Recent progress of ion-doping methods in modifying layered oxide cathode materials for sodium-ion batteries

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Abstract. Typically, the cathode materials contribute the most in achieving the commercialization of sodium-ion batteries (SIBs) as the cathodes take up the most proportion of the full cells cost. Hence, developing cathode materials with a high specific capacity, perfect capacity retention, long cycling lifetime, and strong chemical/environmental stability is of undoubted importance. Researchers are now using many methodologies to improve the performance of different types of cathodes. Among all these, ion-doping used in modifying layered oxide (Na_xTMO_2, in which TM=transition metal; $0<x\leq1$) cathode materials seem to be one of the most popular methods. This is because that the Na_xTMO_2 cathodes offer perfect energy density and Na^+ conductivity, while ion-doping methods could help mitigate the phase transition, sluggish kinetics, and air instability challenges. As a result, this review summarizes the recent progress of ion-doped Na_xTMO_2 cathodes modification strategies, divided into three parts in dealing with the above three challenges respectively. This work targets for facilitating the development of ion-doping methods used in commercial Na_xTMO_2 modification and pave the way for the next generation of energy storage systems.

Keywords: sodium-ion batteries, Na_xTMO_2 cathode, ion-doping.

1. Introduction

Lithium-ion batteries (LIBs) earn a dominant position in the realm of portable electronic devices due to their high density and specific capacity[1]. Unfortunately, Li has only 0.0065% crustal abundance on earth causing its application facing a bottleneck due to high costs[2]. On the contrary, sodium, who has an abundant reserve in the crustal layer, is considered as a potential supplement. Among all the components of SIBs, cathodes are one of the most expensive and important parts as they take up for approximately over 30% of SIBs total cost price and the choice of cathode materials could affect the performance of the full cells. Na_xTMO_2 cathodes, such as P2-type ($x\leq0.7$) and O3-type ($0.7<x\leq1$), materials are considered as appropriate candidates for SIBs because they offer perfect energy density and Na^+ conductivity[3,4].

Nevertheless, the application of Na_xTMO_2 cathodes still encounters many challenges. Firstly, Na_xTMO_2 would face the risk of irreversible phase transition, which can deteriorate structure stability and decrease cycling stability as well as battery lifetime. Besides, the Na_xTMO_2 cathode could face the problem of sluggish kinetics, because the ion radius of Na^+ is large, bigger than that of Li^+. Finally, Na_xTMO_2 cathodes are generally hygroscopic. Even a short period of contact with the air would do harm to their electrochemical performances[5]. In this cases, scientists have been trying to solve these problems through adopting ion-doping methodologies[6].

In this review, recent progress of ion-doping methods in modifying Na_xTMO_2 cathode materials are summarized. Additionally, this review reveals that ion-doping is useful in manipulating Na_xTMO_2 material structure. For phase transition, doping Cu and boron is effective in mitigate Jahn-Teller (J-T) effect in the P2-type. While in the O3-type, doping can prevent O3→P2 or O3→P3 transition during Na^+ intercalation/extraction process. Besides, this review suggests ion-doping in P2-type other than O3-type to gain decent kinetics. Finally, as for air stability problem, doping ions with high redox potential might be a satisfying practice.

2. Effect of ion-doping strategies

2.1. Phase transition

The phase transition is one of the most significant challenges for the commercialization of Na_xTMO_2 cathodes as it can affect the electrochemical performances of the whole cells. In the P2-type Na_xTMO_2, the phase transition generally comes from the unfavorable J-T distortion. Zhou et al. (**Fig.1 a~b**) successfully fabricated the P2-type through Cu-doping, forming a $Na_{0.7}Fe_{0.23-x}Cu_xMn_{0.77}O_2$ (0.09-NFCMO, x=0.09) structure, which presents a specific capacity of 168.6 mAh g^{-1} at 100 mA g^{-1} and a perfect cycling stability of 74.2% retention after being cycled for 50 times at 200 mA g^{-1}. Through the method of hydrothermal Cu-doping, the XPS image shows a lowered Mn^{3+} content in the 0.09-NFMCO compared to the pristine 0-NFMCO, thereby indicating that this method could perfectly reducing J-T effect[7]. For a novel P2&O3 biphasic structure, Yu et al. (**Fig.1 c**) introduced a boron-doping strategy to the full-cell, which presents a decent cycling stability with a capacity retention of 70.8% after being cycled for 150 times at 0.1 C. This job exhibits a novel boron-doped $NaNi_{0.5}Mn_{0.5}O_2$ material called NNMBO and restrains the phase transition through the lattice interlocking effect between P2&O3. Additionally, boron can occupy the interstitial position and reduce the formation energy gap[8]. While in the O3-type Na_xTMO_2, the phase transition usually comes from the unstable structure of O3 itself. As the O3-type has more Na^+ content than P2-type, it is easier for its TMO_2 glide, inducing O3-type to transform into P2 or P3 type during Na^+ intercalation/extraction process. Zhang et al. (**Fig.1 d**) used Nb-doping method and obtained the O3-$NaFe_{0.55}Mn_{0.45-x}Nb_xO_2$ (x=0, 0.01, 0.02, 0.03) structure through solid-state synthesis route. By doping Nb, decreased phases transition irreversibility was seen. The most intriguing part of the research is that when Nb content increased, new ultraweak diffraction peaks were spotted in the XRD patterns. These new peaks may refer to the formation of Na_2CO_3 and NaOH, which indicates air instability of the Na_xTMO_2 cathode. Therefore, it is important to balance the Nb content and the electrochemical performances of this type of SIBs. When x=0.01, the work presents notable results with a specific capacity of 127mAh g^{-1} and a capacity retention of approximately 80% after 100 cycles at 0.1 C[9]. Co-doping methods can also be used to suppress phase transitions. Liang et al. (**Fig.1 e**) successfully doped Sn and Cu towards the O3-type Na_xTMO_2 structure . This SIBs present an astounding rate capability with 108.5 mA h g^{-1} at 1000 mA g^{-1} and maintaining 80.7% retention capacity after 500 cycles. With Sn^{4+} doped, this $Na_{0.993}Ni_{0.382}Mn_{0.428}Cu_{0.098}Sn_{0.049}O_2$ (NaNMCS) structure could have strong electrostatic bonds between Na and O, thereby suppressing the phase transition, especially at high voltages[10]. Besides, there appears the situation when multi-element doping methodology was introduced. For example, Guo et al. (**Fig.1 f**) created $Na_{0.9}Ni_{0.25}Cu_{0.05}Mg_{0.05}Zn_{0.05}Fe_{0.05}Al_{0.05}Mn_{0.40}Ti_{0.05}Sn_{0.05}O_2$ (NCMZFAMTS) through slight concentrations of active (Ni, Cu) and inactive (Mg, Al, Zn) multi-doping. The work achieves superior electrochemical performance of a reversible 120 mAh g^{-1} specific capacity at 2.0-4.0 V voltage range, 90% capacity retention after 500 cycles, and a decent rate capability by maintaining 70% of its original capacity at 5.0 C. The improvements in this SIBs performance may stem from two reasons. One is that the work uses high-entropy materials, suppressing O3→P3 phase transitions and improving cycling stability. Another is that the slight doping of active&inactive could work together to weaken the impact of harmful anisotropic lattice strain and promote chemo-mechanical stability[11].

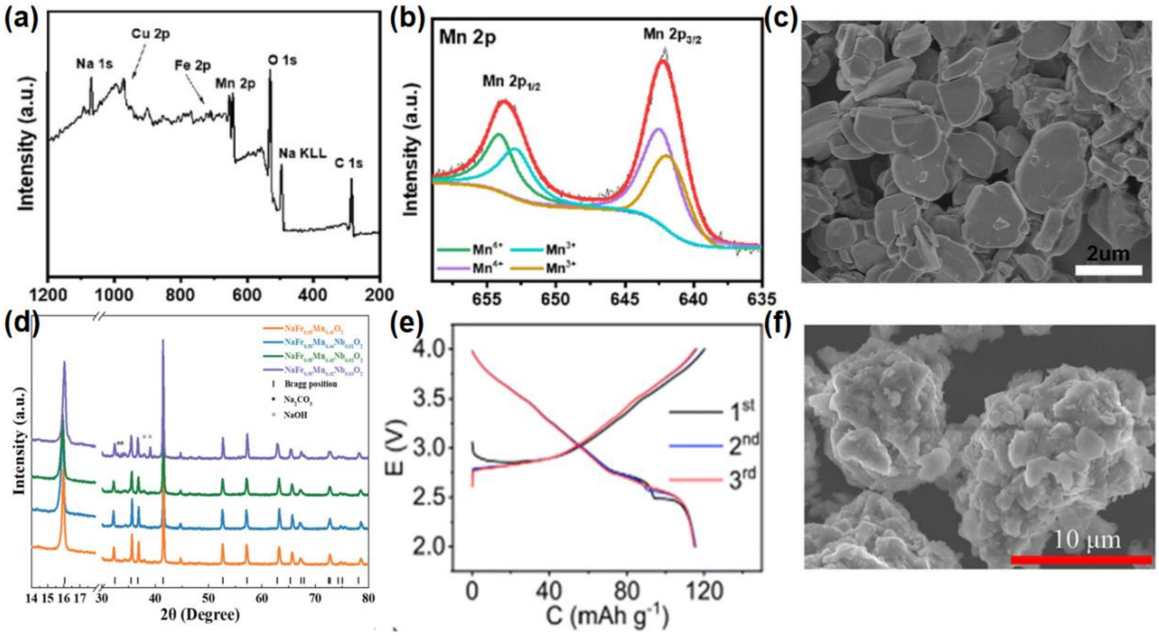

Fig. 1 (a) XPS spectra of 0.09-NFCMO. (b) High-resolution XPS spectra of Mn 2p [7]. Copyright 2024, Energy, Environmental, and Catalysis Applications. (c) SEM image of NNMBO [8]. Copyright 2024, Advanced Functional Materials. (d) XRD patterns of the $NaFe_{0.55}Mn_{0.45-x}Nb_xO_2$ (x = 0, 0.01, 0.02, and 0.03) [9]. Copyright 2020, Applied Energy Materials. (e) Charge and discharge profiles of O3-NaNMCS at 50 mA g^{-1} [10]. Copyright 2023, Inorganic Chemistry Frontiers. (f) Morphology of NCMZFAMTS [11]. Copyright 2023, Energy, Environmental, and Catalysis Applications.

2.2. Sluggish kinetics

Another difficulty faced by SIBs might be the sluggish Na^+ diffusion kinetics due to the large ion radius of Na^+. Usually, different types of ions are doped to enlarge the interplanar spacing, making it easy for Na^+ to intercalate and extract. Recently, Shi et al. (**Fig.2 a**) reported that the niobium-doped P2-type Na_xTMO_2 cathode material, $Na_{0.78}Ni_{0.31}Mn_{0.67}Nb_{0.02}O_2$ (P2-NaMNNb), could help reduce the electronic band gap, while solving the risks of Na^+ immobility caused by the high diffusion energy barrier. Through examining the crystal structure, an increased TM layer distance was gained, doing good to the Na^+ intercalation/extraction process. It is worth noting that this compound is also capable to maintain satisfying electrochemical performance while being charged/discharged at a low temperature of -40℃. Eventually, the work demonstrates an amazing figure of a discharge rate of around 65 mAh g^{-1} at 25℃, and 76% capacity retention after being charged/discharged at 368mA g^{-1} under -40℃ conditions for 1800 cycles[12]. Another useful strategy is co-doping. Huang et al. (**Fig.2 b**) proposed a Zn/Mg co-doping method, resulting in a favorable rate of 67.2 mAh g^{-1} at 10 C and an outstanding cycle stability with 93.8% capacity retention after being cycled for 100 times at 1 C. The compound named $Na_{0.67}Mn_{0.7}Zn_{0.15}Mg_{0.15}O_2$ (NMZMO) could lead to wider ion diffusion channels compared with the initial $Na_{0.67}MnO_2$ (NMO) and effectively increase the Na^+ diffusion coefficient[13]. Yang et al. (**Fig.2 c**) invented a Ti-doped Na_xTMO_2 cathode, $Na_{2/3}Fe_{1/3}Mn_{0.57}Ti_{0.1}O_2$ (NFMTO), which was incorporated with an anode made up of hard carbon. The work gained an amazing capacity retention of 72% after 50 cycles. Moreover, the cyclic voltammetry (CV) curve together with galvanostatic intermittent titration technique (GITT) shows that the Na^+ transmission coefficient in NFMTO is much bigger than that of the original $Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$ (NFMO) compound due to the Na^+/vacancy perturbation triggered by Ti-doping, resulting in improved Na^+ transmission kinetics and prolonged lifetime of this SIBs[14]. Yuan et al. (**Fig.2 d**) synthesized the O3-$NaNi_{0.5}Mn_{0.5-x}Sb_xO_2$ (NaNMS) cathode with high structure stability and wide ion channels for fast Na^+ transmission. Previous work has proven that Sb-doping is effective in enlarging the Na^+ diffusion channel. As a consequence, Yuan's work utilized this theory by manipulating different Sb content (x=0.01, 0.02, 0.03). More specifically, its XRD data reveals the relationship between c/a ratio of the crystal lattice and Na^+ transmission kinetics. The higher the c/a ratio is, the faster the Na^+ will migrate. When Sb was doped into the structure, the c/a ratio increased. Eventually, this research obtained a reversible capacity of 212.3 mAh g^{-1} at 0.2 C, and high capacity retention after being cycled for 100 times at -20°C[15]. When comparing the two types of Na_xTMO_2: P2 and O3, researchers noticed that O3-type may exhibit more sluggish Na^+ diffusion kinetics than P2-type may do. This is because that P2-type possesses a P-type framework structure with high stability and wide path, making it easier for Na^+ diffusion process. Thus, doping specific ions to mitigate the formation of O3 phase is seen as another effective way in boosting the intercalation/extraction mobility. Tang et al. (**Fig.2 e**) invited fluorine into $Na_{0.67}Li_{0.1}Fe_{0.4}Mn_{0.5}O_2$ (NLFMO) structure. Researchers examined the CV curve and found that the F0.1-NLFMO one presents the smallest polarization and the narrowest overlapping pattern. Therefore, this 0.1 mol fluorine content shows the best cycling stability and rate capacity among all the other subjects. In conclusion, through fluorine doping, researchers successfully minimized the TM layer average valence, suppressed extra O3 formation, and obtained SIBs with 90.0% capacity retention after 50 cycles, and rate capacity of 128.7 mAh g^{-1} at 400 mA g^{-1}[16].

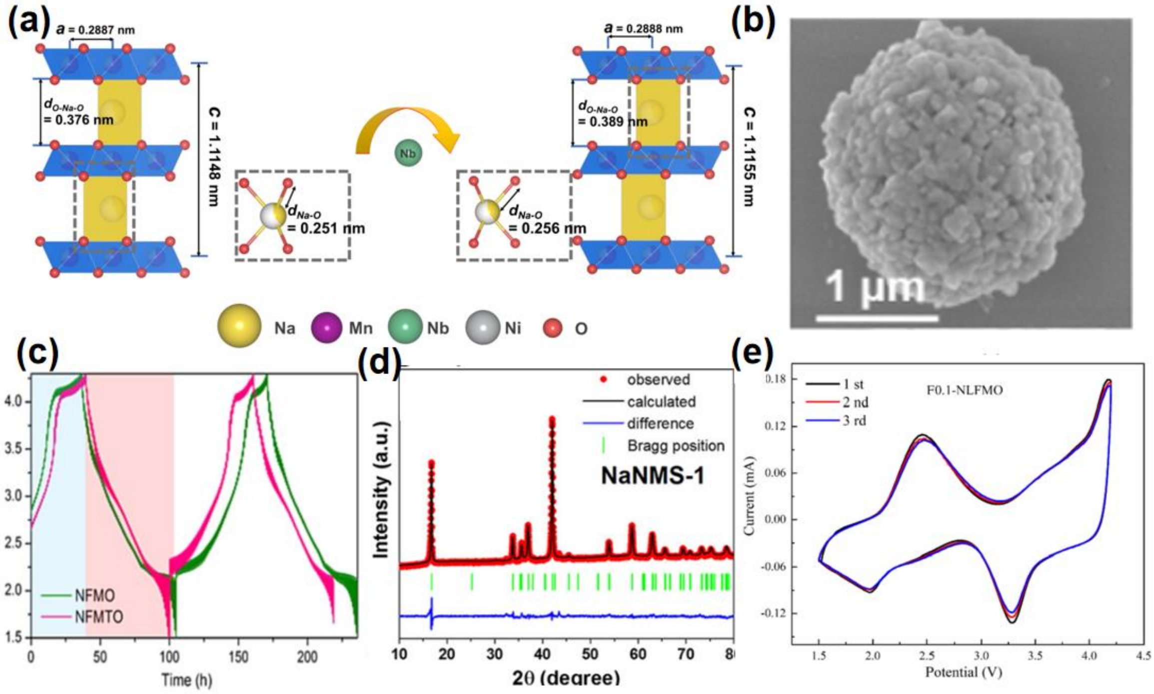

Fig. 2 (a) Schematic diagram of the effect of Nb doping on crystal structure[12]. Copyright 2022, Nature Communications. (b) SEM image of NMZMO[13]. Copyright 2021, Nano Research. (c) The measured GITT curves of NFMO and NFMTO[14]. Copyright 2022, Journal of Energy Chemistry. (d) Rietveld refinement patterns of the XRD data for NaNMS-1[15]. Copyright 2022, ACS Nano. (e) CV curves of the as-prepared material F0.1-NLFMO[16]. Copyright 2019, Electrochimica Acta.

2.3. Air sensitivity

Besides, Na_xTMO_2 cathodes are quite sensitive towards air, making it difficult for the further commercialization of SIBs. In general, SIBs are usually manufactured at one place and moved to another place to be assembled. This points to the importance of building air resistant Na_xTMO_2 materials as the transportation process might involve long time exposure to the oxygen, carbon dioxide, and water, namely causing structure cracks, phase hydration, poor rate capability, and even short lifetime. Encountering such challenges, Li, X et al. (**Fig.3 a**) doped Al into the O3-$NaFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (NFNM) cathode to obtain $NaFe_{(1/3-0.01)}Ni_{1/3}Mn_{1/3}Al_{0.01}O_2$ ($NFNMA_{0.01}$). Because Al element is able to build Al-O covalent bonds, it can help mitigate the reaction between cathode and ambient atmosphere and improve chemical stability. They confirmed the successful introduction of Al into the TM layer through TEM analysis. Moreover, SEM & FTIR figures indicate that Al-doping can restrain the carbonates formation, enhancing the interfacial chemical stability. Beyond that, Li, X also compared the two common doping methods: co-precipitation and direct solid-state method, while examining the differences on XRD patterns. Some impurities were spotted on the surface of α-$NaFeO_2$ phase made from solid-state method, while there are no impurities in the subject made from co-precipitation method. Accordingly, researchers used the co-precipitation method in the study as those impurities might affect the performance of SIBs like capacity retention, discharge capacity, and air stability. The work achieves a rate capacity of 138 mAh g^{-1} and a capacity retention increase from 71.02% to 85.88% after being cycled for 50 times at 0.2 C (compared with the undoped NFNM materials). Furthermore, the most significant outcome of this study shall be the chemical stability improvement of the cell after 30-day air exposure, elevating from 58 mAh g^{-1} (undoped NFNM) to 131 mAh g^{-1} (doped $NFNMA_{0.01}$) at 0.2 C[17]. Typically, a P2-type Na_xTMO_2 is more sensitive to air exposure than a O3-type, so there exists urgent need to find suitable air resistance doping methods especially for the P2-type. To this end, Zuo et al. (**Fig.3 b**) studied the structural and chemical transformation happened on P2- $NaxTMO_2$ structure and tried to explain the rules behind. When comparing the air-stability of 5 different types of Mn-doped Na_xTMO_2, researchers found that there is a close relationship between the ions' valence state (redox potential) and air stability. To be more explicit, Na_xTMO_2 with higher electrochemical redox potential will present better air stability. The finding has been proved by experiment and will pave the way for the future development of air resistant Na_xTMO_2[18].

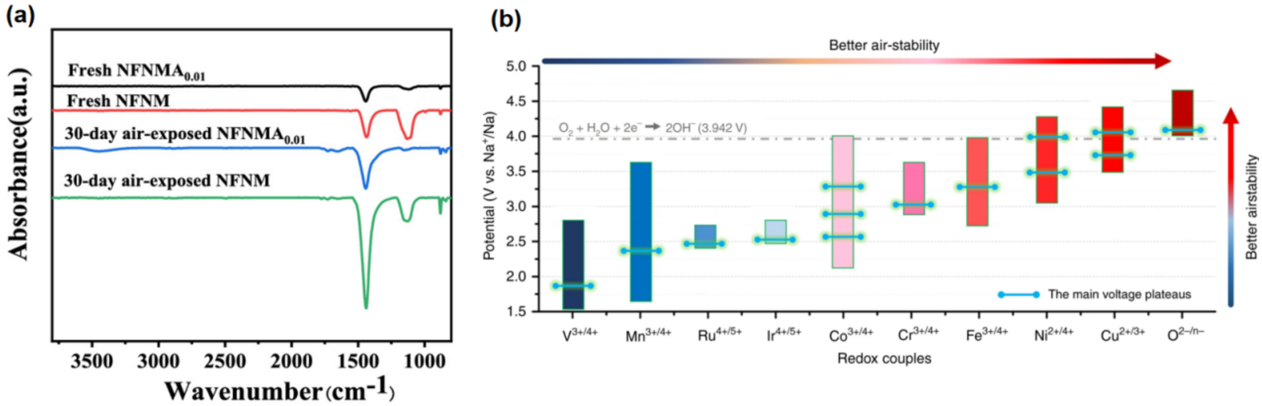

Fig. 3 (a) FTIR spectra of NFNM and NFNMA0.01 before and after the air exposure for 30 days[17]. Copyright 2021, Energy, Environmental, and Catalysis Applications. (b) The comparison of the main redox couples in Na_xTMO_2[18]. Copyright 2020, Nature Communications.

2.4. Summary

The short summary of the comparative electrochemical performance of doped Na_xTMO_2 of previously mentioned works are listed in **Table 1**. It is easy to observe that the integrated performance of the doped Na_xTMO_2 is usually batter than that of the undoped one, showing that ion-doping is a desirable method in SIBs' performance improvement.

Table 1. The Summary of the Comparative Electrochemical Performance of Doped Na_xTMO_2 Cathode Materials in Previous Works

Doped and Undoped Material	Performance/units: mA h g^{-1}	Current Density	Ref
0.09- NFCMO	163.0	200 mA h g^{-1}	[7]
0- NFCMO	137.6		
NNMBO	65.9	0.1 C	[8]
NNMO	<65.9		
$NaFe_{0.55}Mn_{0.44}Nb_{0.01}O_2$	127.4	1 C	[9]
$NaFe_{0.55}Mn_{0.45}O_2$	102.2		
O3-NaNMCS	115.3 (smooth)	50 mA h g^{-1}	[10]
O3- NaNM	130.0 (with platform)		
NCMZFAMTS	120 (90% capacity rentention at 3 C)	0.1 C	[11]
NFM	122 (54% capacity rentention at 3 C)		
P2- NaMNNb	65.8	50 C	[12]
P2- NaMNb	<65.8		
NMZMO	67.2	10 C	[13]
NMO	15.8		
NFMTO	52	3 C	[14]
NFMO	31		
NaNMS-1	131.5	0.2 C (charging cutoff potential limitted to 4V)	[15]
NaNM	130.5		
F0.1-NLFMO	173.0	20 mA h g^{-1} discharge specific capacity	[16]
NLFMO	122.9		
$NFNMA_{0.01}$	138 (85.88% capacity retention)	0.2 C	[17]
NFNM	141 (71.02% capacity retention)		

3. Conclusion

Ion doping has proven to be an effective strategy for enhancing the performance of Na_xTMO_2 cathode materials in SIBs. By substituting specific cations and anions into the host material, researchers have been able to improve key electrochemical properties such as cycling stability, rate capability, and capacity retention. The three main challenges facing the further commercialization of Na_xTMO_2 cathode SIBs might be the phase transition, sluggish kinetics, and air sensitivity. This review suggests effective ion-doping methods to cope with each of them. Firstly, ion-doping can be used to inhibit phase transition in both P2-type and O3-type. As to P2-type, doping ions, such as Cu, can help mitigate J-T distortion. While for O3-type, ion-doping can suppress its transition into P2 or P3-type in the Na^+ intercalation/extraction course. Secondly, the sluggish Na^+ diffusion kinetics can also be weakened through doping as ions can enlarge the interplanar spacing, making it easy for the movement of Na^+. Besides, it is also found that O3-type may exhibit more sluggish Na^+ diffusion kinetics than P2-type may do. Therefore, in the future, researchers can use P2-type for generating batter rate capability results. Finally, this research gives a general advice for modifying air resistant Na_xTMO_2 materials. Na_xTMO_2 with higher electrochemical redox potential will present better air stability. So doping ions with higher electrochemical redox potential shall be effective in promoting the stability of the cell. Overall, the careful selection and incorporation of dopants enable the fine-tuning of the cathode's structure and electronic properties, paving the way for more efficient and durable SIBs. Looking ahead, the development of novel doping strategies, including the exploration of less conventional dopants and doping techniques, will be crucial for the advancement of SIBs. Future research should focus on understanding the synergistic effects of multi-element doping and optimizing the balance between structural stability and electrochemical performance. Additionally, scaling up these doping strategies for commercial production while ensuring cost-effectiveness will be key to the successful deployment of SIBs in real-world applications.

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