

Site-specific gradient Y/F co-doping modulating electronic structure for durable O3-type sodium layered oxide cathodes

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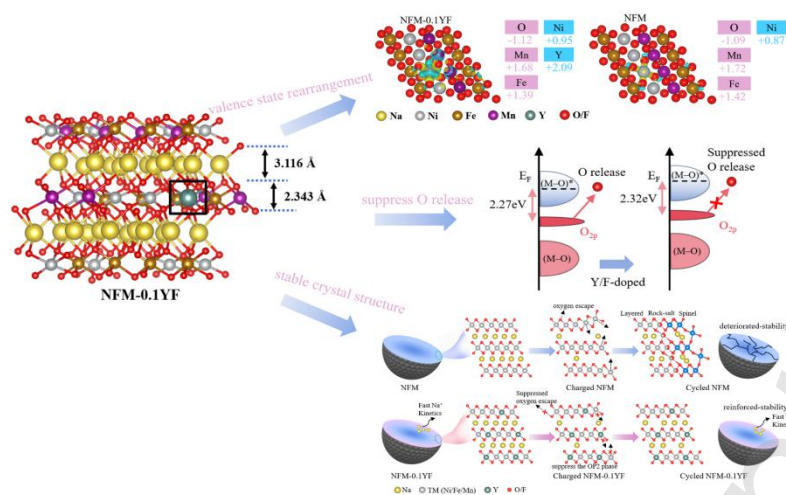
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Via the site-specific surface gradient Y/F co-doping for the $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material, Y element effectively modulates the valence state rearrangement of transition metals in the material and suppresses the release of lattice oxygen. Meanwhile, F-doping alleviates the lattice distortion of transition metals, thus synergistically enhancing the performance of $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes.

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ABSTRACT: O3-type transition metal oxides (TMOs) are among the most promising cathodes for sodium-ion batteries (SIBs) due to their high capacity. However, the local electronic structure arrangement around transition metals (TM) cations directly affects the phase transition behavior and oxygen redox chemistry upon cycling. Herein, we demonstrate that site-specific gradient Y/F co-doping in O3-Na_{0.44}Ni_{1/3}Fe_{1/3}Mn_{1/3}O₂ (NFM) cathode can effectively modulate electron density between TM and O to enhance the structural stability. Extra negative charge density is introduced near the oxygen ligands, resulting in the change of TM valence states, confirmed by comprehensive characterizations and theoretical calculations. Through coordinated Y/F regulation, unfavorable OP2 phases and lattice oxygen release at high voltages is effectively inhibited. Furthermore, gradient distribution of Y/F ions mitigates surface degradation by passivating reactive sites and strengthening the electrode–electrolyte interface. Therefore, the Y/F co-modified NFM cathode demonstrates a high capacity of 99.5 mAh g⁻¹ at 10C (1C = 150 mA g⁻¹) and capacity retention of 80% within the voltage range of 2.0–4.2 V after 150 cycles at 1C, which are higher than their counterpart (67.3% retention, 70.1 mAh g⁻¹ at 10C). This work establishes a universal modification strategy for enhancing the structural stability of O3-type sodium-ion battery cathodes.

KEYWORDS: O3-type layered oxides, site-specific gradient co-doping, electronic structure rearrangement, phase transition suppression, oxygen loss mitigation

1. Introduction

Sodium-ion batteries (SIBs) have garnered substantial attention owing to the abundance and low cost of sodium resources [1-5]. As a key component of SIBs, cathodes are pivotal in governing the overall energy density and economic viability of the batteries. Among SIB cathodes, O3-type layered transition metal oxides (Na_xTMO₂) typically exhibit high sodium content ($x \geq 0.7$) and good reversibility, making them attractive candidates for energy storage devices [6-10]. However, O3-type cathodes are highly air-

sensitive, undergoing spontaneous Na⁺/H⁺ exchange that triggers the formation of residual alkali species and near-surface rock-salt phases on the surface [11, 12]. Moreover, these cathodes often suffer from insufficient capacity stability, particularly under deep sodium (de)intercalation, where severe oxygen loss and irreversible phase transitions (P3 → OP2) are provoked, culminating in structural degradation [13-15]. Furthermore, the variations in local electronic structures between cations and anions in the TMO₂ layers also exert a pronounced impact on the

electrochemical performance of O3-type cathode materials. For instance, Mn^{4+} is electrochemically inert yet functions as a robust structural framework in layered cathodes; in contrast, Mn^{3+} exhibits high electrochemical activity but is prone to disproportionation, followed by dissolution in the electrolyte, resulting in rapid capacity fading and compromised cycling stability [16, 17].

To address the aforementioned challenges, numerous strategies have been proposed [18]. Bulk doping stands out as a widely adopted approach for stabilizing the crystal structure, enhancing air stability, and suppressing irreversible phase transitions [19]. Cationic dopants, such as Zr^{4+} , Ti^{4+} , and Al^{3+} have been widely utilized in bulk doping configurations due to their ability to efficiently modulate local charge environments [20]. Wei et al. [21] demonstrated that Ti-doping in the $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode effectively mitigates the Jahn-Teller distortion while concurrently boosting electrochemical activity via charge compensation-mediated regulation of Ni electronic states, thereby achieving a substantial enhancement in reversible capacity. However, the inherent limitation of this approach lies in its inability to effectively suppress surface degradation processes, as the uniformly distributed heteroatoms within the bulk fail to provide adequate interfacial modification [22]. In parallel, anionic doping strategies, especially F^- incorporation, have demonstrated significant potential in improving cathode performance. The small size mismatch between F^- (1.33 Å) and O^{2-} (1.40 Å) enables its incorporation into the oxygen lattice, while its strong electronegativity tunes O bonding, leading to enhanced Na^+ diffusion and reduced Jahn-Teller distortion [23-25]. However, this benefit is offset by the tendency of F to leach from the lattice during cycling, subsequently reacting with cations in the electrolyte to form fluoride species.

Herein, a site-specific surface gradient Y/F co-doping strategy has been developed to tailor the $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NFM). Through Y/F co-doping, the electronic structure of TM is effectively regulated, leading to enhanced d-p hybridization and increased charge density on oxygen ligands, which in turn suppresses lattice oxygen evolution, stabilizes the crystal structure, and improves Na^+ diffusion kinetics at high voltages. Simultaneously, the gradient surface doping strategy reduces surface degradation by selectively passivating reactive sites and

maintaining a stable electrode-electrolyte interface. Density functional theory (DFT) calculations and X-ray diffraction (XRD) refinement confirm that Y atoms preferentially reside on Ni sites, which alters the electronic structure by regulating the O 2p nonbonding band with high conductivity. Therefore, the site-specific gradient Y/F doped NFM cathodes display an outstanding electrochemical performance with high capacity retention (80% after 150 cycles at 1C) and rate capability (99.51 mAh g^{-1} at 10 C) within the voltage range of 2.0–4.2 V. By precise electronic structure modulation, the unique site-specific gradient Y/F co-doping strategy delivers pronounced enhancements in the electrochemical performance and structural stability of NFM.

2. Experimental Section

2.1. Material synthesis

The bare O3- $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (donated as NFM) is synthesized via the solid phase method. Based on the stoichiometric ratios, Na_2CO_3 (Rhawn; 99.8%), $\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ (Zhongwei; 99%) are weighed and an excess of 5 wt% Na_2CO_3 is added to compensate for the loss of sodium salts at high temperatures, and they are ground and mixed thoroughly. Thereafter, the mixed material is kept in the air at 900 °C for 12 h to obtain a NFM material. To fabricate the Y/F surface gradient doped O3- $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material (donated as NFM-0.1YF), 2mg YF_3 and 2 g NFM are ground and mixed thoroughly. Then, the ground material is placed in a crucible, followed by calcination of the crucible at 600°C for 4 h. For comparison, 1mg YF_3 and 2 g NFM are ground and mixed thoroughly (donated as NFM-0.05YF), 3mg YF_3 and 2 g NFM are ground and mixed thoroughly (donated as NFM-0.15YF), respectively, and other steps are identical to the preparation process of NFM-0.1YF.

2.2. Material Characterization

The structural characteristics of the as-prepared particles are determined via XRD using an X-ray diffractometer (Rigaku Ultima IV) with Cu $K\alpha$ radiation source and scan range from 10° to 80°. The specific structural information is obtained through refined fitting using GSAS2 software. Surface morphologies and microstructure images are acquired via scanning electron microscopy (SEM) using a high-performance field-emission

scanning electron microscope (ZEISS Gemini Sigma 300), energy-dispersive spectroscopy (EDS) using a 200 kV field-emission transmission/scanning transmission electron microscope (FEI, tecnai F20) and a high-performance silicon drift detector (Oxford X-MAX 80T), and transmission electron microscopy (TEM; FEI, tecnai F20). X-ray photoelectron spectroscopy (XPS) is employed using an X-ray photoelectron spectrometer (Thermo Fisher Scientific K-Alpha) to characterize the chemical states of the surface elements. The surface wettability of water is tested using a Contact Angle Tester (KRUS DSA30). Mass composition is tested using Inductively Coupled Plasma Mass Spectrometry (Agilent ICP-MS 7800).

2.3. Electrochemical Measurements

All electrochemical analyses are conducted with coin cells (2025 type). The cathode electrodes are prepared by mixing blending 80 wt% active materials, 10 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The electrodes are dried at 120 °C for 10 h under vacuum. The CR2025 type cells are assembled for electrochemical tests with sodium metal as the counter electrode and porous glass fiber as the separator in a glove box filled with argon (Mikrouna Super 1220/750/900). The electrolyte is 1 m NaPF₆ in propylene carbonate (PC) and ethyl methyl carbonate (EMC) containing 2% fluoroethylene carbonates (FEC) (PC/EMC volume ratio = 1:1). The electrochemical performance and galvanostatic intermittent titration technique (GITT) test are carried out on NEWARE instrument (MIHW-200-160CH) in the voltage range of 2-4 V (1C=130 mA g⁻¹) and 2-4.2 V (1C=150 mA g⁻¹). Cyclic voltammetry (CV) is performed on an electrochemical workstation (CHI 660E). Electrochemical impedance spectroscopy (EIS) tests are performed at the electrical and chemical station with amplitudes of 5 mV and frequencies ranging from 100 kHz to 0.005 Hz.

2.4. Computational Details

A bulk phase of Na₂₄Ni₈Fe₈Mn₈O₄₈ is constructed to simulate the O3-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ system. To determine the detailed positions of Y/F co-doping in layered NFM, we simulated Y/F co-doped O3-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂, constructing Na₂₃YNi₈Fe₈Mn₈O₄₇F (NFM-Na), Na₂₄Ni₇Fe₈Mn₈YO₄₇F (NFM-Ni), Na₂₄Ni₈Fe₇Mn₈YO₄₇F (NFM-Fe), and Na₂₄Ni₈Fe₈Mn₇YO₄₇F (NFM-Mn) models,

corresponding to the replacement sites. DFT calculations are performed with the VASP code using the plane wave (PW) method [26]. The Perdew-Burke-Ernzerhof (PBE) functional is adopted for the exchange-correlation potential, with a cutoff energy of 520 eV set for the system, and the DFT-D correction for weak interactions is included simultaneously [27]. The projector augmented wave (PAW) method is employed to describe the nucleus-electron interaction potential [28]. For electronic step calculations, the system energy is considered converged when the energy change is less than 10⁻⁶ eV. In structural optimization calculations, the optimized configuration is confirmed to reach the local minimum on the potential energy surface when the average atomic force is less than 0.02 eV Å⁻¹. Brillouin zone sampling is carried out using a Monkhorst-Pack 2×2×2 k-point mesh during the calculations. Given the strong magnetism of Fe, Ni, and Mn elements, spin polarization is fully considered in all calculations.

The formation energy of Y substitution is calculated using the following formula:

$$E_{form} = E - E_0 + n\mu_0 - n\mu_i$$

where E₀ denotes the total energy of the pristine structure, and E represents the total energy of the substituted model. μ_i and μ₀ refer to the chemical potentials of the dopant atom and the substituted atom, respectively.

3. Results and Discussion

3.1. Structure and Morphology

The Y/F surface gradient co-doped NFM materials are synthesized through mechanical mixing of NFM and YF₃, followed by high-temperature calcination (as shown in Fig. 1a). The mixed mass ratio of NFM and YF₃ is 1:x (x = 0.0005, 0.001, 0.0015, and these materials are designated as NFM-yYF (y = 0.05, 0.1, 0.15). To elucidate the precise atomic sites of Y-doping within the layered NFM structure, DFT calculations are systematically conducted to evaluate the formation energies of all possible configurations. As demonstrated in Fig. 1b, among the investigated configurations, the NFM-Ni variant (where Y substitutes for Ni) exhibits the most thermodynamically favorable formation energy (1.38 eV), suggesting a strong preference for Y atoms to occupy Ni sites and form YO₆ octahedral coordination environments (Table S1). Mass compositions of these synthesized materials are quantitatively verified using ICP-MS (Table S2), demonstrating excellent consistency with

the experimental design. The crystal structures of NFM and NFM-0.1YF are presented in Fig. 1c-1d. A significant elongation of the TM-O bond length is observed (Y-O/F: 2.262 Å, Ni-O: 2.016 Å; Fig. 1e) due to the larger ionic radius of Y^{3+} (90.0 pm) compared to Ni^{2+} (69.0 pm). The introduction of the larger ionic size Y^{3+} induces a

coordinated expansion of the TM-O layer (NFM: 1.982 Å → NFM-0.1YF: 2.343 Å) concomitant with a contraction of the Na-O layer (NFM: 3.218 Å → NFM-0.1YF: 3.116 Å), ultimately leading to an increase in the lattice parameter c (Table S3) [11, 29].

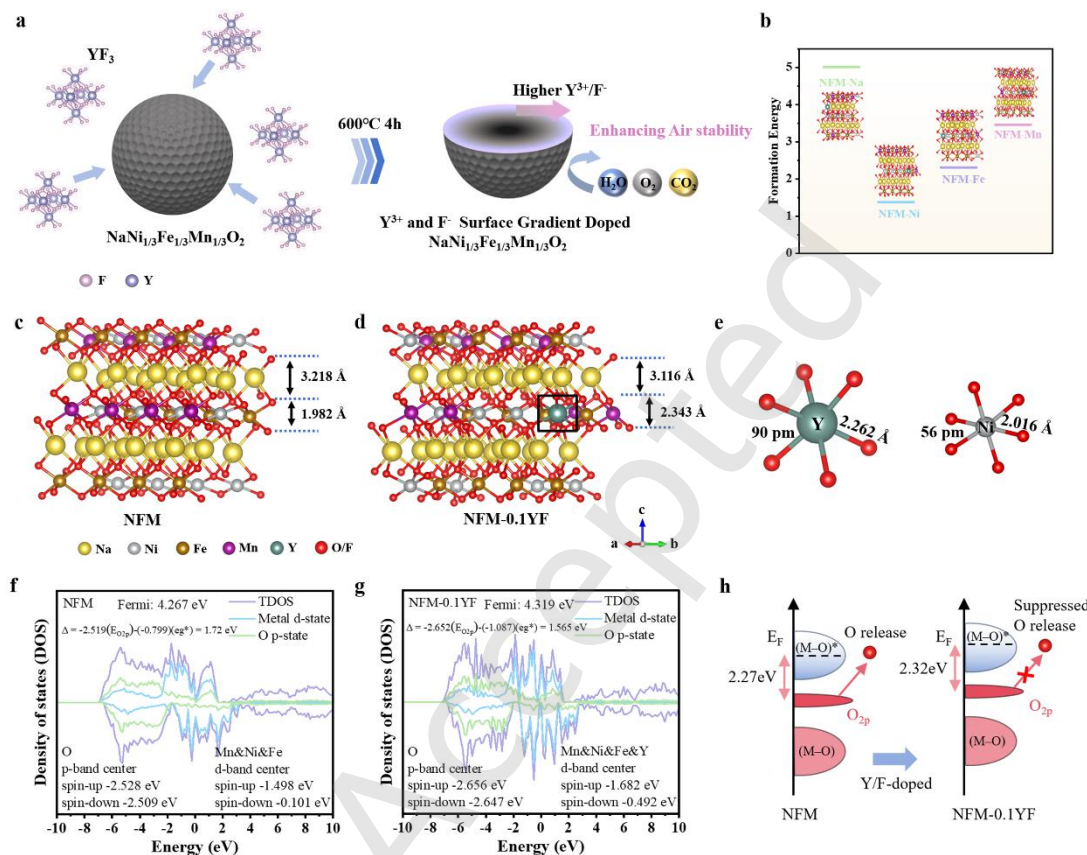


Fig. 1. (a) Schematic of the gradient Y/F-doped O3 phase $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ materials. (b) The formation energy with Y-doping into the Na, Ni, Fe, and Mn sites. Crystal structure view of (c) NFM and (d) NFM-0.1YF materials. (e) Local structures of Y-O/F and Ni-O sites. Part density of states (PDOS) and orbital centers of metal d-orbitals and O 2p orbitals in the (f) NFM and (g) NFM-0.1YF. (h) The band structure diagram after Y/F-doping

The e_g orbitals of TM and O_{2p} orbitals undergo orbital hybridization, resulting in the formation of bonding e_g and high-energy antibonding e_g^* states [30]. The downshift of e_g^* orbitals in NFM-0.1YF facilitates electron transfer, which is manifested in the enhanced redox reversibility of the TM [31]. The energy difference between the band center of the e_g^* orbitals and that of the O_{2p} band ($E_{O_{2p}}$) serves as a key indicator of the charge transfer term Δ . A smaller Δ value correlates with higher electronic conductivity and a kinetically favorable charge transfer process [32]. As shown in Fig. 1f and 1g, the charge transfer term Δ in NFM-0.1YF is calculated to be 1.565 eV, demonstrating that the electron transfer between O_{2p} and e_g^* orbitals in NFM-0.1YF is more

facile than that in pristine NFM ($\Delta = 1.72$ eV). Based on the results of DFT calculations and crystal field theory, we further constructed the TMO_6 band schematics (Fig. 1h). As illustrated, Y-doping can activate TM oxidation and inhibit excessive O stripping, thereby enhancing the reversible capacity and reducing the lattice oxygen loss in NFM-0.1YF [33].

To verify the distribution of Y/F elements, Fig. 2a presents the EDS mapping images of the NFM-0.1YF sample. The results reveal that Na, Ni, Fe, Mn, F, and Y elements are evenly distributed. Fig. 2b and 2c present the Y 3d and F 1s XPS spectra of the NFM-0.1YF sample at various depths, respectively. At a depth of 0 nm, characteristic for Y 3d (The binding energies of Y 3d_{3/2} and Y 3d_{5/2} are 159.3 eV and

157.6 eV, respectively) and F 1s (683.9 eV) peaks are observed. With increasing etching depth from 0 nm to 100 nm, the intensities of the Y 3d and F 1s peaks gradually decrease, indicating the gradient distribution of Y^{3+} and F from the surface to the bulk of the sample. Subsequently, the cross-section of the NFM-0.1YF sample is prepared via argon ion polishing technology. SEM images and EDS linear

scanning of the cross-sections are shown in Fig. 2d–2f. As shown in Fig. 2f, the constituent elements (Na, Ni, Fe, Mn, Y, and F) of NFM-0.1YF demonstrate a gradient distribution, wherein the contents of Y and F decline systematically from the surface to the interior. This observation further validates the successful gradient incorporation of Y/F elements into the NFM matrix.

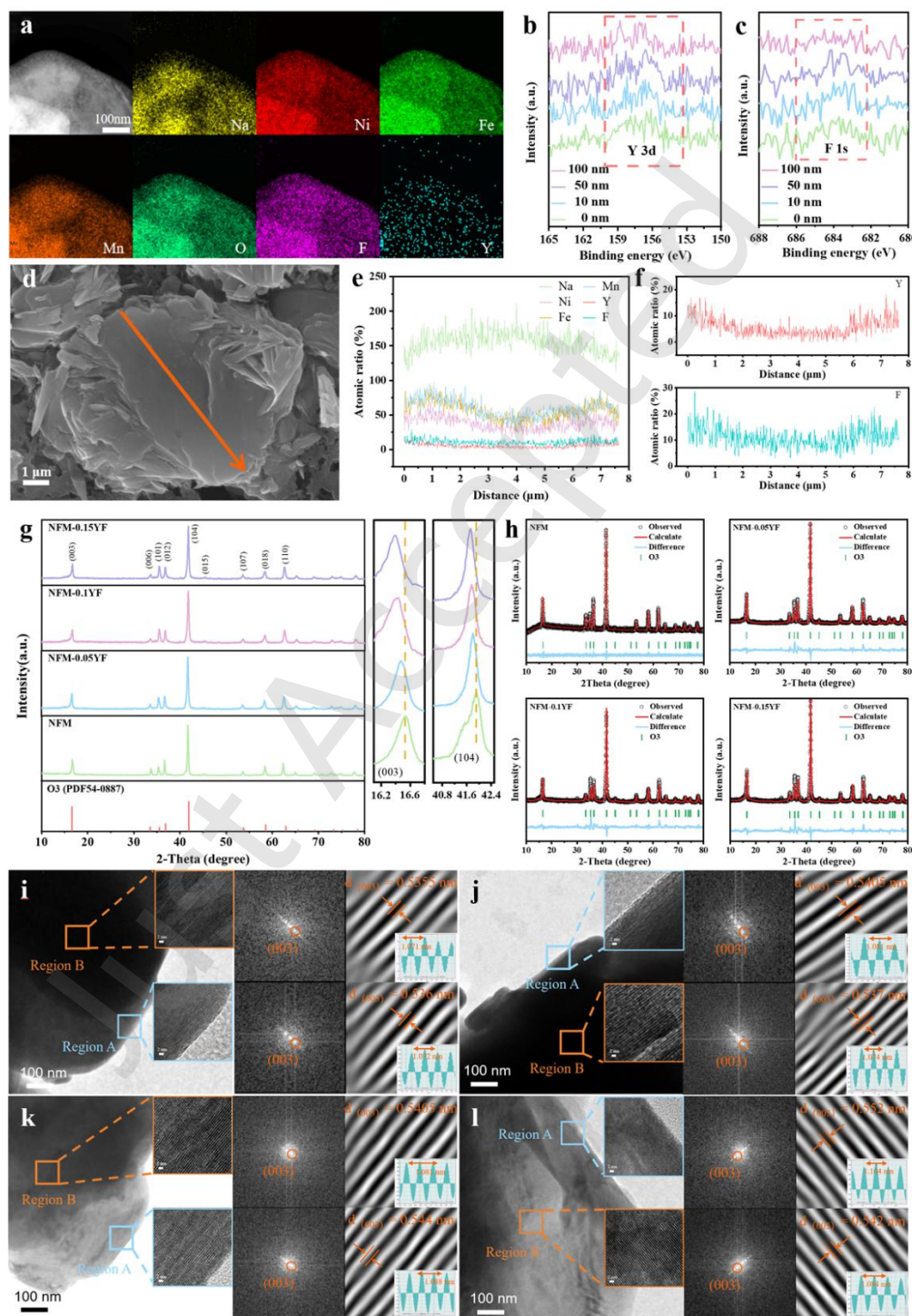


Fig. 2. (a) EDS mapping images of the NFM-0.1YF. XPS spectra of (b) Y 3d and (c) F for NFM-0.1YF at various depths. (d) Cross-sections SEM images and (e) elemental distributions of NFM-0.1YF. (f) Enlarged elemental distributions of Y and F. (g) XRD patterns, relevant standard PDF card, and enlarged plot of the (003) and (104) peaks. (h) XRD refinement patterns of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF. TEM images and high-

The XRD patterns of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF (Fig. 2g) reveal the characteristic diffraction peaks of the hexagonal $\text{O3-NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ phase (JCPDS No. 54-0887, space group R-3m), indicating the preservation of the layered structure upon Y/F-doping [34–36]. Moreover, the XRD results are analyzed by Rietveld refinement to further investigate the effect of modification on the crystal structure. As shown in Fig. 2h and Tables S3–S6, Y occupies the Ni-sites, which is consistent with the DFT simulation results. Additionally, the *c*-axis lattice parameters of NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF are calculated to be 16.06, 16.08, and 16.09 Å, respectively, compared to 16.04558 Å for NFM. This result is consistent with the slight shift of the (003) and (104) diffraction peaks to a lower Bragg angle (Fig. 2g) [33, 37].

Particle morphology and size are characterized by SEM (Fig. S1 in the Electronic Supplementary Material). The Y/F surface gradient-doped samples show spherical secondary particles (10–15 μm), nearly identical to pristine samples. Fig. 2i–2l display the TEM and high-resolution TEM (HRTEM) images along with the FFT patterns of the (003) crystal plane from different regions in NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF. It can be observed that both the near-surface region (Region A) and the region of approximately 250 nm depth exhibit the R-3m crystal structure [29, 38, 39]. To further investigate the effect of surface gradient doping, the interplanar spacing of the (003) plane in the near-surface region (Regions A) and in the bulk material B (Regions A) is compared. Notably, the interplanar spacing during the near-surface region is larger than that of the bulk for all modified samples (NFM-0.05YF: 0.5405 nm vs. 0.537 nm; NFM-0.1YF: 0.544 nm vs. 0.5405 nm; NFM-0.15YF: 0.552 nm vs. 0.542 nm). In contrast, the pristine NFM sample shows nearly identical (003) interplanar spacing in both regions (Region A: 0.536 nm; Region B: 0.5355 nm). This phenomenon can be attributed to the elevated Y/F content in the near-surface region, wherein the large radius of Y^{3+} ions induce expansion of the Y–O/F bonds, resulting in expanded TM–O layers and an increased *c*-axis lattice parameter.

3.2. Charge compensation Mechanism

XPS is initially performed to analyze the effects of Y/F co-doping on the elemental valence of the NFM. The survey XPS spectrum (Fig. S2a) reveals characteristic peaks for Na 1s, Ni 2p, Fe 2p, Mn 2p, O 1s, and C 1s across all samples. Notably, the Y/F co-doped samples exhibit additional peaks at binding energies of 157 eV and 684 eV, which are assigned to the Y 3d and F 1s core levels, respectively. These findings provide direct evidence for the successful incorporation of Y and F elements into the NFM matrix [25, 40]. High-resolution XPS analysis of the Y, F, Ni, Mn, and Fe elements is further conducted to elucidate the effect of Y/F-doping on the valence states of transition metals, with detailed fitting curves presented in Fig. 3a–3d and Fig. S2b, respectively. Fig. 3a shows the Y 3d core-level spectrum after peak deconvolution, revealing $\text{Y}^{3+} 3d_{5/2}$ (157.51 eV) and $\text{Y}^{3+} 3d_{3/2}$ (159.28 eV) components, confirming Y^{3+} incorporation in NFM-yYF samples [41]. As depicted in Fig. 3b, the F 1s core-level spectra of the modified samples exhibit distinct chemical shifts. High-resolution Fe 2p core-level XPS spectra (Fig. S2b) demonstrate the coexistence of Fe^{2+} and Fe^{3+} species in both pristine NFM and Y/F co-doped NFM samples. Notably, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio exhibits a slight increase following Y/F co-doping, as quantified in Table S7. It is reported the presence of Fe^{2+} can significantly enhance the inherent electronic conductivity of the material, thereby facilitating its excellent rate performance [42, 43]. Fig. 3c illustrates the Ni 2p XPS spectra of all samples, confirming the coexistence of Ni^{2+} and Ni^{3+} . Quantitative analysis reveals that the $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio decreases slightly from 37.66%/62.37% for NFM to 35.0%/65.0%, 34.5%/65.5%, and 31.95%/68.05% for NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF, respectively (Table S8). As shown in Fig. 3d, Mn exists in both Mn^{3+} and Mn^{4+} states across all samples. Fitting analysis indicates that the proportion of Mn^{4+} decreases while that of Mn^{3+} increases after modification (Table S9). It is established that the d-orbital overlap and electron cloud sharing between TM and oxygen 2p orbitals induce d-p orbital hybridization, which is further facilitated by the unsaturated $3d^4$ configuration of Mn^{3+} , thereby suppressing oxygen release under high-voltage conditions [44]. Furthermore, as illustrated in Fig. 3e and 3f, the peak intensities of Ni^{3+} and Mn^{3+} in the NFM-0.1YF sample exhibit

a marginal enhancement compared to those in the unmodified NFM sample, as evidenced by the Ni L3-edge and Mn L3-edge soft X-ray absorption spectroscopy (sXAS)

spectra. This observation corroborates with the XPS analysis presented in Fig. 3c-3d, reinforcing the consistency between surface and bulk oxidation states.

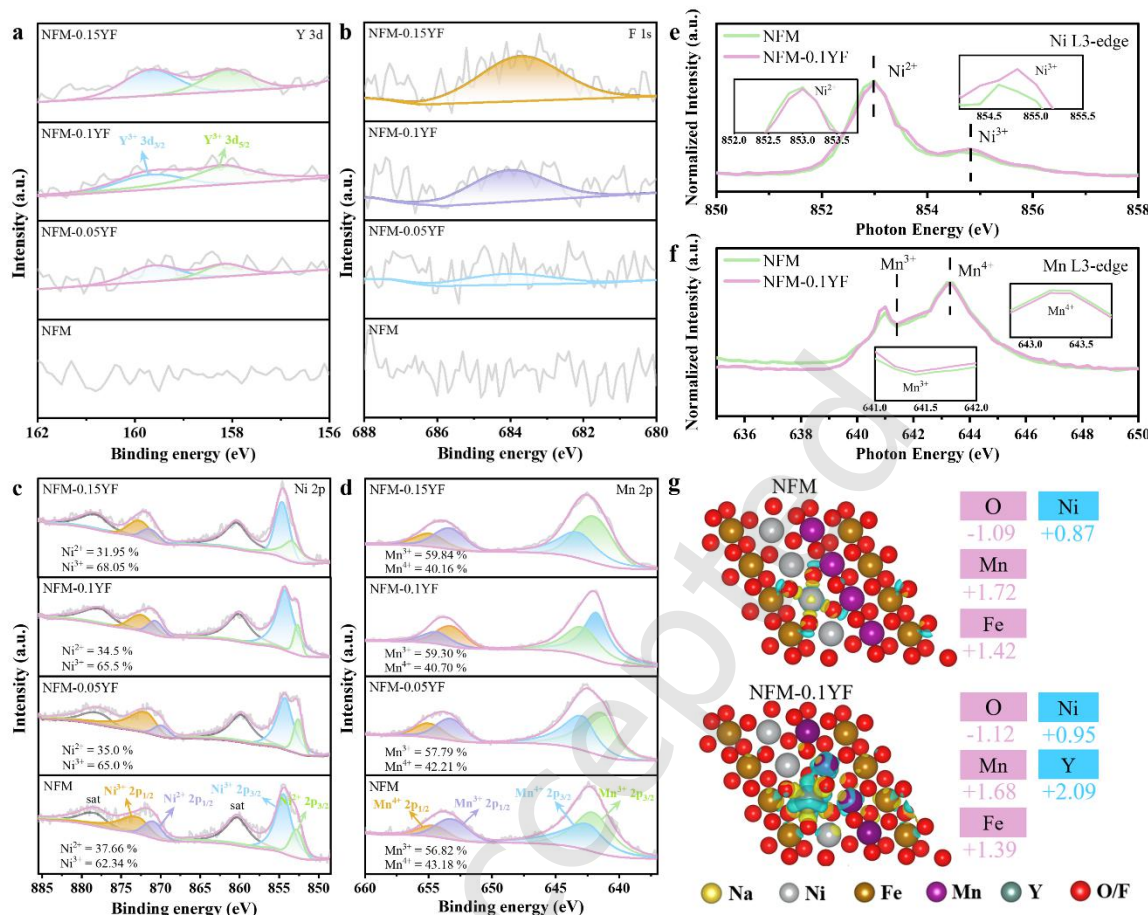


Fig. 3. XPS analysis of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF powders: (a) Y 3d spectra, (b) F 1s spectra, (c) Ni 2p spectra, and (d) Mn 2p spectra. sXAS spectra in NFM and NFM-0.1YF of (e) Ni L3-edge, (f) Mn L3-edge. (g) Supercell atomic structure and Bader charge distribution of each element for NFM and NFM-0.1YF

To elucidate the valence state variations of Ni, Fe, and Mn elements, we conducted a DFT-based Bader charge analysis to determine the average Bader charges for each element in both NFM and NFM-0.15YF materials (as shown in Fig. 3g and Tables S10-S11). It can be observed that in NFM, Ni atoms are coordinated as NiO_6 octahedra, with the charge distributions of surrounding O (-1.09), Fe (+1.42), and Mn (+1.72) being relatively stable, indicating that the local electronic structure in NFM maintains a relatively balanced state. The substitution of Ni by Y leads to the formation of $Y(O/F)_6$ octahedral coordination units. The Bader charge of Y atoms (+2.09) is significantly higher than that of Ni atoms (+0.87 in NFM, +0.95 in NFM-0.1YF), thereby triggering local charge reconstruction around the

doping sites, with the Bader charges of neighboring Ni atoms increasing (some Ni atoms are oxidized from +2 to +3) and the Bader charges of Fe and Mn atoms slightly decreasing (some Fe atoms are reduced from +3 to +2, and some Mn atoms are reduced from +4 to +3) [45]. Notably, the Bader charge of O atoms in NFM-0.1YF (-1.21) is more negative compared with that of O atoms in NFM (-1.09), indicating that the introduction of Y/F provided additional negative charges to O, thereby suppressing lattice oxygen release. These charge distribution characteristics collectively demonstrate the modulatory effect of site-specific surface gradient Y/F-doping on the valence states of TM and the local electronic structure of the material.

3.3. Electrochemical Performance

The electrochemical sodium-ion storage performances (Table S12) of these materials are evaluated using CR2025-

type coin cells. The first charge-discharge curves of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF at 0.1C within the voltage ranges of 2.0 to 4.0 V and 2.0 to 4.2 V are shown in Fig. 4a and 4b, respectively. It is observed that the discharge plateau voltages of all Y/F co-doped samples are significantly higher than those of the pristine NFM electrode. This phenomenon arises from the pronounced electronegativity of fluoride atoms, which strengthens cation-anion interactions and modulates the electronic band structure by lowering the valence band energy in the cathode, thereby substantially elevating the discharge plateau voltages [46]. The cycling performances of all samples at 1C are presented in Fig. 4c (2.0–4.0 V), 4d (2.0–4.2

V). The NFM-0.1YF electrode possesses the highest initial capacity of 119.5 mAh g⁻¹ and maintains a capacity retention of 88.9% after 200 cycles within the 2.0–4.0 V voltage. In contrast, the initial capacity of the NFM, NFM-0.05YF, and NFM-0.15YF electrodes with the capacity retention rates of only 71.8%, 77.5%, and 83.3% after 200 cycles. Similarly, the NFM-0.1YF electrode demonstrates the highest initial discharge capacity of 142.1 mAh g⁻¹ and a supreme capacity retention of 80% after 150 cycles within the 2.0–4.2 V voltage. These improvements are attributed to enhanced d-p orbital hybridization and suppressed oxygen release, which collectively enhance the structural stability of NFM.

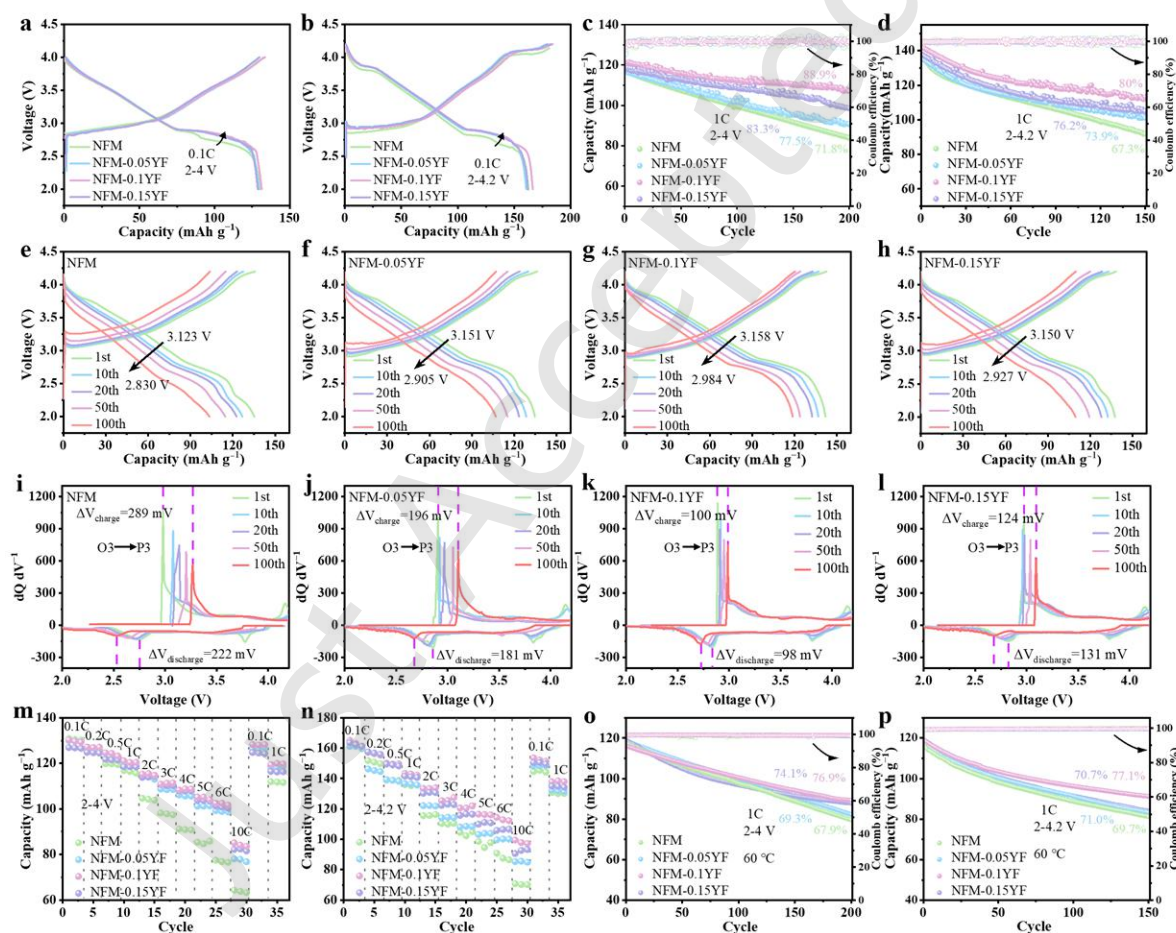


Fig. 4. Initial charge/discharge curves of the NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes at 0.1C: (a) 2.0–4.0 V, (b) 2.0–4.2 V. Coulomb efficiency and cycling performances of the NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes at 1C: (c) 2.0–4.0 V, (d) 2.0–4.2 V. Charge/discharge profiles of (e) NFM, (f) NFM-0.05YF, (g) NFM-0.1YF and (h) NFM-0.15YF during cycles within the voltage ranges of 2.0–4.2 V, and (i, j, k, l) the corresponding dQ dV⁻¹ profiles. Rate performances of NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes: (m) 2.0–4.0 V, (n) 2.0–4.2 V. Cycling performances of NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes at 1C and 60 °C: (o) 2.0–4.0 V, (p) 2.0–4.2 V

As the charge-discharge curves evolved (2.0–4.2 V, Fig.

4e–4h), the discharge midpoint potential of NFM-0.1YF decayed from 3.158 V to 2.984 V, exhibiting a lower discharge midpoint potential decay in NFM-0.1YF ($\Delta V = 174$

mV) than that of NFM (from 3.123 V to 2.830 V, $\Delta V = 293$ mV), NFM-0.05YF (from 3.151 to 2.905 V, $\Delta V = 246$ mV), and NFM-0.15YF (from 3.150 to 2.927 V, $\Delta V = 223$ mV). The corresponding differential capacity curves (dQ/dV^{-1}) of all four samples show clear oxidation/reduction peaks (Fig. 4i–4l). During cycling, the O3–P3 phase transition peaks of NFM ($\Delta V_{\text{charge}} = 289$ mV, $\Delta V_{\text{discharge}} = 222$ mV) demonstrate rapid degradation, in stark contrast to the more gradual decay observed in NFM-0.05YF ($\Delta V_{\text{charge}} = 196$ mV, $\Delta V_{\text{discharge}} = 181$ mV), NFM-0.1YF ($\Delta V_{\text{charge}} = 100$ mV, $\Delta V_{\text{discharge}} = 98$ mV), and NFM-0.15YF ($\Delta V_{\text{charge}} = 124$ mV, $\Delta V_{\text{discharge}} = 131$ mV). Notably, NFM-0.1YF exhibits the most sluggish decay rate among the samples, suggesting that Y/F co-doping significantly enhances the structural stability and electrochemical reversibility of the material [47, 48]. The rate capabilities of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF cathodes within voltages of 2.0–4.0 V and 2.0–4.2 V are presented in Fig. 4m, 4n. Upon increasing the current density to 10C, the NFM-0.1YF electrode exhibits a markedly superior capacity retention (85.1 mAh g⁻¹ for 2.0–4.0 V and 99.5 mAh g⁻¹ for 2.0–4.2 V) compared to NFM (63.8 mAh g⁻¹ and 70.1 mAh g⁻¹). This enhanced rate capability is attributed to the accelerated Na⁺ ion diffusion kinetics resulting from Y/F surface gradient doping. To further investigate the impact of doping on the cycling performance of the NFM materials at elevated temperatures, the effect of Y/F co-doping is systematically evaluated by subjecting all electrodes to high-temperature cycling conditions. As shown in Fig. 4o, the NFM-0.1YF electrode exhibits a capacity retention of 76.9% after 200 cycles at 1 C under 60 °C within the voltage range of 2.0–4.0 V, significantly outperforming NFM (67.9%). Similarly, the NFM-0.1YF electrode achieves a capacity retention of 77.1% after 150 cycles at 1 C within the 2.0–4.2 V voltage (Fig. 4p). It can be observed that all materials exhibit a remarkable convergence in discharge capacities at 1C within the voltage ranges of 2.0 to 4.0 V and 2.0 to 4.2 V. This phenomenon can be attributed to the elevated temperature of 60 °C, which suppresses the electrochemical activity of the Ni³⁺/Ni⁴⁺ redox couple at high voltage (Fig. S3) [49–51]. The Y/F co-doping stabilizes the electrode-electrolyte interface and mitigates oxygen release at high temperatures, thus effectively enhancing the cycling

stability of the material.

To examine the effect of doping on interface properties and air stability. The surface wettability of water on the NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF materials is assessed through contact angle measurements (Fig. S4). The NFM-0.1YF sample exhibited the highest contact angle (23.8°). Notably, the interfacial protection does not increase indefinitely with increasing Y/F content. Excessive Y/F incorporation induce surface compositional segregation, local aggregation, or secondary-phase formation, thereby disrupting the uniformity and continuity of the passivation layer and generating additional local defects and highly reactive sites [52]. Consequently, the interfacial protection effect is weakened, resulting in a decreased contact angle. Furthermore, each material sample is precisely weighed to 200 mg and exposed to ambient air for 5 days, with their mass changes meticulously recorded (Fig. S5). Following the 5-day air exposure, the materials are pressed into electrode pellets for subsequent battery testing (Fig. S6 and S7). It is worth noting that the NFM-0.1YF delivers the best humidity resistance among all the samples.

3.4. Kinetic analysis

The dynamic characteristics of the NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes are explored using CV tests at different scanning rates. Fig. 5a–5d illustrate the CV curves of all samples at scanning rates of 0.1, 0.2, 0.3, 0.4, and 0.5 mV s⁻¹. As the peak current (I_p) is linearly related to the square root of the scan rate ($v^{1/2}$) (Fig. 5e, the slope is recorded in Table S13), D_{Na^+} at the redox peak can be calculated for both electrodes using Equation S1. According to the calculation, the D_{Na^+} at the redox peak is the highest for the NFM-0.1YF (8.48×10^{-8} and 5.48×10^{-8} cm² s⁻¹ for O1 and R1, respectively) among those of the NFM (6.61×10^{-8} and 4.11×10^{-8} cm² s⁻¹ for O1 and R1, respectively), NFM-0.05YF (8.13×10^{-8} and 3.95×10^{-8} cm² s⁻¹ for O1 and R1, respectively), NFM-0.15YF (7.33×10^{-8} and 4.92×10^{-8} cm² s⁻¹ for O1 and R1, respectively). Fig. 5a–5d further demonstrate the variations in redox peak positions across different scanning rates. Notably, the peak shifts observed for NFM-0.1YF (O1 131 mV, R1 104 mV) are significantly smaller than those of NFM (O1 205 mV, R1 193 mV), NFM-0.05YF (O1 189 mV, R1 173 mV), and NFM-0.15Y (O1 145 mV, R1 122 mV).

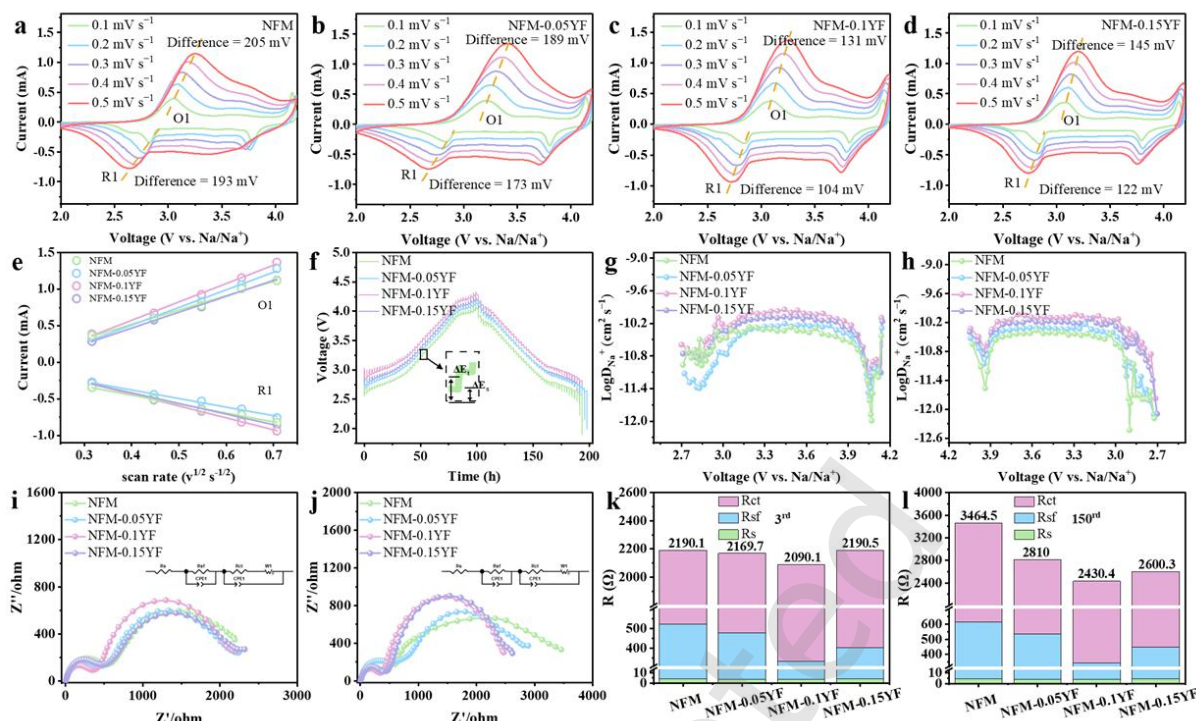


Fig. 5. CV curves of (a) NFM, (b) NFM-0.05YF, (c) NFM-0.1YF, and (d) NFM-0.15YF at various scanning rates in the voltage range of 2-4 V. (e) The linear relationship between the peak currents and scan rates. (f) GITT curves and (g, h) corresponding Na⁺ diffusion coefficients in the voltage range of 2-4 V. The Nyquist plots curves after (i) 3rd cycles and (j) 150th cycles. Impedance variation after (k) 3rd cycles and (l) 150th cycles

Furthermore, we investigated the effect of modification on the kinetic behavior of Na⁺ by employing the GITT to determine the apparent diffusing capacity of Na⁺ during the initial charging/discharging process using the following equation proposed by Weppner and Huggins (Equation S2). As depicted in Fig. 5f-5h and Table S14, it has been observed that compared with pristine NFM, NFM-0.1YF exhibits a higher Na⁺ diffusion coefficients (D_{Na^+}) in all voltage ranges. During the initial charging stage, Y/F co-doping facilitates the free diffusion of Na⁺ ions. When the voltage is in the range of 4.0–4.2 V, the D_{Na^+} undergoes a sharp decline, which is attributed to irreversible O release that impedes the charge compensation of the cathode. However, Y/F co-doping can stabilize O atoms and maintain charge balance, thus facilitating the stable charge flow during the discharge process. To systematically evaluate the effect of doping on the diffusion resistance, the EIS measurements are conducted on the electrode samples after the 3rd and 150th charge-discharge cycles. The fitting results are shown in Fig. 5k and 5l and Table S15. After undergoing multiple charge-discharge cycles, the resistance ($R_{sf} + R_{ct}$) of the NFM

cathode exhibited a progressive increase from 2186.35 Ω (3rd cycle) to 3460.0 Ω (150th cycle). In contrast, the corresponding resistance values for the NFM-0.1YF cathode increased from 2086.64 Ω to 2426.34 Ω , across the same cycling intervals. These observations confirm that site-specific surface gradient Y/F co-doping effectively suppresses the rapid escalation of Na⁺ diffusion resistance and significantly mitigates the electrochemical performance degradation associated with increasing cycle numbers.

3.5. Mitigation of Structural Degradation

To investigate the effect of Y/F gradient co-doping on bulk-phase evolution during cycling, ICP-MS was employed to quantitatively determine the Mn contents in the cycled cathode electrodes, which were compared with those of the pristine cathode materials to indirectly assess Mn dissolution. The ICP-MS results show that the pristine NFM and NFM-0.1YF cathode materials exhibit nearly identical Mn contents of 10.973 and 10.970 wt%, respectively. After 150 cycles at 1C within a voltage range of 2.0–4.2 V, the Mn content of the NFM electrode decreases markedly to 8.253 wt%, whereas the NFM-0.1YF electrode retains a substantially higher Mn content of 9.871 wt%. Considering

their nearly identical initial Mn contents, the enhanced Mn retention in NFM-0.1YF provides strong evidence that Y/F gradient co-doping effectively mitigates Mn loss during prolonged cycling. These results further demonstrate that Y/F gradient co-doping stabilizes Mn within the crystal lattice, thereby enhancing the structural stability of the cathode material during long-term cycling. Subsequently, we conducted in-situ XRD analysis to characterize the phase transition during the initial charge-discharge cycle. Fig. 6a and 6b show the typical contour profile map of the (003), (006), (101), and (012) diffraction peaks for the initial cycle in the voltage range of 2.0–4.2 V. The (003) diffraction peaks of both NFM and NFM-0.1YF split into two peaks during the initial charging stage, indicating the O3 and P3 phases coexist. Upon charging to 3.15 V, the O3 phase transforms into the P3 phase, and the P3 phase remains unchanged until the charging ends. However, during the O3-P3 phase transition stage, the (003) diffraction peak of NFM shifts to a lower angle by 1.06° , which is 0.16° larger than that of NFM-0.1YF (0.9°). When the voltage is raised to 4.1 V, deep desodiation intensifies interlayer electrostatic repulsion and the accumulation of local structural stress, thereby driving the gliding of transition-metal oxide slabs and triggering the OP2 phase transition [53]. Y/F gradient co-doping reconstructs the local electronic environment, while strong Y–O bonds effectively buffer local stress at high voltages and enhance the stability of the layered structure, thereby suppressing the formation of the OP2 phase. Compared with NFM, no OP2 phase is observed in NFM-0.1YF during high-voltage charging, indicating that Y/F gradient co-doping effectively suppresses large-scale cooperative slab gliding and prevents the pronounced lattice distortion, stress concentration, and structural reconstruction associated with the OP2 phase transition. In addition, the gradient-distributed Y/F heteroatoms help stabilize the local Mn–O coordination environment, alleviate lattice mismatch during Na^+ extraction/insertion, and suppress structural damage caused by irreversible slab gliding and excessive oxygen redox. Consequently, NFM-0.1YF maintains a more stable and highly reversible layered structure during cycling, resulting in superior long-term structural stability and enhanced Mn retention. This is highly consistent with the significantly reduced Mn dissolution revealed by ICP-MS measurements, further demonstrating the critical role of Y/F

gradient co-doping in suppressing the high-voltage OP2 phase transition and preserving the integrity of the layered structure. Rietveld refinements are used to further track the evolution of lattice parameters (Fig. 6c, 6d, S8, and Table S17). When focusing on the structural transformations occurring at voltages exceeding 4.0 V, it becomes evident that the OP2 phase maintains the smallest *c*-axis throughout the entire charge-discharge process. The abrupt phase transition from P3 to OP2 in the NFM cathode results in a substantial *c*-axis contraction ($1.12 \text{ \AA}$), which is accompanied by significant reorganization of the internal lattice framework. In stark contrast, the NFM-0.1YF cathode suppresses this detrimental P3-OP2 phase transition and demonstrates more moderate structural evolution, thereby facilitating the Na^+ intercalation/deintercalation. The valence state rearrangement effect induced by Y incorporation effectively suppresses structural degradation while promoting d-p orbital hybridization. Concurrently, the highly electronegative F element enhances the stability of lattice oxygen at elevated voltages, collectively contributing to structural stabilization.

To further verify the effectiveness of the Y/F synergistic regulation strategy in suppressing lattice oxygen release at high potentials, electron paramagnetic resonance (EPR) measurements were performed at 77 K under an Ar atmosphere (Fig. 6e and 6f). Both NFM and NFM-0.1YF exhibit a distinct characteristic signal at $g = 2.003$, which is attributed to paramagnetic centers associated with oxygen vacancies. In the pristine state, NFM-0.1YF shows a higher EPR signal intensity than NFM, indicating a higher initial concentration of oxygen vacancies, mainly arising from defect formation induced by F doping/substitution at O sites. The introduction of an appropriate amount of oxygen vacancies helps lower the Na^+ diffusion barrier, thereby facilitating Na^+ migration and transport. However, after 150 cycles, the EPR signal intensities of the two materials exhibit a reversed trend. NFM displays a stronger EPR signal, indicating more severe accumulation of oxygen vacancies caused by substantial lattice oxygen loss during prolonged cycling. In contrast, the accumulation of oxygen vacancies in NFM-0.1YF is significantly suppressed, further demonstrating that Y/F synergistic regulation effectively stabilizes lattice oxygen and inhibits oxygen release at high potentials. These results are consistent with the XPS

characterization and theoretical calculations.

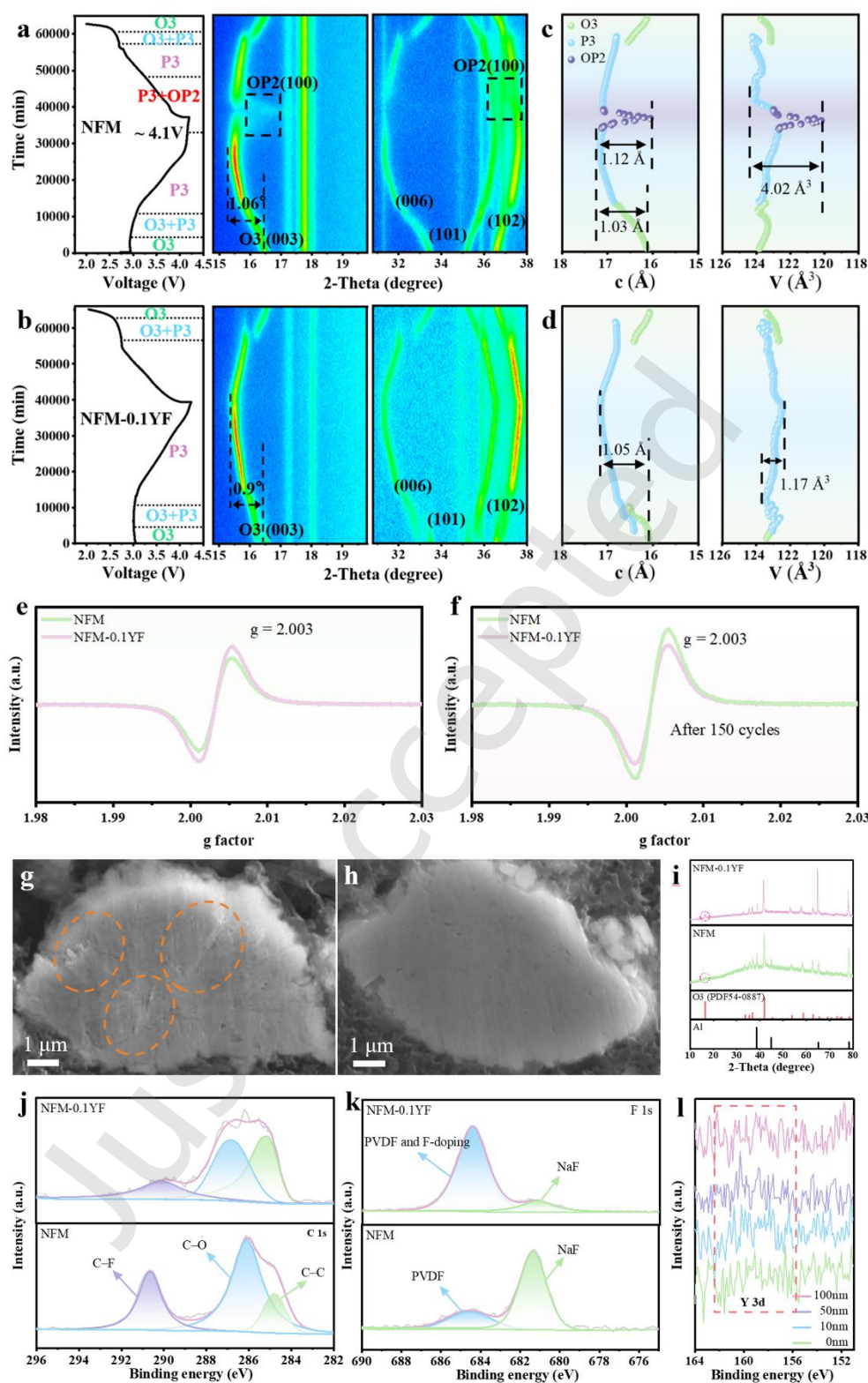


Fig. 6. Contour plots of in situ XRD patterns for pristine (a) NFM and (b) NFM-0.1YF during the initial cycle between 2.0 and 4.2 V at 0.1C. The crystal parameters for (c) NFM and (d) NFM-0.1YF during the initial cycle between 2.0 and 4.2 V at 0.1C. EPR spectra of NFM and NFM-0.1YF electrodes (e) before cycling and (f) after 150 cycles at 1 C within the voltage range of 2.0–4.2 V. Cross-section SEM images for (g) NFM and (h) NFM-0.1YF after 200 cycles at 1C and 2.0–4.2 V. (i) XRD patterns for cycled NFM and NFM-0.1YF after 200 cycles at 1C and 2.0–4.2 V. The XPS spectra of (j) C 1s and (k) F 1s for cycled NFM and NFM-0.1YF after 200 cycles at 1C and 2.0–4.2 V. (l) XPS spectra of Y 3d for cycled NFM-0.1YF at various depths after 200 cycles at

The progressive accumulation of mechanical stress during prolonged electrochemical cycling engenders irreversible mechanical degradation in O3-type layered cathodes from the surface to the interior of the cathode [54]. Cross-sectional SEM characterization demonstrates extensive grain boundary fracture in NFM particles (Fig. 6g), whereas the NFM-0.1YF counterpart exhibits preserved grain structural integrity (Fig. 6h). The XRD patterns of the cycled NFM electrode reveal a pronounced attenuation in the (003) reflection intensity (Fig. 6i), indicative of substantial irreversible phase transformation. In stark contrast, the NFM-0.1YF counterpart maintains a well-defined layered structure with negligible intensity reduction, demonstrating preserved crystallographic integrity and minimal structural deterioration. The cycled NFM and NFM-0.1YF electrodes is further characterized via XPS. As illustrated in Fig. 6j, the C 1s XPS spectra of both NFM and NFM-0.1YF samples demonstrate that the signal intensity of the C–F characteristic peak in NFM surpasses that of NFM-0.1YF. Meanwhile, the NaF signal intensity of NFM is also found to be higher than that of NFM-0.1YF in Fig. 6k, which is attributed to the more severe interfacial side-reactions occurring in the NFM electrode during cycling compared to those in the NFM-0.1YF electrode. Fig. 6l displays the XPS spectrum of the Y element in the cycled NFM-0.1YF material. With increasing etching depth from 0 nm to 100 nm, the

intensity of the Y 3d peak exhibits a gradual decline. This observation unequivocally confirms that electrochemical cycling has not perturbed the inherent tendency of Y^{3+} to adopt a gradient distribution profile from the sample surface to the bulk region.

Fig. 7 depicts the schematic illustration of the structural evolution of NFM and NFM-0.1YF electrodes following prolonged cycling. A pronounced shift in the P3 phase reflection is observed in NFM, accompanied by substantial irreversible oxygen loss during the charging process. Concurrently, an undesirable P3-OP2 phase transition occurs at 4.1 V. Furthermore, Na^+ extraction induces localized lattice stress, thereby promoting the migration of TM ions into Na^+ vacancies. This cation disorder initiates a progressive surface phase transition from the layered structure to the rock-salt or spinel phase, facilitating electrolyte penetration into the cathode and accelerating both structural degradation and electrochemical performance deterioration. In contrast, for NFM-0.1YF, the co-doping of Y and F elements effectively mitigates the P3-OP2 phase transition. Specifically, Y occupies Ni sites while F occupies O sites, which not only suppresses O_2 release and stabilizes the interlayer structure but also reduces TM ion dissolution during cycling. Consequently, the synergistic effects of surface gradient Y/F co-doping culminate in a substantial improvement in the sodium storage capabilities of the NFM material.

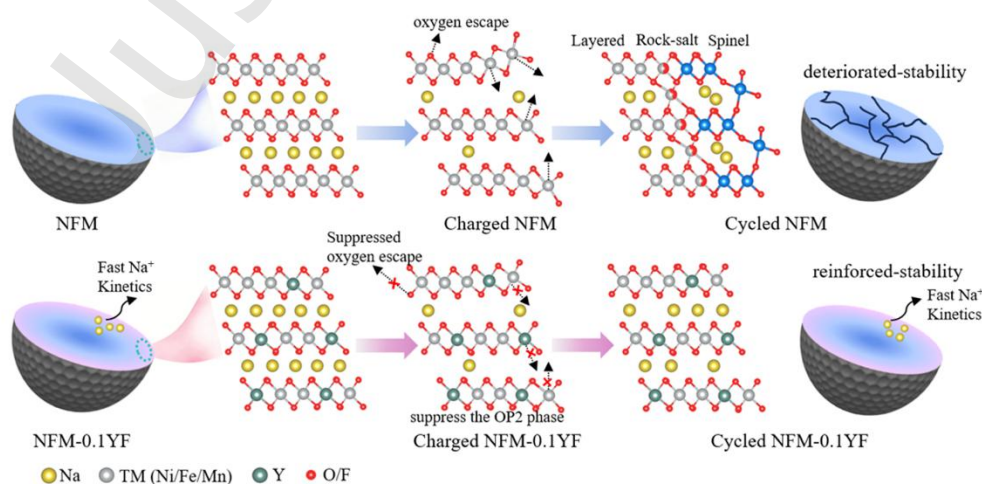


Fig. 7 Schematic illustration of structural evolution in NFM and NFM-0.1YF

In summary, an effective site-specific gradient Y/F

co-doping strategy is proposed to regulate electronic

4. Conclusions

structure, effectively suppressing the oxygen evolution and irreversible phase transition under high-voltage conditions. Specifically, the site occupation of Y at Ni sites can introduce additional negative charge density to oxygen atoms, promoting d-p orbital hybridization between Y and O, while F at O sites can intensify TM-O coupling, together inhibiting the irreversible P3-OP2 transformation and lattice oxygen loss. Additionally, the surface gradient doping strategy can further mitigate the interfacial stability by selectively passivating reactive sites and stabilizing the electrode-electrolyte interface, reducing the grain cracks after cycles. Consequently, the NFM-0.1YF cathode demonstrates remarkable performance enhancements across diverse operating conditions. Within the voltage range of 2.0–4.0 V, the site-specific surface gradient Y/F-doping strategy boosted the capacity retention from 71.8% to 88.9% after 200 cycles at 1C. In the extended 2.0–4.2 V range, capacity retention increases from 67.3% to 80% after 150 cycles at 1C. Even under elevated temperatures (60 °C), the material maintains 76.9% capacity retention after 200 cycles (2.0–4.0 V) and 77.1% after 150 cycles (2.0–4.2 V). This work establishes an effective strategy for advancing high-performance O3-type layered oxide cathodes and provides new insights into the valence state rearrangement mechanism.

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Data availability

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

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Declaration of competing interest

There no conflict of interests in this work.

Author contribution statement

Yang Sun: Writing-original draft, Methodology, Investigation, Conceptualization, Data curation, Software, Validation, Formal analysis, Visualization. Haoji Wang: Writing-original draft, Methodology, Investigation, Conceptualization, Data curation, Software. Yingchang Yang: Writing-review & editing, Funding acquisition, Resources, Supervision, Project administration, Conceptualization, Visualization, Formal analysis, Validation. Wei Shi: Funding acquisition, Resources, Supervision. Yang Liu: Methodology, Investigation. Yanxu Wang: Software, Investigation, Formal analysis. Kaixu Yang: Methodology, Software, Investigation. Jing Chen: Investigation, Methodology. Zinan Xie: Methodology, Software. Hongshuai Hou: Writing-review & editing, Supervision, Resources.

All the authors have approved the final manuscript."

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Site-specific gradient Y/F co-doping modulating electronic structure for durable O3-type sodium layered oxide cathodes

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Equation S1: The Na⁺ diffusion coefficient at the redox peaks was calculated using the Randles- Sevcik equation (1):

$$I_p = 2.69 \times 10^5 n^{3/2} S C_0 D_{Na^+}^{1/2} v^{1/2} \quad (1)$$

where I_p denotes the peak current, n denotes the number of electrons transferred, S denotes the electrode area, v denotes the scan rate, and C_0 denotes the change in Na⁺ concentration.

Equation S2: The Na⁺ diffusion coefficient by Galvanostatic Intermittent Titration Technique is calculated using Equation (2):

$$D_{Na^+} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (2)$$

where D is the apparent diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), τ represents the time of constant current, m_B denotes the amount of active substance, V_M denotes the molar volume, M_B denotes the molecular weight of the active substance, and S denotes the effective contact area between the cathode material and electrolyte. ΔE_s represents the steady-state (balanced) voltage change, and ΔE_t represents the change of voltage when standing still.

1. Supporting Fig.

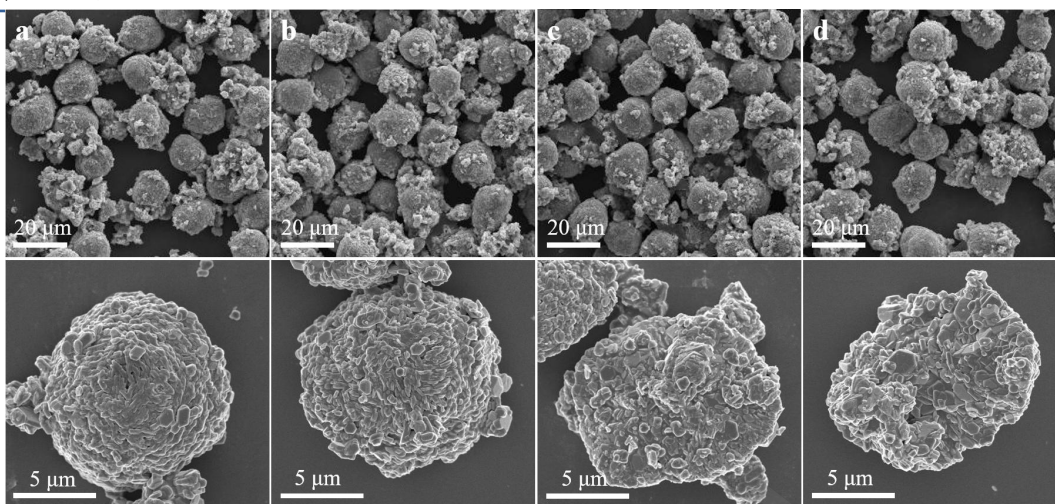


Fig. S1. SEM images of (a) NFM, (b) NFM-0.05YF, (c) NFM-0.1YF, and (d) NFM-0.15YF.

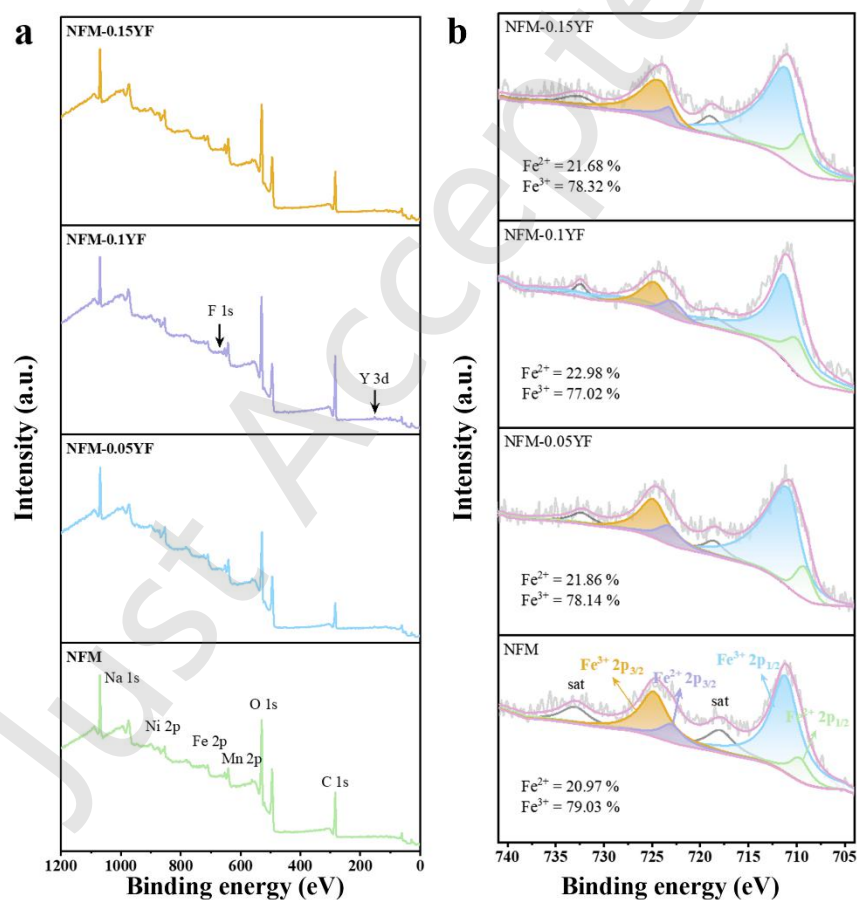


Fig. S2. XPS analysis of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF powders: (a) the survey spectra, (b) Fe 2p spectra.

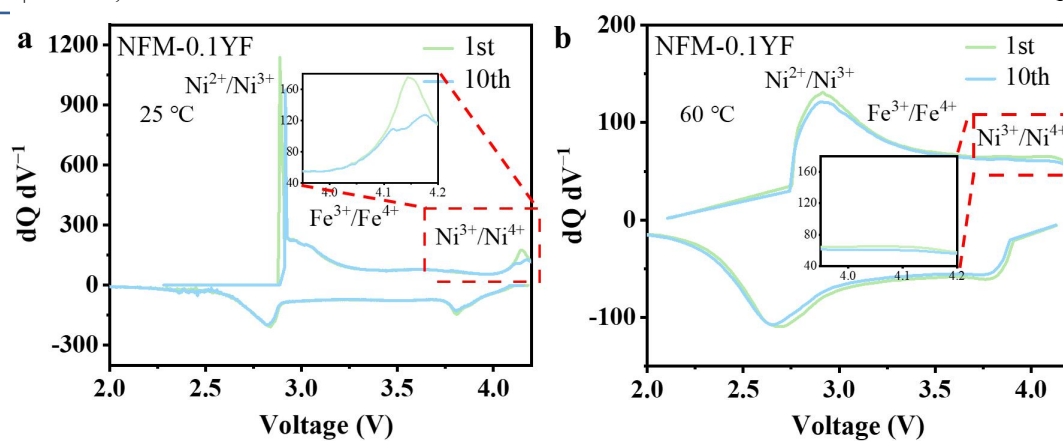


Fig. S3. dQ dV⁻¹ profiles of NFM-0.1YF at 1C (25 °C and 60 °C).

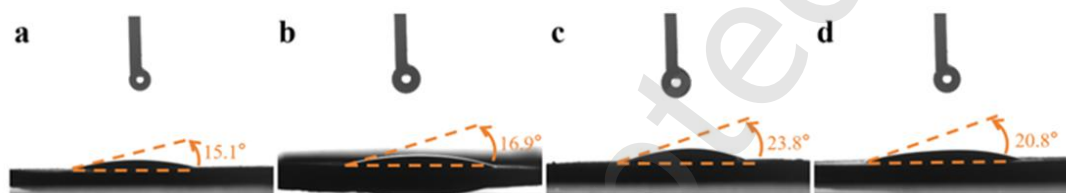


Fig. S4. Water contact angle on the (a) NFM, (b) NFM-0.05YF, (c) NFM-0.1YF, and (d) NFM-0.15YF.

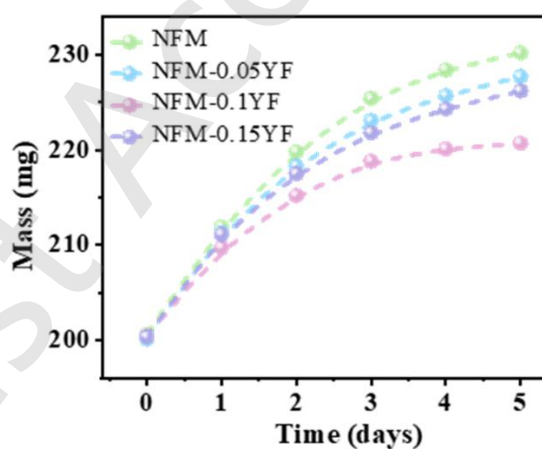


Fig. S5. Mass variation of the material during 5 days exposure to air.

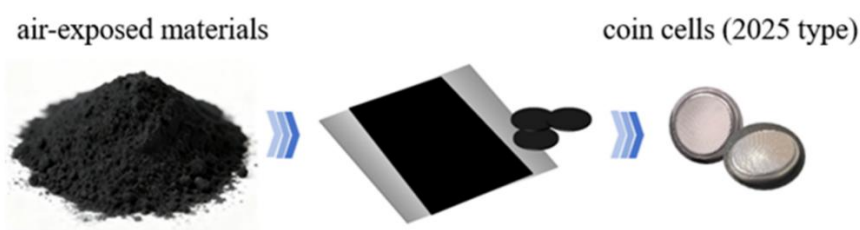


Fig. S6. Schematic of the battery with 5-days air-exposed material.

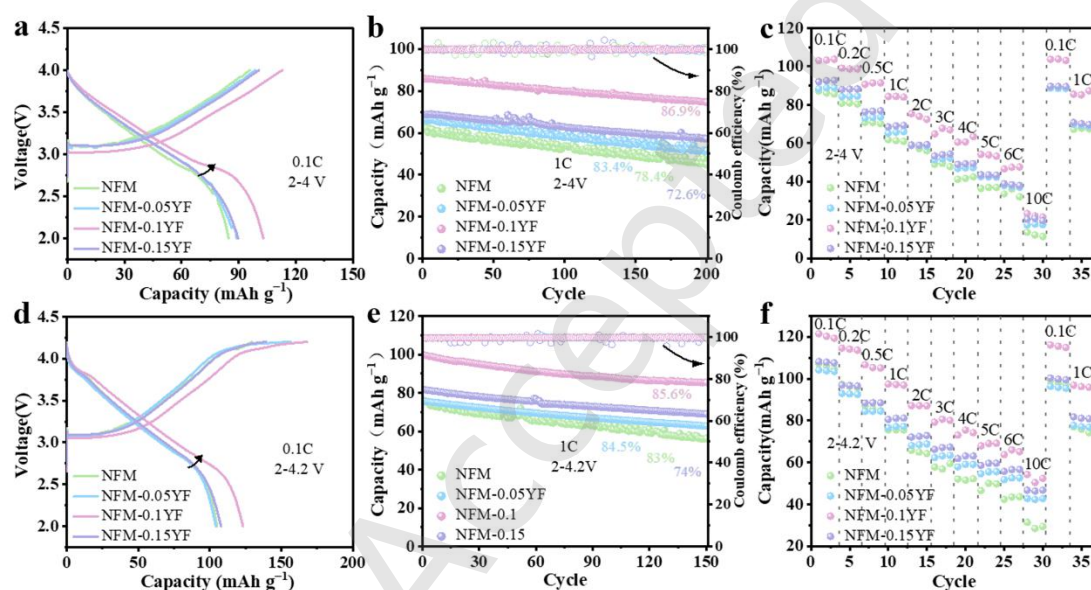


Fig. S7. Initial charge/discharge curves, cycling performance, and rate performance of the NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF samples: (a, b, c), 2.0-4.0 V, (d, e, f), 2.0-4.2 V.

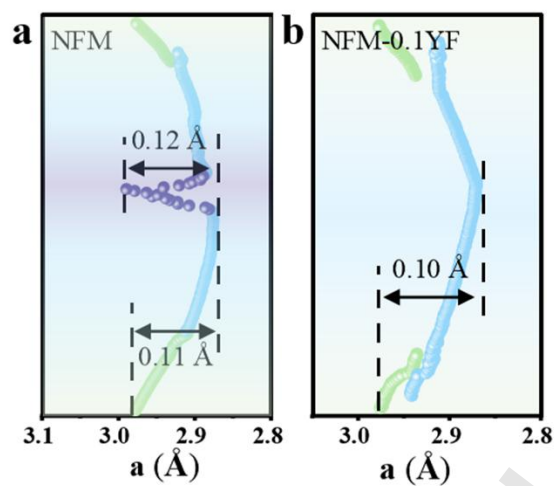


Fig. S8. The lattice parameter a for (a) NFM and (b) NFM-0.1YF during the initial cycle between 2.0 and 4.2 V at 0.1C.

2. Supporting tables

Table. S1 Summary of formation energies for Y doping into the Na, Ni, Fe, and Mn sites.

Structure	Formation energy (eV)
NFM-Na	5.00676
NFM-Ni	1.38055
NFM-Fe	2.30957
NFM-Mn	3.45737

Table. S2 ICP-MS results of NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF samples.

Samples	Measured mass ratio (wt%)				
	Na	Ni	Fe	Mn	Y
NFM	5.309	10.758	10.893	10.973	/
NFM-0.05YF	5.390	10.637	10.840	10.986	0.012
NFM-0.1YF	5.318	10.367	10.816	10.970	0.023
NFM-0.15YF	5.317	10.180	10.841	10.950	0.035

Table. S3 Rietveld refinement results of XRD data for NFM.

NFM

$$R_p = 3.19\%, R_{wp} = 4.02\%, \chi^2 = 2.39$$

Space group: R-3mh (03) $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

$$a = b = 2.98899 \text{ \AA}, c = 16.04558 \text{ \AA}, V = 122.555 \text{ \AA}^3$$

atom	x	y	z	occupancy
Na	0	0	0.5	1.0
Ni	0	0	0	0.3333
Fe	0	0	0	0.3333
Mn	0	0	0	0.3333
O	0	0	0.2678(4)	0.9993

Table. S4 Rietveld refinement results of XRD data for NFM-0.05YF.

NFM-0.05YF				
$R_p = 7.03\%$, $R_{wp} = 9.02\%$, $\chi^2 = 1.77$				
Space group: R-3mh (03) $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
$a=b=2.96863 \text{ \AA}$, $c=16.05781 \text{ \AA}$, $V=122.555 \text{ \AA}^3$				
atom	x	y	z	occupancy
Na	0	0	0.5	1.0
Ni	0	0	0	0.3329
Fe	0	0	0	0.3333
Mn	0	0	0	0.3333
O	0	0	0.2678(4)	0.9989
Y	0	0	0	0.0004
F	0	0	0.2678(4)	0.0011

Table. S5 Rietveld refinement results of XRD data for NFM-0.1YF.

NFM-0.1YF				
$R_p = 7.51\%$, $R_{wp} = 9.92\%$, $\chi^2 = 2.08$				
Space group: R-3mh (03) $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
$a=b=2.96904 \text{ \AA}$, $c=16.08035 \text{ \AA}$, $V=122.761 \text{ \AA}^3$				
atom	x	y	z	occupancy
Na	0	0	0.5	1.0
Ni	0	0	0	0.3326
Fe	0	0	0	0.3333
Mn	0	0	0	0.3333
O	0	0	0.2678(4)	0.9977
Y	0	0	0	0.0008
F	0	0	0.2678(4)	0.0023

Table. S6 Rietveld refinement results of XRD data for NFM-0.15YF.

NFM-0.15YF

$$R_p = 7.41\%, R_{wp} = 9.85\%, \chi^2 = 2.17$$

Space group: R-3mh (03) $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

$$a=b=2.96968 \text{ \AA}, c=16.08539 \text{ \AA}, V=122.852 \text{ \AA}^3$$

atom	x	y	z	occupancy
Na	0	0	0.5	1.0
Ni	0	0	0	0.3322
Fe	0	0	0	0.3333
Mn	0	0	0	0.3333
O	0	0	0.2678(4)	0.9966
Y	0	0	0	0.0011
F	0	0	0.2678(4)	0.0034

Table. S7 Relative percentage content of each valence state of Fe fine XPS spectra of samples NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF.

Sample	Fe 2p (at. %)			
	Fe ²⁺ 2p _{3/2}	Fe ³⁺ 2p _{3/2}	Fe ²⁺ 2p _{1/2}	Fe ³⁺ 2p _{1/2}
NFM	34.62	35.12	13.09	17.17
NFM-0.05YF	31.89	34.09	17.48	16.54
NFM-0.1YF	39.96	38.91	10.47	10.66
NFM-0.15YF	37.37	41.30	12.66	8.67

Table. S8 Relative percentage content of each valence state of Ni fine XPS spectra of samples NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF.

Sample	Ni 2p (at. %)			
	Ni ²⁺ 2p _{3/2}	Ni ³⁺ 2p _{3/2}	Ni ²⁺ 2p _{1/2}	Ni ³⁺ 2p _{1/2}
NFM	27.0	41.73	10.66	20.61
NFM-0.05YF	28.35	38.35	6.65	26.65
NFM-0.1YF	25.33	47.95	9.17	17.55
NFM-0.15YF	23.23	51.96	8.72	16.09

Table. S9 Relative percentage content of each valence state of Mn fine XPS spectra of samples NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF.

Sample	Mn 2p (at. %)			
	Mn ³⁺ 2p _{3/2}	Mn ⁴⁺ 2p _{3/2}	Mn ³⁺ 2p _{1/2}	Mn ⁴⁺ 2p _{1/2}
NFM	40.16	33.60	16.66	9.58
NFM-0.05YF	40.63	32.11	17.16	10.10
NFM-0.1YF	41.93	30.63	17.37	10.07
NFM-0.15YF	42.27	29.97	17.57	10.19

Table. S10 the average Bader charge of each element in NFM.

Elements	Average Bader Charge
O	-1.09
Na	0.84
Ni	0.87
Fe	1.42
Mn	1.72

Table. S11 The average Bader charge of each element in NFM-0.15YF.

Elements	Average Bader Charge
O	-1.12
Na	0.84
Ni	0.95

Fe	1.39
Mn	1.68
Y	2.09

Table. S12 Summary of the electrochemical performance of NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF.

Sample	Capacity Retention (%)		Average Operating Voltage		Rate Capability (mAh g ⁻¹) 2.0-		Energy Density (Wh kg ⁻¹) 2.0-4.2 V/2.0-4.0 V
	2.0-4.2 V/2.0-4.0 V		(V) 2.0-4.2 V/2.0-4.0 V		4.2 V/2.0-4.0 V		
	150th	200th	150th	200th	5C	10C	
NFM	67.3/78.4	-/71.8	2.62/2.58	-/2.49	94.53/84.68	70.21/63.76	130.08/99.74
NFM-0.05YF	73.9/81.4	-/77.5	2.77/2.61	-/2.55	103.83/101.2	85.50/77.79	131.06/99.12
NFM-0.1YF	80.0/90.7	-/88.9	2.93/2.82	-/2.78	116.24/105.21	97.84/84.60	132.72/98.91
NFM-0.15YF	76.2/88.3	-/83.3	2.83/2.77	-/2.70	111.12/103.59	92.70/82.34	131.32/97.31

Table. S13 Slope of the straight line fitted to the square root of the peak current (I_p) versus the scan rate ($v^{1/2}$) at O1 and R1 for NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF, respectively.

Sample	Slope	
	O1	R1
NFM	1.96052(0.04)	-1.21998(0.02488)
NFM-0.05YF	2.40949(0.06173)	-1.1726(0.059)
NFM-0.1YF	2.51225(0.08273)	-1.6245(0.04)
NFM-0.15YF	2.17349(0.09485)	-1.4581(0.0731)

Table. S14 The minimum and maximum values of D_{Na^+} for NFM, NFM-0.05YF, NFM-0.1YF, and NFM-0.15YF.

Sample	D_{Na^+} ($\text{cm}^2 \text{s}^{-1}$)	
	minimum values	maximum values
NFM	3.676×10^{-13}	5.451×10^{-11}
NFM-0.05YF	7.719×10^{-13}	6.242×10^{-11}
NFM-0.1YF	1.869×10^{-12}	1.270×10^{-10}
NFM-0.15YF	7.991×10^{-13}	8.439×10^{-11}

Table. S15 The values of R_s , R_{sf} , and R_{ct} for NFM, NFM-0.05YF, NFM-0.1YF and NFM-0.15YF electrodes after 3rd and 150th cycles at 1 C

Sample	R_s		$R_{sf} \Omega^{-1}$		$R_{ct} \Omega^{-1}$	
	3 rd	150 th	3 rd	150 th	3 rd	150 th
NFM	3.75	4.5	516.65	610.5	1669.7	2849.5
NFM-0.05YF	3.57	4.07	474.73	530.93	1691.4	2275.0
NFM-0.1YF	3.46	4.06	329.54	339.94	1757.1	2086.4
NFM-0.15YF	3.88	4.3	398.12	442.5	1788.5	2153.5

Table. S16 ICP-MS results of the Mn contents in the NFM and NFM-0.1YF electrodes after 150 cycles at 1 C within a voltage range of 2.0–4.2 V.

Samples	Measured mass ratio (wt%)
	Mn
NFM	8.253
NFM-0.01F	9.871

Table. S17 Rietveld refinement results for the lattice parameters a and c, and unit cell volume V of the OP2 phase formed in NFM under high voltage.

NFM		
OP2 phase lattice parameter a ($\text{\AA}$)	OP2 phase lattice parameter c ($\text{\AA}$)	OP2 phase unit cell volume ($\text{\AA}^3$)
2.9074	17.1177	122.58364
2.92235	17.077	122.4739
2.92267	16.9132	122.31509
2.93283	16.9147	122.04705

2.93829	16.8583	121.43945
2.95569	16.613	120.7369
2.9481	16.413	120.53805
2.9632	16.386	120.27564
2.97884	16.051	120.74175
2.98968	16.191	121.00715
2.9408	16.317	121.68025
2.92051	16.51188	122.12025
2.9074	16.632	122.65362
2.90235	16.734	122.76237
2.89267	17.06447	122.88675
2.89283	17.08366	122.96571
2.8892	17.08583	122.9717
