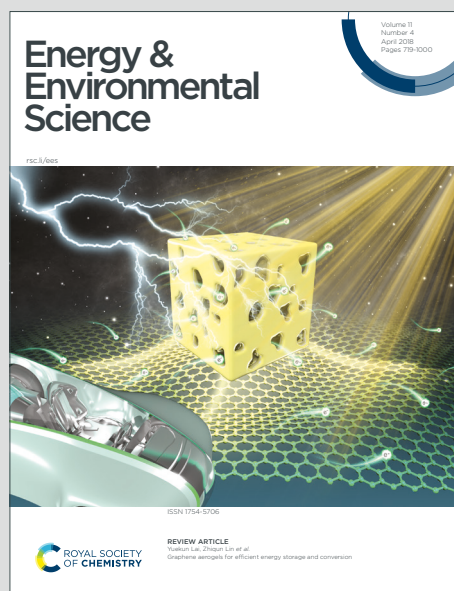


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Broader context

Sodium-ion batteries (SIBs) are premier candidates for sustainable large-scale energy storage. Among potential cathodes, the iron-based mixed-phosphate $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ (NFPP) offers significant safety and cost advantages. However, its commercial deployment is significantly hindered by the persistent formation of electrochemically inert impurities. This work introduces a “dehydration-induced phase engineering” strategy utilizing hydrous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ as a structure-directing precursor. By leveraging the intrinsic structural disorder and dehydration-driven activation of the hydrous precursor, we successfully bypassed the long-standing kinetic barriers inherent in conventional anhydrous FePO_4 route, facilitating the precision synthesis of coherent heterophase intergrowths. The resulting cathode demonstrates exceptional rate capability and extraordinary resilience in extreme environments ($-40\text{ }^\circ\text{C}$), alongside superior durability in practical pouch cells (2000 cycles). Importantly, this strategy eliminates energy-intensive pre-dehydration stages required for anhydrous FePO_4 , offering a pragmatic and low-carbon industrial blueprint for the scalable manufacturing of advanced polyanionic material.

ARTICLE

Dehydration-induced phase engineering of mixed phosphate cathodes for sustainable and low-temperature sodium-ion batteries

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$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ (NFPP) is a highly promising cathode for sustainable sodium-ion batteries (SIBs), yet its scalable application is hindered by the thermodynamically competitive formation of inert maricite- NaFePO_4 (m-NFP) impurity. Herein, we report an eco-friendly and energy-efficient synthesis route utilizing hydrous $\text{FePO}_4 \cdot 1.6\text{H}_2\text{O}$ (FPH) as a structure-directing precursor, which eliminates the energy-intensive dehydration required for conventional anhydrous FePO_4 (FP). Critically, unlike the rigid lattice of FP, the intrinsic structural disorder and *in situ* dehydration-induced activation of FPH synergistically lower the activation energy for $[\text{P}_2\text{O}_7]$ polycondensation. This steers the phase evolution toward an atomic-scale coherent NFPP- $\text{Na}_2\text{FeP}_2\text{O}_7$ intergrowth, effectively bypassing the m-NFP kinetic trap. The resulting seamless heterophase interfaces minimize interfacial resistance, enabling exceptional rate capability (92.2 mAh g^{-1} at 20°C) and extraordinary low-temperature resilience (72% capacity retention at -40°C). Furthermore, practical pouch cells demonstrate superior durability with 81% capacity retention over 2000 cycles. This work elucidates the structure-directing role of precursor disorder and hydration chemistry, providing a scalable pathway for the precision synthesis of advanced polyanionic materials.

1. Introduction

Sodium-ion batteries (SIBs) have emerged as promising alternatives to lithium-ion systems for large-scale energy storage, driven by the natural abundance of sodium, competitive safety profiles, and a broad operational temperature range.¹⁻⁴ Among various cathode candidates, polyanionic materials are particularly distinguished by their robust frameworks anchored by strong P–O covalent bonds, which ensure superior thermal stability and efficient Na^+ transport channels.⁵⁻⁸ Specifically, the iron-based mixed-phosphate $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ (NFPP) has stood out as a premier candidate for commercialization due to its low cost, non-toxicity, and impressive electrochemical performance.⁹⁻¹¹ However, the precise synthesis of phase-pure NFPP remains a formidable challenge due to the intricate thermodynamic competition between $[\text{PO}_4]$ and $[\text{P}_2\text{O}_7]$ units, which often leads

to the unintended formation of maricite- NaFePO_4 (m-NFP) and $\text{Na}_2\text{FeP}_2\text{O}_7$ (NFPO) phases.^{12,13}

While m-NFP is widely dismissed as electrochemically inert due to the lack of efficient Na^+ diffusion channels,^{14,15} the role of NFPO has been recently reevaluated. Although NFPO suffers from limited theoretical capacity (97 mAh g^{-1}) and sluggish kinetics,¹⁶ it can be strategically leveraged through the construction of biphasic or heterostructured architectures. For instance, Hao *et al.*¹⁷ demonstrated that NFPP-NFPO heterostructures facilitate charge redistribution at the heterogeneous interface, enabling enhanced structural stability and charge transport kinetics. Similarly, Wang *et al.*¹⁸ reported that the steric hindrance provided by the NFPO phase effectively restricts intramolecular motion and lattice strain within the NFPP framework. On the other hand, iron-defect engineering has been widely adopted as an effective strategy to suppress the formation of the deleterious m-NFP phase.^{19,20} From the perspectives of industrial scalability and synthetic chemistry, the choice of iron precursor is not merely a cost determinant, but more fundamentally, a structure-directing factor that dictates the competitive phase-evolution pathways during synthesis. While water-soluble salts²¹⁻²³ or oxalates²⁴⁻²⁶ have been widely employed in laboratory research, their large-scale application is hindered by toxic emission and low atomic economy. Consequently, anhydrous FePO_4 (FP) has emerged as the most viable industrial precursor due to its high atomic utilization and environmental friendliness. However, the transition from FePO_4 to phase-pure NFPP persists as a

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formidable challenge.^{27,28} The intrinsic lattice rigidity and thermodynamic stability of crystalline FP create a kinetically hindered reaction interface, imposing a prohibitive activation energy barrier for ionic rearrangement.²⁹ This kinetic inertia leads to incomplete phase transformation and the unintended segregation of $[\text{PO}_4]/[\text{P}_2\text{O}_7]$ units, trapping the system into the thermodynamically stable m-NFP phase. Overcoming this structural rigidity without resorting to exogenous additives remains an unresolved bottleneck in the synthesis of NFPP material.

In this work, we unveil a disorder and hydration-mediated phase engineering strategy utilizing hydrous $\text{FePO}_4 \cdot 1.6\text{H}_2\text{O}$ (FPH) as a functional precursor to circumvent these barriers. We demonstrate that the intrinsic structural disorder of FPH provides greater lattice flexibility for the long-range rearrangement of polyanionic units. Simultaneously, the synchronized *in situ* dehydration triggers a structural fragmentation of the precursor into highly reactive nanodomains, effectively lowering the activation barriers for $[\text{P}_2\text{O}_7]$ polycondensation. This chemical synergy reconfigures the thermodynamic landscape, facilitating the formation of an atomic-scale coherent NFPP-NFPO intergrowth. Crucially, our findings reveal that the coexisting NFPO phase does not impede, but rather synergistically accelerates both ion and electron transport through engineered coherent heterophase

boundaries. The optimized NFPP-FPH cathode achieves a remarkable rate capability of 92.2 mAh g^{-1} at 20°C and exhibits extraordinary kinetic resilience at extreme sub-zero temperature (72% capacity retention at -40°C). More importantly, the pouch cells assembled with NFPP-FPH and hard carbon demonstrate superior durability with 81% capacity retention after 2000 cycles. This study provides fundamental insights into the pivotal role of precursor disorder and hydration chemistry in regulating the phase evolution of advanced polyanionic cathodes. The main text of the article should appear here with headings as appropriate.

2. Results and discussion

2.1 Precursor disorder and dehydration

To elucidate the impact of the iron source on the subsequent phase evolution, the physicochemical properties of both FPH and FP were systematically characterized. The thermal behavior of FPH was first evaluated using thermogravimetric analysis (TGA). As depicted in Fig. 1a, FPH exhibits a distinct weight loss of 16% within the temperature range of $100\text{--}200^\circ\text{C}$, corresponding to the release of approximately 1.6 moles of crystalline water.³⁰ The removal of lattice-bound water molecules is expected to disrupt the initial coordination environment, potentially triggering *in situ* structural fragmentation and creating highly reactive nanodomains at the onset of calcination.

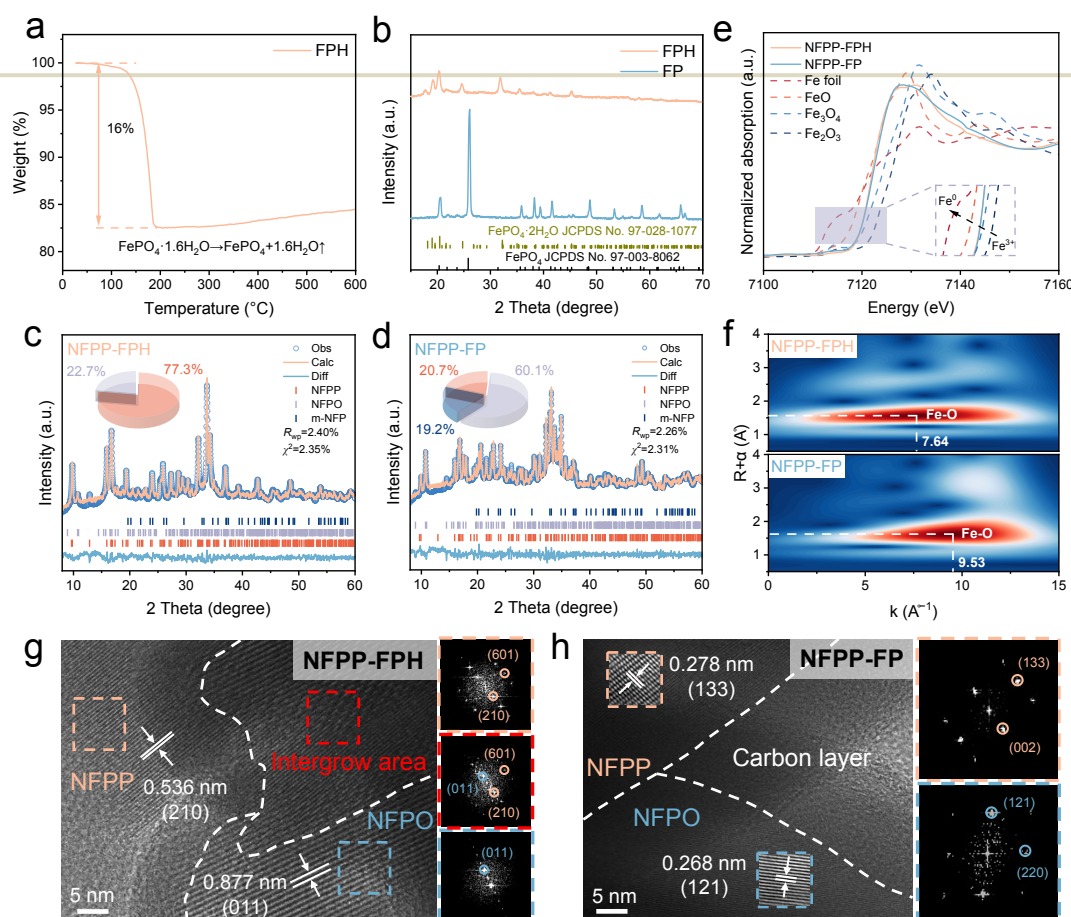


Fig. 1 (a) TGA curve of FPH. (b) XRD patterns of FPH and FP. XRD Rietveld refinement of (c) NFPP-FPH and (d) NFPP-FP. (e) Fe K-edge XANES spectra and (f) wavelet-transformed EXAFS spectra of NFPP-FPH and NFPP-FP. HRTEM images of (g) NFPP-FPH and (h) NFPP-FP.

X-ray diffraction (XRD) patterns (Fig. 1b) reveal a fundamental structural disparity between the two precursors. FP exhibits sharp and well-defined peaks, indicative of a highly ordered and rigid crystalline framework. In stark contrast, FPH displays broad, low-intensity diffraction peaks characteristic of the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ phase, suggesting structural disordered state within the FPH matrix.³¹ Unlike the stable lattice of FP, the intrinsic structural disorder and lower lattice constraints of FPH offer significantly higher structural flexibility. This flexible state is hypothesized to lower the energy barrier for atomic-scale rearrangements, potentially facilitating the direct nucleation of complex mixed-phosphate frameworks. Scanning electron microscopy (SEM) images (Fig. S1a and b) show that both precursors consist of irregular aggregates with morphological parity. This is corroborated by particle size distribution (PSD) analysis (Fig. S1c), which yields comparable median particle sizes (D_{50} of 18.1 μm for FPH and 21.5 μm for FP). This physical equivalence confirms that the divergent phase evolution observed later is intrinsically governed by the internal structural disorder and the hydration process, rather than physical variations in the precursors.

2.2 Material design and structure analysis

Building upon the iron-defect engineering strategy, a series of off-stoichiometric $\text{Na}_4\text{Fe}_x(\text{PO}_4)_2\text{P}_2\text{O}_7$ samples ($x = 3.0, 2.9, 2.85$ and 2.7) were synthesized using both FP and FPH precursors, respectively. As illustrated in the XRD patterns (Fig. S2a), the FP-derived samples (NFPP-FP- x) consistently fail to achieve phase purity regardless of stoichiometry modulation. The persistent characteristic reflections from the NFPO phase ($\sim 10.7^\circ$) and the electrochemically inert m-NFP impurity ($\sim 32.8^\circ, 33.0^\circ$ and 34.7°) underscore a formidable thermodynamic barrier for NFPP formation in anhydrous FP systems.¹⁹ In stark contrast, the FPH-derived samples (NFPP-FPH- x) exhibit a profound suppression of the m-NFP phase (Fig. S2b). Quantitative Rietveld refinement (Fig. 1c and Fig. S3) confirms that the target NFPP phase remains the dominant component in the NFPP-FPH- x samples. Notably, at $x = 2.85$ (NFPP-FPH), the m-NFP impurity is completely eliminated, resulting in a unique biphasic architecture comprising 77.3 wt.% NFPP and 22.7 wt.% NFPO. Further increasing the Fe deficiency to $x = 2.7$ triggers a slight resurgence of m-NFP phase (2.5 wt.%), suggesting that excessive Fe vacancies may destabilize the NFPP framework and shift the phase equilibrium.³² Conversely, for the NFPP-FP- x sample (Fig. 1d and Fig. S4), even at $x = 2.7$ (NFPP-FP), the target NFPP phase accounts for only 20.7 wt.%, reinforcing the kinetic superiority of the hydrous FPH route. Detailed refinement parameters of NFPP-FPH and NFPP-FP samples are summarized in Table S1. The elemental compositions determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Table S2) are in good agreement with the designed stoichiometric ratios.

The microstructural divergence between the FPH and FP-derived samples was further scrutinized *via* SEM. The NFPP-FPH- x samples exhibit a well-dispersed, nanostructured morphology with uniform primary nanoparticles ranging from 50 to 150 nm (Fig. S5). In contrast, the NFPP-FP- x samples suffer from drastic grain coarsening and dense thermal sintering, with

particle size exceeding 300 nm (Fig. S6). This morphological refinement is intrinsically linked to the disordered nature and *in situ* dehydration of the FPH precursor. As previously hypothesized, the inherent structural disorder renders the FPH matrix susceptible to fragmentation into high-activity nanodomains under the localized pressure of released crystalline water. This self-limiting growth mechanism effectively circumvents the excessive grain coarsening typical of conventional solid-state sintering, ensuring a high electroactive surface area. To further substantiate this size reduction on a macro-statistical scale, dynamic light scattering (DLS) analysis was performed (Fig. S7). The measured Z-average diameters of NFPP-FPH (304.8 nm) and NFPP-FP (376.7 nm) characteristically reflect their secondary aggregation states rather than isolated primary crystallite sizes. Crucially, the smaller cluster size of NFPP-FPH consistently echoes the SEM observations, further confirming the robust self-limiting growth effect of the dehydration-induced fragmentation strategy. Fourier-transform infrared (FTIR) spectroscopy was performed to probe the local coordination environment and the integrity of the multi-anion framework. As illustrated in Fig. S8, the spectra exhibit characteristic vibrations categorized into three distinct regions: P–O stretching ($990\text{--}1200\text{ cm}^{-1}$), P–O–P bridge stretching ($700\text{--}990\text{ cm}^{-1}$) and O–P–O bending ($400\text{--}700\text{ cm}^{-1}$). The sharp bands at $\sim 885\text{ cm}^{-1}$ and 720 cm^{-1} are characteristic of the NFPP phase, while the band at $\sim 740\text{ cm}^{-1}$ is primarily attributed to the NFPO phase,³³ confirming the formation of the NFPP-NFPO biphasic architecture. The progressive strengthening of the $\sim 740\text{ cm}^{-1}$ peak with increasing Fe deficiency validates the controlled expansion of the NFPO fraction, consistent with XRD findings. The carbon coating properties were evaluated *via* Raman spectroscopy and elemental analysis (EA). Carbon contents of all samples were maintained within a narrow range of 3.0–3.7 wt.% (Table S3). The Raman spectra (Fig. S9) exhibit the characteristic D-band and G-band of amorphous carbon. Notably, the NFPP-FPH- x samples display consistently higher I_D/I_G ratios compared to the NFPP-FP- x counterparts. This increased degree of carbon disorder is a direct consequence of the *in situ* dehydration process. The localized pressure and precursor fragmentation during calcination likely disrupt the long-range graphitization of the carbon precursor, resulting in a defect-rich and disordered carbon coating. Such an architecture is expected to provide enhanced active sites and accelerated pathways for Na^+ transport at the electrode/electrolyte interface, further boosting the electrochemical performance.³⁴

To further investigate the electronic state and local coordination environment of the Fe species, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were performed. As shown in Fig. 1e, the absorption edge positions for both samples are close to the Fe_3O_4 references, confirming the existence of both Fe^{2+} and Fe^{3+} .³⁵ The Fe^{3+} component is likely attributed to inherent Fe deficiency and partial surface oxidation. The Fourier-transformed (FT) EXAFS spectra in R-space (Fig. S10) reveal a prominent peak corresponding to the Fe–O first coordination shell. Notably, the NFPP-FPH sample exhibits a shorter radial

distance (1.53 Å) compared to the NFPP-FP sample (1.56 Å), suggesting strengthened Fe–O bond and polyanion framework.^{28,36} This structural refinement is further resolved by wavelet-transform (WT) analysis (Fig. 1f), where the maximum intensity for NFPP-FPH is centered at a lower k value (7.64 Å⁻¹) than that of NFPP-FP (9.53 Å⁻¹). This shift, coupled with the bond contraction, indicates that the hydrous FPH route promotes a more robust and ordered local structural environment, which is conducive to the structural stability.³⁷ The interfacial architecture was further elucidated *via* high-resolution transmission electron microscopy (HRTEM). As shown in Fig. S11a, the NFPP-FPH sample exhibits a uniformly encapsulated carbon layer with a thickness of 2–3 nm. Distinct lattice fringes with interplanar spacings of 0.536 nm and 0.877 nm are clearly observed, corresponding to the (210) plane of the NFPP phase and the (011) plane of the NFPO phase, respectively (Fig. 1g). Crucially, a significant intergrowth area is identified between the two phases, characterized by a seamless transition of lattice fringes across the phase boundary. This is further corroborated by the fast Fourier transform (FFT) patterns, which displays a superposition of characteristic reflections from both the NFPP and NFPO phases. Such atomic-scale intergrowth provides direct evidence that the hydrous FPH route facilitates the concurrent nucleation and coherent integration of the two phases, preventing localized phase segregation. This coherent biphasic interface is expected to reduce the interfacial energy and accelerate charge transfer

across the heterostructure. In contrast, the NFPP-FP sample (Fig. 1h and Fig. S12a) exhibits severe phase segregation and excessively thick carbon layer (~16 nm), highlighting the kinetic limitations of the anhydrous FP route. The identifiable lattice fringes of 0.281 nm and 0.277 nm correspond to isolated NFPO and m-NFP crystalline domains, respectively. Although bulk XRD analysis confirms the coexistence of NFPP, NFPO, and m-NFP phase, identifying a triple-phase junction *via* HRTEM is experimentally challenging due to the severe phase segregation and the low concentration of the target NFPP phase (20.7 wt.%). Energy-dispersive X-ray spectroscopy (EDS) mapping confirms the homogeneous distribution of Na, Fe, P, O, and C elements throughout the particles of both samples (Fig. S11b and S12b). In summary, the hydrous precursor FPH shifts the synthesis from a diffusion-controlled regime prone to phase segregation to a kinetically-favored regime that promotes atomic-scale phase coherence.

2.3 Phase evolution and synthetic mechanism

To elucidate the underlying synthetic chemistry, a comprehensive suite of *in situ* and *ex situ* characterizations were conducted. As illustrated in Fig. 2a, *ex situ* XRD patterns collected within the temperature range from 300 °C to 550 °C reveal fundamentally distinct phase evolution pathways for the two synthesis routes. The FPH precursor maintains a long-range disordered state up to 400 °C, establishing a metastable energetic platform that prevents premature crystallization into simple intermediates. In the absence

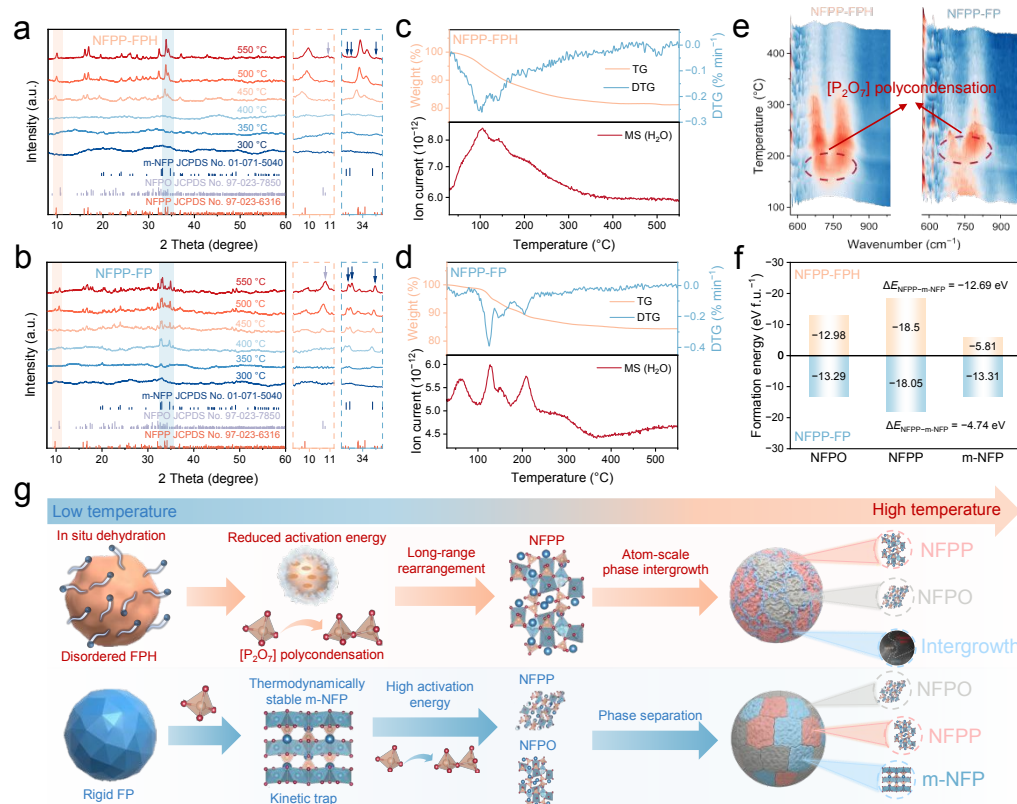


Fig. 2 *Ex situ* high-temperature XRD patterns of (a) NFPP-FPH and (b) NFPP-FP. TG-MS curves of (c) NFPP-FPH and (d) NFPP-FP. (e) *In situ* temperature-dependent FTIR contour plots of NFPP-FPH and NFPP-FP. (f) Calculated formation energies for NFPP, NFPO and m-NFP phases based on DFT. (g) Schematic illustration of the reaction mechanisms of hydrous and anhydrous systems.

of pre-existing rigid lattice, the Na^+ , PO_4^{3-} , and $\text{P}_2\text{O}_7^{4-}$ units possess enhanced kinetic freedom for long-range rearrangement. This facilitates the direct nucleation of the complex NFPP framework at 450 °C and subsequent NFPO crystallization at 500 °C, effectively circumventing the thermodynamically persistent yet electrochemically inactive m-NFP phase. Conversely, the high crystallinity of anhydrous FP imposes a prohibitive lattice constraint, which favors the system toward early-onset nucleation of the simpler m-NFP phase at 400 °C (Fig. 2b). Once formed, the m-NFP phase constitutes a thermodynamic and kinetic trap due to its high grain-boundary energy and limited ion-diffusion channels, hindering further structural evolution toward the target NFPP phase.

The origin of this kinetic divergence was also tracked *via* TG-MS. For the hydrous FPH system (Fig. 2c), a significant and broad weight loss is observed between 50 °C and 250 °C, accompanied by a substantial and continuous H_2O ion current signal ($m/z = 18$). This intense water vapor release originates from the structural dehydration of FPH. The continuous flux of vapor from the particle interior induces the disintegration of the FPH matrix, yielding highly reactive nanodomains. These nanodomains function as preferential nucleation centers, enabling subsequent phase formation to proceed *via* spontaneous nucleation rather than sluggish solid-state diffusion. This process leads to the successful construction of the atomic-scale coherent NFPP-NFPO intergrowth. In contrast, the anhydrous FP system shows multiple discrete, lower-intensity H_2O peaks (Fig. 2d), likely stemming from the release of adsorbed water or the decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$. The absence of *in situ* activation effect leaves the precursor particles relatively dense, limiting the effective interfacial contact and resulting in the sluggish kinetics revealed by XRD. The impact of this disorder and dehydration-induced activation on molecular-level bonding was further corroborated by *in situ* FTIR spectroscopy. A profound divergence in the evolution of $[\text{PO}_4]/[\text{P}_2\text{O}_7]$ units is observed, as highlighted in the spectroscopy (Fig. 2e). In the hydrous FPH system, the $[\text{PO}_4]$ bending modes ($\sim 600\text{ cm}^{-1}$) undergo an accelerated transition into the $[\text{P}_2\text{O}_7]$ stretching vibrations ($\sim 720\text{ cm}^{-1}$) at a significantly lower onset temperature compared to the anhydrous counterpart. This premature transformation provides direct spectroscopic evidence of a reduced activation energy for the polycondensation of $[\text{P}_2\text{O}_7]$ units, a process facilitated by the flexible lattice environment and enhanced atomic mobility post-dehydration. In contrast, the anhydrous FP system exhibits delayed and weakened $[\text{P}_2\text{O}_7]$ signals, reflecting a sluggish structural reorganization that fails to overcome the m-NFP barrier. These molecular-level observations perfectly align with the XRD findings, reinforcing the conclusion that the hydrous route effectively lowers the kinetic threshold for the construction of the target NFPP phase.

Density functional theory (DFT) calculations were performed to evaluate the formation energy landscape (Fig. 2f). For the hydrous FPH system, the target NFPP phase exhibits the lowest formation energy (-18.50 eV), while the m-NFP impurity shows a significantly higher formation energy (-5.81 eV). The substantial energy gap between NFPP and m-NFP ($\Delta E = -12.69\text{ eV}$) explains the complete absence of the m-NFP phase in the FPH-derived product. In the anhydrous FP system, although the NFPP phase still possesses the lowest formation energy (-18.05 eV), the m-NFP phase (-13.31 eV) becomes highly competitive, yielding a markedly narrowed energy gap ($\Delta E = -4.74\text{ eV}$). This reduced thermodynamic driving force,

coupled with the prohibitive kinetic barrier imposed by the rigid FP lattice, causes the system to become kinetically trapped in the m-NFP phase, leading to persistent phase segregation. Notably, the NFPO phase exhibits intermediate formation energies in both systems (-12.98 eV for NFPP-FPH and -13.29 eV for NFPP-FP) that are considerably lower than that of m-NFP in the FPH route, identifying it as a thermodynamically preferred secondary phase that facilitates the concurrent nucleation and atomic-scale coherent integration of the NFPP-NFPO intergrowth.

2.4 Electrochemical performance of half cells

To correlate the precursor-dependent architectures with their sodium-storage capabilities, the electrochemical properties of the NFPP-FPH-*x* and NFPP-FP-*x* series were systematically investigated. As illustrated in Fig. S13a, the NFPP-FPH-*x* electrodes exhibit exceptional rate capability. Among them, the NFPP-FPH electrode demonstrates a clear advantage, delivering superior reversible capacity across all current densities. Furthermore, it maintains the most stable cycling profile at both 1 C and 20 C rates (Fig. S13b and c). This exceptional stability and fast-charge capability are rooted in the synergistic balance between the NFPP-NFPO biphasic ratio and an optimized concentration of Fe vacancy, which collectively facilitate rapid Na^+ transport while accommodating lattice strain through the coherent intergrowth interface. In stark contrast, the NFPP-FP-*x* electrodes display overall inferior electrochemical performance regardless of the Fe deficiencies (Fig. S14). Within this series, the NFPP-FP electrode delivers the highest capacity, correlating with its maximum NFPP phase content as previously identified by XRD. However, all samples in the anhydrous series suffer from abrupt late-stage capacity decay during high-rate cycling. This instability, coupled with poor rate performance, stems from the diffusion-controlled synthesis regime inherent to the anhydrous route. This pathway promotes the formation of the electrochemically inactive m-NFP phase, which undermines the sodium-storage kinetics and structural integrity of the NFPP-FP-*x* samples.

Based on the systematic screening, NFPP-FPH and NFPP-FP were identified as benchmark electrodes to decipher the advantages of the hydrous FPH route. Cyclic voltammetry (CV) was first employed to probe the redox behavior (Fig. 3a). Both electrodes exhibit characteristic multi-electron redox chemistry. For the NFPP-FPH electrode, three distinct pairs of redox peaks at approximately 2.81/2.43 V, 3.00/2.76 V, and 3.28/3.16 V are observed, corresponding to the sequential Na^+ extraction/insertion from Na3, Na1, and Na4 sites within the NFPP lattice, respectively.³⁸ A broader oxidation peak around 2.53 V is specifically attributed to the Na1 extraction within the NFPO phase,¹⁸ confirming the active contribution of the biphasic composite. The significantly higher peak current intensities and excellent overlap of the initial three CV curves (Fig. S15a) in NFPP-FPH underscore accelerated charge-transfer kinetics and minimal structural polarization. In contrast, NFPP-FP exhibits noticeable fluctuations (Fig. S15b), suggesting sluggish activation or localized structural rearrangement during initial cycling. The galvanostatic charge-discharge (GCD) profiles (Fig. 3b) align with the CV curves. The NFPP-FPH electrode delivers a

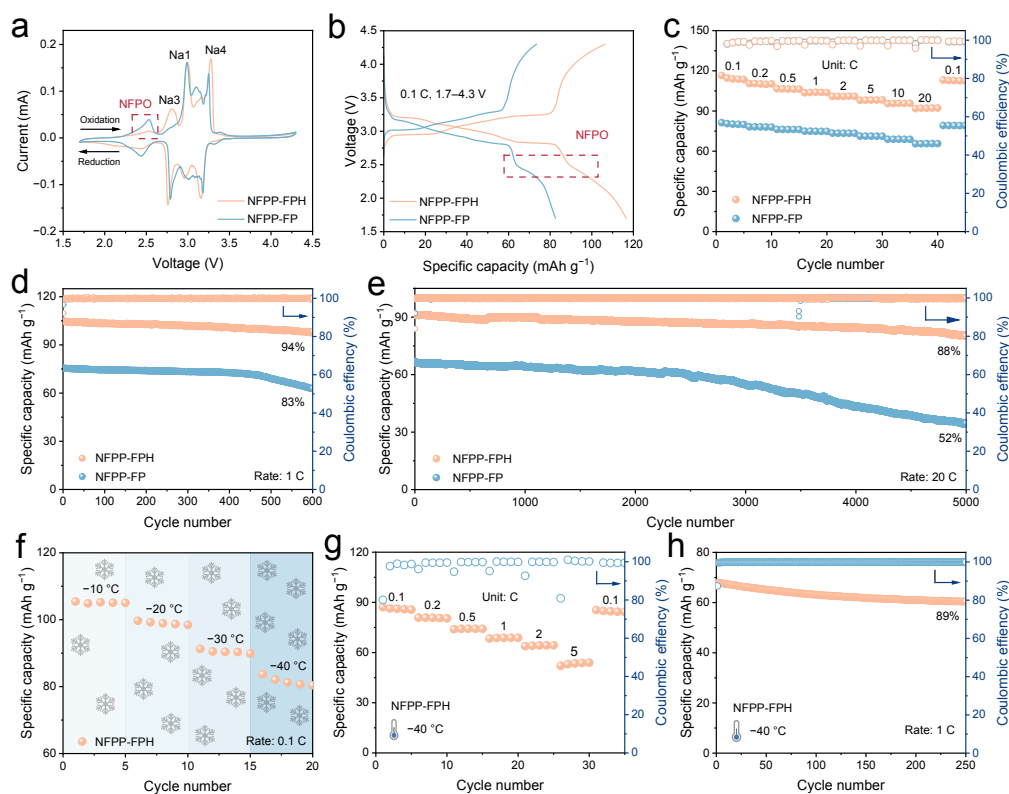


Fig. 3 (a) CV curves at 0.1 mV s^{-1} , (b) GCD profiles at 0.1 C , (c) rate capability from 0.1 C to 20 C , (d) cycling performance at 1 C and (e) long-term cycling stability at 20 C of NFPP-FPH and NFPP-FP electrodes. (f) Specific capacities and corresponding capacity retentions under sub-zero temperatures ($-10 \text{ }^{\circ}\text{C}$ to $-40 \text{ }^{\circ}\text{C}$), (g) rate performance at $-40 \text{ }^{\circ}\text{C}$ and (h) cycling stability at 1 C ($-40 \text{ }^{\circ}\text{C}$) of NFPP-FPH electrode.

discharge capacity of 116.5 mAh g^{-1} at 0.1 C with well-defined voltage plateaus. The additional discharge plateau observed around 2.5 V further confirms the active participation of the NFPO phase in capacity contribution. Its superior rate capability is demonstrated across all current densities (Fig. 3c), maintaining an impressively high capacity of 92.2 mAh g^{-1} at a high rate of 20 C . Cycling tests further validate this structural robustness. NFPP-FPH electrode retains 94% capacity after 600 cycles at 1 C , exhibiting high reversibility. By comparison, NFPP-FP electrode displays a more pronounced capacity fade, with only 83% retention (Fig. 3d). The starkest contrast is manifested during the long-term cycling test with 5000 cycles at 20 C (Fig. 3e). NFPP-FPH electrode demonstrates remarkable durability with 88% capacity retention. Conversely, NFPP-FP suffers a characteristic performance plunge after approximately 2500 cycles, with capacity retention eventually plummeting to 52% . This deterioration is driven by the prevalence of the inactive m-NFP phase and isolated NFPO domains with intrinsic sluggish kinetics, whereas the atomic-scale intergrowth in the hydrous FPH route ensures that the kinetically favored NFPP matrix effectively activates the NFPO nanodomains, ensuring superior rate capability and structural stability.

The practical viability of NFPP-FPH is highlighted by its exceptional low-temperature resilience. As illustrated in Fig. 3f, the NFPP-FPH electrode exhibits remarkable tolerance to extreme cold conditions, maintaining capacity retention rates of 91% , 86% , 78% , and 72% at -10 , -20 , -30 , and $-40 \text{ }^{\circ}\text{C}$,

respectively. The NFPP-FPH electrode also retains substantial rate capability at $-40 \text{ }^{\circ}\text{C}$, delivering nearly 54.0 mAh g^{-1} at a high rate of 5 C (Fig. 3g). Furthermore, the long-term durability was also validated at $-40 \text{ }^{\circ}\text{C}$. The electrode retains 89% capacity after 250 cycles at 1 C (Fig. 3h). Throughout the low-temperature cycling, the Coulombic efficiency remains near 100% , indicating highly reversible Na^+ (de)intercalation and minimal side reaction. These results confirm that the kinetically robust framework and pseudocapacitive charge-storage mechanism of NFPP-FPH effectively mitigate the increased energy barriers imposed by extreme cold conditions, ensuring reliable operation in sub-zero environments.

2.5 Electrode kinetics analysis

The electrochemical kinetics were investigated using galvanostatic intermittent titration technique (GITT), electrochemical impedance spectroscopy (EIS) and scan-rate dependent CV tests to elucidate the origin of the enhanced rate capability. The Na^+ diffusion kinetics were quantified *via* GITT (Fig. S16 and Table S4). The calculated diffusion coefficients (D_{Na^+}) for the NFPP-FPH-x electrodes are consistently higher than those of the NFPP-FP-x counterparts. Specifically, the optimal NFPP-FPH electrode achieves an average D_{Na^+} of $1.19 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, significantly surpassing that of NFPP-FP ($4.60 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$). This enhancement is attributed to the optimized Na^+ vacancy and the coherent biphasic interface, which lower the energy barrier for Na^+ migration. EIS measurements further

evaluate the interfacial charge-transfer kinetics. The NFPP-FPH series displays significantly smaller high-frequency semicircles compared to the NFPP-FP series, indicating reduced interfacial impedance (Fig. S17). Fitting results (Table S5) reveal a dramatic reduction in charge-transfer resistance (R_{ct}), with NFPP-FPH exhibiting a minimal R_{ct} value of 247.2 Ω , substantially lower than that of NFPP-FP electrode (1284.0 Ω). This confirms that the atomic-scale intergrowth of NFPP-NFPO significantly streamlines electron/ion exchange at the electrode/electrolyte interface.

Scan-rate dependent CV was performed to distinguish charge-storage contributions. The NFPP-FPH electrode (Fig. S18a) maintains sharp and well-defined redox peaks even at the highest scan rate of 0.8 mV s^{-1} with minimal potential shifts, demonstrating exceptional kinetic reversibility. Conversely, the NFPP-FP electrode (Fig. S18b) shows substantial peak broadening and voltage shifts as the scan rate increases, particularly for the high-voltage O2 and O3 peaks, reflecting sluggish Na^+ transport in the FP-derived framework. The relationship between peak current i and scan rate v was

quantified using the power-law equation: $i = av^b$, which can be linearized as $\log(i) = \log(a) + b\log(v)$.³⁹ For the NFPP-FPH electrode (Fig. S18c), the calculated b -values for primary redox peaks (O1, O2, R1 and R2) are 1.005, 0.986, 0.830 and 1.017, respectively. These values are remarkably close to 1.0, indicating a dominant surface-controlled pseudocapacitive mechanism. In contrast, the NFPP-FP electrode (Fig. S18d) exhibits generally lower b -values, reflecting a diffusion-controlled process hindered by inactive m-NFP and sluggish solid-state diffusion within the isolated NFPO domains.

2.6 Structural evolution and redox mechanism

To decipher the structural evolution and sodium storage mechanism of NFPP-FPH, *in situ* XRD was performed during the initial galvanostatic cycle (Fig. 4a). The pristine electrode identifies several peaks characteristic of NFPP phase, including the (011), (210), (020), (013), (022), (004), (222), and (602) crystal planes.⁴⁰ Upon charging, the (011), (210), (020) and (022) peaks shift toward higher 2θ angles, reflecting the lattice contraction associated with Na^+ extraction. Notably, the (222) and (004) peaks, which are initially overlapped,

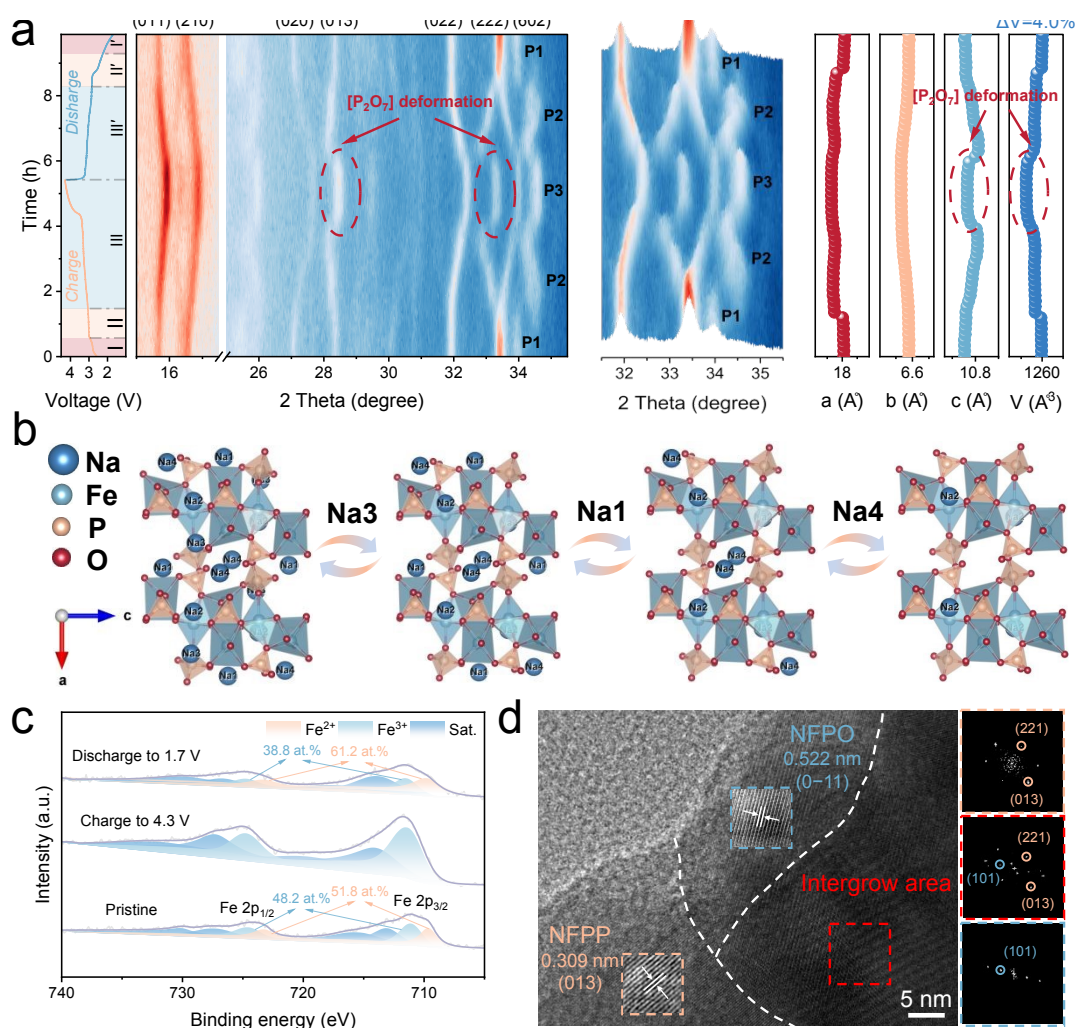


Fig. 4 (a) *In situ* XRD contour plots and corresponding evolution of lattice parameters of NFPP-FPH electrode during the initial GCD cycle. (b) Schematic illustration of the sodium storage mechanism. (c) Valence state evolution of Fe for NFPP-FPH electrode during the charge-discharge process. (d) HRTEM image and corresponding FFT patterns of NFPP-FPH electrode after 100 cycles.

gradually separate as the voltage approaches 3.0 V, confirming a single-phase solid-solution reaction (Region I).²⁸ Within the voltage range of 3.0–3.4 V, the (004) and (222) peaks move toward lower and higher 2θ values, respectively. Beyond 3.4 V, a sharp increase in diffraction angles is observed for the (004) and (013) peaks. This abrupt shift is intrinsically linked to the structural rearrangement and deformation of the $[\text{P}_2\text{O}_7]$ dimer, triggered by the enhanced electrostatic repulsion of Fe^{3+} - Fe^{3+} ions.^{41,42} Simultaneously, the (602) peak progressively fades away at 3.0 V, accompanied by the emergence and continual strengthening of a new metastable P2 phase at the expense of P1 phase. This transition results in a two-phase coexistence region (Region II), corresponding to the prominent voltage plateau at 3.0 V. As Na^+ extraction continues, the peak of P2 phase moves toward lower 2θ angles and eventually transforms into a P3 phase at 3.4 V, which persists until the end of the charge (Region III). An analogous phase transition behavior is observed during the subsequent discharge process. Overall, the *in situ* XRD results demonstrate that NFPP-FPH electrode undergoes a combined biphasic and solid-solution mechanisms throughout the entire sodium storage process.

This phase transition is mirrored by the lattice parameter evolution. During the initial charging stage, the unit cell parameter a and b exhibit continuous contraction. However, at the 3.0 V plateau, the coexistence of P1/P2 phases induces an abrupt decrease of a , while b continued its monotonic reduction. The unit cell volume (V) followed a trend analogous to parameter a . In contrast, parameter c gradually increases during charging and sharply decreases at 3.4 V due to $[\text{P}_2\text{O}_7]$ deformation. The overall volume variation is restricted to approximately 4.0%, and all parameters reversibly recover upon discharge, highlighting the exceptional structural flexibility of the NFPP-FPH framework. The Na^+ extraction sequence is identified as $\text{Na}_3 \rightarrow \text{Na}_1 \rightarrow \text{Na}_4$, while the insertion follows the reverse sequence (Fig. 4b). *In situ* Raman spectroscopy was conducted to evaluate the chemical bond evolution (Fig. S19). Several prominent peaks in the high-frequency region (700–1000 cm^{-1}) are attributed to the stretching vibrations of P–O within $[\text{P}_2\text{O}_7]$ and $[\text{PO}_4]$ units. The signal centered at $\sim 620 \text{ cm}^{-1}$ is assigned to the Fe–O stretching mode,⁴³ serving as a sensitive probe for the iron redox centers. Upon Na^+ extraction, the Fe–O peak undergoes systematic intensity evolution, reflecting the oxidation of Fe^{2+} to Fe^{3+} and dynamic adjustment of FeO_6 octahedra. All characteristic bands reversibly recover their original intensities and frequencies upon discharging to 1.7 V, confirming that the framework effectively buffers local coordination strain.

X-ray photoelectron spectroscopy (XPS) analysis (Fig. 4c) further tracks the charge compensation mechanism. In the pristine state, the Fe 2p spectrum reveals the coexistence of Fe^{2+} and Fe^{3+} species, indicating a relatively high initial oxidation state in the as-prepared sample. Upon charging to the 4.3 V, the Fe^{2+} component completely disappears, signifying its full oxidation to Fe^{3+} to compensate for the charge during desodiation. After discharging to 1.7 V, the Fe 2p peaks return toward lower binding energies, confirming the reduction of Fe^{3+} back to Fe^{2+} .⁴⁴ Although a residual amount of Fe^{3+} remains, its concentration is significantly lower than that observed in the pristine state, indicating a highly active and reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple within the NFPP-FPH framework. The stability of the unique intergrowth architecture was scrutinized *via* HRTEM after 100 cycles

(Fig. 4d). The atomic-scale intergrowth regions remain clearly visible, with no evidence of phase separation or structural collapse. Lattice fringes with d-spacings of 0.309 nm and 0.522 nm correspond to the (013) plane of NFPP and the (0–11) plane of NFPO, respectively. FFT analysis reveals overlapping diffraction spots from both phases, providing direct evidence that the coherent interface was successfully maintained. Crucially, geometric phase analysis (GPA) further reveals relatively higher lattice strain concentration within the NFPP domains, whereas the strain profiles across the NFPO and coherent intergrow areas are more uniform (Fig. S20). This discrepancy characteristically demonstrates that the coherent atomic-scale interface serves as a robust mechanical buffer to effectively homogenize localized stress, thereby preventing structural pulverization during extended cycling.

2.7 Full cell validation

To evaluate the practical application potential of the NFPP-FPH cathode, coin-type and pouch-type full cells were both constructed using hard carbon (HC) as the anode (Fig. 5a). The GCD profiles of the individual NFPP-FPH and HC electrodes in half cells are shown in Fig. 5b. Operating within a voltage window of 1.5–4.0 V, the NFPP-FPH|HC full cell delivers an impressive reversible capacity of 112.2 mAh g^{-1} and robust rate capability, maintaining 76% capacity retention even at 20 C (Fig. 5c). Remarkably, the full cell achieves a competitive energy density of 311 Wh kg^{-1} (based on the cathode mass), outperforming many recently reported NFPP-based SIB systems (Fig. 5d).^{27,35,45–52} Cycling performance shows a capacity retention of 84% after 200 cycles at 1 C (Fig. S21). Furthermore, the synthesis of NFPP-FPH was scaled up for the fabrication of practical pouch cells. XRD and SEM analyses (Fig. S22) confirm that the scaled-up sample exhibit identical crystalline structure and microstructural morphology to its laboratory-scale counterparts, validating the industrial viability of this dehydration-induced phase engineering strategy. The NFPP-FPH|HC pouch cell delivers a capacity of 0.53 Ah within the voltage window of 1.5–4.0 V (Fig. S23). Remarkably, it demonstrates outstanding long-term durability, maintaining 81% capacity retention after 2000 cycles at a high current of 2.4 A (Fig. 5e). These results collectively validate the effectiveness of the hydrous precursor-mediated route in producing high-performance, commercially viable NFPP cathode material.

3. Conclusions

In conclusion, we have elucidated a disorder-mediated and dehydration-triggered synthesis paradigm to engineer an atomic-scale coherent NFPP-NFPO intergrowth architecture. By leveraging the intrinsic structural disorder and dehydration-driven activation of the FPH precursor, we successfully bypassed the long-standing kinetic barriers inherent in conventional anhydrous FP route. Combined *in situ* characterizations and DFT calculations reveal that the disordered lattice provides a metastable environment that significantly lowers the activation energy for structural reorganization. The synchronized release of crystalline water triggers the fragmentation of the precursor into highly reactive nanodomains and facilitating the rapid polycondensation of

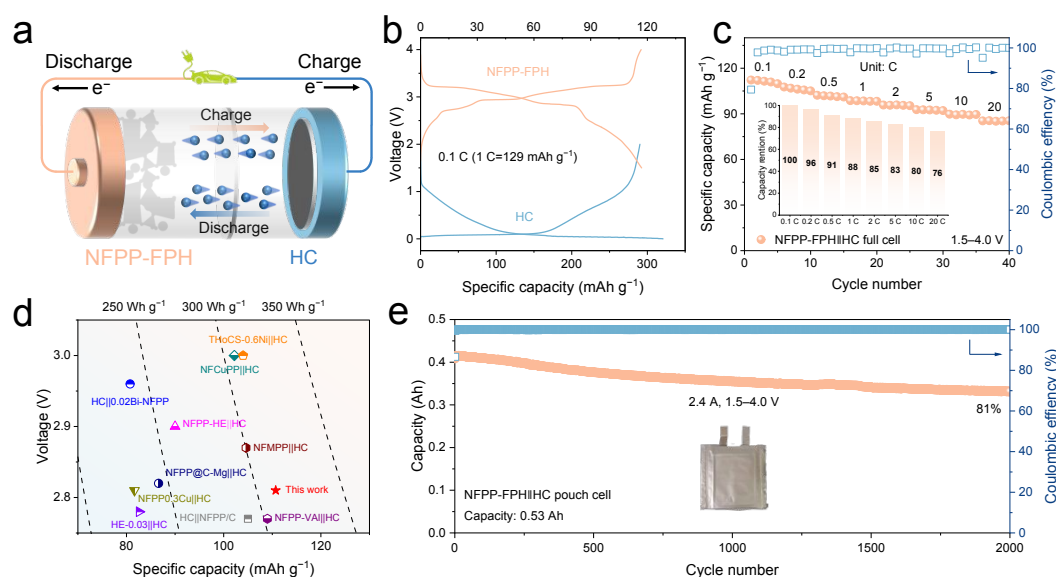


Fig. 5 (a) Schematic illustration of the configuration and working mechanism for the NFPP-FPH || HC full cell. (b) GCD profiles of NFPP-FPH cathode and HC anode in half-cells at 0.1 C. (c) Rate capability of the NFPP-FPH || HC coin-type full cell at various current densities from 0.1 C to 20 C (inset: capacity retentions at different rates). (d) Comparison of energy density and average operating voltage between the NFPP-FPH || HC full cell and previously reported NFPP cathode-based full cells. (e) Long-term cycling performance of the NFPP-FPH || HC pouch cell at 2.4 A.

[P₂O₇] units. This strategy effectively reconfigures the thermodynamic landscape, widening the formation energy gap to circumvent the m-NFP trap and steering the phase evolution toward a synergistic NFPP-NFPO architecture. This unique coherent configuration establishes seamless heterophase interfaces that minimize interfacial resistance and accelerate Na⁺ diffusion kinetics. Consequently, the optimized NFPP-FPH cathode exhibits not only robust long-term durability but also exceptional kinetic resilience that enables high-rate capability and superior performance under extreme sub-zero conditions. The practical robustness of this material is further underscored by the successful validation in pouch cells, which maintain an impressive 81% capacity retention after 2000 cycles. Beyond its outstanding electrochemical merits, this approach offers a highly scalable and pragmatic industrial blueprint by eliminating energy-intensive pre-dehydration stages associated with conventional anhydrous precursor. More fundamentally, this study highlights the pivotal role of precursor disorder and hydration chemistry in dictating the phase evolution of complex polyanionic materials, establishing a broadly applicable strategy for the precision synthesis of advanced polyanionic materials.

Author contributions

Qi Xu: conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing-original draft, writing-review and editing; Ruoyang Wang: formal analysis, visualization, writing-review and editing; Zelin Hao: methodology, writing-review and editing; Xianyan Qiao: resources, writing-review and editing; Haoyu Li: resources, writing-review and editing; Guosong Meng: writing-review and

editing; Chunliu Xu: funding acquisition, methodology, resources, supervision, visualization, writing-review and editing; Zhenguo Wu: conceptualization, funding acquisition, methodology, resources, supervision, visualization, writing-review and editing; Xiaodong Guo: funding acquisition, resources, supervision, writing-review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this work are included in the paper and the supplementary information (SI). Supplementary information is available.

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References

- 1 W. Zuo, Z. Liu, A. Dopilka, Z. Yang, Y. Li, J. Kubal, H. Kim, F. Liu, P. Liu, A. T. Ngo, J. Nelson Weker, Z. Chen, R. Kostecki, J. Wulf-Knoerzer, V. Srinivasan, Y. Cui, K. Amine and G.-L. Xu, *Nat. Rev. Mater.*, 2026, **11**, 117–135.
- 2 L. Yang, X. Yin, J. Wang, Y. Sun, Y. Li, Z. Zhang, Z. Liu, S.-M. Huang, P. Adelhelm and D. Zhou, *Nat. Rev. Chem.*, 2026, **10**, 196–211.
- 3 X. Zhang, F. Ding, K. Han, Z. Chen, H. Wan, X. Xu, X. Wang, J. Meng, Z. Qin, B. Li, X. Liu, T. Chen and C. Niu, *Adv. Mater.*, 2026, **38**, e21756.
- 4 S. Mariyappan, P. Desai, M. Morcrette and J. M. Tarascon, *Nat. Sustain.*, 2026, **9**, 360–371.
- 5 Y. L. Yan, W. X. Zhao, J. Q. Hu, H. L. Wang, Z. Xing, J. R. Geng, S. K. Jiang, Q. F. Gu, H. K. Liu, S. X. Dou, J. W. Zhu, Z. W. Zhao, P. Xiong, L. M. Zhou and M. Z. Chen, *Adv. Energy Mater.*, 2026, **16**, e05808.
- 6 Z. Qayyum, W. Xu, Q. Liu, M. Khan, L. Hou, M. M. Khan, W. He, D. Mu, L. Li, R. Chen and F. Wu, *Mater. Today*, 2026, **94**, 103218.
- 7 Z. Ahsan, Z. F. Cai, S. Wang, M. Moin, H. C. Wang, D. M. Liu, Y. Z. Ma, G. S. Song and C. E. Wen, *Adv. Energy Mater.*, 2024, **14**, 2400373.
- 8 C. Xu, W. Hua, G. Feng, Z. Chen, R. Xiao, Q. Zhang, W. Yang, C. Yang, J. Zhao and Y.-S. Hu, *Angew. Chem. Int. Ed.*, 2025, **64**, e202502758.
- 9 H. Xia, W. Xu, W. Wang, H. Wu, Y. Zhang, W. Cai and K. Wu, *Energy Storage Mater.*, 2026, **84**, 104788.
- 10 X. Xiao, Y. Lan, L. Tan, H. Xu, W. Yao and Y. Tang, *Adv. Funct. Mater.*, 2024, **34**, 2411280.
- 11 H. Kim, I. Park, D. H. Seo, S. Lee, S. W. Kim, W. J. Kwon, Y. U. Park, C. S. Kim, S. Jeon and K. Kang, *J. Am. Chem. Soc.*, 2012, **134**, 10369–10372.
- 12 Y. Wang, F. X. Deng, S. W. Ouyang, C. Jiang and H. X. Li, *J. Energy Chem.*, 2025, **111**, 914–934.
- 13 P. Zhu, Q. Yu, C. Peng, B. Li, Z. Wang, X. Lei, Z. Zhu, X. Tan, Y. Zeng, L. Han, X. Zhang, J. Du, Y. Yin and Y. L. Ding, *Small*, 2026, **22**, e14884.
- 14 H. Liao, Z. Zhang, Y. Zheng and Y. Gao, *Energy Storage Mater.*, 2024, **65**, 103157.
- 15 C. L. Xu, L. Zhou, T. Gao, Z. Chen, X. Y. Hou, J. Zhang, Y. Bai, L. R. Yang, H. Z. Liu, C. Yang, J. M. Zhao and Y. S. Hu, *J. Am. Chem. Soc.*, 2024, **146**, 9819–9827.
- 16 C. Liu, Z. Zhang, H. Liao, Y. Jiang, Y. Zheng, Z. Li and Y. Gao, *Adv. Funct. Mater.*, 2025, **35**, 2424759.
- 17 Z. L. Hao, J. Z. Guo, M. Du, X. R. Zhang, Y. L. Heng, Z. Y. Gu, X. T. Wang, X. X. Zhao, N. Yu, Z. H. Xue, S. H. Zheng, B. Li and X. L. Wu, *J. Am. Chem. Soc.*, 2025, **147**, 13905–13914.
- 18 X. Wang, H. X. Li, X. C. Ge, L. He, S. H. Li, Y. Zhang, J. H. Gu, W. Zhou, Y. Q. Lai and Z. Zhang, *Energy Storage Mater.*, 2025, **79**, 104308.
- 19 L. Ran, B. L. Shen, L. Yue, H. Y. Hu, Y. H. Xiang, Z. F. Jiang, Z. H. Li, Y. C. Duan, Y. N. Zhao, Y. Zheng, M. W. Xu, Y. Xiao and Y. B. Niu, *Angew. Chem. Int. Ed.*, 2026, **65**, e25531.
- 20 A. Zhao, C. Liu, F. Ji, S. Zhang, H. Fan, W. Ni, Y. Fang, X. Ai, H. Yang and Y. Cao, *ACS Energy Lett.*, 2022, **8**, 753–761.
- 21 Y. Shao, C. Y. Liu, H. M. Fan, B. Zhang, L. R. Liao, A. L. Zhao, X. Li, P. Chu and Y. L. Cao, *Small*, 2025, **21**, 2504847.
- 22 W. D. Song, N. Chen, J. P. Wang, W. B. Hua, B. H. Zhang, S. Q. Zhao, X. Ming, Z. X. Shen, G. Chen and F. Du, *J. Am. Chem. Soc.*, 2025, **147**, 39151–39159.
- 23 J. Wang, K. Wang, Q. M. Liu, H. Su and H. J. Zhu, *Chem. Eng. J.*, 2025, **514**, 163122.
- 24 Q. Lu, T. Shen, Y. Zeng, Y. Zhou, M. Su, Z. Sun, L. Liu, A. Jiang, Y. Wan, Y. Liu and R. Wang, *Adv. Funct. Mater.*, 2025, **35**, e09628.
- 25 S. Y. Wang, Q. Zhang, H. Y. Zhu, Y. Y. Du, K. Yu, D. Zhou, Y. H. Deng, J. Wang and J. K. Jian, *Adv. Funct. Mater.*, 2025, **36**, e20871.
- 26 Y. H. Xin, H. X. Zhang, Y. S. Wang, Q. C. Wang, Q. B. Zhou, K. Y. Zhao, F. Wu and H. C. Gao, *Adv. Funct. Mater.*, 2026, **36**, e18331.
- 27 Q. Xia, L. Zhang, D. Wang, J. Wang, Z. Xu, Y. Zhang, Z. Yao, Y. Guo, P. Jia, L. Zhang and Y. Yang, *Energy Storage Mater.*, 2026, **84**, 104849.
- 28 M. L. Cao, M. L. Feng, J. Hu, Y. Xu, C. Fang, J. Peng, J. T. Han and Y. H. Huang, *Adv. Energy Mater.*, 2025, e04854, DOI: 10.1002/aenm.202504854.
- 29 D. D. Yin, Q. Wang, S. C. Liu, L. Y. Lei, B. H. Dai, T. M. Lu, E. M. Li, J. J. Huang, J. H. Teng, K. B. Zhang, X. Tang and J. Li, *J. Energy Chem.*, 2025, **134**, 118157.
- 30 J. Tu, L. Chen, Y. Li, X. Wang and B. Zhang, *J. Alloy. Compd.*, 2025, **1017**, 179168.
- 31 T. Jeong, S. K. Mohanty, W. J. Kwon, S. C. Reddy, A. R. Pati, J. H. Ryu and H. D. Yoo, *J. Mater. Chem. A*, 2025, **13**, 16694–16703.
- 32 B. Dai, T. Lu, J. Huang, E. Li, Q. Tao, J. Teng, K. Zhang, J. Zhou, X. Tang and J. Li, *J. Power Sources*, 2024, **620**, 235266.
- 33 A. Gezović, M. Milović, D. Bajuk-Bogdanović, V. Grudić, R. Dominko, S. Mentus and M. J. Vujković, *Electrochim. Acta*, 2024, **476**, 143718.
- 34 Y. Yan, S. Jiang, L. Zhao, H. Wang, J. An, J. Geng, Y. Li, H. Zhu, P. Xiong, J. Zhu, Q. Gu, G. Wang, R. Yu, L. Zhou, H. Xia and M. Chen, *ACS Energy Lett.*, 2026, **11**, 2885–2895.
- 35 Y. J. Wang, Z. Y. Gu, D. S. Bai, Z. L. Hao, H. W. Huang, Y. Yan, C. J. Li, A. M. Liu and X. L. Wu, *Angew. Chem. Int. Ed.*, 2025, **64**, e202507573.
- 36 H. Wang, Z. Zhang, Y. Chu, A. Lai, S. Kang, G. Xu, F. Peng, W. Li, M. Liu and C. Yang, *ACS Nano*, 2025, **19**, 41824–41835.
- 37 P. Dong, F. Peng, Q. Zhang, H. Wang, Y. Chu, C. Chen and C. Yang, *Angew. Chem. Int. Ed.*, 2025, **64**, e202502693.
- 38 H. Dai, Z. Yang, T. Xie, Z. Zhao, Y. Shang, C. Ai and Q. Yi, *Adv. Funct. Mater.*, 2025, **35**, 2505185.
- 39 X. Wang, Y. Xu, J. Zhang, Y. Xi, N. Hou, Y. Chen, D. Liu, Z. Yang, H. Wen, J. Kang, X. Yang, X. Song, J. Wang, W. Li, J. Zhang, K. Zhang and X. Li, *Nano-Micro Lett.*, 2026, **18**, 237.
- 40 S. K. Jiang, Y. Q. Wang, H. Ge, B. K. Yu, T. Wang, T. Wang, H. L. Wang, X. L. Qu, H. T. Zuo, Z. W. Zhao, L. M. Zhou, W. B. Hua, M. Z. Chen and H. Xia, *ACS Nano*, 2025, **19**, 1499–1508.
- 41 P. Y. Li, Y. D. Huang, Y. J. Chen, M. Chen, W. Yin, S. L. Liu, Q. Wu, H. Z. Chen, J. F. Zhang, X. H. Zhang, G. D. Ren and J. C. Zheng, *Energy Storage Mater.*, 2025, **80**, 104432.
- 42 H. Kim, I. Park, S. Lee, H. Kim, K.-Y. Park, Y.-U. Park, H. Kim, J. Kim, H.-D. Lim, W.-S. Yoon and K. Kang, *Chem. Mater.*, 2013, **25**, 3614–3622.
- 43 Z. Fan, W. Song, N. Yang, C. Lou, R. Tian, W. Hua, M. Tang and F. Du, *Angew. Chem. Int. Ed.*, 2024, **63**, e202316957.
- 44 Q. Lu, T. Y. Shen, C. L. Li, Y. J. Wei, Y. Zhou, M. R. Su, P. P. Zhang, C. T. Sun, J. C. Wu, F. Wang, L. Y. Zhang, Q. Q. Tian, Y. J. Liu and R. H. Wang, *Nano Lett.*, 2026, **26**, 1375–1384.
- 45 X. Qi, H. Dong, H. Yan, B. Hou, H. Liu, N. Shang, L. Wang, J. Song, S. Chen, S. Chou and X. Zhao, *Angew. Chem. Int. Ed.*, 2024, **63**, e202410590.
- 46 J. Q. Gao, H. Y. Chen, Y. Mei, L. S. Ni, H. J. Wang, J. N. Huang, N. Y. Hong, B. Song, Y. Tian, W. T. Deng, G. Q. Zou, H. S. Hou and X. B. Ji, *Nano Energy*, 2023, **115**, 108747.
- 47 X. S. Wang, S. Q. Li, Z. K. Fang, G. B. Zhang, C. P. Han, R. M. Sun and B. H. Li, *Nano Energy*, 2025, **144**, 111397.
- 48 P. Wei, S. Lv, F. Wu, Y. Zhang, F. Cheng, K. Liang, J. Li and Y. Ren, *ACS Mater. Lett.*, 2026, **8**, 1224–1232.
- 49 X. R. Qi, Q. Y. Dong, H. H. Dong, B. X. Hou, H. Y. Liu, N. Z. Shang, S. H. Zhang, L. G. Wang, H. Shao, Y. B. Shen, S. Q. Chen and X. X. Zhao, *Energy Storage Mater.*, 2024, **73**, 103861.
- 50 X. Ge, H. Li, J. Li, C. Guan, X. Wang, L. He, S. Li, Y. Lai and Z. Zhang, *Small*, 2023, **19**, e2302609.
- 51 H. F. Li, M. C. Liu, J. Shi, J. B. Zhu and J. K. Ou, *J. Alloy. Compd.*, 2026, **1051**, 185967.

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52 S. Zhao, H. Li, S. Shi, C. Wang and X. S. Zhao, *J. Mater. Chem. A*, 2026, **14**, 13677–13687.

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Data availability

The data that support the findings of this work are included in the paper and the supplementary information (SI). Supplementary information is available.