

Oxidation-Induced Directional Iron Exsolution Awakens Interfacial Kinetics in Non-Stoichiometric Polyanion Cathodes

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Abstract

Non-stoichiometric polyanion cathodes possess intrinsically favorable bulk-ion-diffusion potential, yet they often remain trapped in a kinetically dormant state. Using non-stoichiometric sodium iron phosphate (NFP) as a model system, we introduce mild thermal oxidation as a thermodynamic perturbation strategy. This treatment drives the directional exsolution of high-energy lattice Fe species toward the particle surface. Analysis of this reconstruction process reveals the underlying origin of the sluggish electrochemical response: the kinetic limitation does not arise primarily from the bulk framework, but rather from local Na/Fe antisite defects at the interface, which impose severe steric obstruction and kinetic barriers and thereby block trans-phase ion-transport pathways. Fe exsolution effectively removes these cationic blockages and simultaneously reconstructs a conductive interfacial network enriched in mixed-valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ species and vacancies. By eliminating the interfacial mass-transfer bottleneck, the intrinsic solid-solution Na-storage capability of the framework is released, delivering an initial discharge capacity of 130 mAh g^{-1} . This work elucidates a microscopic mechanism for actively reconstructing local defects through thermodynamic regulation and provides new interfacial-kinetic insight into activating the intrinsic electrochemical activity of metastable frameworks.

1. Introduction

Sodium-ion batteries (SIBs) have attracted extensive attention as promising alternatives for large-scale energy storage because of the natural abundance and cost advantages of sodium resources [1–4]. Among the various candidate cathode materials, polyanion frameworks, particularly sodium iron phosphates such as NaFePO_4 , are highly attractive because of their excellent structural stability, intrinsic thermal safety, and reliance on earth-abundant Fe [5–8]. However, the thermodynamically stable maricite phase possesses a compact crystal structure without continuous Na^+ diffusion pathways, rendering it nearly electrochemically inactive [9, 10]. Although metastable olivine or amorphous phases can provide accessible ion-percolation pathways, their synthesis generally relies on complex topotactic ion exchange or demanding nanostructure engineering, which presents substantial challenges for large-scale implementation [11–14]. Considerable efforts have also been devoted to directly overcoming the electrochemical inertness of conventional maricite through extreme nanosizing or heteroatom doping [10, 15–17]. Nevertheless, such approaches remain highly dependent on elaborate external structural engineering. In contrast, breaking the conventional 1:1:1 stoichiometric constraint through non-stoichiometric lattice design provides an intrinsically driven route for unlocking the Na-storage potential of this material family.

As pioneering examples of this strategy, Lu et al. [18] first developed $\text{Na}_{2/3}\text{Fe}_{1.33}\text{PO}_4$, followed by the report of another Fe-rich non-stoichiometric phase, $\text{Na}_{0.71}\text{Fe}_{1.07}\text{PO}_4$, by Zhu et al. [19]. Liu et al. [20] further demonstrated that the Na-storage capability of such frameworks can be released through specific electrochemical activation. Although crystallographic evidence indicates that non-stoichiometric design fundamentally reshapes the bulk topology and establishes continuous internal ion-diffusion networks, these materials exhibit strikingly different macroscopic kinetics. Frameworks synthesized

under strictly inert or reducing conditions, such as that reported by Lu et al. [18], retain intrinsic Na-storage capability but remain deeply kinetically dormant, exhibiting severe polarization, limited capacity utilization, and strongly hindered solid-state mass transport at high rates [18]. By contrast, frameworks subjected to specific chemical or electrochemical modulation, including the strong $\text{K}_2\text{S}_2\text{O}_8$ -induced oxidative desodiation reported by Zhu et al. [19] and the activation process described by Liu et al. [20], display excellent high-rate performance.

The pronounced performance disparity among materials with similar bulk topological characteristics points to a critical hidden mechanism: constructing continuous bulk diffusion pathways is necessary, but not sufficient, for achieving high electrochemical activity. We hypothesize that the intrinsic solid-solution reaction potential of these non-stoichiometric frameworks is largely governed by a gatekeeping effect associated with the local cation configuration at the interface. In battery materials, transition-metal ions are prone to antisite occupation at interfaces, where they occupy alkali-metal sites and act as physical plugs that obstruct ion-diffusion pathways [21–24]. We therefore propose that the key gatekeeping mechanism underlying the kinetic dormancy of these frameworks originates from local Na/Fe antisite blocking, which establishes a high mass-transfer barrier at the solid-liquid interface and severely suppresses the intrinsic solid-solution reaction kinetics of the bulk framework.

The pioneering work of Zhu et al. [19] clearly demonstrated the macroscopic effectiveness of a strongly oxidative environment in activating the electrochemical response of such frameworks. However, intense global chemical desodiation not only alters the bulk composition but can also induce substantial surface reconstruction. Consequently, the critical contribution of interfacial kinetics becomes obscured: is the dramatic enhancement in electrochemical activity caused by removal of interfacial antisite blocking, or by the formation of new surface phases after extensive desodiation? In previous strong-oxidation strategies, changes in bulk composition, transition-metal valence, and surface structure were strongly coupled, leaving the true microscopic origin of the activation process unresolved.

To decouple these effects while avoiding the structural damage associated with severe oxidation, we introduce a highly spatially selective mild surface oxidation strategy that preserves the integrity of the bulk framework. Combined experimental characterization and theoretical calculations show that mild surface oxidation selectively induces mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ valence states and local cation vacancies within the outermost surface region while largely preserving the lattice framework. This highly localized chemical reconstruction thermodynamically reorganizes the interfacial cation configuration and effectively dismantles the Na/Fe antisite-blocking bottleneck.

2. Experimental Section

2.1 Synthesis of the Sodium Iron Phosphate Cathode Material

A non-stoichiometric sodium iron phosphate precursor was synthesized via a solvothermal route. Sodium phosphate (10 mmol) and ferrous chloride (10 mmol) were used as the Na/P source and Fe source, respectively, and 1.67 mmol of ascorbic acid was added as a reducing agent to suppress spontaneous oxidation of Fe^{2+} . The reagents were dissolved in a mixed solvent of ethylene glycol and deionized water with a volume ratio of 3:1 and magnetically stirred at room temperature for 30 min to form a homogeneous solution. The initial nominal Na:Fe:P molar ratio was 3:1:1. A Na-rich feed composition combined with a nonequilibrium coprecipitation process was used to capture a Na-deficient, Fe-rich metastable framework. The solution was then transferred into a Teflon-lined autoclave and maintained at 160°C for 6 h. After natural cooling, the precipitate was collected by centrifugation, alternately washed three times with deionized water and absolute ethanol, and finally vacuum-dried at 60°C for 8 h under an absolute pressure of ≤ 0.1 MPa. The resulting gray-green powder was denoted NFP.

2.2 Mild Oxidation Treatment of Sodium Iron Phosphate

The as-prepared NFP powder was evenly spread in a quartz boat and placed in a tube furnace for mild thermal oxidation under flowing air. The samples were heated at 5°C min⁻¹ to 350, 400, or 450°C, held at the target temperature for 10 min, and then naturally cooled to room temperature in the furnace. The products obtained at the different treatment temperatures were denoted NFP-350, NFP-400, and NFP-450, respectively.

2.3 Physical and Chemical Characterization

The crystal structure and phase composition were examined by X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 1.541$ Å). The morphology and aggregation state of the samples were characterized by field-emission scanning electron microscopy (FESEM). Surface elemental chemical states and valence distributions were analyzed by X-ray photoelectron spectroscopy (XPS), with all binding energies calibrated against the C 1s peak at 284.8 eV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to quantitatively determine the actual Na, Fe, and P stoichiometry of the materials.

2.4 Electrode Preparation and Electrochemical Measurements

The active material (NFP or the oxidized samples), acetylene black, and poly(vinylidene fluoride) (PVDF) binder were mixed at a mass ratio of 7:2:1. After thorough grinding, the powder mixture was dispersed in N-methyl-2-pyrrolidone (NMP) and magnetically stirred for 8 h to form a homogeneous slurry, which was subsequently coated onto Al foil current collectors. The electrodes were vacuum-dried at 120°C for 6 h and punched into 14 mm-diameter disks. CR2025-type half-cells were assembled in an Ar-filled glovebox with H₂O and O₂ concentrations below 1 ppm. Sodium metal served as both the counter and reference electrode, glass-fiber filter paper was used as the separator, and the electrolyte was 1 M NaClO₄ dissolved in an EC/PC mixture (1:1 by volume) containing 5 vol% fluoroethylene carbonate (FEC). The cells were rested for 48 h before testing. Galvanostatic charge-discharge and rate-capability measurements were performed using a battery testing system. Cyclic voltammetry (CV) at a scan rate of

0.1 mV s⁻¹ and electrochemical impedance spectroscopy (EIS) over a frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 5 mV were conducted on an electrochemical workstation.

2.5 DFT Calculations

First-principles calculations based on density functional theory (DFT) were performed using the Vienna Ab initio Simulation Package (VASP) [25, 26]. The exchange-correlation energy was described using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [27]. The strong correlation of Fe 3d electrons was treated using the GGA + U approach with an effective Hubbard U value of 4.3 eV for Fe [28]. The interaction between ionic cores and valence electrons was described using the projector-augmented-wave (PAW) method [29], and the plane-wave cutoff energy was set to 520 eV. An olivine-type NaFePO₄ structure was adopted, and a six-layer slab model was constructed along the (010) surface. The bottom two atomic layers were fixed, whereas the remaining atoms were fully relaxed. A 10 Å vacuum layer was introduced to eliminate spurious interactions between periodic images. A 2 × 2 × 1 k-point mesh was used to sample the Brillouin zone. Structural relaxations were considered converged when the total-energy change was below 10⁻⁵ eV and the residual forces were below 0.02 eV Å⁻¹. The formation energy of the Fe/Na antisite defect was determined from the energy difference between the defective system and the pristine surface model.

3. Results and Discussion

3.1 Suppression Followed by Activation: Capture and Spatially Selective Reconstruction of a Metastable Framework

To investigate the crystal structure of the as-prepared NFP, XRD characterization was first performed. As shown in Fig. 1a, the diffraction pattern of NFP was compared with those of conventional maricite (PDF#01-071-5040) and standard olivine (PDF#01-079-6973). Several diffraction features of NFP show clear similarities to those of the known phases. For example, a group of medium-to-strong reflections in the 27°-37° range, particularly those near 32°, 33.5°, and 35°, together with the characteristic reflection near 17°, substantially overlap with corresponding reflections of the two reference phases. These coincident crystallographic features indicate that NFP shares certain local structural motifs with both phases, particularly similar connectivity among PO₄ tetrahedra and FeO₆ octahedra.

Nevertheless, the overall diffraction pattern demonstrates that NFP is neither a simple physical mixture nor a topological variant of the two known phases, but instead represents a distinct phase. Although maricite exhibits a reflection near 29.5°, this peak becomes the most intense reflection in NFP, indicating a fundamental change in relative intensity. In addition, NFP displays new low-angle reflections near 12° and 15° that are absent from both reference phases. These crystallographic features rule out a simple multiphase mixture.

To further interpret these unusual diffraction features, the NFP pattern was systematically compared with complex phase structures reported previously. It should be noted that different X-ray sources were used in earlier studies of related phases: Lu et al. [18] used Co radiation ($\lambda = 1.789 \text{ \AA}$), Liu et al. [20] used Mo radiation ($\lambda = 0.711 \text{ \AA}$), whereas Zhu et al. [19], consistent with the present work, used Cu radiation ($\lambda = 1.541 \text{ \AA}$). To eliminate systematic wavelength-dependent discrepancies during direct comparison, the diffraction data reported in these studies were converted to interplanar spacings (d values) according to Bragg's law. The analysis confirms that the fundamental diffraction characteristics of the present NFP closely match the Fe-rich large-cell superstructure reported in the literature, indicating an enlarged spatial periodicity of the NFP lattice. Combined with the actual composition determined by ICP analysis (Fig. 1b), these results establish that the synthesized NFP is a new non-stoichiometric metastable phase, $\text{Na}_{0.81}\text{Fe}_{1.06}\text{PO}_4$, containing abundant cation vacancies and local structural modulation.

After establishing the bulk crystal-structure characteristics, the morphology of the metastable precursor was further examined by scanning electron microscopy (SEM). As shown in Fig. 1c-1e, the pristine NFP particles predominantly consist of uniform short-rod or thick-plate-like nanostructures. High-magnification images show that the primary particles are approximately 200–500 nm in length and only 50–100 nm in radial thickness. Such nanoscale dimensions not only increase the effective contact area between the electrode material and electrolyte and provide abundant interfacial charge-transfer sites, but also restrict the maximum solid-state ion-transport distance from a geometric perspective. This morphology therefore provides a favorable physical basis for rapid Na^+ -storage kinetics [6, 12].

Given the oxidation sensitivity of Fe^{2+} in this Fe-rich metastable framework, a mild thermal oxidation strategy was introduced to explore the structural-evolution boundary under thermodynamic perturbation and to identify an optimal modulation window that preserves the lattice framework. As shown in Fig. 2a, thermal treatment produces a pronounced powder-color change from the original gray-green to reddish brown, providing a macroscopic indication of surface oxidation and the formation of iron-oxide or oxide-like species. XRD analysis (Fig. 2b) shows that, as the treatment temperature increases from 350 to 450°C, the low-angle characteristic reflections of NFP gradually weaken, while the main reflection near 29.5° continuously shifts toward higher diffraction angles. According to Bragg's law, this evolution indicates lattice contraction during thermal oxidation. A weak diffuse response also appears in the 2θ range of 20°–32°. Notably, despite the pronounced macroscopic color change, no sharp diffraction peaks attributable to crystalline iron oxides such as Fe_2O_3 are detected even after treatment at 450°C. The combination of macroscopic discoloration and the absence of new crystalline reflections, together with the weak diffuse scattering, strongly suggests the formation of an amorphous iron-oxide layer during oxidation. Thermal oxidation therefore drives the material toward a distinctive core-shell-type composite structure.

SEM characterization of the samples after oxidation at different temperatures (Fig. 3) was used to further evaluate their morphological stability during thermal treatment. Relative to the pristine material, the samples treated at 350°C (Fig. 3a,b) and 400°C (Fig. 3c,d) largely retain the original short-rod morphology and nanoscale dimensions without obvious grain coarsening, thereby preserving the

physical mass-transport network favorable for electrochemical reactions. When the treatment temperature reaches 450°C (Fig. 3e,f), the overall particle framework remains largely intact without extensive melting or deformation; however, the particle edges become noticeably blunted and slight local sintering and interparticle adhesion begin to appear.

To directly visualize the spatial character of the oxidation-induced reconstruction, TEM, HRTEM, and STEM-EDS analyses were performed on pristine NFP and NFP-400 (Fig. 4). Pristine NFP retains the anisotropic plate-/short-rod-like morphology observed by SEM (Fig. 4a,b). At higher magnification (Fig. 4c,d), well-resolved lattice fringes remain continuous and comparatively uniform from the particle interior toward the outer boundary, indicating a largely homogeneous crystalline environment before thermal oxidation. The HAADF-STEM image and elemental maps (Fig. 4e-j) further show that Na, Fe, O, and P are broadly co-distributed over the analyzed particles without obvious large-scale elemental segregation. After mild oxidation, NFP-400 preserves the overall particle morphology (Fig. 4k,l), consistent with the XRD and SEM results showing that the bulk framework is not catastrophically reconstructed. A distinct difference, however, emerges in the near-surface lattice contrast. In the HRTEM images of NFP-400 (Fig. 4m,n), clear and periodic lattice fringes are still visible in the inner region, whereas the fringes progressively lose contrast and coherence on approaching the particle surface, producing a more diffuse and structurally disordered outer region. This interior-to-surface crystallinity gradient provides direct microscopic evidence that the structural response to mild oxidation is spatially localized rather than homogeneous throughout the particle. Importantly, this observation should not be interpreted as complete amorphization of NFP-400: the crystalline core remains clearly retained, while only the outermost region exhibits reduced long-range order. When considered together with the increased Fe³⁺ contribution and Fe-O signature revealed by XPS, as well as the absence of sharp diffraction peaks from crystalline iron oxides in XRD, the blurred near-surface lattice is consistent with the formation of an ultrathin, poorly crystalline/amorphous Fe-rich oxide-like reconstructed interphase. Meanwhile, the STEM-EDS maps of NFP-400 (Fig. 4o-t) still exhibit broadly uniform Na, Fe, O, and P distributions at the mapping length scale, indicating that the oxidation treatment does not induce macroscopic phase separation. Such a surface-confined disordered region can provide additional local free volume and a less geometrically constrained interfacial environment, which is compatible with the proposed removal of subsurface Fe-related blocking and the facilitated Na⁺ transport across the particle/electrolyte interface while preserving the crystalline Na-storage framework in the interior.

3.2 Surface Chemical-State Modulation and Release of Electrochemical Kinetics

To elucidate how mild thermal oxidation modulates the surface chemical environment, comprehensive XPS analyses were performed on pristine NFP and NFP-400 (Fig. 5). The survey spectra (Fig. 5a) confirm the presence of Na, Fe, P, O, and C in both samples. More importantly, the high-resolution spectra reveal substantial chemical-state reconstruction within the outermost surface region. The most pronounced evolution occurs in the Fe valence state. The Fe 2p spectrum of pristine NFP (Fig. 5b) is dominated by

Fe²⁺-related features, whereas NFP-400 retains Fe²⁺ while exhibiting markedly enhanced Fe³⁺ features at higher binding energies of 713.7 and 725.8 eV. This partial oxidation is further corroborated by the Fe 3s spectra (Fig. 5c): pristine NFP exhibits a multiplet splitting of approximately 5.6–5.7 eV, characteristic of Fe²⁺, whereas NFP-400 displays an additional splitting of 6.5 eV, a fingerprint of high-spin Fe³⁺ [30].

In addition to oxidation of the Fe centers, the local environments of the coordinating anions and framework atoms undergo pronounced changes. The O 1s spectra (Fig. 5d) show the conventional lattice-oxygen component at approximately 531.0 eV and a higher-binding-energy contribution at approximately 532.8 eV associated with surface-adsorbed and/or defect-related species. More importantly, a strong Fe-O bonding feature emerges at 529.7 eV [31]. This characteristic metal-oxide lattice-oxygen signal strongly suggests that mild thermal oxidation induces substantial chemical reconstruction in the outermost surface region, with a fraction of Fe departing from its original phosphate coordination environment and forming an Fe³⁺-rich iron-oxide or oxide-like interfacial layer in situ. This surface atomic rearrangement also affects the phosphate framework. As shown in Fig. 5e, the main P 2p envelope of NFP-400 broadens markedly toward higher binding energies and can be deconvoluted into additional features at 134.8 and 135.9 eV. These features indicate local structural distortion and redistribution of electron density within interfacial phosphate groups accompanying the oxidative segregation of surface Fe, potentially involving the formation of Fe-deficient polyphosphate-like environments. Together with the slight shift of the Na 1s peak toward lower binding energy from 1071.2 to 1071.0 eV (Fig. 5f), the XPS results collectively demonstrate that moderate thermal oxidation induces heterogeneous surface reconstruction in NFP-400, producing an interfacial layer enriched in Fe³⁺ species and structural defects.

The reconstructed surface chemical state produces a pronounced macroscopic activation of Na-storage kinetics (Fig. 6a,b). At a current density of 15.5 mA g⁻¹ (Fig. 6a), pristine NFP remains trapped in an interfacial kinetic lock, delivering an initial discharge capacity of only approximately 70 mAh g⁻¹ followed by continuous capacity decay. By contrast, optimally activated NFP-400 exhibits markedly enhanced Na-storage activity, with the initial discharge capacity increasing to approximately 130 mAh g⁻¹ and approximately 105 mAh g⁻¹ retained after 100 cycles. Considering that the Fe-rich defective layer induced by mild thermal oxidation is spatially confined to the outermost surface region, such a substantial increase in accessible capacity demonstrates that reconstruction of the surface microenvironment removes the interfacial ionic lock and releases the otherwise inaccessible bulk Na-storage potential of the NFP lattice. Surface modulation also markedly improves rate capability (Fig. 6b). When the current density is stepwise increased from 15.5 to 310 mA g⁻¹, NFP-400 maintains superior capacity retention, and the capacity nearly fully recovers when the current is returned to the initial value, indicating excellent structural resilience under high-rate perturbation.

To distinguish the Na-storage mechanism and polarization evolution before and after activation, the dynamic electrochemical response was systematically tracked (Fig. 6c-5h). The cyclic-voltammetry response first reveals a fundamental change in the electrochemical reaction behavior. Pristine NFP (Fig. 6c) exhibits a very weak current response and strongly hysteretic redox features, indicating severely

restricted interfacial charge transfer. This behavior directly reflects the kinetically dormant state originally reported for this class of materials by Lu et al. [18]. In sharp contrast, the CV envelope of NFP-400 (Fig. 6d) expands dramatically and evolves into a broad, continuous, slope-like response without sharp phase-transition features. This broadened response is highly consistent with an efficient solid-solution reaction mechanism in the non-stoichiometric framework promoted by abundant surface defects. From a kinetic perspective, it also provides a direct macroscopic manifestation of rapid charge exchange once the continuous bulk ion-transport network is released from the interfacial barrier.

Further dQ/dV analysis quantitatively reveals the evolution of reaction kinetics during prolonged cycling. The redox features of pristine NFP (Fig. 6e) are weak and decay markedly with cycling. By contrast, NFP-400 (Fig. 6f) exhibits substantially improved reaction kinetics and excellent cycling reversibility. Apart from a modest first-cycle variation associated with irreversible interfacial wetting and initial structural reconstruction, the dQ/dV curves at the 30th, 60th, and 100th cycles nearly overlap, with highly consistent peak positions and response intensities. This high degree of electrochemical fidelity indicates that the amorphous iron-oxide layer constructed by surface exsolution remains robust during cycling and functions as an electrochemically active interfacial layer that facilitates ion transport while stabilizing the bulk framework.

Under stepwise high-current perturbation, the dQ/dV profiles further reveal the origin of the reduced polarization (Fig. 6g,h).

For pristine NFP (Fig. 6g), the main redox feature rapidly shifts toward higher potential and broadens substantially, highlighting the large mass-transfer resistance at the solid-liquid interface. NFP-400 (Fig. 6h), however, exhibits distinctly improved resistance to polarization. As the current density increases to 155 and then 310 mA g⁻¹, its initially sharper redox features gradually evolve into broad, continuous response bands. The flattening of the dQ/dV profiles at high rates indicates a highly linear correspondence between voltage and capacity during charge/discharge. This macroscopic electrochemical behavior is consistent with the solid-solution reaction mechanism observed by Zhu et al. [19] using operando XRD and further reflects the ability of efficient interfacial kinetics to unlock a continuous solid-solution response under extreme ion flux. These results demonstrate that localized chemical reconstruction effectively removes the ion-transport bottleneck and broadly releases the kinetic potential of the framework.

Consistent with the reconstructed surface chemical state, the interfacial kinetics are markedly improved, as further evidenced by EIS. In addition to optimized interfacial charge transfer, the low-frequency impedance response reveals enhanced ion-diffusion kinetics. The Nyquist plots before and after cycling are shown in Fig. 7a,b. In the high-frequency region, the semicircle diameter reflects the charge-transfer resistance (R_{ct}) at the solid-liquid interface. Before cycling, pristine NFP exhibits an R_{ct} of approximately 380 Ω , whereas the polarization semicircle of NFP-400 is markedly contracted, corresponding to an R_{ct} of approximately 260 Ω . The large initial charge-transfer resistance of pristine NFP provides a physicochemical explanation for why similar metastable frameworks in the work of Liu et al. [20]

required prolonged electrochemical cycling and strong electric-field driving to passively overcome the interfacial barrier. By contrast, the substantially lower initial R_{ct} of NFP-400 demonstrates that mild thermal oxidation acts as a pre-activation treatment that proactively removes the mass-transfer bottleneck and reduces the dependence on field-driven activation. After prolonged cycling (Fig. 7b), the impedance of both electrodes increases, but the R_{ct} of NFP-400 (approximately 450 Ω) remains substantially lower than that of pristine NFP (approximately 600 Ω), indicating that the modified interface alleviates charge-transfer resistance and maintains improved cycling stability. In the low-frequency region, NFP-400 also exhibits a steeper Warburg response than pristine NFP. According to classical electrochemical impedance theory, changes in the low-frequency Warburg response reflect changes in solid-state ion-diffusion kinetics [32]. This result suggests that local vacancies introduced by surface treatment may improve continuity of the internal lattice transport pathway and thereby enhance Na^+ diffusion within the bulk material.

The Bode phase-angle plots (Fig. 7c-f) provide complementary evidence for the precision and mildness of the surface-reconstruction strategy. Although the Nyquist plots show clear differences in absolute impedance, the Bode phase-angle responses of NFP and NFP-400 substantially overlap, with the characteristic relaxation maxima remaining near 1000 Hz and no additional time constants or pronounced peak shifts observed. In general, formation of a thick, inert surface byproduct layer, such as an excessively thick passivation film, would introduce additional phase-angle/time-constant features in the Bode response [33]. The absence of such features indicates that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ -rich amorphous oxide composite interphase generated by mild oxidation does not behave as an inert dead layer. Instead, the amorphous structure, with its abundant free volume and isotropic transport pathways, preserves the intrinsic charge-relaxation behavior while acting as an active ion/electron transport network that substantially lowers the energetic barrier for Na^+ transfer across the solid-liquid interface. Overall, this in situ formed amorphous composite interphase, together with improved transport through the internal lattice, provides microscopic kinetic support for the excellent high-rate performance.

To determine whether the interfacial reconstruction induced by mild oxidation continues to influence the electrode after prolonged electrochemical operation, post-cycling XPS was further performed on NFP-400 and pristine NFP (Fig. 8). Panels (a–h) correspond to the performance-enhanced NFP-400 electrode, whereas panels (i–p) correspond to pristine NFP. The P 2p and O 1s spectra of the two electrodes remain highly similar after cycling, indicating that the phosphate framework and the dominant lattice-oxygen environment are largely preserved. In contrast, pronounced differences are observed in the interfacial decomposition products. The F 1s spectra show that NaF remains the dominant fluorinated CEI component in both electrodes, while its relative contribution decreases from approximately 81.9% in pristine NFP to 73.0% in NFP-400, accompanied by an increase in C–F-related species from approximately 18.1% to 27.0%. NaF, C–F species, sodium carbonates, and organic carbonate-derived species have been widely identified as characteristic constituents of cathode–electrolyte interphases in sodium-ion batteries containing carbonate electrolytes and FEC additives [34, 35]. Consistently, the high-binding-energy carbonate/ $\text{O}-\text{C}=\text{O}$ /PVDF- CF_2 -related contribution in C 1s increases from approximately 2.9% to 6.6% after mild oxidation. Importantly, previous studies have demonstrated that the surface

chemistry and exposed atomic environment of polyanionic cathodes can directly regulate the adsorption and decomposition of FEC and ClO_4^- species, thereby altering the chemical composition of the subsequently formed CEI [34]. Thus, the present results suggest that the preconstructed surface state of NFP-400 modifies the subsequent electrolyte-decomposition pathway rather than simply increasing the total amount of CEI. More importantly, under identical fitting constraints, the post-cycling Fe 2p spectrum of NFP-400 exhibits a stronger low-binding-energy Fe^{2+} -associated contribution than pristine NFP. $\text{Fe}^{2+}/\text{Fe}^{3+}$ constitutes the principal redox couple of NaFePO_4 , and in situ X-ray absorption studies have directly demonstrated the reversible evolution of Fe valence during Na^+ extraction and reinsertion [36]. The Fe 2p binding-energy assignment is also consistent with previous XPS studies of NaFePO_4 , in which the lower-binding-energy Fe 2p components were attributed predominantly to Fe^{2+} species [37]. Considering that the initial thermal treatment partially oxidizes surface Fe^{2+} to Fe^{3+} , the recovery of a more Fe^{2+} -like state after cycling suggests that the reconstructed Fe-rich interphase remains electrochemically responsive rather than behaving as an inert oxidized layer. Provided that the two electrodes were harvested at the same terminal electrochemical state, this behavior is consistent with more complete $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox and Na^+ reinsertion in NFP-400. These post-cycling results therefore provide complementary evidence that directional Fe exsolution and the removal of subsurface Na/Fe antisite blocking exert a persistent influence on both interfacial chemistry and reaction reversibility.

The long-term structural integrity of the optimized electrode was further evaluated by post-cycling SEM (Fig. 9). Across progressively higher magnifications (Fig. 9a-d), the cycled NFP-400 electrode maintains a continuous and densely packed surface in which the active-material layer remains well interconnected. Although several micrometer-scale cracks are visible over the electrode surface, no extensive delamination, large-area peeling, or severe pulverization-induced void formation is observed. Such cracks are commonly associated with drying, electrode handling, and accumulated mechanical stress in composite electrodes and therefore should not by themselves be interpreted as catastrophic failure of the active material. More importantly, the high-magnification images show that the material surrounding the cracks remains compact and densely assembled rather than collapsing into isolated fragments. The preservation of a coherent electrode architecture after prolonged cycling is consistent with the stable capacity retention and the highly reproducible dQ/dV response of NFP-400. Together with the post-cycling XPS results, these observations indicate that the surface reconstruction generated by mild oxidation does not evolve into a mechanically destructive or highly porous interphase during cycling. Instead, the NFP-400 electrode retains an integrated particle/conductive-network contact at the electrode scale, supporting the view that the reconstructed surface layer can accommodate repeated Na^+ insertion/extraction while maintaining the structural continuity required for sustained ion/electron transport. Thus, the post-cycling morphology provides complementary evidence that the kinetic activation achieved by mild oxidation is accompanied by robust electrode-level structural stability rather than being obtained at the expense of mechanical integrity.

3.3 Mechanistic Origin: Directional Fe Exsolution and Thermodynamic Removal of Interfacial Blocking

To identify the fundamental origin of the kinetic limitation in pristine NFP, density functional theory calculations were performed (Fig. 10). As discussed above, NFP is a non-stoichiometric large-cell superstructure containing abundant internal defects. Because the real lattice contains substantial long-range disorder, direct full-scale atomistic modeling would introduce excessive variables and obscure the central mechanism. Nevertheless, unlike dense and electrochemically inactive conventional maricite, the NFP investigated here exhibits clear intrinsic activity, implying the presence of continuous Na^+ diffusion pathways within the framework. To isolate the core physical picture of how Fe ions obstruct these transport channels, the influence of long-range disorder was intentionally removed and a classical olivine configuration with well-defined one-dimensional diffusion channels was selected as a thermodynamic probe model. This locally simplified structural model allows the intrinsic migration tendency and thermodynamic preference of interfacial Fe species to be quantitatively evaluated.

Within this theoretical reference model, isolated Na/Fe antisite defects were introduced into the ideal lattice to mimic local cation occupation in the Fe-rich system. As shown in Fig. 10a, extending the truncated surface model from the bulk toward the outermost layer produces a gradient lattice expansion, with the interlayer spacing increasing from 3.14 to 3.36 Å. The accompanying increase in free volume caused by surface relaxation disrupts the local chemical-potential balance within the lattice. The calculated defect-formation energies (Fig. 10b) reveal the thermodynamic consequence of this structural evolution: for each Na layer, the Fe species most favorable for Na/Fe exchange consistently originates from the site below the Na layer (site 6, i.e., Fe below Na layer). This repeated thermodynamic preference for Fe to move upward from the underlying Fe layer into the Na channel indicates an intrinsic driving force for directional Fe segregation toward the surface. However, as surface stress is released, the defect-formation energy does not reach its minimum at the outermost layer (Layer 1); instead, a V-shaped energy trap emerges in the subsurface region (Layer 2). Thus, under reducing conditions in pristine NFP, Fe species with an intrinsic segregation tendency cannot readily reach the outermost surface and are prone to becoming trapped in the subsurface region. These retained Fe ions physically occupy the Na^+ insertion/extraction exits, creating an interfacial channel-blocking effect and leading to severe kinetic sluggishness in pristine NFP.

External chemical driving through thermal oxidation is therefore critical for overcoming this energetic barrier. Although EDS elemental mapping (Fig. 10c-f) confirms that the overall frameworks of all treated samples remain stable and that the elements are macroscopically homogeneous, compositional comparison reveals a subtle interfacial evolution. ICP-OES, which reflects the average bulk composition, gives an overall Fe/P mass ratio of 1.916, whereas local EDS mapping of the particle-surface region shows that this ratio increases to 2.021 near the surface of optimally activated NFP-400. This difference provides initial experimental evidence for directional Fe migration toward the outermost surface. Together with the mixed-valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxide layer observed by surface-sensitive XPS, these results strongly support the occurrence of an Fe-exsolution process.

Combining the experimental results with DFT analysis suggests the following mechanism. Mild thermal treatment at 400°C provides the kinetic activation required to overcome the subsurface V-shaped energy

barrier, while the oxidizing surface environment establishes a strong thermodynamic chemical-potential gradient. The coupled effects of heat and oxygen drive the high-energy Fe ions trapped near the subsurface channel exits to follow their intrinsic segregation tendency and exsolve toward the outermost surface. This process not only converts the channel-blocking Fe species into the mixed-valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxide layer observed by XPS, but also leaves abundant cation and oxygen vacancies in situ. Through this microscopic exsolution-driven reconstruction, interfacial antisite blocking is effectively removed without disrupting the bulk framework.

Spontaneous segregation of transition-metal cations such as Ni, Co, and Mn toward outer surfaces, driven by surface energy and local chemical-potential differences, has been reported in layered cathodes as well as in classical LiFePO_4 systems [38–41]. The directional Fe exsolution revealed here in Fe-rich NFP therefore suggests that thermodynamic-gradient-driven interfacial cation reconstruction may represent a broadly applicable physical phenomenon.

More importantly, the interfacial ion-blocking mechanism established in this work resolves a hidden variable underlying the long-standing discrepancy in macroscopic performance among non-stoichiometric NFP systems. In the pioneering study by Lu et al. [18], the synthesized framework possessed intrinsic Na-storage capability but remained strongly kinetically dormant. The present results suggest that conventional bulk-sensitive characterization techniques, such as XRD and Mössbauer spectroscopy, cannot readily detect local chemical states in the outermost surface and subsurface regions, leaving Na/Fe antisite blocking near the interface unresolved. Subsequent studies therefore relied on strong external driving forces to activate these metastable materials. Liu et al. [20] found that prolonged electrochemical activation was required, which can be understood as the passive overcoming of the interfacial structural barrier under a strong electric field. Zhu et al. [19], by contrast, employed $\text{K}_2\text{S}_2\text{O}_8$ as a strong oxidant for chemical desodiation followed by high-temperature annealing. Although this strategy successfully enabled excellent solid-solution behavior, the intense global oxidation inevitably coupled extensive bulk-composition changes with deep surface reconstruction, making it difficult to isolate the independent contribution of interfacial kinetics.

In comparison, the mild thermal-oxidation strategy developed here is highly spatially selective. It demonstrates that bulk topological design alone is insufficient to guarantee high electrochemical activity: even a continuous bulk diffusion network can remain inaccessible if steric blocking associated with subsurface Fe segregation is not removed. At the microscopic level, the chemical or electrochemical oxidation processes involved in previous activation strategies may likewise function by eliminating local surface blocking and introducing active vacancies. This finding highlights the decisive role of the outer-surface microenvironment in macroscopic kinetics and extends the design paradigm from bulk-structure optimization alone toward coordinated regulation of bulk topology and local interfacial states.

This conceptual separation and coordinated regulation of interfacial kinetics and bulk transport not only provides a route for overcoming kinetic bottlenecks in polyanion frameworks, but may also offer useful

guidance for other advanced battery systems suffering from interfacial polarization or passivation. The restrictive influence of nanoscale interfacial layers on overall electrochemical performance is widely recognized across energy-storage chemistries. For example, nanoscale rock-salt surface reconstruction in layered oxide cathodes can strongly impede bulk ion diffusion, making precise surface regulation an established strategy for preserving cycle life [21, 22]. Likewise, the mechanism demonstrated here, in which vacancy introduction through surface-defect engineering promotes ion transport, parallels interfacial-regulation strategies in multivalent batteries such as Zn^{2+} systems, where interfacial defects can mitigate electrostatic repulsion and transport barriers for highly charged ions [23]. Finally, the mechanism identified here is also consistent with interface-design principles in all-solid-state batteries (ASSBs), where preserving the bulk framework while selectively regulating surface chemistry is an important route for reducing resistance at rigid solid-solid contacts [24]. Thus, extending electrode design from bulk-structure optimization to precise regulation of microscopic interfacial transport resistance may provide a general framework for continuously activating high-energy electrode materials across diverse storage chemistries.

4. Conclusions

In this work, we propose and demonstrate an interfacial-activation mechanism based on directional Fe exsolution induced by mild surface oxidation, which successfully breaks the kinetic dormancy of a non-stoichiometric sodium iron phosphate (NFP) cathode. Experimental characterization and theoretical calculations consistently indicate that the poor electrochemical activity of pristine NFP originates from Na/Fe antisite defects in the subsurface region that occupy Na-transport channels and create severe interfacial blocking. Mild oxidation at 400°C provides the key driving force for high-energy antisite Fe species to exsolve toward the outermost surface. Without disrupting the bulk topology, this process removes the interfacial mass-transfer bottleneck in situ and constructs a low-resistance transport network composed of mixed-valence $\text{Fe}^{2+}/\text{Fe}^{3+}$ species and local vacancies, thereby enabling excellent high-rate Na-storage activity and cycling stability. These results demonstrate that directional reconstruction of unfavorable subsurface defects through controlled thermodynamic perturbation is an effective route for breaking kinetic dormancy. More broadly, this strategy transforms local defects from features to be passively avoided into active elements that can be deliberately exploited, providing a rational and potentially general microscopic intervention paradigm for interface engineering in metastable electrode materials.

Declarations

Ethical Approval Statement

Not applicable. This study did not involve human participants, human data, or animals.

Conflict of Interest Statement

The authors declare that they have no conflicts of interest.

Financial Disclosure

This research received no external funding.

Author Contributions

Lin Zhu: Conceptualization, methodology, investigation, formal analysis, visualization, and writing - original draft. Aoran Sui: Investigation, validation, and data curation. Huichun Xue: Supervision, resources, and writing - review and editing. All authors have read and approved the final manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figures

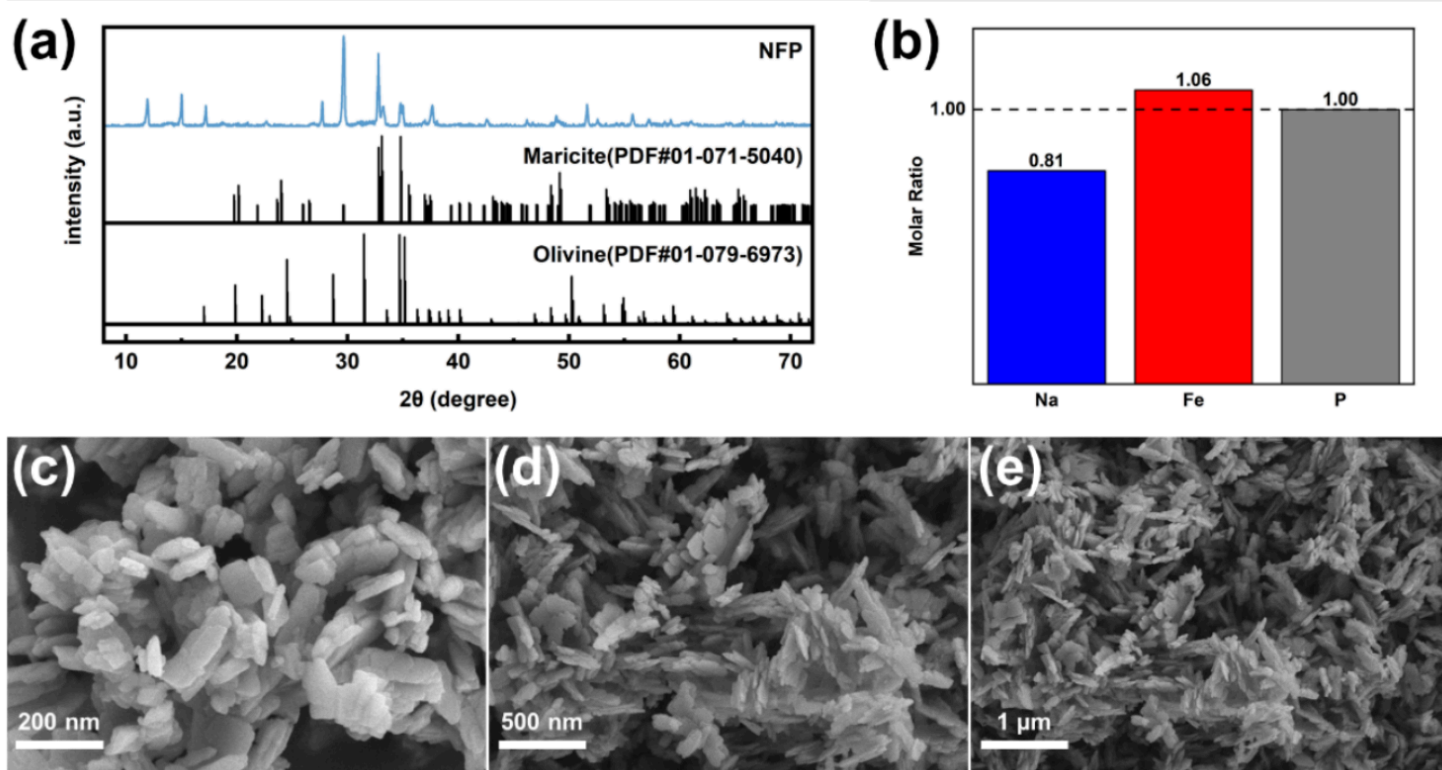


Figure 1

Structural and morphological characterization of the NFP precursor: (a) XRD pattern of NFP, with reference patterns for maricite and olivine shown at the bottom; (b) Na, Fe, and P molar ratios determined for the synthesized NFP; and (c-e) SEM images of NFP at different magnifications.

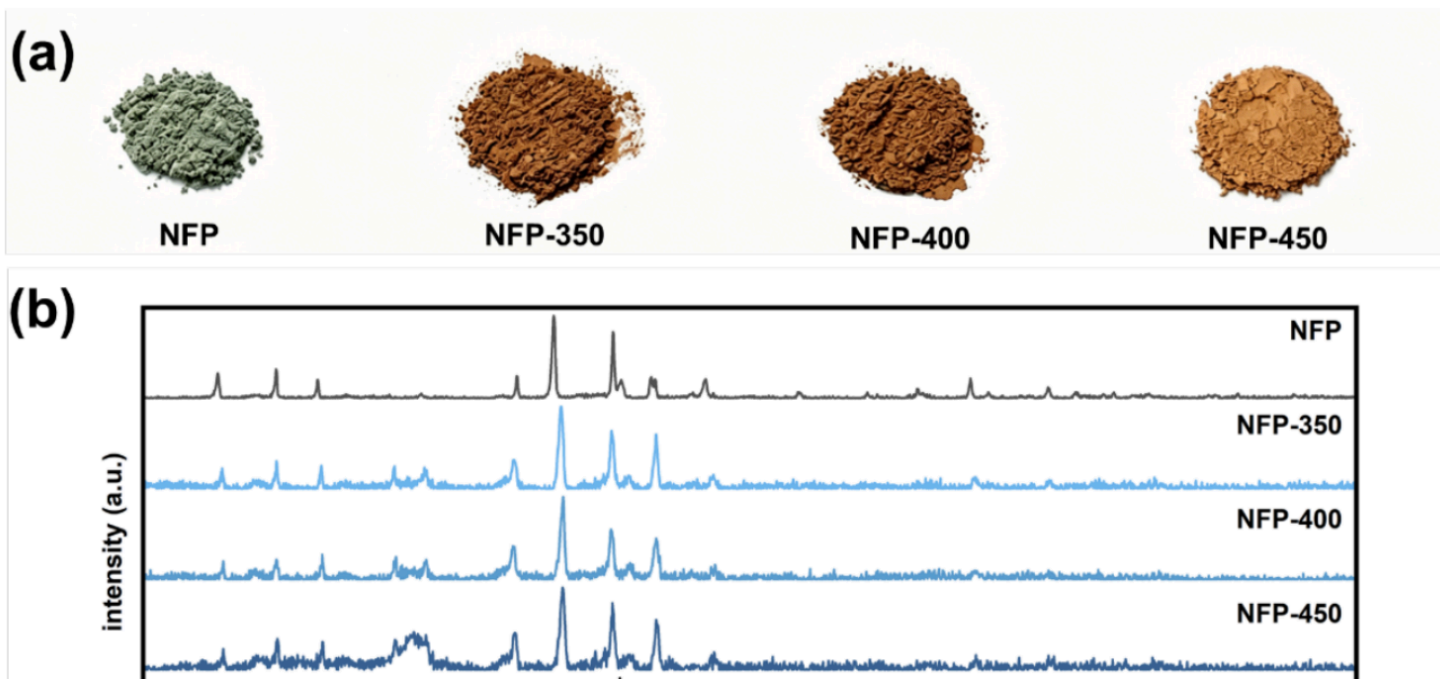


Figure 2

Phase, composition, and structural evolution before and after oxidation treatment: (a) photographs showing the macroscopic powder-color evolution from pristine NFP to NFP-350, NFP-400, and NFP-450 from left to right; and (b) corresponding powder XRD patterns, with the Fe₂O₃ reference pattern shown at the bottom.

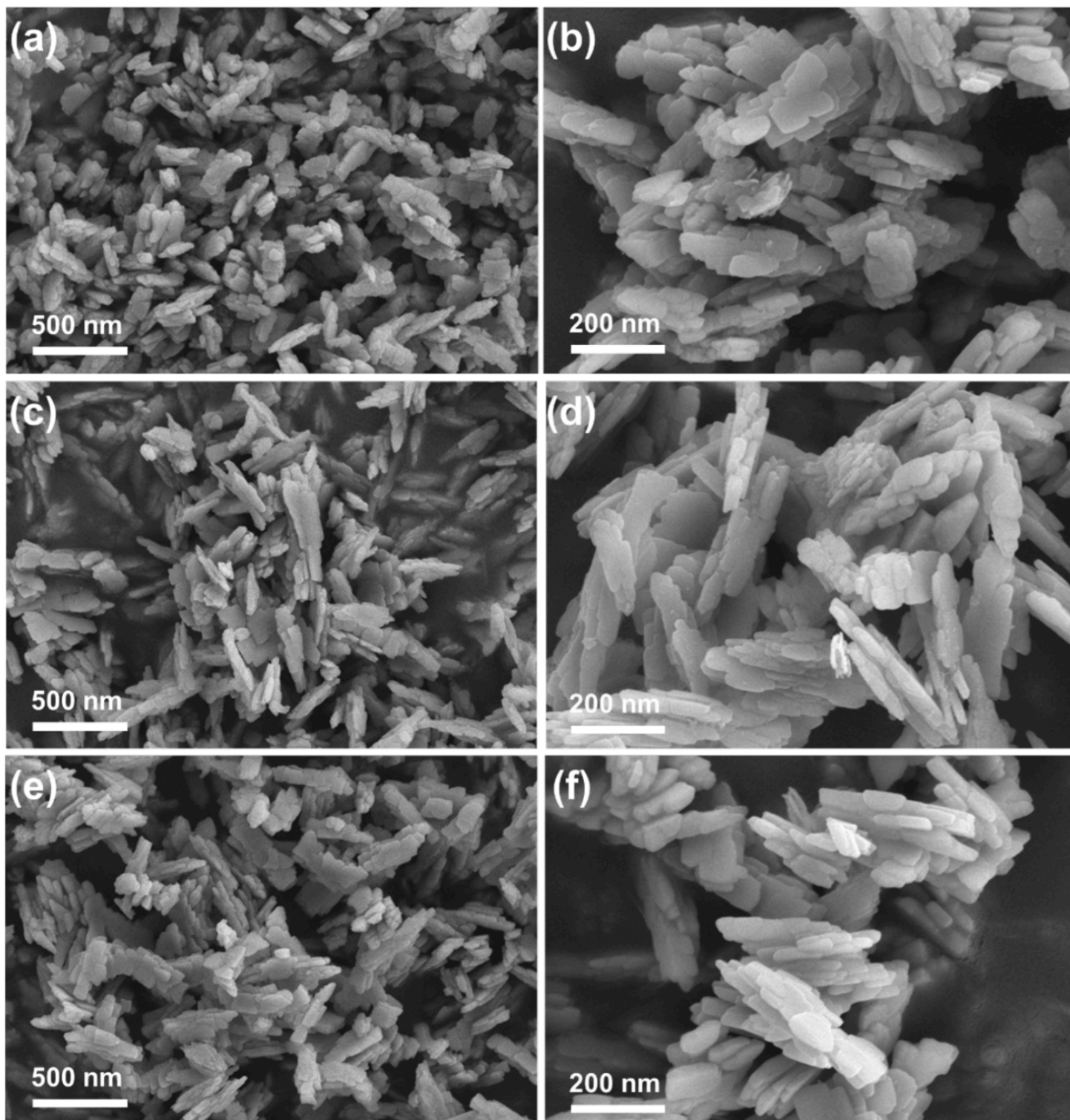


Figure 3

SEM images of samples oxidized at different temperatures. Panels (a,c,e) and (b,d,f) show lower- and higher-magnification images, respectively. Panels (a,b), (c,d), and (e,f) correspond to NFP-350, NFP-400, and NFP-450, respectively.

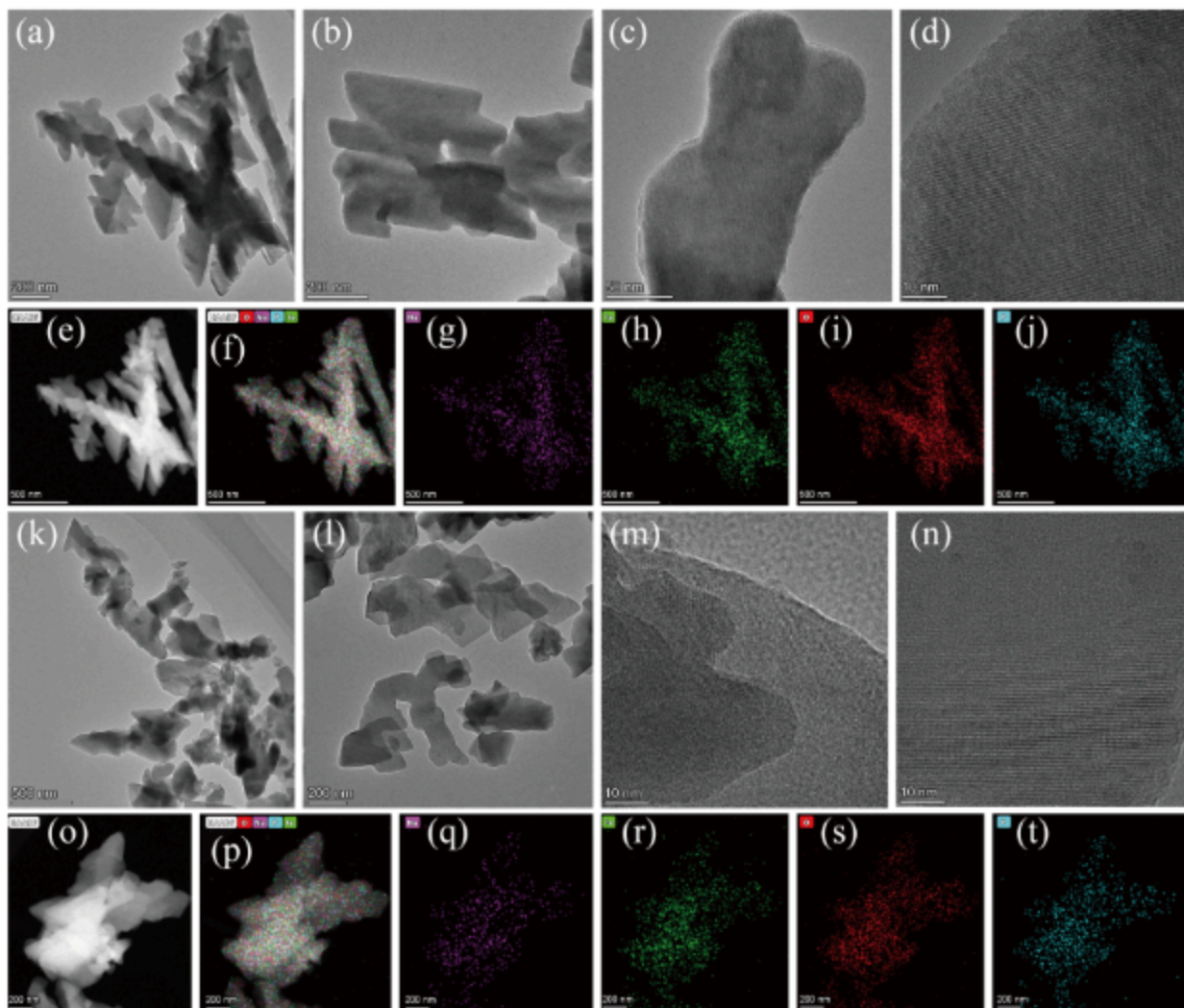


Figure 4

TEM/STEM characterization of pristine NFP and NFP-400. (a,b) TEM images and (c,d) higher-magnification/HRTEM images of pristine NFP; (e) HAADF-STEM image, (f) overlaid elemental map, and (g-j) individual Na, Fe, O, and P maps of pristine NFP. (k,l) TEM images and (m,n) HRTEM images of NFP-400; (o) HAADF-STEM image, (p) overlaid elemental map, and (q-t) individual Na, Fe, O, and P maps of NFP-400.

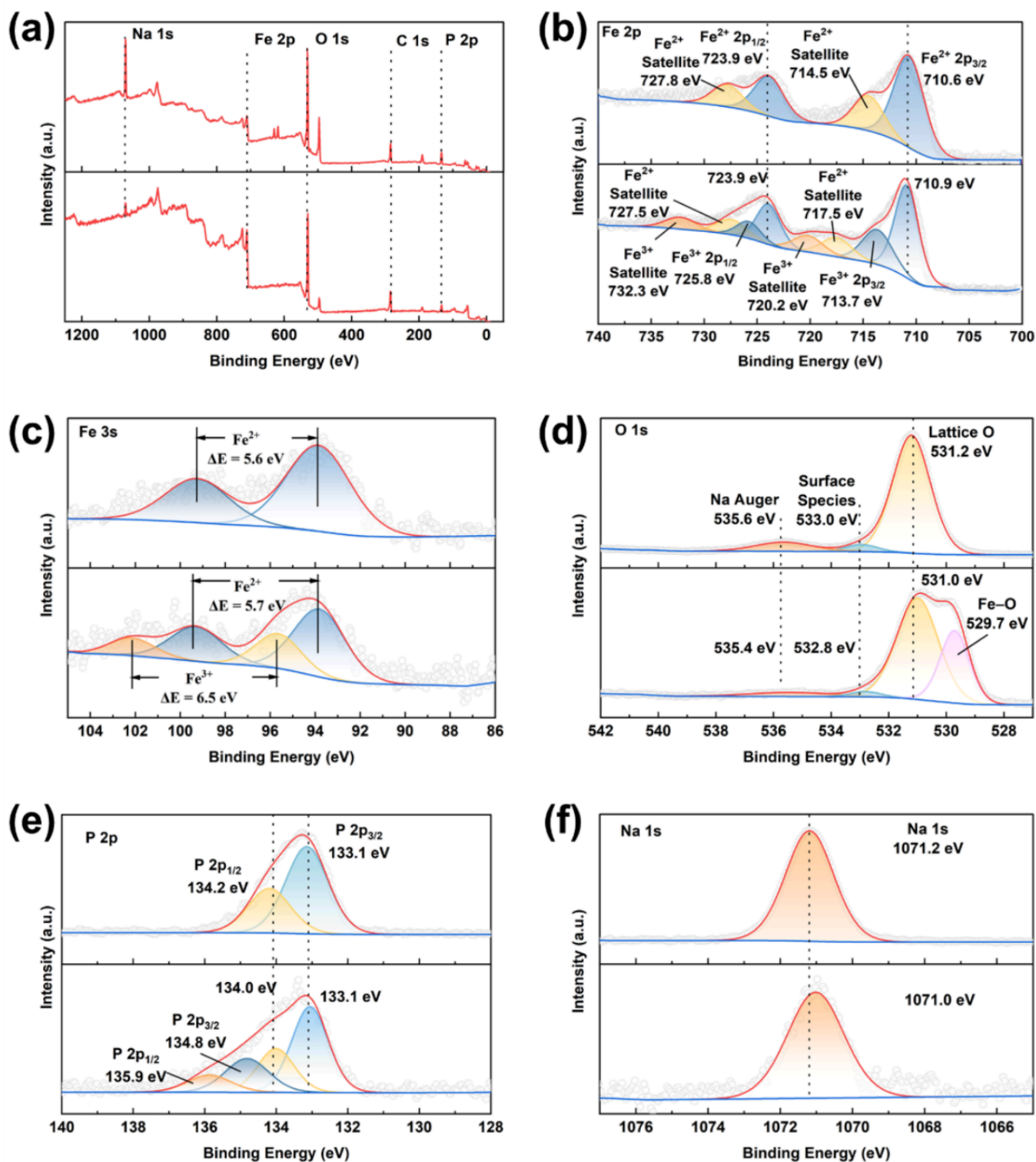


Figure 5

XPS spectra of NFP and NFP-400: (a) survey spectra and high-resolution spectra of (b) Fe 2p, (c) Fe 3s, (d) O 1s, (e) P 2p, and (f) Na 1s.

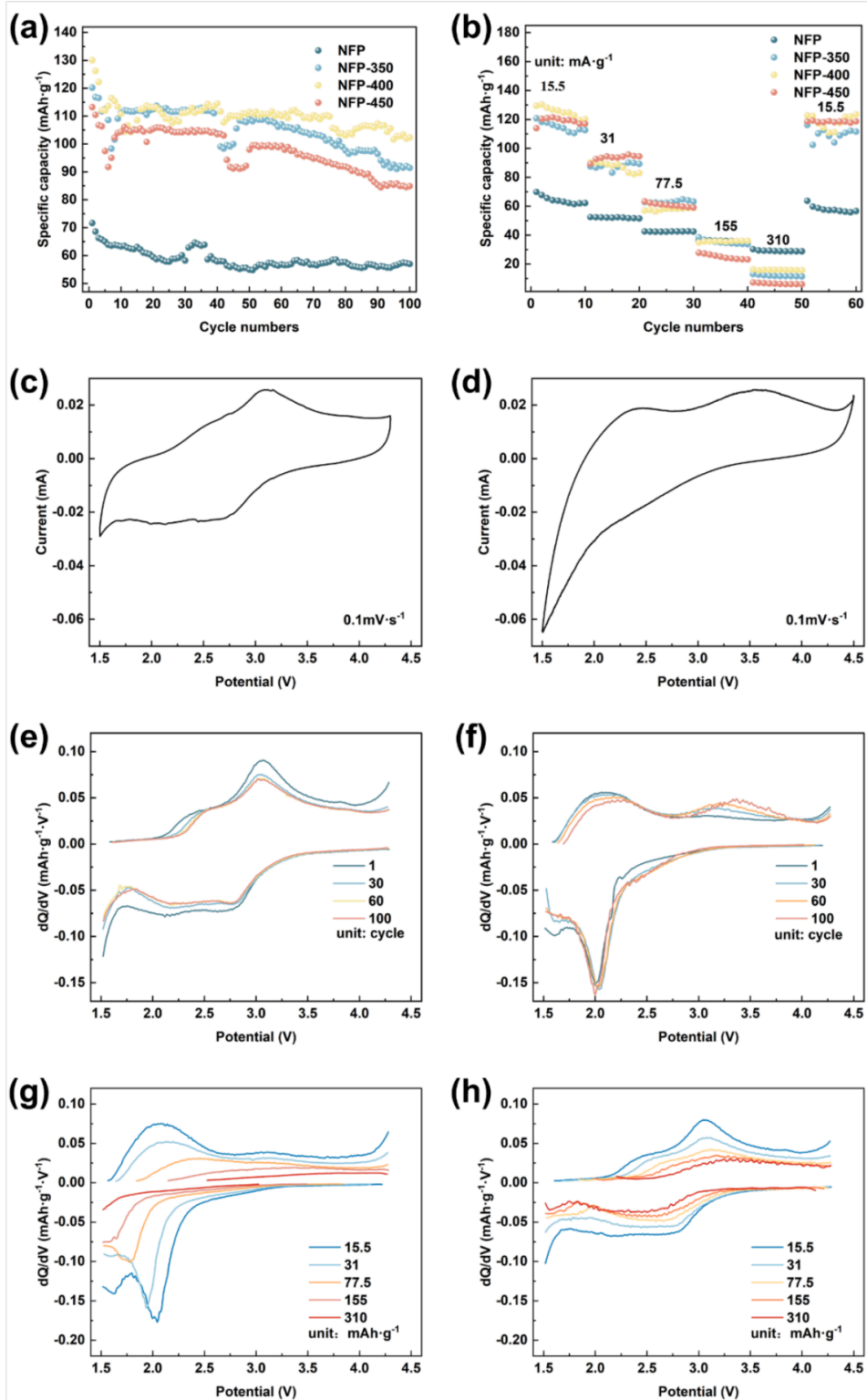


Figure 6

Electrochemical performance and kinetic analysis of pristine NFP and optimally activated NFP-400: (a) cycling performance at 15.5 mA g⁻¹; (b) rate capability; CV curves of (c) pristine NFP and (d) NFP-400; dQ/dV-V profiles of (e) pristine NFP and (f) NFP-400 at different cycle numbers; and dQ/dV-V profiles of (g) pristine NFP and (h) NFP-400 at different current densities.

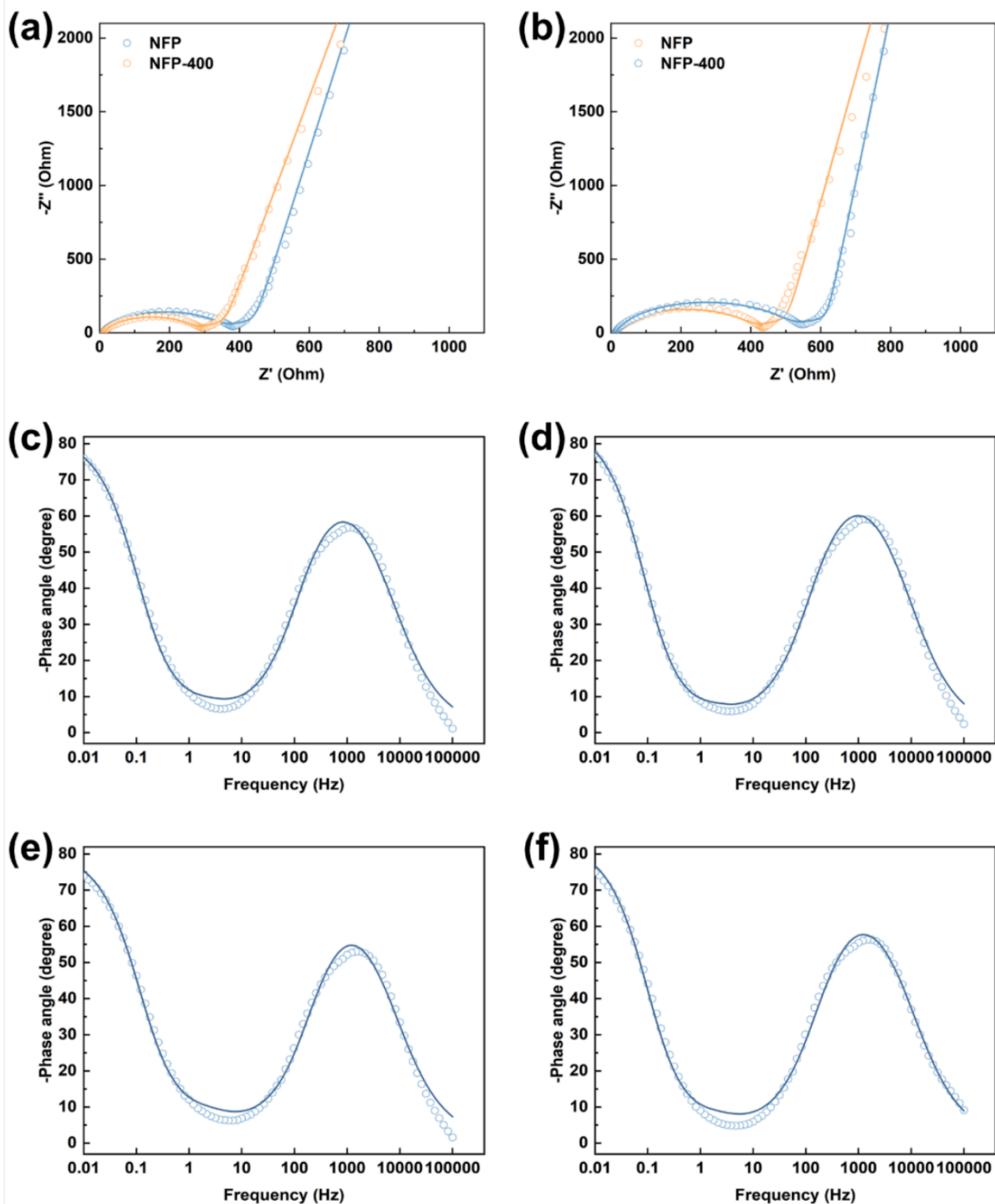


Figure 7

EIS characterization of NFP and NFP-400: Nyquist plots (a) before cycling and (b) after cycling; and phase angle-frequency plots of NFP and NFP-400 (c,e) before cycling and (d,f) after cycling.

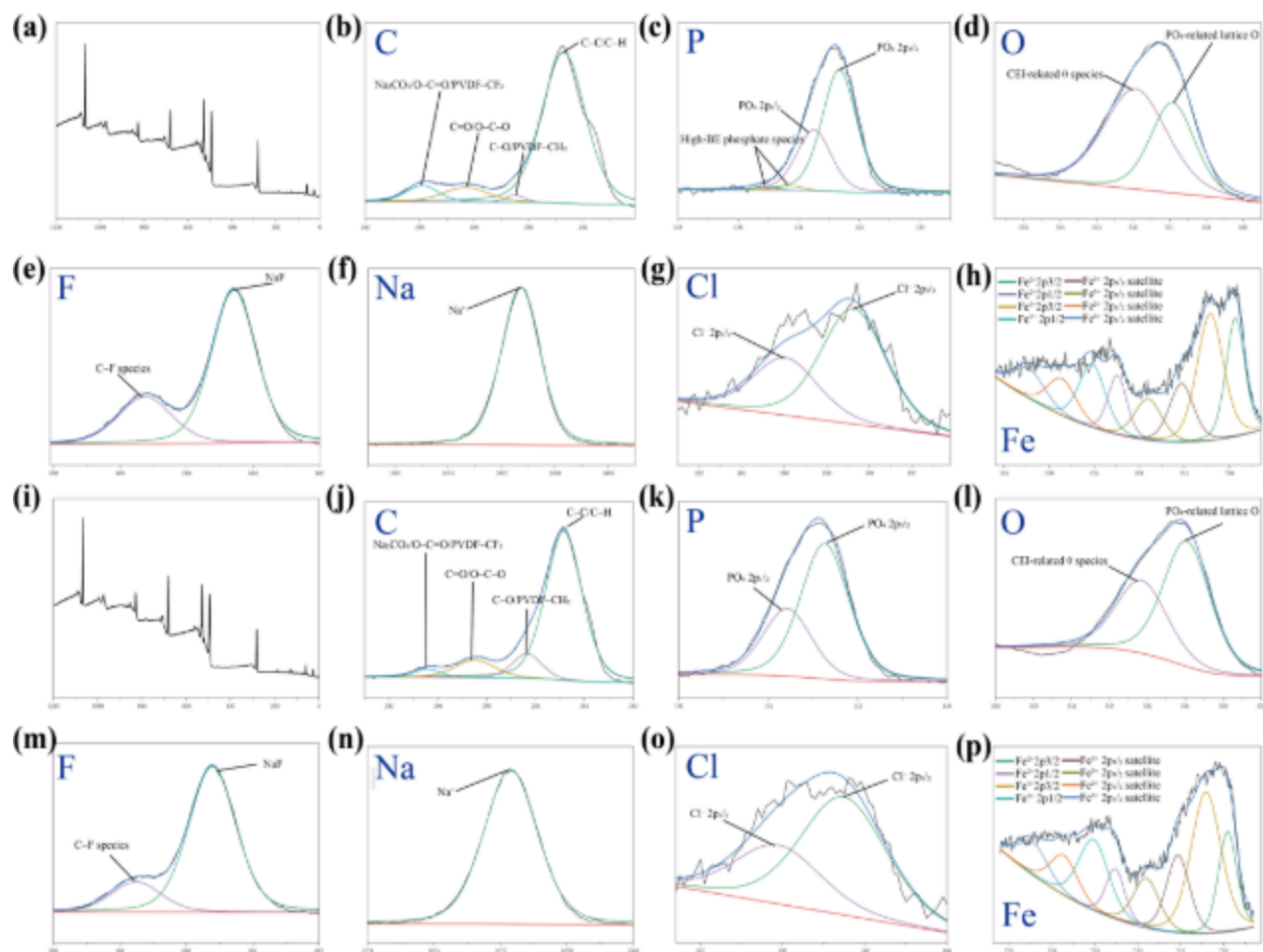


Figure 8

Post-cycling XPS comparison of NFP-400 and pristine NFP electrodes: (a–h) NFP-400 and (i–p) pristine NFP. (a,i) survey spectra; (b,j) C 1s; (c,k) P 2p; (d,l) O 1s; (e,m) F 1s; (f,n) Na 1s; (g,o) Cl 2p; and (h,p) Fe 2p spectra.

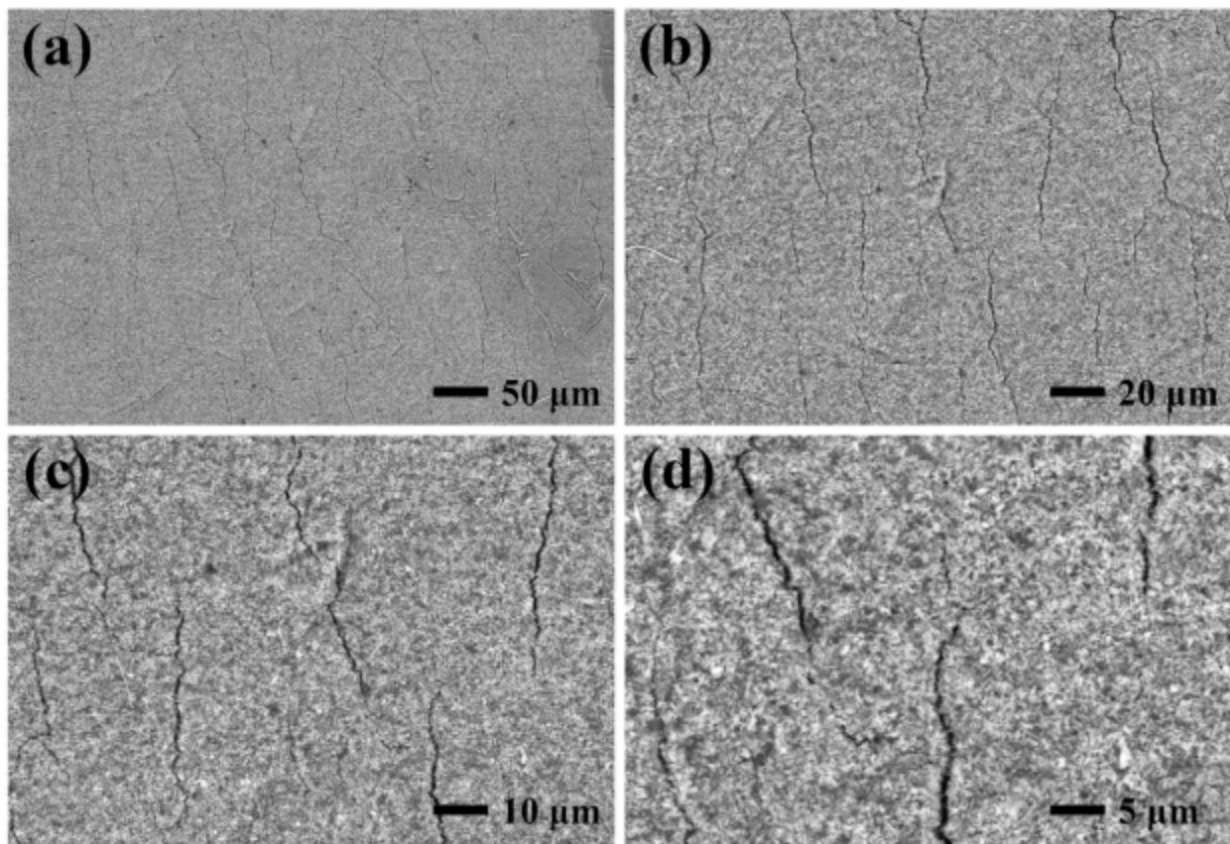


Figure 9

Post-cycling SEM images of the NFP-400 electrode at progressively higher magnifications. Scale bars: (a) 50 μm , (b) 20 μm , (c) 10 μm , and (d) 5 μm .

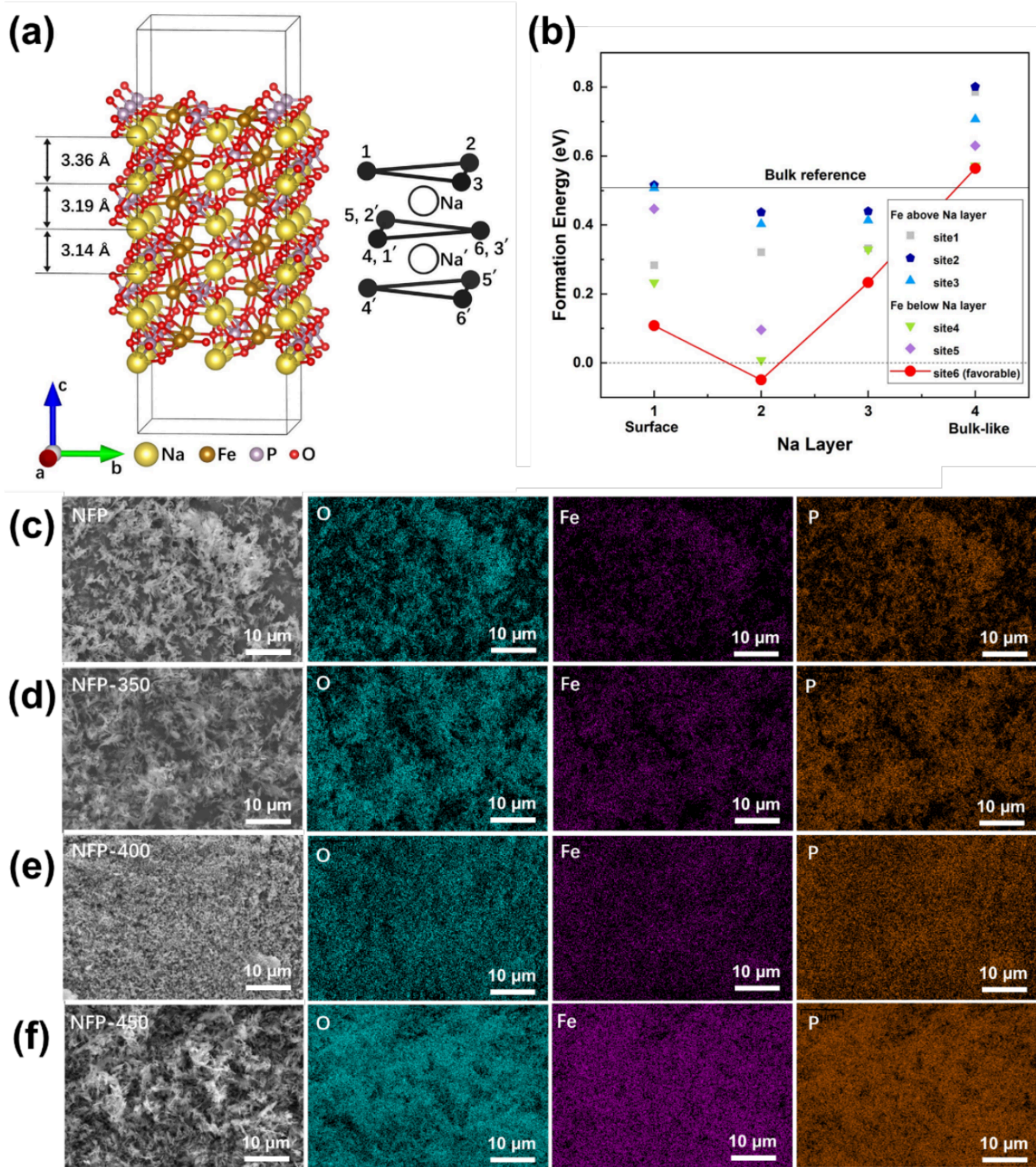


Figure 10

DFT-derived truncated-surface properties and elemental mapping of the different samples: (a) gradient-expansion model of the (010) surface lattice; (b) thermodynamic gradient of defect-formation energy as a function of Na-layer depth; and (c-f) elemental mapping of pristine NFP, NFP-350, NFP-400, and NFP-450, respectively.