

# Key Issues and Modification Strategies for Layered Oxide Cathode Materials in Sodium-Ion Batteries

Qianqian Ma

School of Materials and Chemistry, University of Shanghai for Science & Technology, Shanghai 200093, China

---

## Abstract

Sodium-ion batteries, with their advantages of abundant sodium resources, low cost, and excellent safety performance, represent a potential alternative to lithium-ion batteries for large-scale grid energy storage. The cathode material plays a crucial role in determining the battery's energy density, cycle life, and cost. Layered transition metal oxides, due to their well-ordered layered structure, good electrical conductivity, and two-dimensional ion transport pathways, are highly promising cathode materials for sodium-ion batteries. However, their practical application is hindered by various challenges, including irreversible phase transitions, high sensitivity to air, loss of lattice oxygen under high pressure, local structural distortions, and slow sodium ion diffusion, all of which significantly impede their commercialization. This paper systematically reviews the research progress of layered oxide cathodes for sodium-ion batteries, analyzes the key challenges faced in their application, outlines effective modification strategies such as element doping, surface coating, and structural design, and discusses future research directions. The aim is to provide theoretical insights and technical support for the development and industrialization of high-performance sodium-ion battery cathode materials.

## Keywords

Sodium-ion Batteries; Cathode Materials; Layered Oxides; Modification.

---

## 1. Introduction

Against the backdrop of rapid transformation in the global energy landscape, developing green energy technologies has become a crucial approach to addressing environmental and energy challenges. Efficient and stable energy storage and conversion systems are key components for building sustainable energy systems. Lithium-ion batteries, with their excellent overall performance, have been widely used in consumer electronics, electric vehicles, and grid energy storage applications [1]. However, the limited reserves and uneven distribution of key resources such as lithium, cobalt, and nickel, along with growing demand, have led to increasing concerns regarding supply chain security and costs, thereby restricting their widespread use on a large scale. Sodium-ion batteries, with their advantages in terms of resource availability and cost, represent a promising alternative and complementary technology [2]. Sodium is much more abundant in the Earth's crust than lithium, making its raw materials readily available and inexpensive. Additionally, sodium-ion batteries exhibit better thermal stability and a wider operating temperature range, resulting in higher safety levels. These advantages make them particularly suitable for large-scale grid-level energy storage applications, providing an important direction for the development of cost-effective and safe energy storage solutions [3].

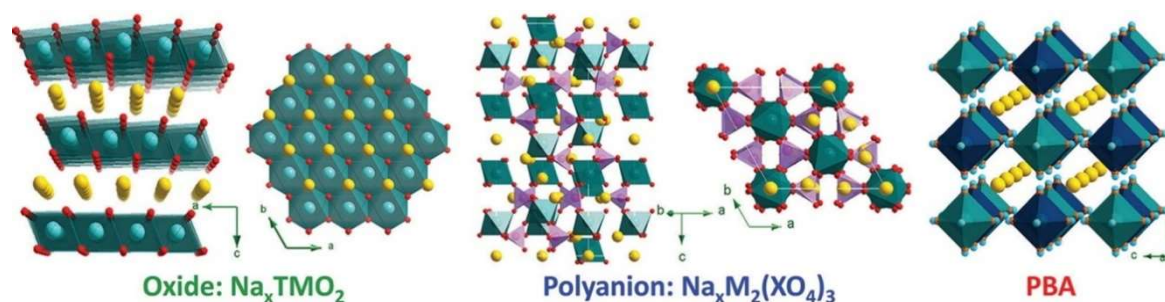
Although sodium-ion batteries have significant advantages in terms of resources and cost, their energy density remains limited due to the relatively large atomic mass and low reduction potential of

sodium ions itself. This theoretical limitation constitutes a major obstacle to their commercial application. To meet the high energy-density requirements of applications such as electric vehicles, improving their performance has become a key research focus [4]. According to the energy-density formula ( $E=QV$ ), improvements can be made in two main areas: first, by developing electrode materials with higher specific capacities [5]; second, by increasing the average operating voltage of the battery. Among these, the cathode material, which is responsible for storing sodium, directly determines the battery's capacity and voltage level, making it a crucial factor in overcoming energy-density limitations [6]. To further enhance the electrochemical performance of layered oxide cathodes, increasing the battery's operating voltage is a key approach.

However, when the charging voltage exceeds 4.0 V, a series of severe performance degradation issues occur in the battery system. These include: (1) irreversible phase transitions and structural damage to the cathode; (3) increased release of oxygen, which accelerates electrode deterioration [7]; (2) Jahn-Teller distortion and dissolution of transition metals, leading to loss of active material; (4) reduced kinetic efficiency [8]. These factors significantly limit the practical application of layered oxide cathodes. In recent years, researchers have made significant progress by employing strategies such as element doping, structural design, and entropy control to enhance the materials' stability under high voltages. This article summarizes the challenges faced by layered oxide cathodes and the corresponding modification techniques, while also outlining future research directions. The aim is to provide insights for the development of sodium-ion batteries with high energy density and long lifespan.

## 2. Classification of Cathode Materials for Sodium-Ion Batteries

Currently, research on cathode materials for sodium-ion batteries focuses primarily on three key categories: layered transition metal oxides, polyanion compounds, and prussian blue analogs (Figure 1). Layered transition metal oxides ( $\text{Na}_x\text{TMO}_2$ ) exhibit outstanding advantages such as high specific capacity and simple synthesis methods, making them promising for commercial applications [9]. Polyanion compounds use  $(\text{XO}_4)^{n-}$  units (where  $X = \text{P}, \text{S}, \text{Si}, \text{etc.}$ ) as their basic structural units. Their strong covalent bonds create stable three-dimensional frameworks that effectively prevent structural degradation and oxygen loss during charging and discharging. These materials also demonstrate excellent thermal safety and cycle stability. However, their intrinsic electronic conductivity is low, requiring improvements through techniques like carbon coating, nanostructure modification, and element doping [10]. Prussian blue analogs are cost-effective and have open-framework structures. Their crystal structure is closely related to the sodium content and crystalline water content. They also possess high ionic conductivity. However, their electrochemical properties vary significantly depending on the redox mechanism involved. Current research focuses on adjusting the composition and reducing crystalline water content to balance capacity and stability. Among these cathode materials, layered oxides have gained widespread attention in recent years due to their high energy density, diverse types, simple synthesis methods, and environmental friendliness.



**Figure 1.** Structures of three cathode materials: layered transition metal oxides, polyanionic compounds, and prussian blue [11]

### 3. Introduction to Layered Transition Metal Oxides

The basic structure of layered oxides consists of alternating layers of TMO<sub>6</sub> octahedra with shared edges and sodium layers. As shown in Figure 2, depending on the coordination environment of sodium ions (prismatic or octahedral) and the stacking pattern of oxygen layers, these structures can be classified as P-type (e.g., P2, P3) or O-type (e.g., O2, O3). Here, “P” and “O” denote the types of coordination polyhedra around sodium ions, while the subscript numbers indicate the number of repeating oxygen layers per unit cell. When the sodium content  $x$  is between 0.6 and 0.8 and the average valence state of the transition metal is higher than 3.3, a P2-type structure is likely to form [12]. This structure belongs to the P6<sub>3</sub>/mmc space group, with oxygen atoms stacked in an AB BA pattern. All sodium ions occupy prismatic sites (N<sub>ae</sub> and N<sub>af</sub>). However, due to the large radius of Na<sup>+</sup> ions, it is impossible for them to occupy both adjacent sites simultaneously. During the removal of sodium ions, the TMO<sub>6</sub> layers may slide, leading to a transformation into the O<sub>2</sub> phase or a distorted P'2 phase. In the O<sub>2</sub> phase, the excessively large interlayer spacing hinders the reversible insertion and extraction of sodium ions, thereby affecting cycle stability[13].

When the sodium content is high, an O3-type structure is formed. This structure belongs to the R3m space group. The arrangement of oxygen atoms follows the pattern AB CA BC, while sodium ions are located entirely in octahedral sites. During sodium removal, the O3 phase undergoes a reversible structural change: as sodium ions are removed, the remaining ions tend to form triangular coordination arrangements, creating vacancies. At the same time, the repulsion between oxygen atoms between layers increases, leading to elongation along the c-axis [14]. Compared to the P2 phase, the O3 phase generally has a higher specific capacity due to the larger number of sodium sites. However, the longer migration paths for sodium ions result in lower rate performance compared to P2-phase materials. Additionally, during charging and discharging, continuous sliding of the TMO<sub>2</sub> layers can induce a transformation from the O3 phase to the P3 phase. In the P3 phase, the oxygen atoms are arranged in a AB BC CA pattern, still belonging to the R3m space group. The interlayer distance in the P3 phase is typically larger than that in the O3 phase, which facilitates sodium ion diffusion [15]. It should be noted that the O<sub>3</sub>↔P3 phase transition involves only overall layer sliding without disrupting the basic crystal structure. However, due to the high energy barrier, the P2 phase generally does not transform directly into the P3 phase.

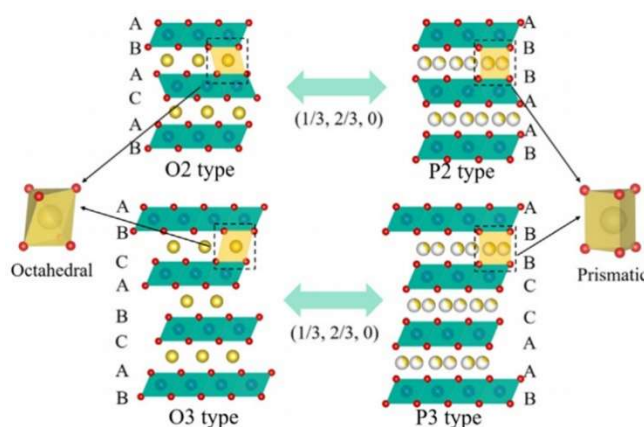


Figure 2. Schematic diagrams of the crystal structures of types O2, O3, P2, and P3 [16]

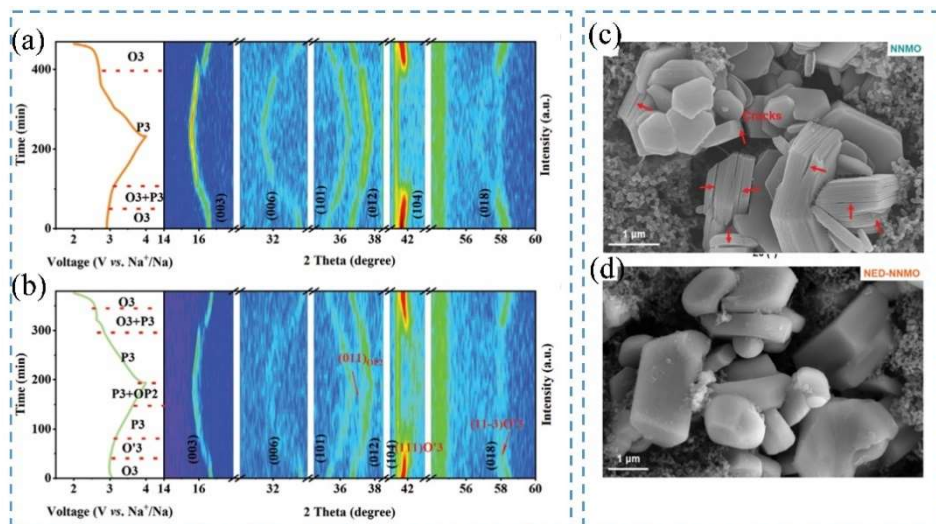
### 4. Challenges Faced by Layered Oxide Cathode Materials

#### 4.1 Irreversible Phase Transitions

In the practical engineering applications of sodium-ion battery cathode materials, irreversible phase transitions have become one of the key bottlenecks hindering further improvements in their electrochemical performance. Under high-pressure operating conditions, sodium-ion battery cathode materials undergo crystal structure transformations, which is a major cause of rapid capacity

degradation. As the battery voltage increases, many  $\text{Na}^+$  ions are expelled from the lattice structure. This process leads to relative sliding of the transition metal layers, triggering rearrangements in the crystal structure and initiating various complex phase transformation processes [17]. At the microscopic level, these multi-step phase transitions are closely related to the arrangement of vacancies formed after  $\text{Na}^+$  insertion/extraction and the degree of relative sliding in the transition metal oxide layer. As a result, the materials exhibit complex electrochemical responses, and their lattice volume undergoes repeated expansion and contraction during charge-discharge cycles [18].

From a macroscopic particle perspective, the stress and strain generated by the periodic changes in lattice volume gradually lead to the formation of microcracks within the cathode material particles. These microcracks directly block the diffusion pathways for  $\text{Na}^+$ , resulting in a significant decrease in ion transport rates. Taking the O3-type  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode material as an example (Figures 3a, b), this material undergoes multiple phase transitions during charging and discharging cycles: O3-O'3-P3-OP2-P3-O3 [19]. The main reason for these transitions is that the migration and rearrangement of transition metal ions disrupt the reversibility of the crystal structure. Additionally, the incorporation of external ions further hinders the reinsertion of  $\text{Na}^+$ , preventing the original O3 structure from being fully restored during discharge. The formation of the O'3 phase is closely related to the Jahn-Teller effect, while both the O'3 and OP2 phases significantly impede the  $\text{Na}^+$  desorption process. Furthermore, high-pressure conditions combined with mechanical strain can induce microcracks within the cathode material particles [20] (Figures 3c, d). These microcracks not only increase battery impedance and reduce the contact area between the electrolyte and active materials but also cause degradation of the active substances, hindering  $\text{Na}^+$  conduction and leading to a continuous decline in battery voltage and capacity over time. Therefore, effectively suppressing unfavorable phase transitions is crucial for  $\text{Na}_x\text{TMO}_2$  cathode materials to achieve excellent long-term cycle stability and electrochemical performance.



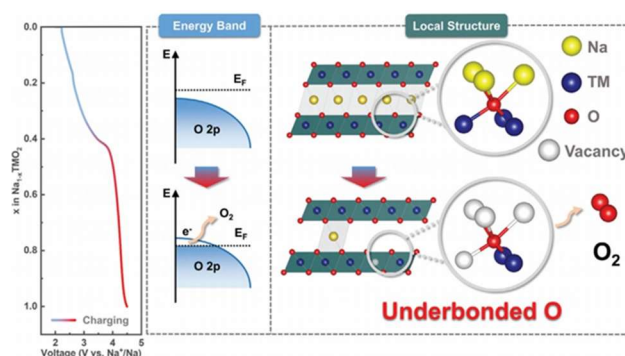
**Figure 3.** (a), (b) In-situ XRD contour maps of NNFM-S and NNFM samples [19]; (c), (d) SEM images of NNMO and NED-NNMO electrodes after cycling [20]

#### 4.2 Irreversible Oxygen Loss

In layered oxide cathode materials, irreversible losses are one of the key factors contributing to battery performance degradation. By activating the redox activity of oxygen anions, anions can participate in charge compensation, thereby enabling additional specific capacity at high voltages. However, when a large amount of  $\text{Na}^+$  is removed, the 3d orbitals of the transition metals in their higher oxidation states strongly hybridize with the 2p orbitals of oxygen. This leads to the oxidation of some lattice oxygen atoms, resulting in the formation of peroxide species [21]. This process is often accompanied by the generation of oxygen vacancies, and at high voltages, it can further trigger the release of

oxygen, causing irreversible oxygen loss and the migration of transition metal ions. From the perspective of band structure (Figure 4), during charging, electrons are removed from the transition metal 3d bands, causing the Fermi level to decrease while the O2p bands shift upward relative to it. When the charging voltage is high enough, the O2p bands may cross the Fermi level, at which point charge compensation is primarily driven by the oxidation of lattice oxygen. If the coupling between the O2p bands and the transition metal 3d bands is weak, the oxidized  $O^{n-}$  species can easily convert back into  $O_2$ . From the perspective of local coordination environments, when the coordination number of oxidized oxygen atoms is less than 3, their stability significantly decreases, making oxygen escape very likely [22].

Under high-voltage, deep desodiation conditions, transition metal ions migrate into the sodium layer, leaving behind vacancies. The in-plane migration of residual transition metal ions facilitates the formation of  $(O_2)^{n-}/O-O$  dimers from unpaired oxygen atoms, while also contributing to the formation of vacancy clusters. These vacancy clusters provide a site for further oxidation of oxygen species, ultimately leading to the generation of  $O_2$  molecules. Since the kinetics of  $O_2$  molecules being reduced to  $O^{2-}$  during discharge is slow, this results in a significant voltage hysteresis [23]. More seriously, the escape of  $O_2$  from the lattice causes irreversible oxygen loss and the formation of an inert phase on the particle surface. Meanwhile, the remaining oxygen vacancies can easily induce defects such as stacking faults and microcracks. Additionally, reactive oxygen species released under high voltage can react with the electrolyte, accelerating electrolyte decomposition and irreversible capacity loss [24]. Therefore, developing effective strategies to suppress oxygen loss at high voltages is crucial for creating sodium-ion battery cathode materials with high energy density and long lifespan.

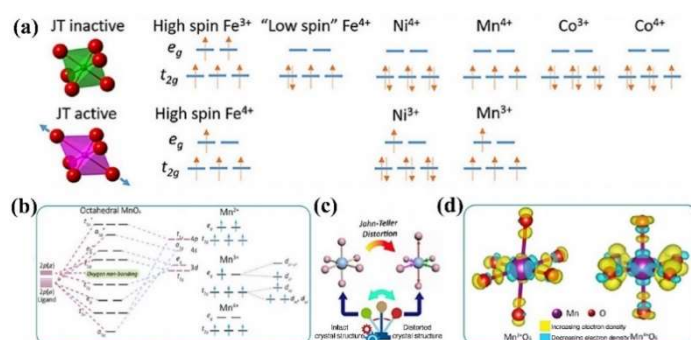


**Figure 4.** Schematic diagram illustrating the mechanism of reactive oxygen loss from the perspectives of band theory and local structure [25]

### 4.3 Jahn-Teller distortion

The local structural distortion in transition metal oxides induced by the Jahn-Teller effect is a crucial factor affecting the long-term cycle stability of sodium-ion batteries. As shown in Figure 5a, this effect occurs readily when the  $e_g$  orbitals are occupied by an odd number of electrons. Typical examples include high-spin states like  $Mn^{3+}$  and  $Fe^{4+}$ , as well as low-spin states like  $Ni^{3+}$ . In manganese-based layered oxides,  $Mn^{3+}$  inevitably induces Jahn-Teller distortion [26]. As depicted in Figure 5b, when one electron occupies the  $e_g$  orbital, the electron distribution becomes asymmetric along the  $z^2$  and  $x^2-y^2$  directions, destabilizing the regular  $Mn^{3+}O_6$  octahedral structure. Since the  $dx^2-y^2$  orbitals remain empty, the coordinating oxygen ions experience a stronger attraction from the central ion in the  $xy$  plane, causing them to move closer to the  $Mn^{3+}$  and forming four shorter Mn-O bonds [27]. At the same time, these shorter bonds increase the repulsion in the  $dx^2-y^2$  orbitals, raising their energy levels. This leads to an axial elongation and equatorial compression of the octahedron, resulting in a configuration with four short and two long Mn-O bonds (Figure 5c). This distortion not only alters the local atomic arrangement but also affects the electronic structure and ion transport, thereby impairing the material's electrochemical properties (Figure 5d). Therefore, to develop high-performance layered oxide cathode materials, it is necessary to systematically study and implement

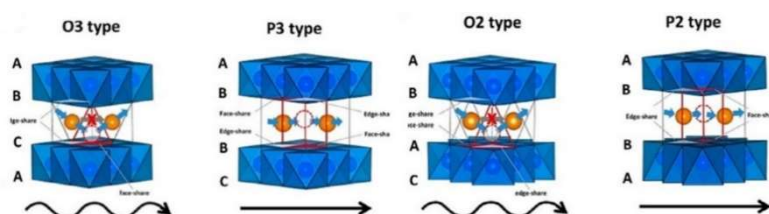
strategies to effectively suppress Jahn-Teller distortion, thereby enhancing structural stability and cycle life.



**Figure 5.** (a) Electron structures of inactive (upper) and active (lower) TMO<sub>6</sub> octahedra with Jahn-Teller effect [28]; (b) Molecular orbital energy diagram of octahedral MnO<sub>6</sub>, along with electron orbitals of Mn<sup>2+</sup>/Mn<sup>3+</sup>/Mn<sup>4+</sup>; (c) Schematic diagrams of octahedral MnO<sub>6</sub> before and after Jahn-Teller distortion; (d) Calculated charge densities for octahedral Mn<sup>3+</sup>O<sub>6</sub> and Mn<sup>4+</sup>O<sub>6</sub> [29]

#### 4.4 Electrochemical Kinetic Limitations

For O3-type sodium-ion battery cathode materials, their electrochemical kinetics are constrained by the inherent characteristic that the radius of Na<sup>+</sup> is larger than that of Li<sup>+</sup>. This directly results in a lower diffusion rate for Na<sup>+</sup> and increased ion migration resistance within the cathode material (Figure 6). Due to both the limited Na<sup>+</sup> diffusion and the rigidity of the crystal structure, the efficiency of ion transport within the battery is poor. This not only significantly reduces the battery rate performance but also limits the effective utilization of active materials under high current density conditions. This kinetic bottleneck highlights the importance of enhancing Na<sup>+</sup> migration capabilities and facilitating efficient charge transfer within the battery for the development of high-performance sodium-ion batteries.



**Figure 6.** Sodium ion diffusion paths in different layered transition metal oxides [30]

### 5. Modification Strategies for Layered Oxide Cathode Materials

Layered oxide cathodes face various structural challenges in practical applications, including irreversible phase transitions, lattice oxygen loss, Jahn-Teller distortions, and slow ion diffusion kinetics. These issues significantly affect their cycling and rate performance. To address these problems, we have summarized several effective modification strategies, such as element doping, surface coating, and structural design, to enhance the material's structural stability and prevent unfavorable structural changes.

#### 5.1 Element Doping

Element doping is a key strategy for optimizing the performance of electrode materials in sodium-ion batteries. By replacing atoms at the atomic scale with other elements (such as cations or anions), it's possible to simultaneously regulate the structure, electronic state, and electrochemical behavior of the material.

Cation doping primarily regulates material properties by replacing transition metal sites or sodium sites with metal ions. The mechanisms of action vary depending on the doping element used. For example, the introduction of  $\text{Li}^+$ ,  $\text{Cu}^{+2+}$  etc. can facilitate the formation of  $\text{Mn}^{4+}$  oxidation states, thereby effectively suppressing the Jahn-Teller distortion caused by  $\text{Mn}^{3+}$ . An et al [31] found that in Ca-doped  $\text{Na}_{0.95}\text{Ca}_{0.025}\text{Ni}_{0.9}\text{Ti}_{0.1}\text{O}_2$ ,  $\text{Ca}^{2+}$  not only prevents irreversible phase transitions and lattice volume collapse at high potentials but also increases the interlayer spacing through its steric effect, stabilizes the cathode/electrolyte interface, and reduces lattice oxygen loss and transition metal migration. Yuan et al [32] replaced some of the Mn with  $\text{La}^{3+}$ , utilizing the “atomic knife” effect to refine grain sizes and increase the sodium interlayer spacing. This reduced the severe phase transitions experienced by the O3-phase material during cycling. Additionally, the perovskite phase formed on the surface improved ion transport properties. Qiu et al [33] modified sodium sites with  $\text{Rb}^+$ , widening the sodium ion channels and strengthening the TM-O bonds. This prevented the formation of the harmful O3” phase in  $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  during high-dehydration conditions, thereby enhancing both structural reversibility and electrochemical performance.

Anionic doping mainly involves the substitution of oxygen sites by ions with radii like that of  $\text{O}^{2-}$ , such as  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ . This enhances the structural stability of lattice oxygen, thereby suppressing cation intercalation and oxygen loss. Among these,  $\text{F}^-$  doping has been most extensively studied. Song et al [27] introduced  $\text{F}^-$  into P2- $\text{Na}_{0.75}\text{Zn}_{0.28}\text{Mn}_{0.72}\text{O}_2$ . The stronger Zn-F bonds not only stabilized the crystal structure but also disrupted the electronic symmetry of the  $\text{MnO}_6$  octahedrons, reducing the Jahn-Teller distortion. As a result, the material exhibited improved rate performance and cycle stability. More importantly, the stable TM-F bonds formed through  $\text{F}^-$  substitution effectively prevented interlayer migration of  $\text{Zn}^{2+}$  during deep desodiation and stabilized the redox chemistry of oxygen. Chen et al [34] further demonstrated that  $\text{F}^-$  doping reduced the sodium layer spacing, mitigated structural degradation, and the Mn-F bonds suppressed spontaneous  $\text{Na}^+$  desorption and the formation of surface basic by-products. Compared to  $\text{F}^-$ , research on other anionic dopants in sodium-based layered oxide electrolytes is relatively limited. Early studies in lithium batteries showed that  $\text{Cl}^-$  doping increased the cell volume, reduced structural distortions, and improved cycle stability. Additionally, polyanionic groups like  $\text{BO}_3^{3-}$  and  $\text{PO}_4^{3-}$  have been used as dopants; they can prevent irreversible phase transitions and electrolyte decomposition under high pressure/high temperature conditions. However, these findings are still in the preliminary stage.

## 5.2 Surface Coating

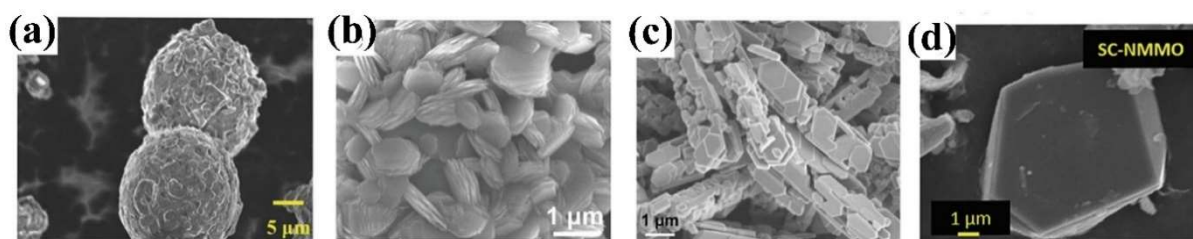
Surface coating involves creating a uniform and dense protective layer on the surface of the active material, thereby achieving multi-dimensional optimization of its electrochemical properties. The core principle of this approach is to utilize the physical barriers and chemical modifications provided by the coating to address the key challenges faced by electrode materials during cycling. On one hand, the coating prevents direct contact between the active material and the electrolyte, thereby reducing side reactions such as electrolyte decomposition and the dissolution of transition metal ions. It also protects the material from damage caused by moisture and carbon dioxide in the air, thereby enhancing its storage stability. On the other hand, a well-designed coating can serve as a structural support, helping to mitigate lattice strain and volume expansion during sodium ion insertion and extraction. This prevents particle agglomeration, cracking, and structural collapse, ensuring the long-term integrity of the electrode structure. Additionally, coatings with high electrical conductivity or ion-conducting properties can create efficient ion transport pathways, compensating for any deficiencies in the conductivity of the active material itself and thereby improving the battery’s rate performance.

Zhao et al [35] prepared a  $\text{NaTi}_2(\text{PO}_4)_3$  coating on the O3- $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  surface. This coating effectively prevented electrolyte erosion and inhibited the dissolution of transition metals. As a result, the material maintained 77.5% of its capacity after 100 cycles at 1C, while its capacity at 5C was 103.1 mAh/g. Li et al [36] used a solvothermal method to coat the P2- $\text{Na}_{0.7}\text{MnO}_{2.05}$  surface with the ion/electron conductor  $\text{NaPO}_3$ . This coating improved charge transfer and stabilized the interface,

enabling the material to exhibit excellent cycle stability in both liquid and solid-state batteries. These studies demonstrate that surface coatings can effectively enhance interfacial stability, reduce side reactions and harmful phase transitions, thereby improving the electrochemical performance of the materials.

### 5.3 Morphological Design

Optimizing the microstructure and morphology of the cathode material is a crucial approach to enhancing its structural stability under high voltages. Properly designed morphology can improve the lattice's ability to resist stress during cycling, while a robust micro- and nano-structured surface effectively prevents particle fragmentation and surface reactions, thereby hindering electrolyte penetration into the material. For example,  $\text{Na}_{0.66}(\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13})\text{O}_2$  with a uniform spherical morphology (Figure 7a) maintained 90% of its capacity after 150 cycles in the 2.0-4.7 V voltage range [37]. Additionally, low-dimensional structures such as nanosheets and nanowires can reduce the diffusion paths for ions and electrons, thereby accelerating reaction kinetics. For instance, the  $\text{O3-Na}[\text{Li}_{0.05}\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Cu}_{0.1}\text{Mg}_{0.05}]\text{O}_2$  prepared by Guo et al [38] consists of nanosheets arranged in an ordered manner (Figure 7b). The exposed (010) crystal plane increases the electrode/electrolyte contact area, thereby enhancing  $\text{Na}^+$  transport rates. Similarly,  $\text{P2-Na}_{0.67}\text{Ni}_{0.23}\text{Mg}_{0.1}\text{Mn}_{0.67}\text{O}_2$  exhibits a one-dimensional rod-like nanosheet structure (Figure 7c), and the strong interlayer interactions grant the material high mechanical stability. Creating single-crystal particles with high crystallinity and low specific surface area is another effective strategy to mitigate grain boundary stresses and cracks caused by anisotropic volume changes under high pressures. Single-crystal particles lack grain boundaries (Figure 7d), resulting in higher density and mechanical strength. Their excellent thermal stability also contributes to improved battery safety.



**Figure 7.** (a) Scanning electron microscope image of Na-NMC microspheres [37]; (b) SEM of  $\text{O3-Na}[\text{Li}_{0.05}\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Cu}_{0.1}\text{Mg}_{0.05}]\text{O}_2$  nanosheets [38]; (c) SEM Image of  $\text{P2-Na}_{0.67}\text{Ni}_{0.23}\text{Mg}_{0.1}\text{Mn}_{0.67}\text{O}_2$  [39]; (d) SEM Image of Single Crystal Grains

## 6. Conclusion and Outlook

Despite significant progress in areas such as electronic structure regulation, surface modification, functional structure design, and the utilization of anion/cation redox reactions in layered oxides, research in this field still faces several challenges. Firstly, current efforts mostly focus on optimizing individual components or interfaces, with limited understanding of the overall compatibility between the cathode and electrolyte systems under high-pressure conditions, as well as the electrochemical coupling mechanisms involved. Secondly, material synthesis and modification strategies are still largely based on empirical approaches, lacking systematic theoretical frameworks and coordinated design approaches. Thirdly, as research moves towards practical applications, issues arise when transitioning from half-cell evaluations to full-cell systems—specifically, irreversible sodium ion loss and matching problems with the anode. When scaling up from button cells to soft-pack or cylindrical batteries, challenges related to process complexity and maintaining electrochemical consistency become prominent.

Additionally, the economic benefits of recycling used sodium-ion batteries are low, making it difficult to encourage the development of large-scale recycling industries. Therefore, it is necessary to enhance the resource-recycling value through material regeneration and valorization processes. Future

research should aim to expand the range of cathode materials by combining layered oxides with prussian blue analogs and polyanionic materials, thereby leveraging the complementary advantages of different materials and improving design and evaluation at the full-cell level. Practical anode systems that can replace metallic sodium should also be developed to overcome engineering challenges associated with battery scaling. Through multidimensional collaborative innovation, it is possible to accelerate the commercialization of sodium-ion batteries, enabling them to complement lithium-ion batteries in supporting the development of sustainable energy storage systems.

## References

- [1] X. Cui, S. Ding, Y. Niu, H. Wang, Y. Lu, Y. Hu, W. Xue, 4.2 V O<sub>3</sub>-Layered Cathodes in Sodium-Ion Pouch Cells Enabled by an Intermolecular-Reinforced Ether Electrolyte, *Adv. Mater.* 37 (2025) e2415611.
- [2] Y. Shen, C. Cheng, X. Xia, L. Wang, X. Zhou, P. Zeng, J. Zeng, L. Zhang, Achieving structurally stable O<sub>3</sub>-type layered oxide cathodes through site-specific cation-anion co-substitution for sodium-ion batteries, *J. Energy Chem.* 93 (2024) 411-418.
- [3] J. Jin, Y. Liu, X. Zhao, H. Liu, S. Deng, Q. Shen, Y. Hou, H. Qi, X. Xing, L. Jiao, J. Chen, Annealing in Argon Universally Upgrades the Na-Storage Performance of Mn-Based Layered Oxide Cathodes by Creating Bulk Oxygen Vacancies, *Angew Chem Int Ed Engl.* 62 (2023) e202219230.
- [4] X. Yang, Y. Li, X. Li, T. Lin, W. Lin, P. Li, D. Xiao, S. Wang, H. Pan, Binary eutectic fluoride salts modification enhancing structural stability of layered oxide cathodes for Na-ion batteries, *Energy Storage Mater.* 76 (2025)
- [5] T. Cui, X. Li, Y. Fu, Characteristics, materials, and performance of Ru-containing oxide cathode materials for rechargeable batteries, *eScience.* 4 (2024)
- [6] D. Yang, C. Liu, X.W. Gao, Z. Zhao, Q. Gu, Y. Long, Q. Lai, H. Chen, Z. Liu, W.B. Luo, Constructing Mechanical-Chemical Stability via Multiphase Riveting and Interface Optimization Toward Layer-structured Oxide Cathode Material, *Angew Chem Int Ed.* 64 (2025) e202500939.
- [7] J. Shen, Y. Lou, J. Sun, H. Li, L. Li, W. Jang, S. Ye, X. Wu, H. Yang, Y. Yu, Achieving High Reversible Anionic Redox Activity of Li-Rich Layered Oxides via Mg and Mo Co-Doping, *Adv. Funct. Mater.* 35 (2025)
- [8] P. Li, T. Yuan, J. Qiu, H. Che, Q. Ma, Y. Pang, Z.-F. Ma, S. Zheng, A comprehensive review of layered transition metal oxide cathodes for sodium-ion batteries: The latest advancements and future perspectives, *Mater. Sci. Eng. R-Rep.* 163 (2025)
- [9] Y. Jin, Y. Peng, Y. Li, H. Zhou, J. Feng, Q. Fan, Q. Kuang, Y. Dong, X. Yang, Y. Zhao, Cu doping in TM ordered and disordered layered oxides for Sodium-Ion Batteries: Electrochemical Properties, structure evolution and Cu-Ion migration, *Chem. Eng. J.* 495 (2024)
- [10] K. Zhang, Y. Pan, X. Guo, J. Wang, C. Li, J. Li, M. Liao, Y. Jiang, W. Li, K. Zhang, Q. Ye, L. Ma, X. Gong, K. Li, Y. Wang, Y. Gao, X.-G. Gong, H. Peng, B. Wang, Connecting adjacent active layers with structural pillars for high-performance Li-organic batteries, *eScience.* 5 (2025)
- [11] X. Liang, J.Y. Hwang, Y.K. Sun, Practical Cathodes for Sodium-Ion Batteries: Who Will Take The Crown?, *Adv. Energy Mater.* 13 (2023)
- [12] M. Li, H. Zhuo, J. Lei, Y. Guo, Y. Yuan, K. Wang, Z. Liao, W. Xia, D. Geng, X. Sun, J. Hu, B. Xiao, Unravelling the structure-stability interplay of O<sub>3</sub>-type layered sodium cathode materials via precision spacing engineering, *Nat Commun.* 16 (2025) 2010.
- [13] X. Gao, G. Chen, W. Yao, Y. Mu, L. Hu, T. Zeng, W. Zhao, Z. Huang, M. Yang, Y. Pu, W. Ji, Z. Tan, P. Miao, N. Zhang, L. Yu, L. Zeng, R. Wang, Y. Xiao, Unlocking the ultra-high capacity and cost-effectiveness of cobalt-free lithium-rich cathode materials, *Energy Storage Mater.* 76 (2025)
- [14] T. Yang, Q. Li, Z. Liu, T. Li, K.M. Wiaderek, Y. Liu, Z. Yin, S. Lan, W. Wang, Y. Tang, Y. Ren, Q. Liu, Stabilizing the Deep Sodiation Process in Layered Sodium Manganese Cathodes by Anchoring Boron Ions, *Adv. Mater.* 36 (2024) e2306533.
- [15] X. Yin, L. Yang, W. Zhao, Z. Li, J. Xu, Y. Du, Z. Liu, Y. Sun, Y. Deng, J. Wang, P. Adelhelm, X. Yao, R. Si, D. Zhou, Synergetic Modulation of Interlayer–Intralayer Spacings for P2-Type Layered Oxide Cathode with Superior Rate Performance, *ACS Energy Lett.* 9 (2024) 3922-3930.

- [16] X.-Y. Zhou, Z.-X. Huang, X.-Y. Liu, B.-J. Xin, M. Du, D.-H. Liu, D.-M. Dai, X.-L. Wu, Air sensitivity of layered oxides for practical sodium-ion batteries, *J. Mater. Sci. Technol.* 269 (2026) 183-199.
- [17] K. Zhang, J. Zou, Z. Xu, G. Liu, L. He, Q. Yu, F. Wang, Y. Xia, Suppressing Fe Migration for Highly Reversible Oxygen Redox of Sodium-Ion Layered Oxide Cathode, *J. Am. Chem. Soc.* (2025)
- [18] H. Ji, H. Ren, G. Chen, W. Ji, F. Zhou, H. Qu, H. Fang, M. Chu, R. Qi, J. Zhai, W. Zeng, T. Liu, G. Zhou, Y. Xiao, J. Lu, Structural Insights Into Phase Formation of Sodium Layered Cathodes Materials with Prominent Electrochemical Performances, *Angew Chem Int Ed Engl.* 64 (2025) e202510981.
- [19] J. Yao, X. Wang, P. Hu, J. Fan, X. Yang, W. Jiang, S. Jiang, P. Dong, Y. Zhang, J. Duan, Z. Zhou, Local Electron Spin-State Modulation at Mn Site for Advanced Sodium-Ion Batteries with Fast-Kinetic  $\text{NaNi}_{0.33}\text{Fe}_{0.33}\text{Mn}_{0.33}\text{O}_2$  Cathode, *Adv. Funct. Mater.* (2024)
- [20] Y. Huang, S. Gu, X. Xu, Z. An, X. Han, Y. Cao, D. He, F. Zhang, H. Guo, Y. Liu, X. Liao, G. Liu, P. Liu, F. Wu, Y. Li, Z. Wang, Z. Wang, C. Ding, Y. Wang, J. Chen, M. Yang, F. Jiang, Y. Deng, Z. Xu, Z. Lu, Negative Enthalpy Doping Stabilizes P2-Type Oxides Cathode for High-Performance Sodium-Ion Batteries, *Adv. Mater.* 37 (2025) e2408012.
- [21] C. Zhang, B. Wei, M. Wang, D. Zhang, T. Uchiyama, C. Liang, L. Chen, Y. Uchimoto, R. Zhang, P. Wang, W. Wei, Regulating oxygen covalent electron localization to enhance anionic redox reversibility of lithium-rich layered oxide cathodes, *Energy Storage Mater.* 46 (2022) 512-522.
- [22] C. Cheng, Z. Zhuo, X. Xia, T. Liu, Y. Shen, C. Yuan, P. Zeng, D. Cao, Y. Zou, J. Guo, L. Zhang, Stabilized Oxygen Vacancy Chemistry toward High-Performance Layered Oxide Cathodes for Sodium-Ion Batteries, *ACS Nano.* 18 (2024) 35052-35065.
- [23] Z.-X. Huang, X.-L. Zhang, X.-X. Zhao, H.-Y. Lü, X.-Y. Zhang, Y.-L. Heng, H. Geng, X.-L. Wu, Suppressing oxygen redox in layered oxide cathode of sodium-ion batteries with ribbon superstructure and solid-solution behavior, *J. Mater. Sci. Technol.* 160 (2023) 9-17.
- [24] A.G. Squires, L. Ganeshkumar, C.N. Savory, S.R. Kavanagh, D.O. Scanlon, Oxygen Dimerization as a Defect-Driven Process in Bulk  $\text{LiNiO}_2$ , *ACS Energy Lett.* 9 (2024) 4180-4187.
- [25] Z. Chen, Y. Deng, J. Kong, W. Fu, C. Liu, T. Jin, L. Jiao, Toward the High-Voltage Stability of Layered Oxide Cathodes for Sodium-Ion Batteries: Challenges, Progress, and Perspectives, *Adv. Mater.* 36 (2024) e2402008.
- [26] Rambukwella, K.L. Firestein, Y. Xu, Z. Sun, S. Zhang, C. Yan, Unveiling the effect of molybdenum and titanium co-doping on degradation and electrochemical performance in Ni-rich cathodes, *Mater. Rep. Energy.* 5 (2025)
- [27] X. Song, R. Liu, J. Jin, X. Zhao, Y. Wang, Q. Shen, Z. Sun, X. Qu, L. Jiao, Y. Liu, Unraveling the functioning mechanism of fluorine-doping in Mn-based layered oxide cathodes toward enhanced sodium-ion storage performance, *Energy Storage Mater.* 69 (2024)
- [28] T. Yang, X. Wang, Z. Liu, Q. Liu, Cation Configuration and Structural Degradation of Layered Transition Metal Oxides in Sodium-Ion Batteries, *ACS Nano.* 18 (2024) 18834-18851.
- [29] S. Liu, B. Wang, X. Zhang, S. Zhao, Z. Zhang, H. Yu, Reviving the lithium-manganese-based layered oxide cathodes for lithium-ion batteries, *Matter.* 4 (2021) 1511-1527.
- [30] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, *Chem. Rev.* 114 (2014) 11636-82.
- [31] S. An, L. Karger, P. Müller, J. Lin, S. Vasala, V. Baran, S.L. Dreyer, R. Zhang, F. Ulusoy, A. Kondrakov, J. Janek, T. Brezesinski, Exploring calcium pillaring of O3-type  $\text{NaNi}_{0.9}\text{Ti}_{0.1}\text{O}_2$  cathodes to advance Na-ion battery technology, *Chem. Eng. J.* 509 (2025)
- [32] T. Yuan, P. Li, Y. Sun, H. Che, Q. Zheng, Y. Zhang, S. Huang, J. Qiu, Y. Pang, J. Yang, Z.F. Ma, S. Zheng, Refining O3-Type Ni/Mn-Based Sodium-Ion Battery Cathodes via "Atomic Knife" Achieving High Capacity and Stability, *Adv. Funct. Mater.* 35 (2024)
- [33] J. Qiu, P. Li, M. Jiang, Z. Fan, S. Wang, Q. Huang, W. Peng, G. Yang, Y. Ma, T. Yuan, Y. Pang, S. Zheng, Unleashing O3-Type Layered Cathode Capacity via Rb-Modulation for Advanced Sodium-Ion Batteries, *ACS Nano.* 20 (2026) 3762-3775.
- [34] X. Chen, S. Zheng, P. Liu, Z. Sun, K. Zhu, H. Li, Y. Liu, L. Jiao, Fluorine Substitution Promotes Air-Stability of P2-Type Layered Cathodes for Sodium-Ion Batteries, *Small.* 19 (2023) e2205789.

- [35] S. Zhao, Q. Shi, R. Qi, X. Zou, J. Wang, W. Feng, Y. Liu, X. Lu, J. Zhang, X. Yang, Y. Zhao, NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> modified O<sub>3</sub>-type NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> as high rate and air stable cathode for sodium-ion batteries, *Electrochim. Acta.* 441 (2023)
- [36] W. Li, Z. Yao, S. Zhang, X. Wang, X. Xia, C. Gu, J. Tu, Building superior layered oxide cathode via rational surface engineering for both liquid & solid-state sodium ion batteries, *Chem. Eng. J.* 421 (2021)
- [37] K. Kaliyappan, W. Xaio, T.K. Sham, X. Sun, High Tap Density Co and Ni Containing P2-Na<sub>0.66</sub>MnO<sub>2</sub> Buckyballs: A Promising High Voltage Cathode for Stable Sodium-Ion Batteries, *Adv. Funct. Mater.* 28 (2018)
- [38] Y. Xiao, P.F. Wang, Y.X. Yin, Y.F. Zhu, Y.B. Niu, X.D. Zhang, J. Zhang, X. Yu, X.D. Guo, B.H. Zhong, Y.G. Guo, Exposing 010 Active Facets by Multiple-Layer Oriented Stacking Nanosheets for High-Performance Capacitive Sodium-Ion Oxide Cathode, *Adv. Mater.* (2018) e1803765.
- [39] B. Peng, Z. Sun, L. Zhao, J. Li, G. Zhang, Dual-Manipulation on P2-Na<sub>0.67</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> Layered Cathode toward Sodium-Ion Full Cell with Record Operating Voltage Beyond 3.5 V, *Energy Storage Mater.* 35 (2021) 620-629.