).

3.3. Failure Mechanism of P2-Na$_x$MnO$_2$

The aggressive phase transition accumulates throughout the cycling process, which may lead to ultimate failure of the layered materials. Generally, the failure mechanisms are divided into two categories: bulk cracking and surface degradation. For the basic Mn-rich P2-type Na$_x$Ni$_{1/3}$Mn$_{1/3}$O$_2$ (P2-NM) composition, the intragranular cracks induced by the P2-O2 phase transition are confirmed to be the main cause for capacity decay during high voltage cycling. The cross-sectional STEM-HAADF
images in Figure 11d–f shows P2-NM cathode cycled at 2.0–4.25 V after 1 cycle, 10 cycles and 50 cycles. High density of intergranular and intragranular cracks develop, resulting in grain disintegration as the cycle number increases. The intragranular cracks propagate along the (002) planes, showing strong crystallographic preference. This phenomenon was not observed in the sample cycled below the P2-O2 phase transition voltage. Analysis shows huge internal strain built up at the P2/O2 phase boundary, which could initialize crack nucleation. Based on TEM statistical results, Figure 11g shows the crack density at different voltages and cycles. The high voltage cycling plays an important role in cracking nucleation, and longtime cycling will result in the density of cracks increasing. Moreover, the trend of crack density increase is consistent with the capacity decay. Hence, cracking related degradation is the main cause for performance decay.

Since the P2-O2 phase transition is the driving force of the crack nucleation for the P2-NM during high voltage cycling, doping with different element has been demonstrated to be an effective approach to suppress the P2-O2 phase transition and improve the cycling performance. Jin et al. demonstrated that doping with Li can produce a complete solid-solution reaction process of a P2-Na0.85Li0.12Ni0.22Mn0.66O2 material.[76] Wang et al. carried out a comparison between Cu, Ti, Mg and Zn substituted P2-NM materials.[77] Although the cathode materials doped with different elements can effectively suppress the P2-O2 phase transition, the dopants have different effects on the improvement of cycle stability. The enhancement effectiveness of the elements follows the order of Zn>Mg>Ti>Cu.

3.4. Cation Migration Behaviors

Apart from the intrinsic effect of the dopants to the structural stability, different elements may also experience distinct migration behaviors during the cycling process. Moreover, the same dopant may also experience different reversibility depending on the parent structure. Irreversible cation migration has been a major problem in layered lithium cathode materials, which includes the cation exchange of Li−Ni, as well as the migration of other transition metals to the empty lithium layer. Mn is prone to such migration, particularly in materials with transition metal layer vacancies, such as de-lithiated Li-rich NMC materials.[33,34] This process leads to the transformation from layered to spinel phase. Mn migrates to the tetrahedral sites when trivacancies are formed in the lithium layer. Trivacancies form when a lithium ion from the adjacent empty lithium layer moves to the tetrahedral site and a Li/Mn dumbbell structure forms, which serves as a nucleus for the growth of spinel phase. However, due to the difficulty of squeezing a sodium ion into the tetrahedral site, it is energetically unfavorable for a spinel phase to form in NaNiO2 materials, which is beneficial for the structure stability.[78] This example epitomizes that the migration behavior of specific elements is not always the same in different structures. This part discusses several examples of how reversible and irreversible cation migrations can impact the material performance.

3.4.1. Reversible Cation Migrations

The reversible migration of cations normally happens at restricted voltage regions. Li are Mg are often reported to migrate reversibly in layered sodium cathode materials. As
an example, ex situ NMR was used to track Li-ion site occupation changes at different states of charge/discharge for the Na$_{0.80}$[Li$_{0.12}$Ni$_{0.22}$Mn$_{0.66}$]O$_2$ samples, which confirms the Li dopant is mobile. Some Li ions migrate from the TM layer to the Na layer at high voltage, and this process is highly reversible. Recent work confirms the Mg dopant can also migrate into the tetrahedral and octahedral sites in the sodium layers during charging process and return to the TM layers after discharging process as confirmed by the presence of an extra Mg O scattering peak during the use of Fourier transformed extended X-ray absorption spectroscopy. Zhou et al. used HAADF-STEM to monitor the reversible cation migration in a Na$_{0.8}$Co$_{0.4}$Ti$_{0.6}$O$_2$ material, and concluded that such migration behavior was correlated with the large voltage hysteresis.

A direct positive effect of the reversible cation migration to the electrochemical behavior was reported by Xiao et al. In an earlier study using a finite difference method near edge structure (FDMNES) method to reproduce the features of the Mn K edge XANES during in situ operation of a Li-rich NMC material, the authors discovered that the Mn migration was...
partially reversible during the charging/discharging process. Following this discovery, the authors used a de-lithiated Li-rich NMC material as a host for sodium intercalation. This sodiated phase demonstrates an O3 structure with a reversible capacity of 220 mAh g\(^{-1}\), which is very impressive. More importantly, the whole process does not involve any O3-P3 phase transition. The authors compared the in situ XRD of this process as compared to the sodiation of a de-lithiated regular NMC material (without transition metal Li, thus resulting in less TM migration). As shown in Figure 12a, the de-sodiation of a regular NMC structure involves the shift of the (003) peak in a negative direction, implying an expansion of the layers. This is expected since removing sodium from the structure leads to a drop in the screening effect, where the repulsion force of lattice oxygen forces layer expansion. However, in a fully sodiated structure using a de-lithiated Li-rich NMC material as the host, removing the sodium results in a positive shift of the (003) peak (Figure 12b). Such contractions that happen since the beginning of the de-sodiation process can be explained by the migration of cations to the sodium layer, which acts as a screening agent to replace the sodium-ions. Figure 12c shows the density function theory (DFT) energy calculation of how the migration process changes the phase transition behavior. For an O-type dominating structure to convert into a P-type dominating structure, the system has to undergo a series of intermediate metastable phases triggered by the cation migration. Figure 12d shows no presence of an extra bonding environment after 100 cycles, implying that the migration is highly reversible.

3.4.2. Irreversible Cation Migrations

There are two fundamental consequences of irreversible cation migration processes. The first one is the loss of the dopant from its original site that prevents it from continuing to counter adverse phase transitions. The second one is the accumulation of the migrated cations in the Na layer. Fe migration is perhaps the most studied irreversible case in layered sodium materials. The study originated from NaFeO\(_2\), which is the typical layered sodium cathode material. Due to the accessibility of the redox couple of Fe\(^{3+}/Fe^{4+}\) in sodium cathode materials, high voltage increases the chance of Fe\(^{3+}\) migration to the Na layer, thus causing structural degradation. Studies have revealed that nearly 29% of Fe ions can migrate into the Na layer in a NaFeO\(_2\).
sample charged to 4.4 V.\[85\] Ni migration is another typical irreversible case, and the same trend is generally observed in Ni-rich layered lithium cathode materials. To understand how the Ni\(^{2+}\) migration happens, consider the ligand field stabilization energy of Ni\(^{2+}\) in both octahedral and tetrahedral sites. Calculations have unambiguously indicated that Ni\(^{2+}\) has a very strong preference to octahedral sites rather than tetrahedral sites, which facilitates the Ni migration from the TM layer, and fixes the octahedral sites in the Na layer.\[86,87\]

Wang et al. carried out a thorough study on how dopants (Mg, Zn, Cu, Ti) precipitate within the layers in case of migration in Mn-rich P2 materials. Figure 13a demonstrates that the Mg-doped cathode has uniform contrast in the grain interior before cycling.\[88\] However, a high density of bright stripes develop in the grain bulk after cycling at 4.5 V, as shown in Figure 13b,c. As the cycling number increases, the size and density of the bright stripes increase significantly. As shown in Figure 13d–f, the STEM-HAADF and corresponding EDS mapping of Mg-doped cathode shows the bright stripes are Na-deficient and Mg-rich regions that appeared as precipitates. As shown in Figure 13g–i, the Zn-doped cathode reveals a similar high density of precipitates in the grain bulk, and the STEM-EDS shows Na element is uniform and Zn is rich in the precipitate region, which is different from the Mg-rich precipitates. The precipitate regions in Mg-doped cathode and Zn-doped cathode have a similar feature, where the concentrations of Ni and Mn remain uniform between the precipitates and the matrix. The lattice images in Figure 13j–l show that precipitates have different stacking sequences and plane spacing within the P2 layered cathode. The yellow circuit in Figure 13k shows the lattice change form the end of a precipitate (top) to the P2 layered structure (bottom), which indicates that the atom shuffle mechanism play an essential role on the formation of precipitates. In combination with EDS mapping, the lattice image in Figure 13l confirms that the Zn dopant migrates into the Na layer.

On the other hand, the Cu and Ti dopant remain uniform in Cu-doped and Ti-doped cathode after cycling. The uniform doping can suppress the P2-O2 phase transition and undergo a P2-OP4 phase transition with smaller volume change. The single atom pillars in a uniform doping cathode are too weak to counter the internal strain induced by phase transition, so the intragranular cracks still nucleate and propagate into the grain interior. However,
the Mg-rich and Zn-rich precipitates can act as strong pillars to strengthen the bonding between TM layer and improve the material’s mechanical properties, which counters the strain induced by phase transition and effectively suppress the nucleation and propagation of bulk cracks. Although dopant-rich precipitates can effectively suppress intragranular cracks, the surface region still suffers from significant surface cracking and corrosion.

Further analysis shows that the surface de-precipitation process leads to the nucleation and propagation of surface cracks. The STEM-HAADF image and corresponding EDS mapping in Figure 14a–d shows the loss of Zn-dopant and Na, which results in the formation of surface de-precipitation regions after long cycles. As the cycle number increases, the surface de-precipitation region propagates into the grain interior. When the surface undergoes the de-precipitation process, the role of the precipitates in acting as the pillars and countering strain induced surface phase transition are weakened, which leads to the nucleation and propagation of surface cracks. Figure 14f–h shows the lattice images of precipitates at the surface de-precipitation region of Zn-doped cathode after long cycling (Figure 14e). As shown in Figure 14e–h, the thickness of the precipitates increases gradually from the surface to the grain bulk. The schematic illustration in Figure 14i shows Zn loss results in the thickness of precipitates decreasing, de-precipitation process occurring, and the formation of surface de-precipitation layer. After prolonged cycles, the surface de-precipitation layer expands into the grain interior and leads to the propagation of surface cracks and surface corrosion.

Although the high density of nano-sized precipitates at the particle surface can effectively mitigate the nucleation and propagation of surface cracks and surface corrosion, at the same time, these precipitates also introduce the following drawbacks. Firstly, the precipitates will block Na diffusion and lower rate capability. Secondly, substantial dopant migration and segregation into precipitates will result in a high density of nanovoids and even nano-cracks after many cycles. Thirdly, these precipitates will lead to decreases in initial capacity and energy density. So, synthesizing the cathode material with precipitates can take advantage of their ability to suppress intragranular cracks and avoid the negative effects induced by the formation of the precipitates.

![Figure 14. STEM-HAADF images and corresponding EDS mapping of the Zn-doped cathode at 2.0–4.5 V after a,b) 50 cycles, and c–h) 200 cycles. (e–h) Lattice images from the yellow frames in the low magnification STEM-HAADF image (e). Schematic illustration showing surface degradation process initialized by surface de-precipitation. Reproduced with permission. Copyright 2022, Elsevier.](https://www.afm-journal.de)
3.5. Morphology Effect on the Performance Degradation

Scaling-up of the layered Mn-rich materials follows two major approaches in practical. The first one is solid-state synthesis, which adopts metal oxides as the precursors and anneal at high temperature after thorough mixing. This approach utilizes readily available materials and the procedure is overall economic. However, materials synthesized through this approach do not generally have very high stability or tap density due to the particulate morphology. In spite of this, the solid-state synthesis approach is still a very important method it is used to screen composition for less cost and better performance is the very first step taken before upscaling or commercialization. The second approach is co-precipitation, which has been fully proven to be ideal for designing spherical structures with high tap density. More importantly, materials synthesized through this approach show more stable performance, despite extra cost may be incurred during the synthesis process.


Degradation of layered materials in ambient atmosphere has been a major concern in practical applications. The process generally involves 1) loss of Na in the forms of Na₂CO₃, NaHCO₃, NaOH, 2) intercalation of water molecules and 3) structural degradation such as cracking. These side reactions may lead to performance decay, as well as gelling issues during electrode slurry preparation. In Ni-rich compositions, the loss of Na from the material surface leads to NiO accumulation. Compared with its lithium counterpart with the same transition metal composition, layered sodium cathode material demonstrates much higher dynamic affinity with both water and CO₂ as has been revealed by Manthiram et al.[90] Losing Na from the layered structure inevitable leads to charge imbalance, which needs to be compensated by the oxidation of other elements. When intaking CO₂, the reaction in a Mn-rich P2-type materials is proposed as follows:

\[
\text{CO}_2 + 1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-} \quad (2)
\]

\[
\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + e^- \quad (3)
\]

The CO₃²⁻ ions are supposed to insert into the layers accompanied with Mn⁴⁺ oxidation, which can be ameliorated by Ni substitution.[91]

On the other hand, when reacting with water, the charge balance is observed to take place through a Na⁺/H⁺ exchange process, along with water molecule intercalation. The reaction takes place as following:

\[
x\text{H}_2\text{O} + \text{Na}_{0.67}\text{TMO}_2 \rightarrow \text{Na}_{0.67-x}\text{H}_x\text{TMO}_2 + x\text{NaOH} \quad \text{(without CO}_2\text{ in the atmosphere)} \quad (4)
\]

\[
x\text{CO}_2 + x\text{H}_2\text{O} + 2\text{Na}_{0.67}\text{TMO}_2 \rightarrow 2\text{Na}_{0.67-x}\text{H}_x\text{TMO}_2 + x\text{Na}_2\text{CO}_3 \quad \text{(with scarce CO}_2\text{ in the atmosphere)} \quad (5)
\]

\[
x\text{CO}_2 + x\text{H}_2\text{O} + \text{Na}_{0.67}\text{TMO}_2 \rightarrow \text{Na}_{0.67-x}\text{H}_x\text{TMO}_2 + x\text{NaHCO}_3 \quad \text{(with abundant CO}_2\text{ in the atmosphere)} \quad (6)
\]

\[
\text{Na}_{0.67-x}\text{H}_x\text{TMO}_2 + y\text{H}_2\text{O} \rightarrow \text{Na}_{0.67-x}\text{H}_x(\text{H}_2\text{O})_y \text{TMO}_2 \quad \text{(when the sodium content in the electrode is below a critical value n.)} \quad (7)
\]

From the above discussion, it can be concluded that the affinity to both water and CO₂ in the ambient atmosphere is the direct reason leading to air instabilities. In order to deal with this problem, strategies such as surface coating, element doping, as well as re-heating process have been proposed.[93–98]

4. Anionic Redox Behaviors in Mn-Rich Layered Materials

Triggering anionic redox reactions (ARR) in layered cathode materials is a proven strategy to effectively elevate their capacity. Tremendous efforts have been made in improving the reversibility as well as understanding the underlying process of ARR.[105] Introducing Li to the transition metal layer causes anionic redox reactions. This principle has been utilized in Li-rich layered cathode materials that demonstrate exceptionally high capacity. In general, the analysis of occupied states at the Fermi level in cathode materials can be utilized to determine the redox behavior. There is a very weak interaction between oxygen and alkali metal ions in the coordination configuration of layered alkali metal oxides, and most of the 2p electrons of O interact with 3d electrons of the TM ions to form antibonding (M=O)* and bonding (M−O). As shown in Figure 15A, (M−O)* with cationic character contributed by the electron from TM ions is closer to the Fermi level, such as the e6 orbital from Ni, while the electron contribution from O 2p is mainly filled in the states far from the Fermi level, showing anionic character.[99,106] In conventional systems, cationic characteristic electrons are engaged in reversible charge-discharge reactions whereby cationic redox behavior is achieved, while the lower energy states with anionic characteristic are stable and do not change with the reaction. For Mn-based oxides, particularly in layered oxides with a Mn valence of +4, the regular electrons of both Mn and O are extremely far away from the Fermi level and cannot perform charge compensation. Therefore, additional 2p states of oxygen caused by the changes of electron structure near the Fermi level allow for ARR to be realized. As in the case of the typical Li₂MnO₃ structure in Li-ion system, the non-bonding O 2p states that result from the appearance of excess Li in the TM layer are the key to ARR.[106] However, the mechanism of ARR in Mn-rich layered sodium oxides is more complex and is not exactly identical to the non-bonding O 2p states in layered oxides like Li-rich NMC. Several behaviors that increase oxygen density near the Fermi level promote ARR.

4.1. Li Substitution Effect

The substitution of Li in transition metal layers is the major approach to utilizing ARR in Mn-rich layered cathode materials.[107]
Similar to the ARR mechanism in typical Li$_2$MnO$_3$, the coordination configuration of O with four Li ions and two Mn ions drives the generation of the non-bonding O 2p states.$^{[108]}$

The approach of Li substitution in the TM layer generates non-bonding O 2p states in layered Mn-rich Na-ion oxides through the weak electron overlap between alkali metal ions (Na and Li) and oxygen, such as P2-Na$_{5/6}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$,$^{[100]}$ P3-Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$,$^{[47]}$ and P2-Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$,$^{[109]}$ with different contents of Li substitution in the TM layer. The first cycle curve of P2-Na$_{5/6}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ is shown in Figure 15b, and the first charging plateau $\approx$ 4.3 V is similar to that of Li$_2$MnO$_3$. Such charge compensation behavior can be attributed to the ARR of the lattice oxygen due to the electrochemical inactivity of Mn$^{4+}$. As shown in Figure 15c, DFT calculations confirmed that the non-bonding 2p state of oxygen was distributed along the Na-O-Li configuration, which is consistent with the electronic behavior in the Li-O-Li configuration.$^{[103]}$

Recently, Wang et al.$^{[110]}$ reported an ARR-type O3-NaLi$_{1/3}$Mn$_{2/3}$O$_2$ with an ultra-high Na content, delivering a high reversible capacity of 190 mAh g$^{-1}$ and a suppressed voltage decay behavior during cycling, which is promising for high-capacity, low-cost ARR applications.

Although the non-bonding O 2p states and ARR behavior are both triggered from the existence of Li in TM layer, there are differences in ARR between the layered sodium material and Li-rich NMC that deserves a careful comparison and discussion. Compared with the layered Li-ion oxides, the presence of Na ions expands the interlayer spacing, and the distance between TMO$_6$ slabs is extended, which inevitably weakens electron overlapping between O and Na further or even localizes the 2p electrons of O along the direction of the TMO$_6$ slab. Whether such a difference in electronic structure causes the difference in ARR behavior between sodium-ion and lithium-ion materials needs further investigation.

Figure 15. a) Schematic band structure of oxides with ARR behavior. Adapted with permission.$^{[99]}$ Copyright 2018, Nature Publishing Group; b) Charge and discharge curves of layered Mn-rich sodium cathode materials with ARR behavior. Adapted with permission.$^{[56,100–102]}$ Copyright 2021, Wiley-VCH GmbH. Copyright 2021, Wiley-VCH GmbH. Copyright 2014, Wiley-VCH GmbH. Copyright 2018, Wiley-VCH GmbH. Copyright 2014, Royal Society of Chemistry; c) Electron distribution along Na-O-Li configuration and Li-O-Li configuration, respectively. Adapted with permission.$^{[103]}$ Copyright 2017, Wiley-VCH GmbH; d) O K-edge mRIXS for NNMO and NLNMO at first charging states (4.4 V). Adapted with permission.$^{[56]}$ Copyright 2021, Wiley-VCH GmbH; e) First charge and discharge curves, crystal structure and HAADF-STEM image for Na$_{0.75}$[Li$_{0.25}$Mn$_{0.75}$]O$_2$ with honeycomb superstructure and Na$_{0.6}$[Li$_{0.2}$Mn$_{0.8}$]O$_2$ with ribbon superstructure. Adapted with permission.$^{[104]}$ Copyright 2020, Nature Publishing Group.
however, the variability in layer spacing contributes to a moderate disparity in ARR behavior. Jia et al. conducted a comparison of O3 and P2 materials with ARR behavior that were both triggered by Li substitution. P2-Na\(_{0.66}\)Li\(_{0.15}\)Fe\(_{0.15}\)Ru\(_{0.75}\)O\(_{2}\) was more likely to trigger reversible ARR at relatively low cutoff voltages and has higher capacity than P3-Na\(_{0.67}\)Li\(_{0.2}\)Mn\(_{0.8}\)O\(_{2}\).[101] In addition, there are Na ion vacancies in the alkali layer for many layered sodium-ion cathode materials, which induce local coordination distortions. The resulting variability in electronic structure as well as the non-bonding 2p states demand further discussion. In an earlier study, Lee et al.[132] demonstrated that the ordering of Na sites and vacancies in the alkali metal layers significantly affects the voltage distribution in the electrochemical profile, accompanied by the effects of different Na occupancies (Na\(_2\) sites and Na\(_3\) sites) on the energy in the P2 structure. By extension, it should be investigated whether the differences in local structure caused by Li doping will govern the oxygen non-bonded 2p state and shift the ARR behavior subtly.

4.2. Non-Li Substitution Effect

With Li in the transition metal layers, the ARR is triggered by local holes due to the lack of O 2p and TM 3d hybridization. However, recent reports showed that P2-type Mn-rich layer materials that contain Mg, Ni, Zn, Cu, and even vacancies also display anomalous ARR behaviors. Yet, the underlying mechanisms of how the ARR was triggered is under debate. For a non-transition metal such as Mg, the ARR behavior of Mn-rich layered Na\(_{2/3}\)[Mg\(_{0.28}\)Mn\(_{0.72}\)]O\(_2\) was ascribed to the interaction of the Mg\(_{2+}\) 3s orbital with the O 2p orbitals that leads to a weak ionic bond similar to Li–O. This places the O 2p states in a higher energy condition and thus accessible within the electrolyte stability window. Furthermore, due to the immobility of the Mg\(_{2+}\) in the transition metal layer, the P2-Na\(_{2/3}\)[Mg\(_{0.28}\)Mn\(_{0.72}\)]O\(_2\) material does not demonstrate any oxygen loss.[30] Unlike the ARR incurred by Li incorporation that experiences oxygen loss due to the presence of non-bonded O 2p states, the Mg-incurred ARR shows that oxygen is always coordinated by at least three cations and the O 2p orbitals interact with at least one cation. The A–O bond (A = Mg or Li) formed by the oxygen and ions with weak electronegativity is highly polarized and the electrons are more localized around oxygen, resulting in ARR behavior. In addition, the substituted transition metal vacancies within the TM layer likewise contribute to the non-bonding O 2p state with ARR behavior. The typical Mn-rich Na\(_3\)Mn\(_2\)O\(_4\) material, also written as Na\(_4[\alpha\text{Mn}_6\beta\text{Mn}_7\gamma\text{O}_{22}]\)O\(_2\) (\(\alpha,\beta,\gamma\) is the Mn vacancy), possesses ARR activity since the non-bonding 2p state is activated with oxygen coordinated to two Mn\(_{4+}\) and one Mn\(_{3+}\). Na\(_3\)Mn\(_2\)O\(_4\) is capable of delivering 120 mAh g\(^{-1}\) on the first charge to 4.7 V and a discharge capacity of 200 mAh g\(^{-1}\) to 1.5 V.[102] Ni and Cu substituted Na\(_2\)MnO\(_2\) also demonstrate ARR on some occasions. Abate,[111] Kim,[114] and Xiao[106] et al. all applied RIXS to confirm the independent ARR behavior exhibited by Ni– or Cu substituted Na\(_2\)MnO\(_2\). This phenomenon cannot be explained completely by the absence of O 2p and TM 3d hybridization. A reductive coupling mechanism was therefore proposed to address this. An earlier study in Li-rich layered Li\(_2\)Ru\(_{0.5}\)Sn\(_{0.5}\)O\(_4\) has revealed that the oxidation of the oxygen ions is accompanied by the reduction of the adjacent TM, that is, the reductive coupling mechanism, in the form of local charge transfer to implement ARR behavior.[115] The reductive coupling mechanism can account for the anomalous ARR behavior in Ni or Cu substituted Na\(_2\)MnO\(_2\). Kim et al.[114] revealed that during the first charging process of P3-type Na\(_{0.66}\)Ni\(_{0.25}\)Mn\(_{0.75}\)O\(_2\), Ni was slightly oxidized from 3.8 to 4.1 V, but was subsequently reduced when the charge voltage was further increased from 4.1 to 4.4 V, which indicates the ARR behavior is accomplished in the form of charge transfer from O to Ni, that is, reductive coupling. In addition, Abate et al.[111] utilized DFT calculations to confirm that covalently enhanced Cu–O or Fe–O bonds increase the oxygen density near the Fermi energy level, thus contributing to the tendency of ARR.

4.3. Co-Substitution Effect

Despite the fact that having Li or Ni in the transition metal layer can trigger the ARR independently, there is an abnormal scenario where the combination of these two does not boost the ARR synergistically. An in-depth investigation of this phenomenon was carried out by Xiao et al.[56] As shown in Figure 15d, RIXS revealed the strong ARR activity of Ni-doped P2-Na\(_{0.66}\)Ni\(_{0.25}\)Mn\(_{0.75}\)O\(_2\) (NNMO), yet P2-Na\(_{0.66}\)[Ni\(_{0.25}\)Mn\(_{0.75}\)]\(_{0.9}\)Li\(_{0.1}\)O\(_2\) (NLNMO) with 10% Li substitution in the TM layer resulted in an impressive suppression of the ARR behavior. DFT calculations for different de-sodiated states verified that the density change of oxygen near the Fermi level has been significantly reduced for NLNMO compared to NNMO. The substitution of Li in NLNMO has suppressed the redox activity of Mn and promoted the redox activity of Ni, increasing the energy density and providing a new idea for the modification of ARR-type Mn-rich sodium cathode materials. In addition, the discovery of this phenomenon also inspired further ideas on the ARR mechanism for Ni or Cu substituted Na\(_2\)MO\(_2\). XANES showed that more Ni in NLNMO was oxidized to Ni\(^{4+}\), implying the suppression of the charge transfer from O to Ni and also strengthened the reductive coupling effect. However, the substituted Li ions were found to be distributed around Mn, while additional investigation is required to determine whether the presence of Li causes the ordered-separation of Mn from Ni and further influences the ARR behavior. A more complete interaction theory is needed to complement the ARR mechanism in addition to the non-bonding O 2p states and reductive coupling. When investigating the ARR behavior of P2-Na\(_{0.75}\)[Li\(_{0.15}\)Ni\(_{0.15}\)Mn\(_{0.7}\)]O\(_2\), Myung et al. found that instead of fully suppressed ARR, the material demonstrated ARR with decreased voltage hysteresis.[116] This difference with P2-Na\(_{0.66}\)[Ni\(_{0.25}\)Mn\(_{0.75}\)]\(_{0.9}\)Li\(_{0.1}\)O\(_2\) implies that the relative amount of Li and Ni should also play critical roles in tailoring the ARR behaviors.

4.4. Reversible Behavior of the ARR

Although the ARR behavior has offered an effective strategy for capacity enhancement of the layered sodium Mn-rich materials, the reversibility retention and mechanism as well as irreversible losses remain a long-standing issue for ARR-type cathode...
materials, which are relevant to achieving high capacity, low cost and long cycle life. Compared with the structure changes in cat-ionic redox-behavior cathode materials during electrochemical processes, ARR-type oxides undergo more complex structure transformations. However, the structure transformation of the intermediate state is closely related to the reversible behavior of the reaction, and the interrelationship between the structure transition undergone by ARR and the reversibility is explored to contribute to the improvement of the cycle stability.\cite{127}

Rong et al.\cite{118} applied NPDF to detect the shortening and reversible recovery of the local O–O bond in P3-Na0.6[Li0.2Mn0.8]O2 triggered by ARR, and such O–O dimers boost the high reversible capacity during the charging and discharging process. The reversible mechanism of the O–O dimer in the sodium-ion system is more useful compared to the Mn-rich Li-ion oxides that are predicted to not be conducive for the reversibility of O–O dimer;\cite{119} and the stabilization is highly correlated with the expanded interlayer spacing and oxygen trapped within the P-type structure. With an increase in Na content, P2-Na0.76[Li0.25Mn0.75]O2 was proposed to further increase reversibility and energy density.\cite{120} In the case of Li-doped Na0.6MnO2, however, the P2 and P3 type structures display completely different ARR-reversible behaviors. The P3-type structure material possesses a reversible charge/discharge plateau at \(\approx 4.2\) V, while the P2-type structure material presents a significant voltage hysteresis behavior when discharged with a sloping discharge curve. The mechanism of this phenomenon is poorly elucidated and is probably related to the migration of transition metals and the change in electronic structure during the de-intercalation of sodium ions.

The voltage hysteresis phenomenon, which is strongly associated with the reversibility of ARR and the nature of the reaction, has been widely discussed in Li-rich cathodes, and is the consequence of the combined effect from the kinetic hysteresis of TM migration and the thermodynamic hysteresis corresponding to the change in electron structures around lattice oxygen guided by the structure transition. As shown in Figure 15c, Bruce et al.\cite{104} concluded that the ARR reversibility as well as the voltage hysteresis behavior was distinctly regulated by the superstructure within the TM layer, Na0.6[Li0.2Mn0.8]O2 with a ribbon superstructure possesses high ARR reversibility and apparently suppressed voltage hysteresis behavior in contrast to the Na0.75[Li0.25Mn0.75]O2 with a honeycomb superstructure and significant voltage hysteresis behavior, and the reversible discharge plateau of ARR is distributed \(\approx 4.0\) V. They suggested that the ribbon superstructure inhibited the migration of Mn with the formation of O\(^2\)-, which further suppressed the hysteresis and promoted a stable electron-hole around oxygen. Recently, Eum et al.\cite{121} compared the reversibility of ARR in Na0.6[Li0.2Mn0.8]O2 and Na0.6[Li0.2Ti0.2Mn0.6]O2 and constructed a correlation between TM migration, lattice oxygen stability and ARR reversibility. The conversion kinetics from \(\pi\) to \(\sigma\) interactions for oxygen was determined by the TM migration pathway, and the \(\pi\)-type stabilization mechanism contributed to the reversibility of ARR, while the \(\sigma\) interactions facilitated by TM migration resulted in O–O dimers and structure instability. For Non-Li substituted Na0.6MnO2, despite the improved structure and ARR reversibility of P2-Na2/3[Mg0.28Mn0.72]O2, which recapitulated the charging plateau during the subsequent charging process, it still possessed voltage hysteresis behavior of the ARR during the discharging process.\cite{109} It was also reported that even though NNMO is found to show ARR under most occasions, its oxygen may also be irreversibly released from the structure instead. This discrepancy reveals that the anionic redox behavior is also related to many other factors such as the synthesis approach, morphology, crystallographic orientation and so forth.\cite{122} The vacancy-type Na2MnO2 possesses reversible ARR with minimal voltage hysteresis. Song et al.\cite{123} attributed this phenomenon to the minimal strain response of the structure and the excellent maintenance of the stacking order for the oxygen layer, in the absence of irreversible structure transformations like sliding and TM migration. Rather than the poor ARR reversibility and severe voltage hysteresis exhibited in Li and Mn rich materials, different types of Mn-rich sodium cathodes exhibit different ARR reversibilities and inconsistent voltage hysteresis behaviors. However, the mechanisms involved are also controversial, and a more unified theory is needed to describe the reversible behavior and voltage hysteresis of ARR from transformations in crystal structures and electronic structures.

5. Conclusion

This review provides a timely update for the latest advancements of Mn-rich layered materials for sodium-ion batteries. Through a comparison between the development pathways for layered lithium and sodium-based materials, we have highlighted that the most critical barriers that slowed down layered sodium material development are the composition uncertainty and microscopic structure complexity. Recent reports have shown remarkable progress on the rational design on the composition with tailored structures. Once these obstacles are removed, it is anticipated that layered materials for sodium-ion batteries will experience a quick shift to maturity. With that in mind, this review focused on fundamental understandings of the underlying principles dictating the obstacles. First, we have reviewed multiple structures that were well documented in the family of layered sodium materials. Despite making attempts to synthesize these structures under various conditions, recent advances have revealed the underlying principle of how the material composition determines its structure using the cationic potential concept. We have listed examples of experimental results that match well with predictions based on theoretical concepts, as well as overlooked exclusions (such as the presence of vacancies) in such predictions. Second, we have emphasized that the Mn-rich nature would inevitably induce a P2, or at least a P2-dominating structure. Through analysis of the electrochemical behaviors of P2 materials, we have shown that despite having lower capacity, P2 materials still demonstrate huge potential due to its elevated average voltage. Third, we have discussed the phase transitions of various Mn-rich layered materials and proposed many approaches that can potentially benefit the structural integrity. Last, we discussed the anionic redox behaviors of Mn-rich layered materials, in particular several abnormal phenomena that need further investigation.

The utilization of Mn-rich composition for layered sodium cathode materials is by far demonstrated to be promising,

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however, challenges still remain before they can be deployed in practical applications. Several topics require further attention as listed below.

1) The dissolution of Mn into the electrolyte, particularly using PF6−-based salt, has been notoriously known as a major reason for capacity fade. Previous attempts have been made to counteract the dissolution by introducing surface coating, electrolyte additive and HF scavengers, it is expected that the same approaches should be considered in layered sodium cathode materials as well. Remedies also include the use of non-NaPF6-based electrolyte. It is true that NaPF6 is anticipated to be the dominating electrolyte salt to be used in SIBs, other options such as NaFSI might also be considered.[56] The role has been demonstrated in the use localized high concentrated electrolyte, which shows outstanding capabilities of forming stable cathode electrolyte interphase, as well as low presence of proton with the absence of PF6− salts.

2) Mn3+ is prone to Jahn–Teller distortion, which results in structural disintegration. With such a high amount of Mn in the structure, the distortion can easily take place in local areas even if the voltage range is intentionally restricted to a range that does not activate the Mn redox reaction. This mainly includes the material surface and subsurface, where electron exchange and side reactions with the electrolyte take place. Therefore, more attention should be paid on the surface reactions that may lead to the Jahn–Teller distortion and structural transformation.

3) Constructing spherical secondary particles is a chief way to improve the material tap density, as has been widely adopted in layered lithium cathode materials. For Mn-rich layered sodium materials, the optimization of the secondary particle morphology is still at a nascent stage. There is a lack of study on how the spherical morphology, the primary particle size and distribution and even composition affect the material performance. There is a need to learn from the experience in layered lithium cathode materials to facilitate the development of layered sodium materials with the morphology suitable for large-scale applications.

4) The practical application of Mn-rich layered sodium cathode materials requires demonstration in large format cells with extensive evaluations. Current studies have been mostly focused on lab-scale material development that has somehow underestimated many factors such as gassing issues.

The recent burgeoning attention on SIBs calls for a thorough evaluation of potentially applicable materials. This review has primarily focused on Mn-rich layered materials, particularly those with P2-type structures. However, due to the various deployment field of SIBs, other materials such as O3-type layered materials, polyanionic materials, and Prussian blue analogues may be used to meet practical needs. It is anticipated that in the next few years, a revolution in SIBs will occur and create unprecedented opportunities in both academia and industry.

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Conflict of Interest

The authors declare no conflict of interest.

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