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Predominant P3-Type Solid–Solution Phase Transition Enables High-Stability O3-Type Na-Ion Cathodes

Hao Guo,* Chenglong Zhao,* Dong Zhou, Jianlin Wang, Xiaobai Ma, Jianxiang Gao, Xuesheng Jiao, Xufeng Hu, Xuedong Bai, Kai Sun,* and Dongfeng Chen*



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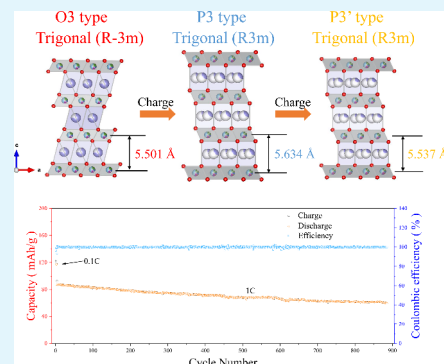
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Supporting Information

ABSTRACT: Layered O3-type oxides are one of the most promising cathode materials for Na-ion batteries owing to their high capacity and straightforward synthesis. However, these materials often experience irreversible structure transitions at elevated cutoff voltages, resulting in compromised cycling stability and rate performance. To address such issues, understanding the interplay of the composition, structure, and properties is crucial. Here, we successfully introduced a P-type characteristic into the O3-type layered structure, achieving a P3-dominated solid–solution phase transition upon cycling. This modification facilitated a reversible transformation of the O3–P3–P3' structure with minimal and gradual volume changes. Consequently, the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode exhibited a specific capacity of approximately 113 mAh/g, coupled with exceptional cycling performance (maintaining over 70% capacity retention after 900 cycles). These findings shed light on the composition–structure–property relationships of Na-ion layered oxides, offering valuable insights for the advancement of Na-ion batteries.

KEYWORDS: Na-ion batteries, O3-type cathode, $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$, P3-dominated phase transition, O3–P3–P3'



1. INTRODUCTION

Li-ion batteries (LIBs) have been widely applied to consumer devices and electric vehicles due to their high energy density and excellent cycling stability.¹ However, the increasing demand and uneven distribution of Li resources hinder the extensive application of LIBs in the field of energy storage, in which cost is the most important factor. Na-ion batteries (SIBs) are expected to be an alternative to LIBs in energy storage systems because of the stable supply and even distribution of Na resources.^{2–4} In the current SIBs, cathode materials play a significant role in energy density, cycling life, and rate property.^{5,6} Therefore, an in-depth investigation into cathode materials and their corresponding reaction mechanisms during (de)sodiation is of great importance for both the engineering and scientific point of view.^{7–10} Among the reported cathode materials, Na-ion layered transition metal oxides (Na_xTMO_2) have gained significant attention owing to their great compositional diversity, relatively easy preparation process, and highly reversible specific capacity.^{11–16} O3-type and P2-type Na_xTMO_2 are the widely studied layered structures used for cathode materials, which are composed of TMO_6 octahedra sheets, where Na ions occupy the octahedral (O) and prismatic environment (P) sites between the octahedra sheets, respectively. The figure (e.g., 3 in O3) represents the stacking number of TMO_6 octahedra sheets in a structure cell.¹⁷ Generally, high Na content can screen the electrostatic repulsion effect between the two oxygen sheets,

leading to a reduction in the $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer space, which contributes to the emergence of an O3-type structure. On the contrary, low Na content leads to a larger $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer space, therefore promoting the formation of a P2-type structure.^{18,19}

O3-type $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ can exhibit high capacity that benefited from high Na content and adequate $\text{Ni}^{2+/4+}$ redox couple. Nevertheless, it suffers irreversible phase transformation with great volume variation at elevated cutoff voltages, which is detrimental for cycling stability.^{20,21} The substitution of Ni^{2+} and Mn^{4+} with inert and/or active elements (Zn^{2+} , Mg^{2+} , Ti^{4+} , Cu^{2+} , etc.) can help to suppress the undesirable phase transformation when the voltage exceeds 4 V, consequently elevating the structure stabilization and cycling stability, but at the expense of capacity.^{22,23} Also, it should be mentioned that the long-term cycling stability of layered O3-type oxides can be further improved by limiting the cutoff voltage. As a result, the practical capacity of O3-type oxides^{24–27} is restricted to about 110–130 mAh/g. Therefore, it is clear that an in-depth understanding of the composition–

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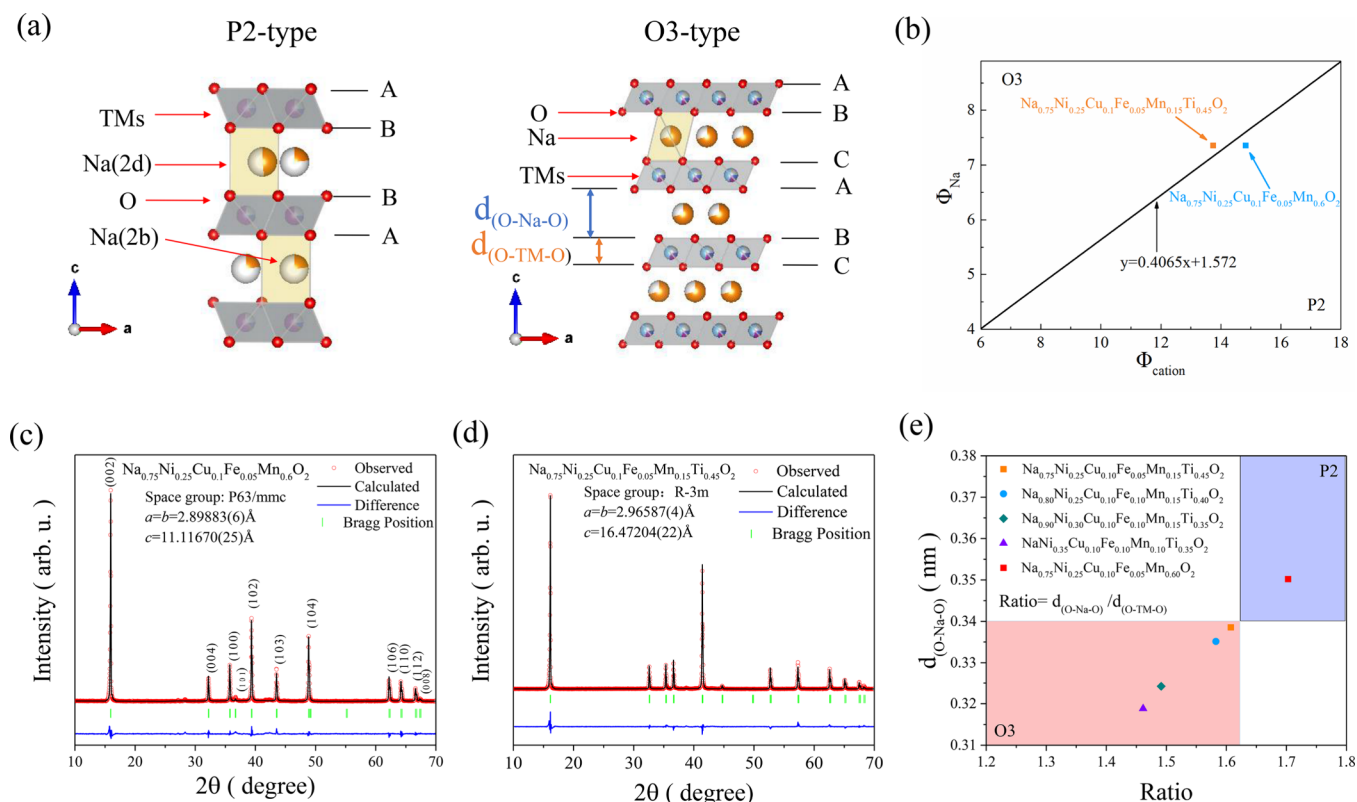


Figure 1. Designing the O3-type structure with P-type structural characteristics. (a) Representation of P2-type and O3-type crystal structures. (b) Prediction of phase structure according to the cationic potential. (c and d) XRD data and refinement results of P2-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$ and O3-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ materials. (e) $d_{(\text{O}-\text{Na}-\text{O})}$ versus the ratio of $d_{(\text{O}-\text{Na}-\text{O})}/d_{(\text{O}-\text{TM}-\text{O})}$ for O3- $\text{Na}_x[\text{Ni}_a\text{Cu}_b\text{Fe}_c\text{Mn}_d\text{Ti}_e]\text{O}_2$ and P2- $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$.

structure–property of O3-type Na_xTMO_2 contributes to the design of optimal cathodes presenting the desired properties: large capacity, high structural stability, and excellent cycling stability.

In this work, we designed an O3-type layered oxide with a larger $d_{(\text{O}-\text{Na}-\text{O})}$ interlamellar spacing, featuring a distinctive attribute of P-type structures.²⁸ The incorporation of the P-type characteristic into the O3-type framework led to a brief O3–P3 phase transition and an extended P3-type solid–solution phase transformation during cycling. This design effectively mitigates irreversible phase transitions and minimizes strain induced by volume changes, resulting in outstanding cycling stability and rate capabilities. Notably, the material exhibited a reversible capacity of approximately 113 mAh/g between 2 and 4.2 V, maintaining a remarkable capacity retention of 70% after 900 cycles and a conservation rate of 63% at 5C charging/discharging rates.

2. EXPERIMENTAL SECTION

2.1. Sample Synthesis. The $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$, $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$, $\text{Na}_{0.8}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.15}\text{Ti}_{0.4}\text{O}_2$, $\text{Na}_{0.9}\text{Ni}_{0.3}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.15}\text{Ti}_{0.35}\text{O}_2$, and $\text{NaNi}_{0.35}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.35}\text{O}_2$ samples were synthesized via a high-temperature calcination process, following our previous report.²⁴

2.2. Material Characterization. X-ray powder diffraction measurements were conducted on an X-ray diffractometer (D8 Advance, equipped with Cu K α radiation, Bruker, Germany) to study the phase purity and phase structure of the obtained materials. In addition, neutron powder diffraction was applied to further verify the crystal structure as well as transition metal ordering. The used facility is a high-resolution powder diffractometer (HRPD, $\lambda = 1.889$ Å),

which is located in the China Advanced Research Reactor (CARR, China Institute of Atomic Energy, China). Electron microscope techniques were used to characterize the microstructure information of samples, as described in the Supporting Information.

2.3. Electrochemical Measurements. The preparation process of positive electrodes, the fabrication procedure, and the measurement method of coin-type cells were in agreement with those reported in the previous work,²⁹ as shown in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Compositional Design. The previous work indicated O3- and P2-types can be distinguished according to the ratio of $d_{(\text{O}-\text{Na}-\text{O})}$ to $d_{(\text{O}-\text{TM}-\text{O})}$ in a unit cell. It can be found that a precise dividing line to distinguish O3-type and P2-type structures is at ~ 1.62 .³⁰ Therefore, designing an O3-type layered oxide with a big $d_{(\text{O}-\text{Na}-\text{O})}$ interlamellar spacing, which facilitates the value of $d_{(\text{O}-\text{Na}-\text{O})}/d_{(\text{O}-\text{TM}-\text{O})}$ close to the boundary line of the O3- and P2-type structures, can introduce the P-type structural characteristic into the O3-type structure. We speculated that adjusting the P2-type composition with intermediate Na content can pass through the division between O3- and P2-type structures, promoting the attainment of an O3-type structure with P-type structural characteristics. Here, we selected the composition of P2-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.1}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$ as a candidate, considering that the combination of multiple transition metals has a positive effect on Na storage performance. Inspired by the cationic potential method,^{31,32} we found that substituting partial Mn^{4+} with appropriate Ti^{4+} makes the cationic potential (Φ_{cation}) pass through the dividing line between two stacking

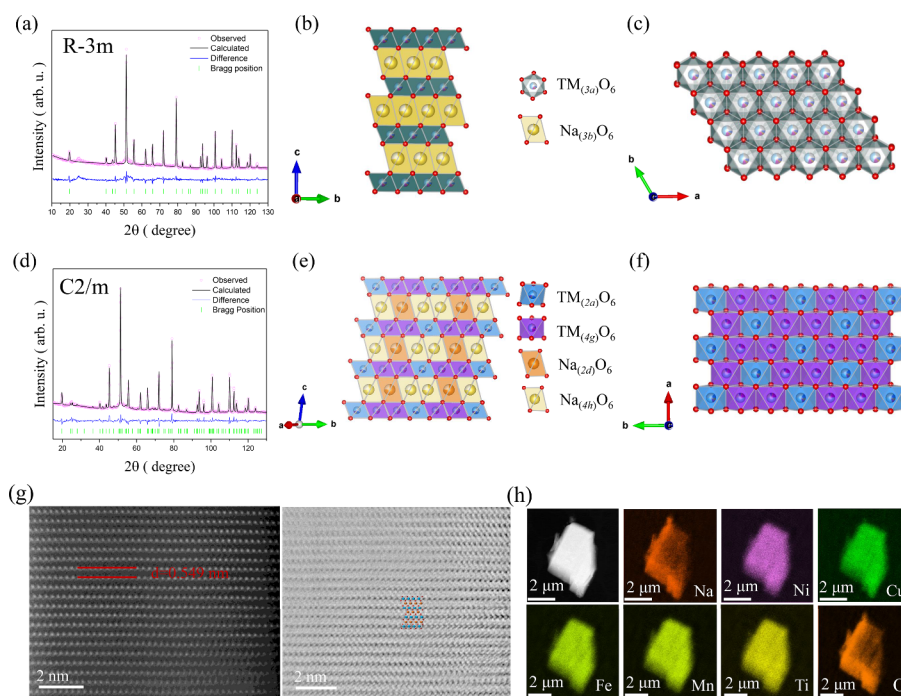


Figure 2. Structural characterization. NPD pattern and Rietveld refinement, schematic crystal structure, and transition metal arrangement of O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ using (a–c) $R\text{-}3m$ and (d–f) $C2/m$ space groups, respectively. (g and h) High-angle annular dark field and annular light field STEM images and energy dispersive X-ray spectroscopy (EDS) mappings of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ sample.

structures, indicating that the adjusted $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ material has an O3-type stacking structure while possessing a characteristic of P-type structures (Figure 1b).

To prove the prediction, we prepared $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$ and $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ samples using a high-temperature solid-state method. The phase purity and phase structure of two samples were first analyzed by means of X-ray diffraction (XRD) and Rietveld refinement. As illustrated in Figure 1c, the diffraction peaks of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$ sample can be well indexed with the space group of $P6_3/mmc$. The relevant P2-type stacking structure, depicted in Figure 1a, was composed of TMO_6 octahedra sheets with oxygen stacking arrangements of ABBA. Na ions occupied the two prismatic environment (P) sites between the octahedra sheets. The $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ sample crystallized to an O3-type structure with repeating ABCABC stacking (Figures 1a and 1d), corresponding to the NaFeO_2 structure with $R\text{-}3m$ symmetry. The detailed crystal structure parameters of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.6}\text{O}_2$ and $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ samples are displayed in Tables S1 and S2, respectively. These results demonstrated that the $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer distance of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ material was 0.339 nm, larger than those of other high-Na O3-type layered oxides (Figure 1e and Table S4). The resulting value of $d_{(\text{O}-\text{Na}-\text{O})}$ to $d_{(\text{O}-\text{TM}-\text{O})}$ for O3-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ was 1.607, which is close to the boundary line of the P2-type structure, demonstrating that this O3-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ material has P2-like characteristics and may exhibit improved Na storage performance.

The crystal structures of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ samples were further characterized by neutron powder diffraction (NPD). It is worth noting that some weak diffraction peaks in the NPD pattern, which were absent in the XRD pattern, cannot be indexed with the $R\text{-}3m$ space group (Figure 1d and Figure 2a). Instead, good fitting results can be obtained by using the $C2/m$ space group involving 3d transition metal (TM) ordering (Figure 2d). The relevant crystal structure parameters of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ material obtained by using $R\text{-}3m$ and $C2/m$ space groups are shown in Tables S5 and S6, respectively. As shown in Figures 2e and 2f, in the crystal structure with the $C2/m$ space group, Na atoms occupied two octahedral sites (2d and 4h) between the TMO_2 slabs. Ni/Cu/Fe/Mn/Ti atoms simultaneously occupied two sites (2a and 4g) within the TMO_2 slabs but presented the separately predominant occupations. In other words, most of the Ni, Cu, and Fe atoms were located in 2a sites, while the great mass of Mn and Ti atoms occupied the 4g sites. As a result, the specific transition metal ordering results in the broadened and weak superlattice peaks in the NPD pattern, which cannot be observed in the XRD pattern owing to the similar scattering ability of 3d transition metals with the near atomic number Z. In addition, we also investigated the TM ordering in the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ sample by using scanning transmission electron microscopy (STEM). Nevertheless, the ordered distribution of TM elements with regular ‘bright–bright–dark–bright–bright’ arrangements was not visible in STEM images due to the similar atomic numbers between Ni/Cu/Fe/Mn/Ti (Figure 2g).

The crystal structure and element distribution of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ sample were also studied using high-resolution transmission electron microscopy (HRTEM). By analyzing the selected area electron diffraction pattern (Figure S1), the diffraction spots correspond to the

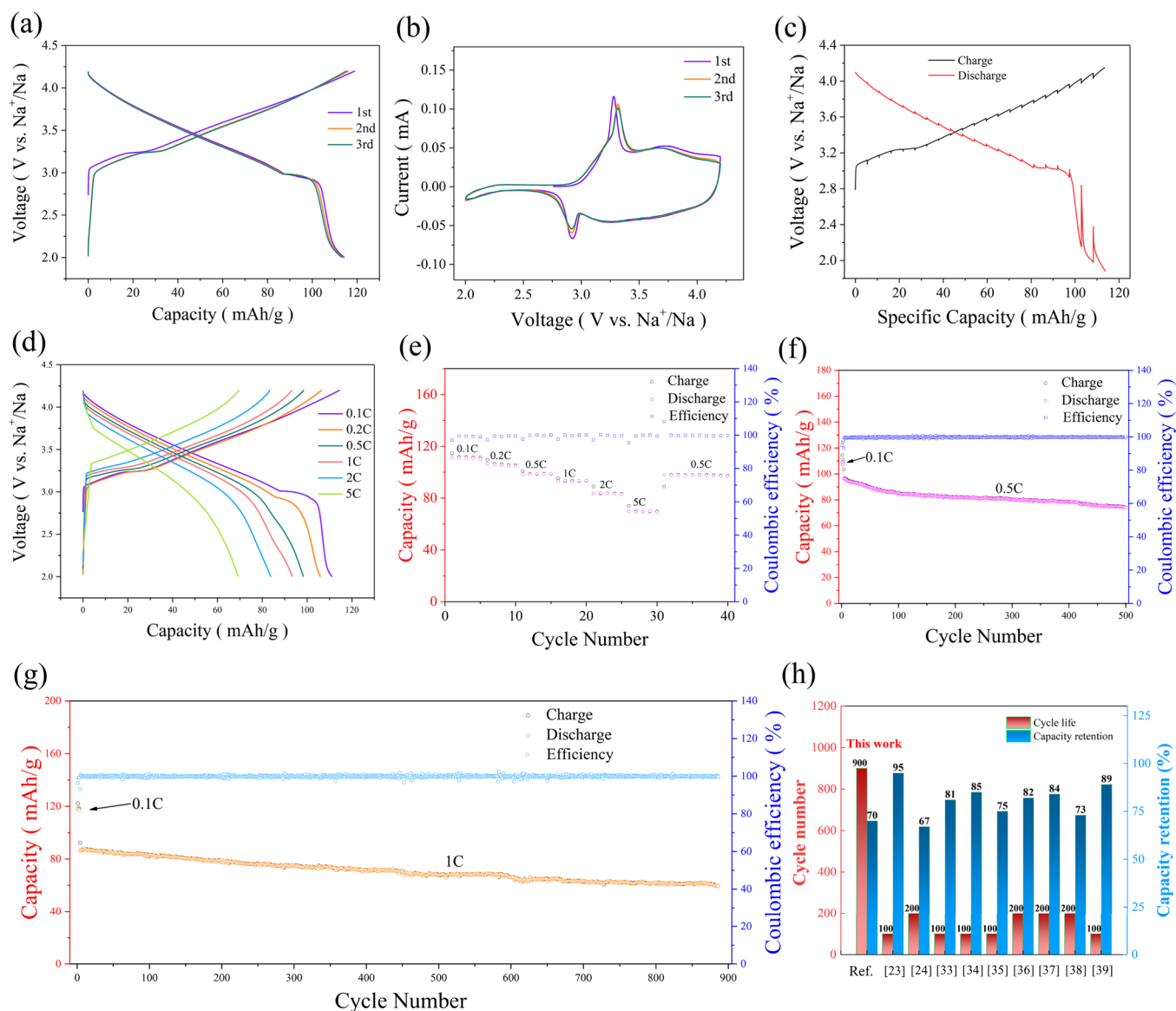


Figure 3. Electrochemical performance. (a) Charge–discharge curves and (b) cyclic voltammetry profiles of the O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes when cycled in the voltage region of 2.0–4.2 V. (c) GITT profiles for the first charging and discharging at 0.1C and (d and e) rate capability of the O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes at different rates. (f and g) Capacity retention of $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes at 0.5C and 1C rates, respectively. (h) Comparison of cycling performance with other O3-type cathodes.^{23,24,33–39}

(101) and (012) planes of the crystal structure with the *R*-3*m* space group, respectively, compatible with the results of XRD refinement. As presented in Figure 2g, the distances between the neighboring lattice fringes were 0.549 nm, corresponding to the (003) lattice planes, which was also consistent with the HRTEM result. In addition, energy dispersive X-ray spectroscopy (EDS) mappings (Figure 2h and Figure S1) indicated that the elements in the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ materials presented a uniform distribution.

3.2. Electrochemical Performance. To investigate the influence of large $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer distance on the electrochemical property, $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes were tested by coin-type half cells. The $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode showed a discharge capacity of 113 mAh/g between 2.0 and 4.2 V at a current density of 12 mA/g (0.1C). Notably, the charge–discharge profiles and CV curves of the

$\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes displayed high coincidence (Figures 3a and 3b). As shown in Figures 3c and S2, the galvanostatic intermittent titration technique (GITT) measurement indicated that the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode exhibited a high Na-ion diffusion coefficient (stabilizes at 10^{-10} – 10^{-11} cm^2/s), therefore resulting in improved rate capabilities. As presented in Figures 3d and 3e, the reversible capacities of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode were 112, 106, 98, 90, 80, and 70 mAh/g at 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C rates, respectively, demonstrating outstanding rate performance. In addition, it can be clearly seen from Figures 3f and 3g that $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathodes have a remarkable cycling performance with 70% capacity retention after 900 cycles at a 1C rate, which is superior to that of other O3-type layered oxides (Figure 3h and Table S7). Consequently, the superior cycling performance and rate

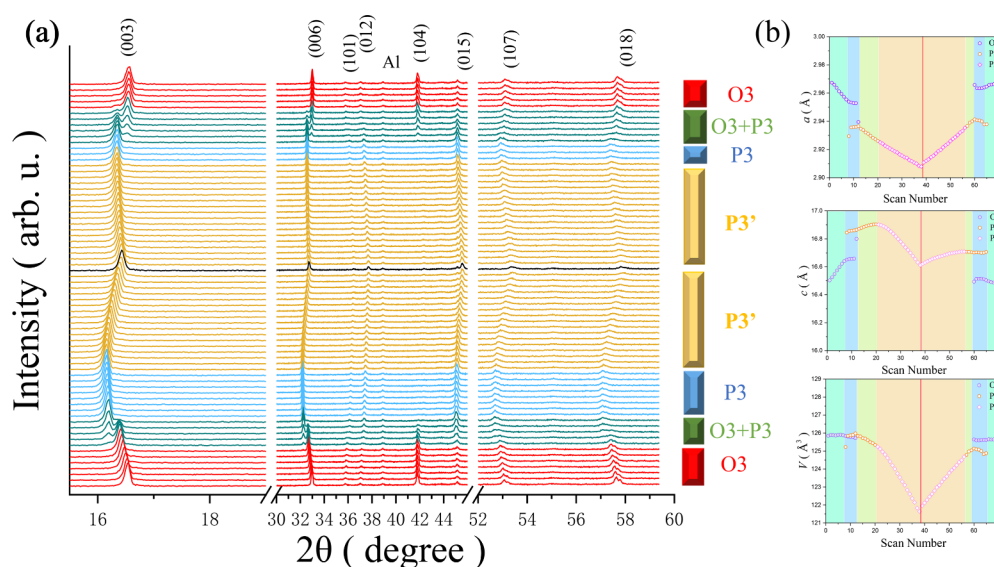


Figure 4. Structural transformation during cycling. (a) In situ XRD patterns of the O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode upon cycling. (b) Cell parameter evolution of the O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode during charging and discharging.

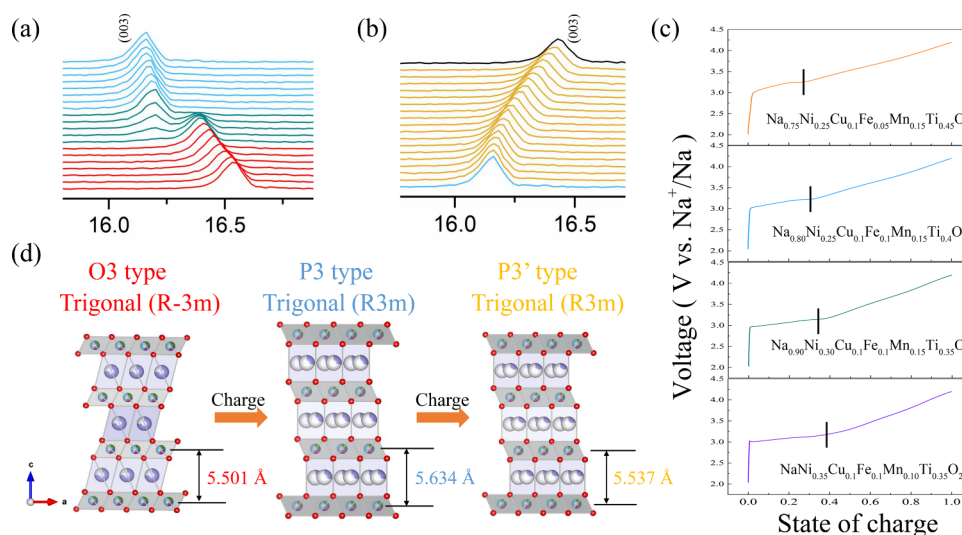


Figure 5. Performance enhancement mechanism. The (003) peak evolution when the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode is at the low charging voltage region (a) and the high charging voltage region (b), indicating an O3–P3 phase transition and a P3–P3' phase transition, respectively. (c) The normalized charge profiles of O3-type $\text{Na}_x[\text{Ni}_a\text{Cu}_b\text{Fe}_c\text{Mn}_d\text{Ti}_e]\text{O}_2$; the black line represents the boundary of capacity stored in O3-type and P3-type regions. (d) The evolution of crystal structure and interlayer distance (1/3 of cell parameter c) when the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode is at different charging states.

capabilities of the O3-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ prove its potential for future application.

3.3. Structural Evolution. To understand the effect of large $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer space on the structure evolution and electrochemical performance of the O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode, we conducted in situ XRD measurements during charging and discharging. As shown in Figure 4a, upon initial charging, the (003) diffraction peaks and (101) peaks of the O3-type $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode moved to a lower and a higher 2θ angle, respectively, suggesting the solid-soluble reaction (Figure 4b). With subsequent charging, the O3-type cathode underwent a phase transformation from the O3- to P3-type phase, corresponding to the short low-voltage plateau region in charge–discharge curves (Figure 3a).

Upon further charging, it is noteworthy that the (003) peaks of the P3 phase unexpectedly and gradually moved to higher 2θ angles, demonstrating the gradual decrease of the interlayer distance. This phenomenon is different from those of other O3-type cathode oxides.^{24,40–42} It is generally known that the (003) peaks of the P3 phase will gradually shift to a lower 2θ angle upon the deintercalation of Na^+ , corresponding to the increase of the interlayer distance.^{41,43} Until the end of charging, no new peak was observed and the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode maintained a P3-type structure but with different cell parameters (Figure 4b). To further confirm the crystal structure of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode at high voltage, we performed the ex situ XRD measurements of this cathode when charged to 4 and 4.2 V, respectively. It can be found from Figure S3 that both XRD patterns can be fitted with the

$R\bar{3}m$ space group, proving the same P3-type structure. Consequently, we denote this type of structure at high voltage as the P3' type. During discharging, the P3' structure changed back to the initial O3 structure in an opposite way (Figure 4a and Figure 4b), indicating a high reversibility.

3.4. Performance Improving Mechanism. Generally, O3-type cathode oxides usually suffer performance degradation during charging and discharging, resulting from the appearance of a distorted phase and large-volume phase transition during deep desodiation.^{20,22,33,44,45} For example, $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ exhibited a complicated phase evolution (O3–O3'–P3–P3'–P3'') upon deintercalation and intercalation of Na, which has a detrimental influence on the electrochemical performance.²⁰ It is generally appreciated that the appearance of distorted phases including O3' and P3' upon deintercalation and intercalation of Na results from the Jahn–Teller effect of Ni^{3+} and Na^+ /vacancy ordering, which can be suppressed by rational element substitution.^{21,46} As shown in Figures 5a and 5d, in the case of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode, any distorted phase including O3' and P3' structures were absent owing to the synergism of multiple 3d transition metals. The reversible O3–P3 phase transformation at the low-voltage region contributes to the promotion of cycling performance (Figure 5d). In addition, when O3-type cathode oxides are in the state of deep deintercalation of Na, the large-volume phase transition such as P3–O3'' frequently occurs.³³ The crystal structure of the O3'' phase is analogous to that of the initial O3 phase but with a lower interlayer distance. This P3–O3'' phase transition is always accompanied by a significant lattice volume change, which will result in structural degradation and cracking generation during repeated charge and discharge, leading to the performance fading.^{22,33,44} Instead of a P3–O3'' phase transition at the high-voltage region, a P3–P3' phase transition was present in the case of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode (Figures 5b and 5d). Specifically, the lattice volume of the P3 phase decreased slowly upon charging to high voltage (Figure 4b), which facilitates the enhancement of the cycling property when operating at high cutoff voltage. To further prove the benefit of the P3-dominated solid–solution phase transition, we designed a series of layered oxide cathodes with the same transition metal (TM) elements but with different Na content. When designing the TM components, we adopted the approximate ratio of Ti to Mn to reduce the effect of undesirable phase transitions at high voltage. It can be seen from Figure 5c that the proportion of the capacity stored in P3-type region during the electrochemical Na^+ deintercalation grew linearly with the decrease of Na in $\text{Na}_x[\text{Ni}_a\text{Cu}_b\text{Fe}_c\text{Mn}_d\text{Ti}_e]\text{O}_2$. As a result, the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode with the most predominant P3-type solid–solution phase transition showed the best cycling stability and rate capabilities (Figure S4). Moreover, we investigated the structure evolution of $\text{NaNi}_{0.35}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.10}\text{Ti}_{0.35}\text{O}_2$ during charging and discharging via ex situ XRD. As shown in Figure S5, while charging, the structure transformation of the $\text{Na-Ni}_{0.35}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.10}\text{Ti}_{0.35}\text{O}_2$ cathode was similar to that of $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ (O3–P3–P3'). However, in the course of discharging, the P3'-type structure changed back to the O3-type structure in an asymmetric way, demonstrating the poor reversibility. Therefore, the $\text{Na-Ni}_{0.35}\text{Cu}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.10}\text{Ti}_{0.35}\text{O}_2$ material with an asymmetric and O3-dominated phase transition exhibited the worst cycling stability and rate performance. Ultimately, we concluded that

the highly reversible and P3-dominated solid–solution phase transformation with minimal and slow volume change during the charge–discharge course results in the excellent cycling stability and rate capabilities of the $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$ cathode.

4. CONCLUSIONS

In conclusion, we successfully incorporated the P-type characteristic into the O3-type structure through strategic adjustments in composition and the $d_{(\text{O}-\text{Na}-\text{O})}$ interlayer space. The cathode, denoted as O3– $\text{Na}_{0.75}\text{Ni}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.05}\text{Mn}_{0.15}\text{Ti}_{0.45}\text{O}_2$, presented remarkable cycling stability, with a capacity retention of 70% after 900 cycles at a current rate of 1C. Additionally, it demonstrated outstanding rate capabilities, with 63% capacity retention even at a high 5C rate. These findings suggest that the exceptional cycling performance and rate capabilities stem from the dominance of the P3-driven solid–solution phase transition and the controlled volume changes during charging and discharging. This study provides valuable insights for the rational development of high-stability O3-type layered oxide cathodes tailored for SIBs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c02889>.

The obtained crystal structure parameters via refinement, ICP results, the values of $d_{(\text{O}-\text{Na}-\text{O})}$ and $d_{(\text{O}-\text{Na}-\text{O})}/d_{(\text{O}-\text{TM}-\text{O})}$, HRTEM images, SAED, EDS mappings, Na^+ diffusivity, ex situ XRD, comparison of cycling stabilities of O3-type layered cathodes at elevated cutoff voltages, and the rate capabilities and cycling performance of $\text{Na}_x[\text{Ni}_a\text{Cu}_b\text{Fe}_c\text{Mn}_d\text{Ti}_e]\text{O}_2$ with high Na content (PDF)

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Notes

The authors declare no competing financial interest.

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