



High-entropy lattice pinning effect enables long lifespan and air stability in O3-type sodium-ion battery cathodes

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ABSTRACT

O3-type $\text{NaNi}_{0.4}\text{Fe}_{0.2}\text{Mn}_{0.4}\text{O}_2$ cathodes suffer from harmful phase transitions and large volume strains, leading to sluggish Na^+ kinetics and poor cyclability. To address these issues, we propose dual-site doping via a high-entropy strategy, O3- $\text{Na}_{0.96}\text{Ca}_{0.02}\text{Ni}_{0.27}\text{Fe}_{0.2}\text{Mn}_{0.35}\text{Al}_{0.02}\text{Cu}_{0.1}\text{Ti}_{0.05}\text{O}_2$ (NCNFMACTO) cathode. Based on the Rietveld refinement of X-ray diffraction (XRD) data and DFT calculations, it is inferred that Ca^{2+} doping occupies the sodium sites, generating an “anchoring effect” that stabilizes the transition metal layer during the desodiation process. Concurrently, doping the transition-metal layer with multi-principal elements (Al, Cu, Ti) induces a lattice-regulating effect. This reinforces TM-O covalency and impedes slab gliding, thereby suppressing detrimental phase evolution and minimizing volume change. As a result, the material undergoes a reversible O3-P3-O3 phase transition with only 1.1% volumetric strain, significantly enhancing Na^+ diffusion kinetics. The doped cathode exhibits remarkable cycling stability (91% capacity retention after 200 cycles at 1C and 80.1% capacity retention after 1000 cycles at 5C) and excellent air stability. Moreover, the NCNFMACTO//HC full cell maintains 85.2% capacity retention over 400 cycles at 1C. The full cell demonstrates an excellent energy density of $264.87 \text{ Wh}\cdot\text{kg}^{-1}$ at $44.42 \text{ W}\cdot\text{kg}^{-1}$, fully demonstrating its feasibility. This work provides key insights for designing high-stability sodium-layered oxide cathodes.

KEYWORDS

sodium ion batteries, high entropy, cathode materials, O3 phase material, suppressing complex phase transition

1 Introduction

With the rapid growth in demand for large-scale energy storage and the increasingly prominent issues of energy crises and uneven resource distribution, there is an urgent need to develop cost-effective energy storage materials with superior performance [1–3]. Sodium-ion batteries, with their unique resource and performance advantages, are rapidly developing into a novel energy storage technology [4–6]. Compared with lithium-ion batteries, sodium-ion batteries offer advantages such as lower cost and abundant resource reserves, providing a more economical solution for the large-scale application of clean energy [7]. However, SIBs' cathodes remain limited by anisotropic lattice expansion/contraction during sodium-ion intercalation/deintercalation causing cycling instability, air sensitivity, and phase transitions [8–11]. Among various cathode materials, layered

oxides ($(\text{Na}_x\text{TMO}_2)$, TM = transition metals), which include O3-phase (Na^+ in octahedral sites) and P2-phase (Na^+ in prismatic sites) structures, have emerged as highly promising energy storage materials due to their straightforward synthesis, high capacity, and superior energy density [12–15]. O3-phase material has an oxygen atom stacking sequence of ABCABC with a space group of $R\bar{3}m$; P2-phase material exhibits an ABBA oxygen stacking arrangement and belongs to the $P6_3/mmc$ space group [16, 17]. Compared to P2-phase materials, O3-phase materials exhibit advantages such as higher theoretical capacity, superior initial Coulombic efficiency and enhanced energy density. Therefore, the rational design of O3-phase layered oxides can significantly improve the electrochemical performance of layered oxides [18].

Despite their high capacity, O3-phase materials face significant challenges, such as complex phase transitions (O3-O'3-P3) and

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interlayer sliding during electrochemical process, resulting in structural collapse and consequently poor cycling stability and rate capability [19–23]. Additionally, the material surface readily reacts with ambient $\text{H}_2\text{O}/\text{CO}_2$ to form $\text{NaOH}/\text{Na}_2\text{CO}_3$, leading to severe air sensitivity [24, 25]. Previous studies have demonstrated that structural stability can be enhanced through metal doping strategies, such as incorporating elements such as Ca [26, 27], Ti [28], and Al [29, 30] into the O3-phase lattice. High-entropy strategy offers a promising pathway to enhance the electrochemical performance of sodium-ion cathode materials. Qiu et al. proposed a high-entropy doped material, $\text{Na}_{0.85}\text{Li}_{0.1}\text{Al}_{0.02}\text{Sn}_{0.08}\text{Cu}_{0.1}\text{Ti}_{0.1}\text{Ni}_{0.3}\text{Mn}_{0.3}\text{O}_2$, demonstrating that the high-entropy doping strategy effectively improves structural stability by suppressing phase transitions and lattice distortion [24]. However, their long-term cycling stability still unsatisfactory [31–34]. Therefore, achieving cycling stability under high current densities, robust air stability and reversible phase transitions remains a critical challenge.

It is noteworthy that the intrinsic mechanism of this dual-site high-entropy strategy fundamentally surpasses traditional multi-element doping. Conventional doping typically introduces foreign ions as isolated point defects into the host lattice, primarily leveraging local size mismatches to alleviate volume strain. In contrast, our high-entropy approach achieves a multi-principal component configuration in both the sodium layer and the transition metal layer, resulting in a configurational entropy as high as 1.62R. This entropy driven homogenization leads to a collective pinning effect rather than localized defect engineering. The synergy among multiple elements not only physically pins the slippage of TMO_2 layers to inhibit complex phase transitions but also chemically stabilizes the oxygen framework by enhancing the covalency of TM-O bonds [35]. Therefore, this dual-site high-entropy design constructs a three-dimensional pinning network that simultaneously provides structural and chemical stability, a synergistic effect unattainable with conventional doping strategies. This study developed a high-performance sodium-ion cathode material by dual-site doping through high-entropy strategy with the composition of $\text{Na}_{0.96}\text{Ca}_{0.02}\text{Ni}_{0.27}\text{Fe}_{0.2}\text{Mn}_{0.35}\text{Al}_{0.02}\text{Cu}_{0.1}\text{Ti}_{0.05}\text{O}_2$ (NCNFMACTO). Ca^{2+} in the sodium layers while optimizing the ordered distribution of the transition metal layers and the sodium-ion diffusion pathways, thereby enhancing the kinetic processes. Al, Cu and Ti co-doped in the TM layer synergistically regulate the crystal lattice. As a result, NCNFMACTO achieves fully reversible O3-P3-O3 phase transition with only 1.1% volumetric strain during charge/discharge. Notably, NCNFMACTO exhibits a fully reversible O3-P3-O3 phase transition with only 1.1% volumetric strain during charge/discharge, alongside superior electrochemical performance retained even after 7 days of air exposure [36–38]. Furthermore, it shows superior cycling performance with 80.1% capacity retention after 1000 cycles at 5C ($1\text{C} = 150\text{ mAh}\cdot\text{g}^{-1}$) and 82% after 500 cycles at 1C within 2.0–4.0 V. Notably, the full cell delivers a high energy density of $264.87\text{ Wh}\cdot\text{kg}^{-1}$ while achieving 82.0% capacity retention over 100 cycles at 0.1C. These results collectively demonstrate strong potential for practical applications.

2 Result and discussion

$\text{Na}_{0.96}\text{Ca}_{0.02}\text{Ni}_{0.27}\text{Fe}_{0.2}\text{Mn}_{0.35}\text{Al}_{0.02}\text{Cu}_{0.1}\text{Ti}_{0.05}\text{O}_2$ (NCNFMACTO) and the control samples, including undoped $\text{NaNi}_{0.4}\text{Fe}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (NFM424) and co-doped $\text{NaNi}_{0.27}\text{Fe}_{0.2}\text{Mn}_{0.35}\text{Al}_{0.02}\text{Cu}_{0.1}\text{Ti}_{0.05}\text{O}_2$ (NNFMACTO), were synthesized via a simple solid-state

method as detailed in the supporting information. The bulk compositions of these three sodium-ion cathode materials were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) as shown in Table S1 in the Electronic Supplementary Material (ESM). The structural characteristics were verified using XRD patterns measured with Rietveld refinement. Figures 1(a) and 1(b) and Fig. S1 in the ESM present the Rietveld refinement results of three samples. Detailed crystallographic data are shown in Tables S2 and S3 in the ESM. The results indicate that all three samples adopt the NaFeO_2 -type structure belonging to the $R\bar{3}m$ space group. No impurity phases were detected in NCNFMACTO and NNFMACTO, whereas NFM424 contains a minor NiO phase (5.52 wt.%). This confirms that entropy regulates the formation of solid solutions by reducing the Gibbs free energy, consistent with the theoretical principle $\Delta G = \Delta H - T\Delta S$ [34]. It is generally accepted that high-entropy materials exhibit a configurational entropy greater than 1.5R [39]. As shown in Fig. 1(c), the structure of NCNFMACTO is illustrated, accompanied by a pie chart detailing the specific composition of transition metal ions based on ICP-MS results. The calculation results show NCNFMACTO (1.62R) > NNFMACTO (1.5R) > NFM424 (1.05R) [33, 40]. By doping four elements, this study successfully synthesized a high-entropy material with a configurational entropy reaching 1.62R. Notably, while NNFMACTO also falls within the high-entropy regime (1.5R), the absence of Na-site regulation limits its ability to suppress interlayer gliding. The dual-site configuration in NCNFMACTO was therefore designed to achieve not merely high configurational entropy, but a synergistic combination of Na-site anchoring and TM-site lattice pinning for optimal electrochemical stability. In Fig. 1(d), it can be observed that compared to NNFMACTO ($a = 2.9859\text{ Å}$, $c = 15.9817\text{ Å}$), the lattice parameters of NCFMACTO ($a = 2.9863\text{ Å}$, $c = 15.9552\text{ Å}$) exhibit an expansion in the a - b plane and a contraction along the c -axis. This phenomenon may be attributed to the preferential occupation of Ca^{2+} ions at the 2a sites rather than the 2d sites (sodium sites). The primary reasons for this behavior are the enhanced electrostatic repulsion between $\text{Na}^+\text{-Na}^+$ in the NaO_2 layer along the planar direction and the strengthened electrostatic cohesion of $\text{O}^{2-}\text{-Na}^+\text{-O}^{2-}$ between two TMO_2 layers, consistent with previous reports [41]. Figure 1(e) revealed the hexahedral morphology of NNFMACTO via scanning electron microscopy (SEM), which was similar to the morphological features of NFM424 and NNFMACTO (Fig. S2 in the ESM). Figure 1(f) shows a high-resolution transmission electron microscopy (HRTEM) image with distinct lattice fringes, revealing that NCNFMACTO exhibits a typical O3-type structure with an interplanar spacing of 0.252 nm (101 plane). The elemental mapping images of NCNFMACTO in Fig. 1(g) demonstrate the uniform distribution of Na, Ca, Ni, Fe, Mn, Al, Cu, Ti, O throughout the material, while Figs. S3 and S4 in the ESM further confirm that NFM424 and NNFMACTO samples also exhibit homogeneous elemental distribution.

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the electronic structure and chemical valence states of compounds NFM424, NNFMACTO and NCNFMACTO, as detailed in Fig. S5 in the ESM. Figure S5(a) in the ESM displays the high-resolution Na 1s spectrum, where the peak positioned at 1070.9 eV confirms the presence of Na^+ in the layered structure [42]. The Ni 2p spectrum in Fig. S5(b) in the ESM was deconvoluted into four peaks, peaks at 854.7 and 872.1 eV can be assigned to Ni^{2+} , while at 860.4 and 878.6 eV are

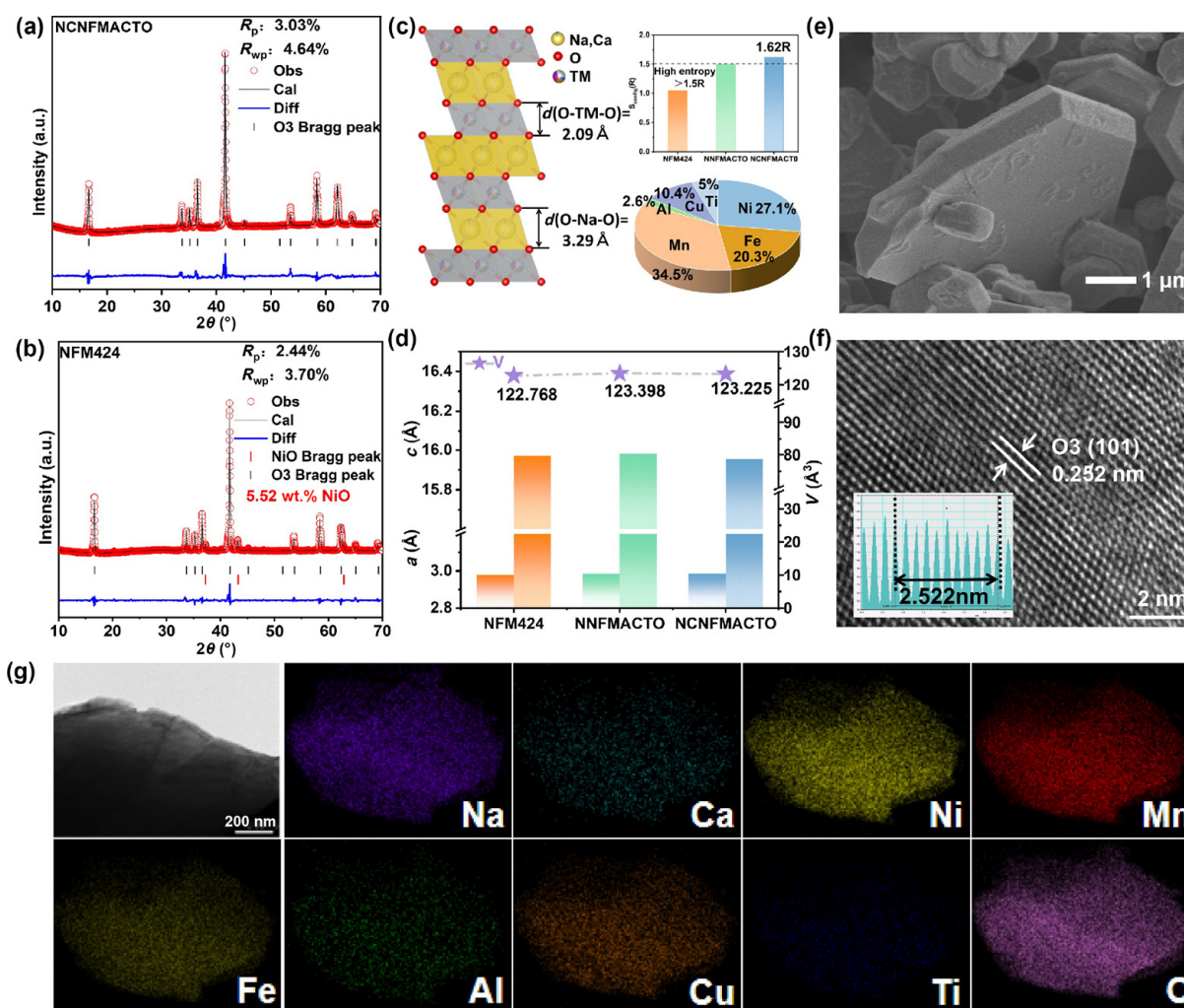


Figure 1 Structural properties: (a, b) Rietveld refinement of the XRD patterns for NCFMACTO and NFM424, respectively. (c) Schematic illustration of the O3-type crystal structure, with the interlayer spacing indicated. The pie chart shows the transition metal composition determined by ICP-OES and the bar graph displays the configurational entropy values of the three materials. (d) Comparison of lattice parameters a , c and volume V for NCFMACTO, NNFMACTO and NFM424. (e) SEM image of NCFMACTO. (f) HRTEM analysis results of NCFMACTO. (g) Elemental mapping results of NCFMACTO.

classified as satellite peaks [43]. The Fe 2p spectrum in Fig. S5(c) in the ESM was deconvoluted into four peaks, peaks at 710.6 and 724.0 eV can be assigned to Fe^{3+} , while peaks at 717.4 and 732.0 eV are classified as satellite peaks [44, 45]. The Mn 2p high-resolution spectrum in Fig. S5(d) in the ESM exhibits two peaks located at 642.1 and 653.5 eV, which can be assigned to Mn^{4+} [46, 47]. This result demonstrates that the co-doping of Ca, Cu, Al and Ti ions effectively stabilizes the crystal structure and enhances cycling stability while maintaining the original oxidation states of Ni, Fe, and Mn ions. In NCFMACTO, the Ca 2p XPS spectrum (Fig. S5(e) in the ESM) exhibits two distinct peaks at binding energies of 346.9 eV (Ca $2p_{3/2}$) and 350.4 eV (Ca $2p_{1/2}$), which clearly confirms the divalent state of calcium (Ca^{2+}) [48]. The Al 2p spectrum (Fig. S5(f) in the ESM) shows a binding energy of 75.33 eV, indicating the trivalent state of aluminum (Al^{3+}) [49]. The Cu 2p spectrum (Fig. S5(g) in the ESM) exhibits characteristic peaks at 933.2 eV (Cu $2p_{3/2}$) and 953.0 eV (Cu $2p_{1/2}$), demonstrating the divalent oxidation state (Cu^{2+}) [50]. Similarly, the Ti 2p spectrum (Fig. S5(h) in the ESM) presents binding energies at 457.6 eV (Ti $2p_{3/2}$) and 463.4 eV (Ti $2p_{1/2}$), verifying the tetravalent state of titanium (Ti^{4+}) [7]. High-resolution XPS analysis of the O 1s spectrum reveals three distinct peaks at 529, 531, and 535.4 eV, corresponding to TM-O bonds, sodium

carbonate (Na_2CO_3), and sodium Auger features, respectively (Fig. S5(h) in the ESM) [51]. These findings provide clear evidence of sodium precipitation on the material surface.

To evaluate the impact of dual-site modification on electrochemical performances, we examined the Na^+ storage behaviors of NFM424, NNFMACTO and NCFMACTO using half-cells with sodium metal anodes. Figure 2(a) displays the charge-discharge curves of three samples at 0.1C ($1\text{C} = 150 \text{ mA}\cdot\text{g}^{-1}$) within 2.0–4.0 V. The specific capacities of NFM424, NNFMACTO, and NCFMACTO at 0.1C are 133.69, 130.37 and 128.7 $\text{mAh}\cdot\text{g}^{-1}$, respectively. The slightly lower capacity of the NCFMACTO cathode compared to the NFM424 cathode may be attributed to the substitution of electrochemically active Ni^{2+} with inactive elements (Cu, Al), leading to reduced electrochemical activity [22]. The first five galvanostatic charge-discharge curves of NCFMACTO (Fig. 2(b)), NFM424 (Fig. 2(c)), and the control sample NNFMACTO (Fig. S6 in the ESM) measured at 0.1C demonstrate negligible capacity decay for NCFMACTO, clearly proving the superior structural stability of the NCFMACTO material. Figures 2(d), 2(e) and Fig. S7 in the ESM present the comprehensive rate capability evaluation of NCFMACTO, NFM424 and NNFMACTO cathodes across a wide range of current rates (0.1C–5C). The data points in the

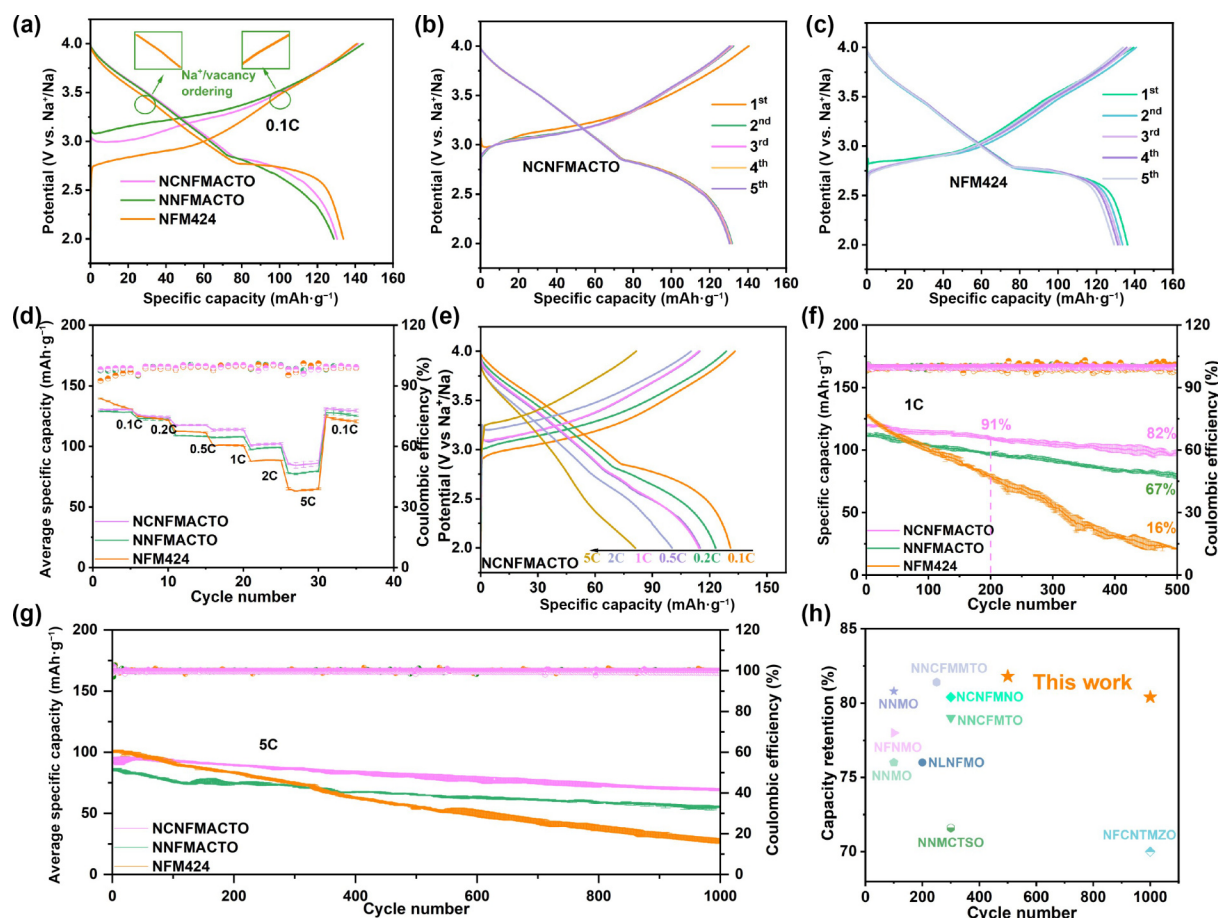


Figure 2 Electrochemical performance of the NCNFMACTO, NNFMACTO and NFM424 for Na⁺ storage. (a–c) Galvanostatic charge-discharge curves at 0.1C. (d, e) Rate capability and corresponding charge-discharge curves at different current densities from 0.1C to 5C. (f, g) Long-term cyclic performance at 1C and 5C. (h) Comparative cycling performance evaluation of NCNFMACTO relative to other reported electrode materials.

figure represent the average capacity from five independent half-cells ($n = 5$), with error bars indicating standard deviation. The complete replicate datasets are shown in Fig. S32 in the ESM. The NCNFMACTO cathode demonstrates superior electrochemical performance, delivering a remarkable discharge capacity of 85.71 mAh·g⁻¹ at an extremely high rate of 5C (corresponding to 66% retention of its initial 0.1C capacity). Notably, the material exhibits excellent capacity recovery, completely restoring its original capacity after the rigorous rate testing protocol. Compared with NFM424 and NNFMACTO, NCNFMACTO demonstrates significantly enhanced rate capability and superior cycling stability. These improvements clearly indicate that the dual-site doping effectively promotes reaction kinetics and enhances structural integrity. Additionally, as illustrated in Figs. 2(f) and 2(g) and Fig. S8 in the ESM, the NCNFMACTO cathode demonstrates exceptional cycling performance within 2.0–4.0 V voltage. The data points in the figure represent the average capacity from five independent half-cells ($n = 5$), with error bars indicating standard deviation. The complete replicate datasets are shown in Figs. S33 and S34 in the ESM. At 0.1C, the NCNFMACTO maintains a reversible capacity of 115.96 mAh·g⁻¹ after 100 cycles, demonstrating an excellent capacity retention of 89%. At 1C, it maintains a reversible capacity of 108.64 mAh·g⁻¹ after 200 cycles, achieving an impressive capacity retention of 91%. Remarkably, even after 500 cycles, the material retains 97.48 mAh·g⁻¹ with 82% of its initial capacity. At 5C, compared to the pristine NFM424 (with a capacity retention of 26.8% after

1000 cycles at 5C), the NNFMACTO sample exhibits significantly enhanced cycling stability (with a capacity retention of 66.8%), fully demonstrating the intrinsic advantages of high-entropy doping at the TM site. Notably, with the further introduction of Ca²⁺ (NCNFMACTO), the capacity retention under the same testing conditions is further improved to 80.1%, which clearly confirms that Ca doping at the Na site provides an additional stabilizing effect beyond the original high-entropy configuration. Additionally, the long-term stability of the average potential in NCNFMACTO cathode materials indicates their promising application prospects (Fig. S9 in the ESM). As shown in Fig. 2(h), a comparison with other sodium-ion battery cathodes demonstrates that NCNFMACTO exhibits significant competitive advantages.

As shown in Figs. 3(a) and 3(b), and Fig. S10 in the ESM, the cyclic voltammetry (CV) curves clearly demonstrated that the NCNFMACTO sample exhibits more symmetrical anodic/cathodic peaks at higher voltages (3.24/2.77 V), while NFM424 displays extra anodic and cathodic peaks at 3.4–3.5 V, which are attributed to the Na⁺/vacancy order-disorder. However, such peaks are absent in the NCNFMACTO and NNFMACTO materials. This phenomenon results from the homogeneous charge distribution enabled by the multi-component distribution in the TM layer through high-entropy doping, thereby promoting rapid kinetics and reversibility while reducing the disorder of Na⁺/vacancy during the Na⁺ extraction/insertion process which is consistent with the charge-discharge curves [34]. This corresponds

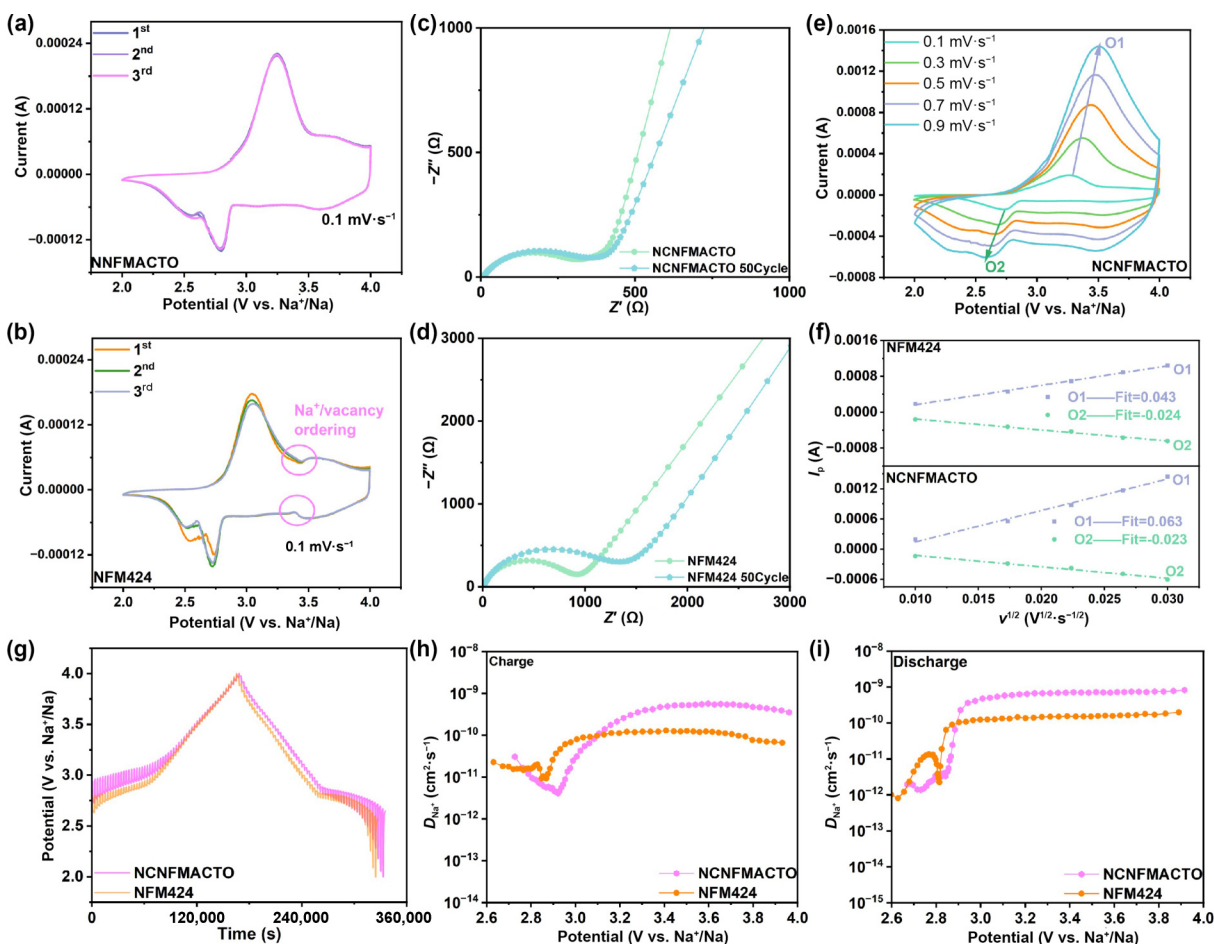


Figure 3 Shows the kinetics of the materials. CV curves performed at the scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ in the voltage range of 2.0–4.0 V for NCNFMACTO (a) and NFM424 (b). EIS evolution at 1st and 50th cycles collected at 0.1 C of NCNFMACTO (c), NFM424 (d). (e) NCNFMACTO at varying scan rates, accompanied by (f) the linear relationship between the peak current and the square root of the scan rate. (g) GITT profiles and (h–i) the determination of Na^+ diffusion coefficients from GITT of NCNFMACTO and NFM424.

to the charge-discharge curves in Fig. 2(a). Furthermore, the phase transition peaks of the NCNFMACTO sample demonstrate significantly higher overlap compared to the other two samples, indicating substantially improved structural stability after modification [52]. This observation is well corroborated by the electrochemical cycling test results. The CV tests revealed the redox reaction characteristics of the material. However, to further investigate the kinetic behavior during the electrochemical process, electrochemical impedance spectroscopy (EIS) was conducted to systematically study the impedance properties of the electrode/electrolyte interface. Figure S11 in the ESM presents the equivalent circuit model employed for interface characterization. Figures 3(c), 3(d) and Fig. S12 in the ESM respectively display the EIS evolution results of NCNFMACTO, NFM424, and NNFMACTO in their initial state and after 50 cycles. The high-frequency intercept corresponds to the Ohmic resistance (R_s), the semicircular region from high to medium frequency reflects the charge transfer resistance (R_{ct}), and the low-frequency slope is attributed to the diffusion of sodium ions. It can be clearly observed that NCNFMACTO exhibits the smallest charge transfer resistance (R_{ct}), demonstrating the most favorable charge transfer kinetics among the three. After 50 cycles, NFM424 and NNFMACTO exhibited rapid resistance increase, whereas the NCNFMACTO sample demonstrated significantly slower resistance growth. This result indicates that the modified material can effectively suppress side reactions between the cathode and

electrolyte, thereby inhibiting SEI layer formation. The detailed fitted resistance values for all three samples are presented in Fig. S13 in the ESM. Figure 3(e) and Fig. S14 in the ESM display the CV curves of NCNFMACTO, NFM424, and NNFMACTO cathodes at different scan rates ranging from 0.1 to $0.9 \text{ mV}\cdot\text{s}^{-1}$. As the scan rate increases, the redox peaks undergo slight shifts due to the influence of electrode polarization. Based on the linear relationships in Fig. 3(f) and Fig. S15 in the ESM, the sodium ion diffusion coefficient D_{Na^+} can be calculated using the Randles-Sevcik equation. Compared to NFM424 (D_{Na^+} of $8.39 \times 10^{-11} \text{ cm}^2\cdot\text{s}^{-1}$), NCNFMACTO demonstrates superior diffusion kinetics (D_{Na^+} of $3.16 \times 10^{-10} \text{ cm}^2\cdot\text{s}^{-1}$). To further elucidate the kinetics of Na^+ storage, we quantified the capacitive and diffusion-controlled contributions using variable scan rate CV measurements (Fig. 3(e)). Based on the b -values determined from the $\log(i)$ versus $\log(v)$ plots (Fig. S16 in the ESM), the anodic peak of NCNFMACTO is 0.92 and the cathodic peak is 0.65, indicating a mixed kinetic regime. As shown in Fig. S16 in the ESM, the capacitive contribution increases from 42% at $0.1 \text{ mV}\cdot\text{s}^{-1}$ to 74% at $0.9 \text{ mV}\cdot\text{s}^{-1}$. This substantial capacitive behavior is attributed to the high-entropy-induced structural disorder, which creates abundant active sites for surface reactions and shortens Na^+ diffusion pathways, thereby enabling rapid charge storage even at high current densities. To gain deeper insights into the improvement mechanism of sodium-ion diffusion kinetics, we conducted galvanostatic intermittent titration technique (GITT) tests on three

samples, with the results presented in Figs. 3(g)–3(i) and Fig. S17 in the ESM. The D_{Na^+} was calculated using the Weppner-Huggins method. The reported D_{Na^+} values represent the average of three independent GITT measurements, with the standard deviation reflecting the measurement variability. In the error analysis, factors including electrode loading and fitting window selection were taken into account. Based on the GITT results, the D_{Na^+} were calculated, confirming that the average D_{Na^+} of NCNFMAC TO is approximately $2.94 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, significantly higher than that of NFM424 ($7.61 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$).

To investigate the structural evolution, *in-situ* XRD was performed during the initial charge/discharge cycle at 0.2C within 2.0–4.0 V. Figures 4(a), 4(b), 4(d), 4(e) and Fig. S18 in the ESM display the initial charge/discharge curves of NFM424, NNFMAC TO and NCNFMAC TO, respectively, with the evolution of their main diffraction peaks visually presented through overlaid graphs and two-dimensional (2D) contour maps. The unchanged peaks are likely attributed to the Al, Be/BeO window, etc. During charging, the (003) and (006) diffraction peaks shift toward lower angles, while the (101) and (012) reflections migrate to higher angles [53]. A new peak emerges at lower 2θ angles in NCNFMAC TO, which can be attributed to the P3 phase. Furthermore, a two-phase coexistence region is observed below 3 V. Upon further charging, the O3/P3 biphasic region undergoes complete transformation into a single P3 phase through gliding of TMO_2 slabs. The diffraction peaks of the P3 phase undergo continuous shifting throughout the charging

process without emergence of new reflections, indicating a solid-solution reaction mechanism [54]. During discharge, all diffraction peaks reversibly evolve through inverse pathways, ultimately restoring the original O3 phase structure. A fully reversible O3-P3-O3 phase transition occurs during cycling, it provides compelling evidence for the enhanced structural stability of NCNFMAC TO. Ca^{2+} acts as a "pillar" within the Na layer, forming stronger electrostatic cohesion with the adjacent oxygen layers ($\text{O}^{2-}\text{-Ca}^{2+}\text{-O}^{2-}$). This anchoring effect physically constrains the interlayer spacing and restricts the gliding of TMO_2 slabs. In contrast to NFM424, the latter exhibits splitting of the (003) diffraction peak into two distinct peaks, unequivocally confirming the formation of an O3 phase. This structural transition is triggered by Jahn-Teller distortion resulting from increased concentration of Ni^{3+} during sodium deintercalation. The peak intensity contour plots in Figs. 4(b) and 4(e) provide direct visual confirmation of the aforementioned results, demonstrating that the synergistic effect of TM-site and Na-site substitution effectively suppresses complex phase transitions. Figures 4(c), 4(f) and Fig. S18 in the ESM present the Rietveld-refined operando XRD data, providing deeper insights into the evolution of lattice parameters. The χ^2 for all refinements ranged from 1.23 to 1.48, the R_{wp} value ranged from 4.59% to 5.6% and the R_p value ranged from 3.8% to 4.5%, confirming the reliability of the refined parameters. The phase transitions are accompanied by pronounced variations in both the a -axis and c -axis dimensions. The observed increase in lattice parameter c indicates an expansion of the interlayer spacing,

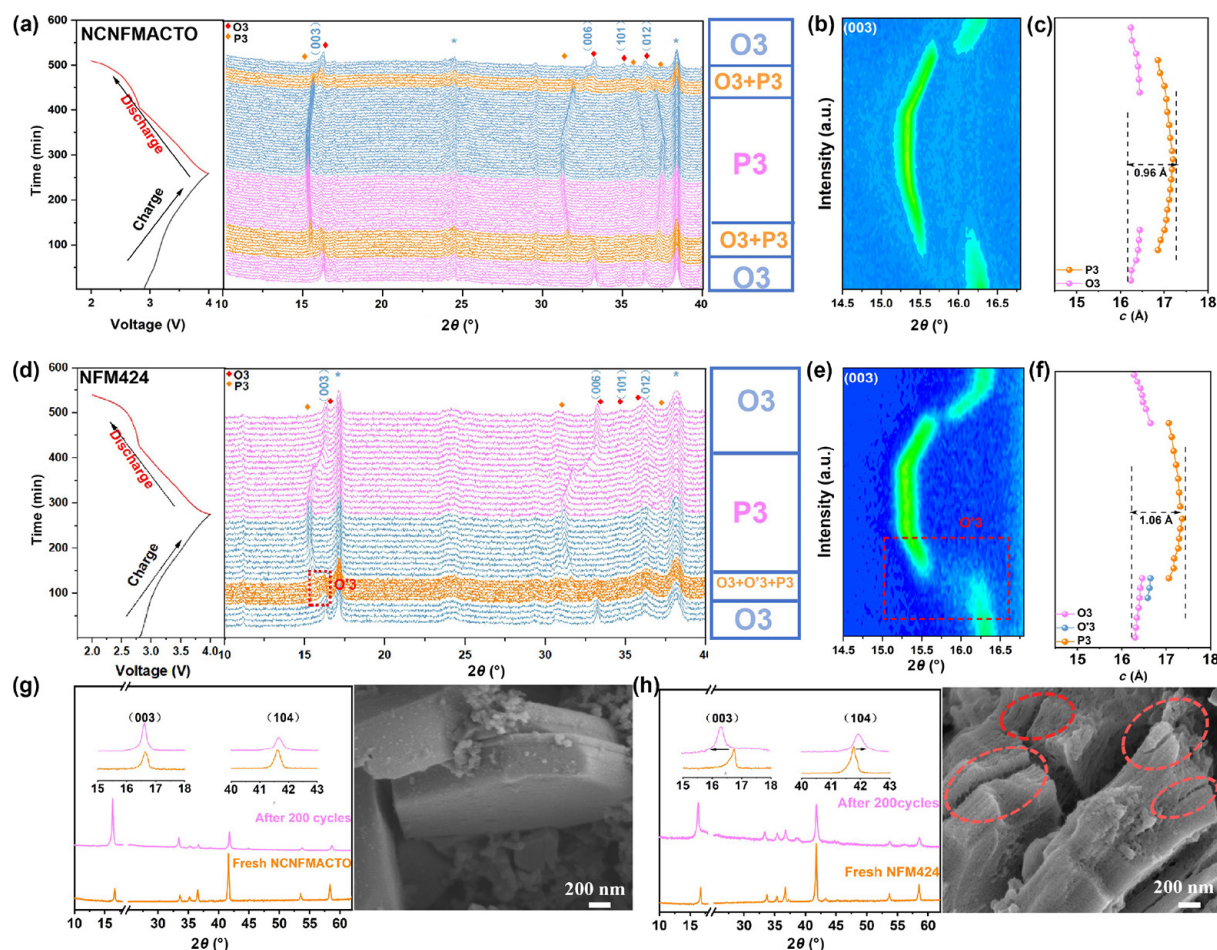


Figure 4 *In-situ* X-ray diffraction analysis and post-cycling structural examination: *in-situ* XRD with intensity contour maps of NCNFMAC TO (a, b) and NFM424 (d, e); (c, f) the calculated lattice parameters (c) evolution of during the charging process. The comparative XRD patterns and SEM images of the pristine electrode and the cycled electrode (after 200 cycles at 1C rate) of (g) NCNFMAC TO and (h) NFM424.

likely attributed to enhanced electrostatic repulsion between O^{2-} anions. Concurrently, the reduction in lattice parameter a arises from the contraction of in-plane distances due to diminished ionic radii of the oxidized species. The results demonstrate that the maximum change in the c -axis in NCNFMACTO is 0.96 Å, which is significantly lower than that of the NFM424 (1.06 Å) and NNFMACTO (1.03 Å) systems. Notably, computational analysis reveals a mere 1.1% volume expansion of NCNFMACTO at full sodiation (Fig. S19 in the ESM), unequivocally validating its exceptional structural stability and outstanding capacity retention during prolonged cycling.

To investigate structural integrity after cycling, comparative XRD measurements of pristine and cycled electrodes were performed (Figs. 4(g), 4(h) and Fig. S20 in the ESM). After 200 cycles, NFM424 shows a (003) reflection shift to lower angles while (104) peak to higher angles, indicating c -axis expansion, a -axis contraction exhibited its severe volumetric strain, whereas NNFMACTO showed significantly mitigated volume variation. While NCNFMACTO demonstrated no discernible peak shift in its diffraction pattern, indicating minimal volumetric strain. The field-emission scanning electron microscopy (FESEM) images of the cycled NFM424 electrode revealed distinct cracks, while NNFMACTO showed significantly improved crack resistance, and NCNFMACTO maintained intact morphology. This demonstrates that dual-site doping significantly enhance structural stability. Additionally, *in-situ* XPS measurements were conducted to monitor the charge compensation behavior during charge/discharge processes (Fig. S21 in the ESM). In the Ni 2p spectra, the binding energy of Ni shifts toward higher energies during the charging process, indicating the oxidation of Ni^{2+} to Ni^{3+} . Conversely, during discharge, the binding energy shifts back to lower energies, suggesting the reduction of Ni. Notably, when discharged to 2.0 V, Ni^{3+} cannot be fully reduced to Ni^{2+} , preventing the Ni species from completely returning to their initial state, which is consistent with previous reports [55]. In contrast, Mn ions maintain Mn^{4+} , demonstrating the absence of Jahn-Teller

effects in NCNFMACTO, which aligns with previous studies [56]. Throughout the entire Na^+ deintercalation process, no additional peaks were observed in the Cu 2p, Ti 2p or Fe 2p spectra, demonstrating the electrochemical inertness of these elements in the NCNFMACTO material.

Air stability is one of the critical factors determining the practical applicability of materials. However, most reported O3-type layered transition metal oxides to date are highly sensitive to humid air. To investigate the structural evolution during air exposure, the three samples were simultaneously exposed to ambient air at room temperature for seven days. Figures 5(a) and 5(b) and Fig. S22 in the ESM present comparative XRD patterns of the as-prepared NCNFMACTO, NFM424 and NNFMACTO materials and their counterparts after 7-day air exposure, respectively. For the NFM424 and NNFMACTO samples, their diffraction peaks can be attributed to hydrated phases and sodium carbonate hydrate (marked with *), indicating that these materials react with both water and carbon dioxide in air. In contrast, no obvious characteristic peaks of hydrated phases were observed in the NCNFMACTO sample after 7-day air exposure, demonstrating that the calcium-substituted NCNFMACTO exhibits superior air stability. The “anchoring effect” of Ca^{2+} ions anchors them within the sodium layers, effectively suppressing excessive expansion of the interlayer spacing and lattice distortion during desodiation, thereby reducing the tendency for water molecule incorporation. The electrochemical performance after 7-day air exposure was investigated (Figs. 5(c) and 5(d) and Fig. S23 in the ESM). The data points in the figure represent the average capacity from five independent half-cells ($n = 5$), with error bars indicating standard deviation. The complete replicate datasets are shown in Fig. S35 in the ESM. NCNFMACTO exhibited a significantly lower capacity loss of 4.34 $mAh \cdot g^{-1}$ after air exposure compared to NFM424 (27.17 $mAh \cdot g^{-1}$). It is noteworthy that the NCNFMACTO sample after 7-day air exposure demonstrates comparable electrochemical performance to the freshly synthesized NCNFMACTO, achieving similar cycling stability

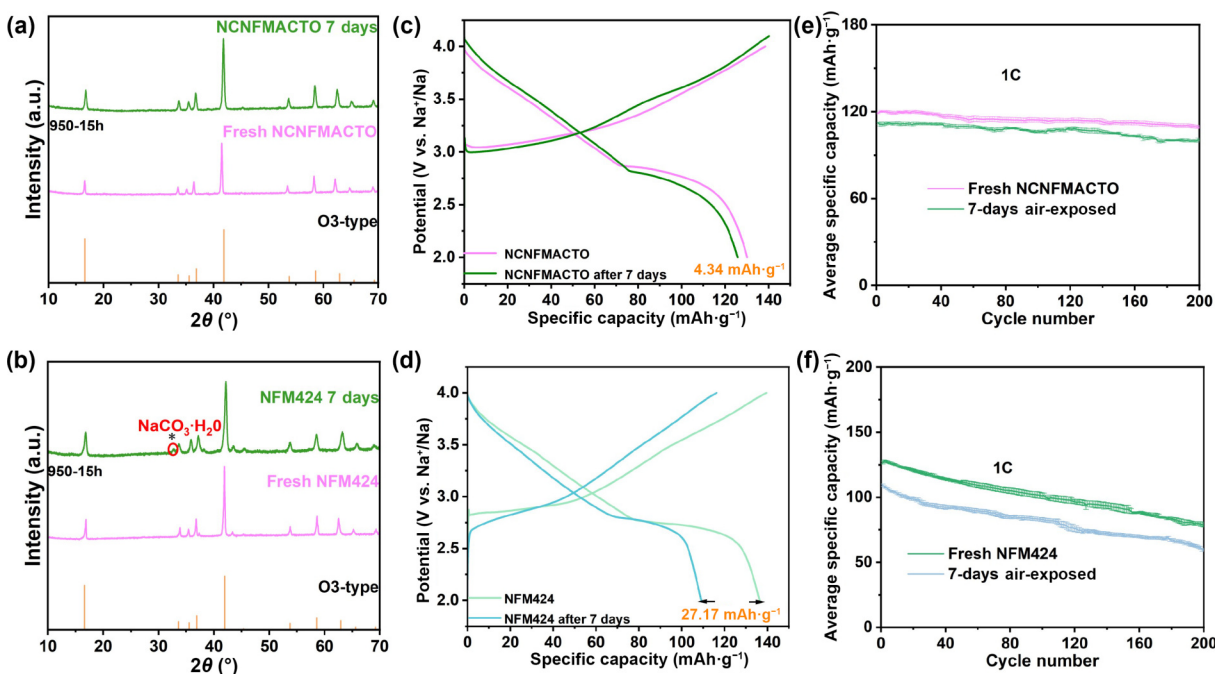


Figure 5 The feasibility and practicality of NCNFMACTO. The XRD patterns of (a) NCNFMACTO and (b) NFM424 powder exposed in air for 7 days and the corresponding GCD curves of pristine and exposed (c) NCNFMACTO and (d) NFM424 cathodes. Cycling performance at 1C among pristine and air-exposed NCNFMACTO (e) and NFM424 (f) samples, respectively.

under both 0.1C for 100 cycles and 1C for 200 cycles (Fig. 5(e) and Fig. S24 in the ESM). However, both NFM424 and NNFMCTO exhibit significant degradation in capacity and cycling stability (Fig. 5(f) and Fig. S25 in the ESM). This exceptional performance aligns with prior theoretical predictions, demonstrating that dual-site doping synergistically enhance the material's air stability [57]. XPS surface analysis (Fig. S26 in the ESM) reveals that after seven days of air exposure, the intensity of the Na_2CO_3 peak for NFM424 increases dramatically, while that for NNFMCTO shows only a moderate increase. In contrast, the O 1s spectrum of NCNFMCTO remains almost unchanged. This result demonstrates that Ca doping effectively impedes surface attack by H_2O and CO_2 [58, 59]. To gain deeper insight into the origin of this enhanced surface stability, we performed Bader charge analysis based on DFT calculations (Fig. S27 in the ESM). The results reveal that after Ca^{2+} incorporation, the Bader charge of the lattice oxygen atoms directly coordinated to Ca^{2+} increases from 1.185 e^- to 1.237 e^- . This indicates that Ca^{2+} , with its strong ionic character, donates more electrons to the surrounding oxygen atoms, leading to enhanced electron localization and increased electron cloud density around these oxygen sites. From a chemical perspective, oxygen atoms with higher electron density become less susceptible to electrophilic attack by the carbon atoms in CO_2 molecules, thereby suppressing the formation of carbonate (CO_3^{2-}) species and improving the material's air stability. This localized enhancement of electron density serves as a direct manifestation of the “anchoring effect” exerted by Ca^{2+} .

The structural stability and electrochemical kinetics of three materials were evaluated using density functional theory (DFT) calculations. To elucidate the dual-site doping effect, the spin-polarized density of states (DOS) of the three materials (Figs. 6(a) and 6(b) and Fig. S28 in the ESM) was compared. The results indicate that both NNFMCTO and NFM424 exhibit half-metallic characteristics. Specifically, NNFMCTO shows a DOS close to 0 eV at the Fermi level, while NFM424 possesses a band gap of 0.466 eV in its spin-down state, which is consistent with previously reported literature [60]. In contrast, the Fermi level of NCNFMCTO shifts toward the valence band, resulting in a pronounced density of states at the Fermi level. This suggests that dual-site doping effectively enhances the electrical conductivity and structural stability of NCNFMCTO. Figure 6(c) presents the calculated formation energies and corresponding structural diagrams for Ca doping at the Na and TM sites. The formation energies for Ca doping at the Na and TM sites are -0.292 and -0.214 eV , respectively. This suggests a thermodynamically more favorable tendency for Ca to occupy the Na site, which is consistent with the structural refinement observations. To investigate the correlation between the enhanced structural stability and the strength of the TM-O bonds, we employed the Crystal Orbital Hamiltonian Population (COHP) method (Fig. 6(d) and Fig. S29 in the ESM). This analysis compared the bond strengths of Ni-O, Fe-O and Mn-O bonds across the three structures. The COHP analysis reveals that the $-\text{ICOHP}$ values for the Ni-O, Fe-O and Mn-O bonds in NCNFMCTO are 1.121,

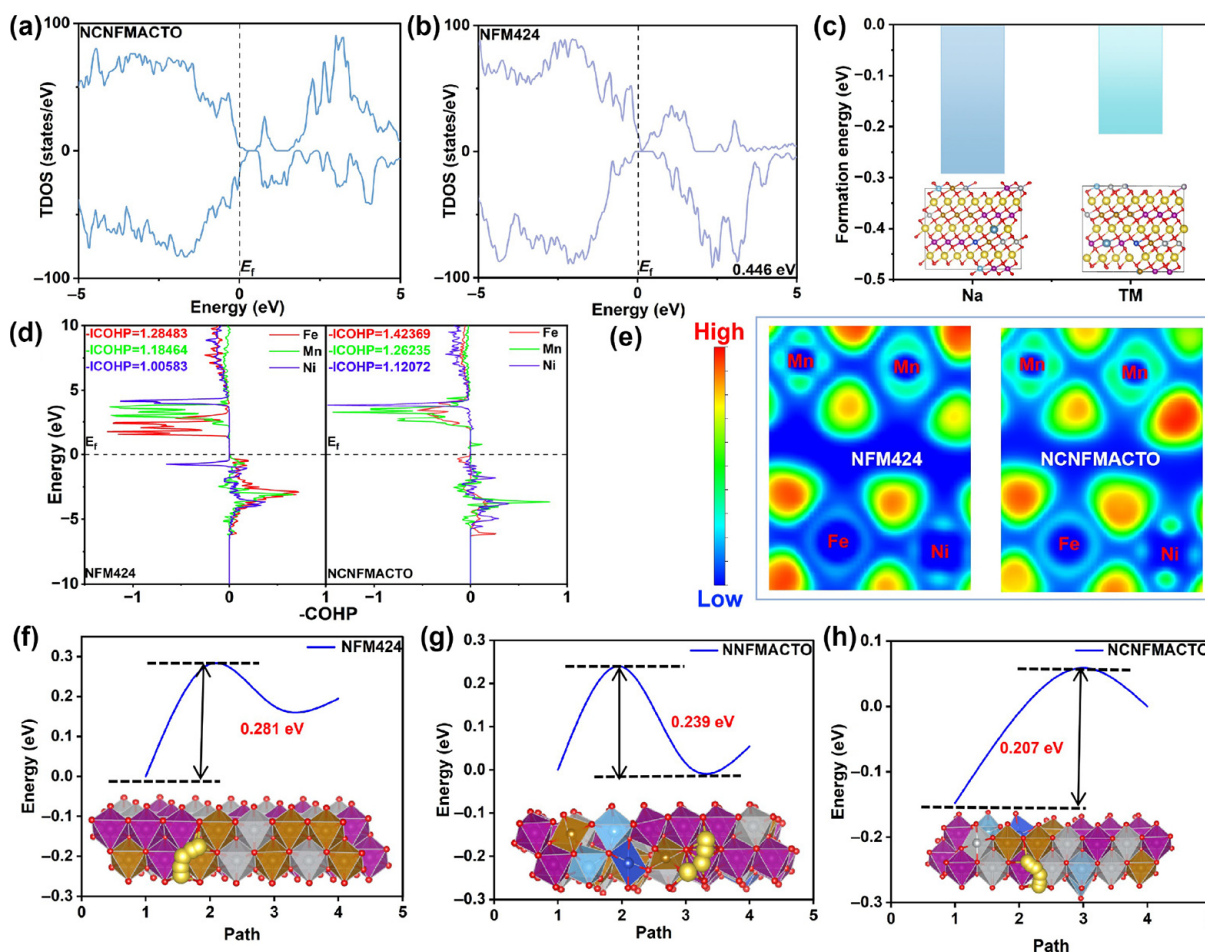


Figure 6 The calculated density of states (DOS) of NCNFMCTO (a) and NFM424 (b). (c) Formation energy of Ca at Na sites and TM sites. (d) The COHP values of Ni-O, Fe-O, and Mn-O bonds in NCNFMCTO and NFM424. (e) Electron localization function (ELF) for NCNFMCTO and NFM424. Diagrams of sodium ion diffusion energy barrier and diffusion pathways of (f) NFM424, (g) NNFMCTO, and (h) NCNFMCTO.

1.424 and 1.262 eV, respectively. These values are higher than those in NFM424 and NNFMACTO, indicating stronger bond strengths [61]. The structural cross-sections shown in Fig. 6(e) and Fig. S30 in the ESM display the electron localization function (ELF) of the three materials. Charge density analysis reveals that the electron density between Mn-O, Ni-O and Fe-O bonds in NCNFMCTO is the highest, which is consistent with the COHP results. The dual-site doping strategy enhances the TM-O interactions, thereby effectively stabilizing the lattice oxygen and crystal structure. Notably, the enhanced charge distribution reduces the electron density between Na-O bonds, thus promoting the diffusion kinetics of sodium ions [62]. Figures 4(f)-4(h) illustrates the sodium ion diffusion pathways along the sodium layers in the NCNFMCTO, NNFMACTO and NFM424 crystal structures, as calculated based on DFT structures, along with the corresponding diffusion and migration energy barriers of sodium ions in the three structures determined using the climbing image nudged elastic band (CI-NEB) method. The diffusion energy barrier of NCNFMCTO (0.207 eV) is significantly lower than those of NFM424 (0.281 eV) and NNFMACTO (0.239 eV), indicating that the dual-site doping strategy significantly enhances the diffusion kinetics of sodium ions, leading to a notable improvement in their diffusion rate.

To further evaluate its practical application potential, full-cell tests were conducted by pairing the NCNFMCTO as cathode with a commercial hard carbon (HC) as anode (NCNFMCTO//

HC) as illustrated in Fig. 7(a). During charging, sodium ions are extracted from the NCNFMCTO cathode and inserted into the HC anode, accompanied by the flow of electrons from the cathode to the anode; the reverse electrochemical reaction occurs during discharging. Based on the charge balance principle and electrochemical characteristics (Fig. 7(b)), the mass ratio between cathode and anode was optimized to 1.4-1.6, with the full-cell operating voltage window set at 1.9-3.9 V during testing. As shown in Fig. 7(c), the NCNFMCTO full-cell exhibits smooth charge-discharge profiles, with negligible capacity decay observed during the first five cycles. NCNFMCTO//HC full cell demonstrates outstanding rate capability (Figs. 7(d) and 7(e)), delivering a high capacity of 120.11 mAh·g⁻¹ at 0.1C. Remarkably, it maintains superior capacity retention of 80.54 mAh·g⁻¹ even under 5C. The data points in the figure represent the average capacity from five independent full-cells ($n = 5$), with error bars indicating standard deviation. The complete replicate datasets are shown in Fig. S36 in the ESM. The calculated Ragone plot is shown in Fig. 7(f). Based on the total mass of active cathode and anode materials, an impressive energy density of 264.87 Wh·kg⁻¹ is achieved at a power density of 44.42 W·kg⁻¹. Remarkably, even under a high-power density of 829.23 W·kg⁻¹, the full cell maintains an excellent energy density of 165.33 Wh·kg⁻¹. Remarkably, the cell maintains a substantial working voltage of 2.96 V at 44.42 W·kg⁻¹, under high-power density of 829.23 W·kg⁻¹, it sustains an exceptional operating voltage of

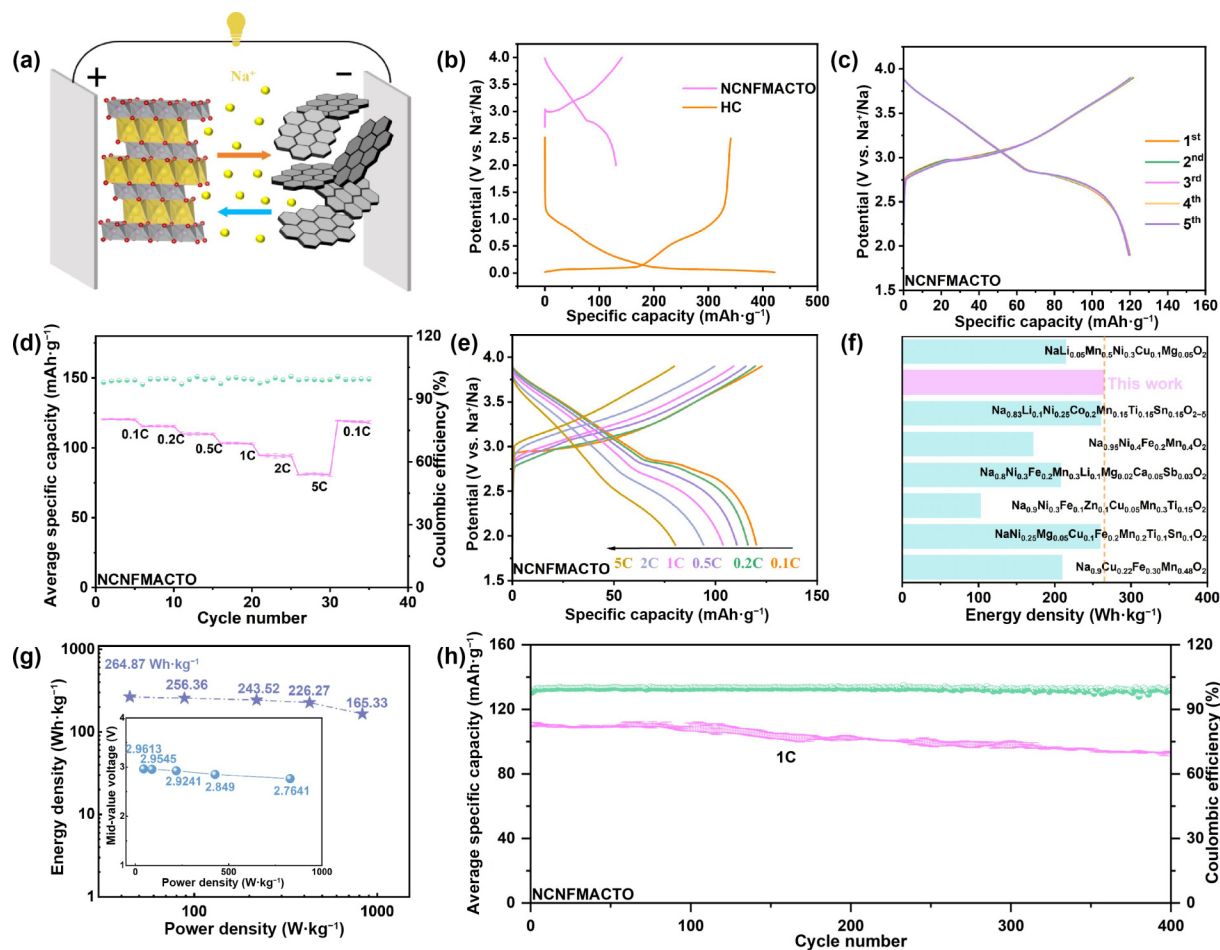


Figure 7 Sodium-ion full cell properties assembled by NCNFMCTO cathode and commercial HC anode. (a) Schematic illustration of the work process; (b) Galvanostatic charge/discharge curves of NCNFMCTO based full cell device for the first cycle; (c) Galvanostatic charge-discharge curves at 0.1C; (d, e) Rate properties under different currents; (f) Comparative evaluation of energy density between NCNFMCTO and other reported electrode materials; (g) The corresponding energy density versus power density plot; (h) Cycling stability at 1C rate.

2.76 V (Fig. 7(f)). Notably, compared with other sodium-ion full cells reported in the literature (Fig. 7(g)), our developed NCNFMACTO||HC full cell achieves an energy density of 264.87 Wh·kg⁻¹, demonstrating promising commercialization potential. The cycling performance of the NCNFMACTO||HC full cell was evaluated in Fig. 7(h) and Fig. S31 in the ESM. The data points in the figure represent the average capacity from five independent full-cells ($n = 5$), with error bars indicating standard deviation. The complete replicate datasets are shown in Fig. S36 in the ESM. Notably, it delivers an 81.57% capacity retention after 100 cycles at 0.1C, while maintaining 85.66% capacity retention after 400 cycles at 1C. These results confirm the material's long-term cycling stability and underscore its outstanding performance at the material level.

3 Conclusion

In summary, we have synthesized a high-entropy O3-Na_{0.96}Ca_{0.02}Ni_{0.27}Fe_{0.2}Mn_{0.35}Al_{0.02}Cu_{0.1}Ti_{0.05}O₂ (NCNFMACTO) cathode material via a dual-site doping strategy, that significantly enhances reaction kinetics and structural stability. Mechanistically, the Rietveld refinement of XRD data is consistent with the DFT calculations, both indicating that Ca²⁺ preferentially occupies Na-site, where it is proposed to provide an electrostatic anchoring effect that physically constrains interlayer expansion, while multi-principal elements in the TM layer strengthen TM-O covalency and impede slab gliding [63]. NCNFMACTO exhibits fully reversible phase transitions, facilitating rapid Na⁺ diffusion and substantially reducing volume strain during desodiation/sodiation processes, thus ensuring exceptional cycling stability and electrochemical performance. Therefore, the prepared NCNFMACTO demonstrates exceptional long-term cycling stability with 80.1% capacity retention after 1000 cycles at 5C. Notably, the cathode material exhibits excellent air stability, showing no significant capacity degradation after being exposed to air for 7 days. Through theoretical calculations and systematic *in situ/ex situ* characterization, we elucidated the sodium storage mechanism and its kinetic advantages, including high ion mobility and low charge transfer resistance. Furthermore, the NCNFMACTO//HC full cell exhibited exceptional long-term cycling stability at 1C, retaining up to 85.66% of its capacity after 400 cycles. This study not only provides practical strategies and a theoretical basis for the rational design of high-performance O3-type cathode materials for sodium-ion batteries, but also offers new insights into the application of stabilized layered oxide materials in advanced sodium-ion batteries. Under optimized experimental conditions, NCNFMACTO exhibits excellent electrochemical performance, highlighting its promising potential as a candidate material for practical sodium-ion batteries.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content

of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

Electronic Supplementary Material: Supplementary material (experimental details; materials characterizations; electrochemical characterizations and addition details about DFT calculations) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120231>.

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