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Leidenfrost-Assisted Synthesis of Indium-Substituted Mixed Phosphate Cathodes with Superior Cycling Stability and Enhanced Sodium Storage Kinetics

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ABSTRACT

The unavailability of high-performance cathodes hinders large-scale adoption of sodium-ion batteries (NIBs). In this work, we report for the first time a Leidenfrost-assisted synthesis as a low-cost and scalable approach for designing In³⁺-doped mixed phosphate ([PO₄]³⁻-[P₂O₇]⁴⁻) cathodes. The strategic substitution of In³⁺ at the Fe site induces lattice expansion, thereby facilitating enhanced Na⁺ diffusion and improved electrochemical performance. The optimized cathode composition, Na₄Fe_{2.97}In_{0.03}(PO₄)₂P₂O₇ (NFIPP03), exhibits exceptional electrochemical performance, with a specific capacity of 129.3 mAh g⁻¹ at 0.05 C, corresponding to an energy density of ~359 Wh kg⁻¹, and a stable cycling performance more than 10 000 cycles at 20 C. Temperature-dependent magnetic susceptibility (M–T) and electron paramagnetic resonance (EPR) measurements reveal an enhanced spin state in NFIPP03 compared to the pristine sample, as well as improved electrical conductivity. Ex situ XRD and XPS analyses confirm excellent structural and chemical stability during (de)sodiation. Furthermore, density functional theory (DFT) calculations indicate significantly widened Na⁺ migration pathways, reduced activation energy barrier, and an attenuated bandgap in NFIPP03 which corroborates our experimental observations. Our findings highlight the synthesis for developing cost-effective, high-performance iron-based mixed-phosphate cathodes, advancing the sustainability and scalability of NIB technology.

1 | Introduction

The growing global shift toward renewable energy sources has created an urgent demand for cost-effective and scalable energy storage systems to support decarbonization efforts [1]. While lithium-ion batteries (LIBs) have been successfully implemented in powering portable electronics and electric vehicles [2], their

reliance on scarce and geographically concentrated lithium resources has led to concerns over supply security, cost volatility, and geopolitical risks. As a result, there is a strong push for alternative battery technologies [3]. Sodium-ion batteries (NIBs) have emerged as a compelling alternative due to the natural abundance and low cost of sodium, along with their promising electrochemical performance [4]. However, the advancement of

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NIB technology hinges on the development of cathode materials that can deliver high capacity, long cycling stability, and rapid charge–discharge capability [5].

Among the available cathode materials, the polyanionic-type cathodes have garnered significant attention for NIBs due to their open 3D frameworks and robust structural stability during Na^+ (de)intercalation [6]. In polyanion cathodes, sodium superionic conductor (NASICON)-type phosphates, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ [7], $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ [8], $\text{Na}_3(\text{VO}_x)_2(\text{PO}_4)\text{F}_{3-2x}$ ($x = 0$ or 1) [9] etc. have attracted considerable attention in recent years. These materials offer high operating voltages and enable multi-electron redox reactions ($\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$), contributing to superior energy densities. However, their practical deployment is mainly hindered by the high-cost and toxicity of vanadium [10]. NASICON-type materials utilizing cost-effective iron as the redox-active center present a promising solution to the limitations associated with vanadium-based cathodes [11]. Iron-based systems not only reduce production cost but also improve the practicality of NIBs for large-scale energy storage applications [12].

However, synthesizing electrochemically active iron-rich phosphate-type cathodes remains challenging. The commonly formed maricite polymorph of iron phosphate lacks viable Na^+ diffusion pathways, making it unsuitable for practical application [13]. In contrast, iron pyrophosphate offers a stable 3D Na^+ conduction framework and a relatively high operating voltage (~ 3.0 V), attributed to the inductive effect of the $\text{P}_2\text{O}_7^{4-}$ group [14]. Yet, its reversible capacity is limited (<100 mAh g^{-1}) due to its high molecular weight. To address these challenges, recent efforts have focused on designing mixed-polyanion frameworks that combine both PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ groups [15]. These hybrid structures aim to leverage the structural stability of phosphates and the voltage-enhancing inductive effects of pyrophosphates, thereby offering an effective route to improve energy density and cycling performance in next-generation NIB cathodes. In this regard, Kang and co-workers reported $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ (NFPP) [16], a mixed phosphate–pyrophosphate with a NASICON-type structure, offering high theoretical capacity (129 mAh g^{-1}), a favorable operating voltage (~ 3.1 V), and minimal volume change ($\sim 4.1\%$) during cycling. Despite these advantages, NFPP suffers from poor electronic conductivity and sluggish Na^+ diffusion, limiting its practical performance. To overcome these issues, strategies such as cation/anion doping [6, 17–20], dual-doping (e.g., Mn/F) [21, 22], carbon coating [23], morphology tuning [24], and high-entropy engineering [25–27] have been explored to improve conductivity and structural stability. However, most of these approaches rely on conventional synthesis methods, which restrict scalability and sustainability.

In this work, we present a novel and environmentally friendly synthesis strategy (Figure 1) for $\text{Na}_4\text{Fe}_{3-x}\text{In}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ cathodes, utilizing the Leidenfrost effect, this effect occurs when a liquid comes into contact with a surface significantly hotter than its boiling point, causing it to levitate on a vapor cushion [28–30], which enables rapid solvent evaporation and instantaneous nucleation followed by annealing. This approach ensures excellent phase purity, and scalable production. The resulting materials exhibit a porous morphology that promotes electrolyte percolation and efficient Na^+ transport. To enhance

electrochemical performance, indium (In^{3+}) was introduced as a dopant at the Fe site, inducing lattice expansion, improving electronic conductivity, and accelerating charge storage kinetics. The complete compositional series is labeled as NFIPP00, NFIPP01, NFIPP03, NFIPP05, NFIPP07, and NFIPP10 corresponds to $\text{In}(x) = 0, 0.01, 0.03, 0.05, 0.07,$ and 0.10 moles respectively. Notably, NFIPP03 emerges as the optimal candidate. It delivers a high specific capacity of 129.3 mAh g^{-1} at 0.05 C (energy density ~ 359 Wh kg^{-1}), retains $\sim 90\%$ capacity over 1000 cycles at 2 C, and demonstrates remarkable long-term cycling stability over 10000 cycles at 20 C, underscoring its structural and electrochemical resilience under high-rate conditions. Temperature-dependent magnetic susceptibility (M – T) and electron paramagnetic resonance (EPR) measurements reveal an enhanced spin state relative to the pristine sample, correlating with a reduced bandgap and increased electrical conductivity. Ex situ XRD and XPS confirm the structural and chemical stability of NFIPP03 during Na^+ insertion/extraction. Furthermore, density functional theory (DFT) calculations indicate widened Na^+ migration pathways, a lower activation energy barrier, and a narrower bandgap, all of which corroborate the experimental observations. Together, these findings validate the effectiveness of In^{3+} doping and Leidenfrost-assisted synthesis as a scalable and sustainable strategy for advancing iron-based phosphate cathodes in NIBs technology.

2 | Results and Discussion

2.1 | Material Characterizations

NFIPP samples were prepared via a Leidenfrost-assisted spray-drying process followed by annealing, as shown in Figure 1. Aqueous precursor solutions were sprayed onto a heated surface, where rapid evaporation and precursor fusion occurred. The resulting powder was subsequently annealed at 550°C under an inert atmosphere to yield NFIPP. Detailed synthesis procedures are provided in the experimental section of the supporting file. To gain insight into the crystal structure and phase stability of the NFIPP cathodes, X-ray diffraction (XRD) analysis was performed. All the samples exhibit a well-defined diffraction pattern consistent with an orthorhombic phase of the $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ framework [16]. As shown in Figure 2a, the patterns of the doped NFIPP compositions closely align with the NFIPP00, suggesting that the incorporation of a small amount of In^{3+} does not alter the parent structure. Interestingly, some diffraction peaks, from 15° to 21° in the magnified XRD regions (Figure 2b) corresponding to the planes (0 1 1), (2 1 0), and (4 0 0), reveal a shift toward lower 2θ angles upon In^{3+} doping. These shifts are indicative of a slight lattice expansion, likely resulting from the substitution of Fe^{2+} (ionic radius ≈ 0.78 Å) [6] by the larger In^{3+} ions (≈ 0.80 Å) [31]. Such lattice expansion may play a pivotal role in enhancing Na^+ diffusion by broadening the ionic transport channels and lowering migration barriers during electrochemical cycling.

To further validate the structural integrity and cationic substitution, Rietveld refinements were performed for both NFIPP00 and the optimized NFIPP03 composition (Figure 2d,e). The diffraction data were indexed to the orthorhombic $Pn2_1a$ space group with the lattice parameters $a = 18.1379$ Å, $b = 6.5572$ Å, $c = 10.5278$ Å, and $V = 1252.106$ Å³ for NFIPP00, consistent with previous reports on NFPP [15]. The refined lattice parameters

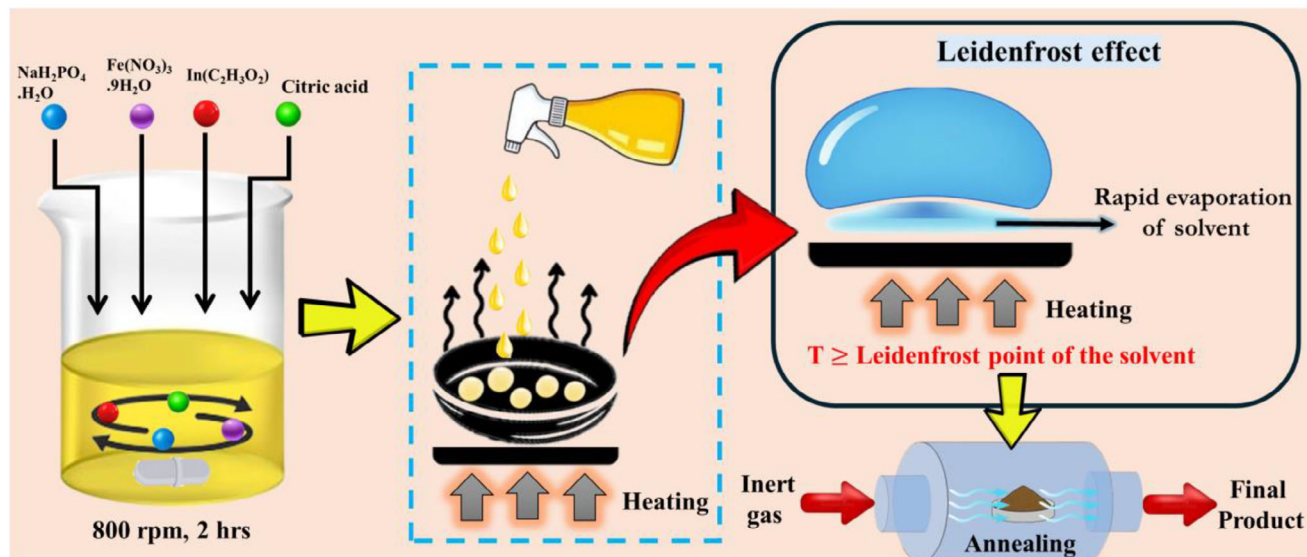


FIGURE 1 | Schematic diagram of the synthesis process of NFIPP material.

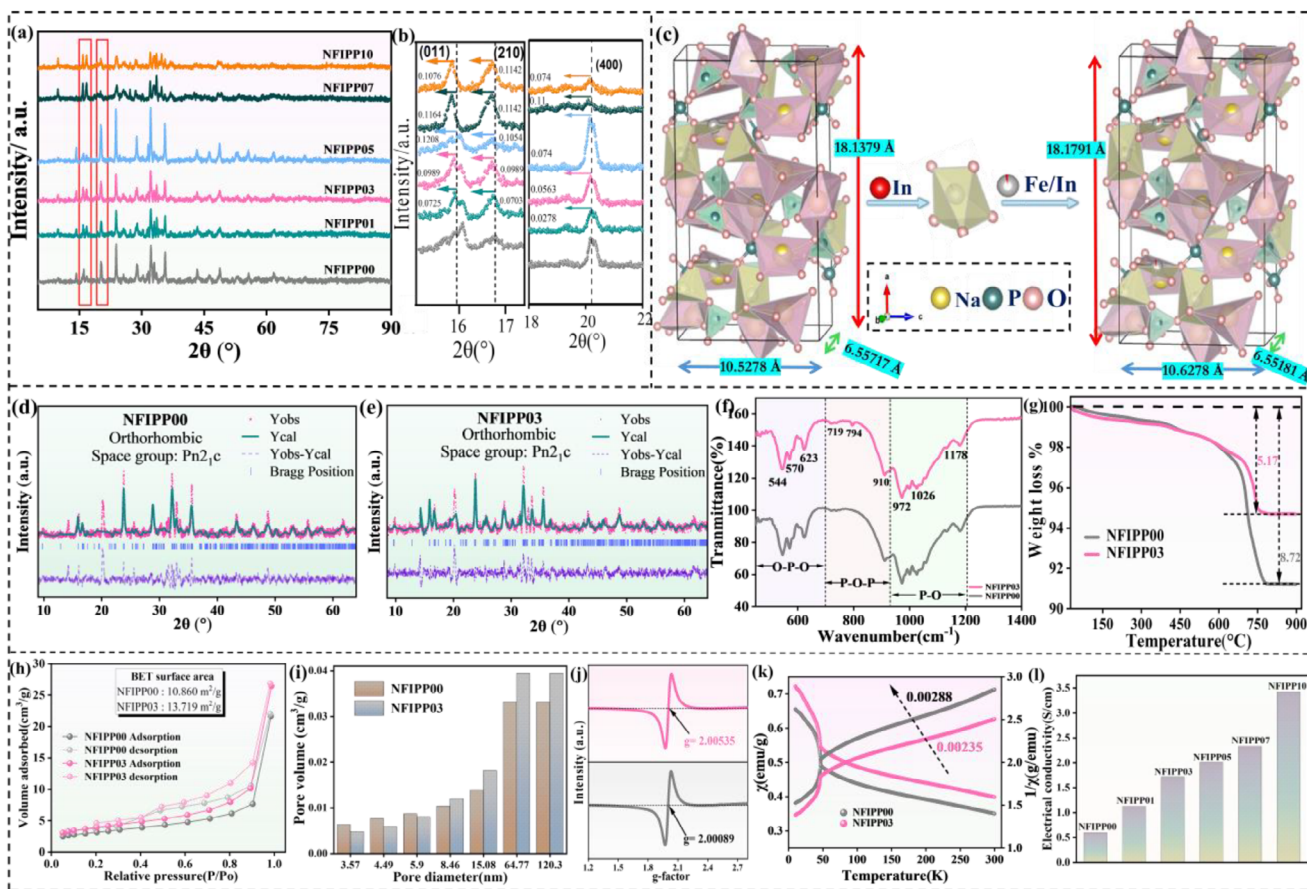


FIGURE 2 | (a) XRD patterns (b) XRD shifts corresponding to (011), (210) & (400) planes of all NFIPP samples. (c) Schematic crystal structure of NFIPP00 & NFIPP03. (d,e) XRD Rietveld refinement results for NFIPP00 & NFIPP03 respectively. FTIR spectra (f) & TG analysis (g) of NFIPP00 & NFIPP03 respectively. N_2 adsorption/desorption isotherms (h) and equivalent pore size distribution analysis (i) of NFIPP00 and NFIPP03. EPR spectrum (j) and temperature-dependent magnetic susceptibility profile (k) for NFIPP00 & NFIPP03. (l) Electrical conductivity measurement for all NFIPP samples.

exhibit a satisfactory fitting quality with low residual values, confirming the successful incorporation of In^{3+} into the host lattice. Full crystallographic details before and after doping, including unit cell dimensions, are provided in Tables S1 and S2. The typical crystalline structure is depicted in Figure 2c. Structurally, the NFPP framework is composed of $[\text{Fe}_3\text{P}_2\text{O}_{13}]$ clusters, built from edge-sharing FeO_6 octahedra and PO_4 tetrahedra, forming a 3D skeleton with extensive Na^+ diffusion pathways [10]. In^{3+} substitution at the Fe site, introduces minimal local distortion while retaining the 3D network essential for fast Na^+ transport. These structural features, together with the phase purity and subtle lattice tuning, underpin the enhanced electrochemical behavior observed in the doped compositions. Furthermore, the average Na–O distance is increased from 2.492 to 2.535 Å after In^{3+} -doping, which is capable of weakening the Na–O bonds, thus facilitating the Na^+ diffusion. Fourier-transform infrared (FTIR) spectroscopy was employed to investigate the functional groups present in the NFPP material, as shown in Figure 2f. The absorption bands observed in the 700–970 cm^{-1} region correspond to the stretching vibrations of the P–O–P bonds, characteristic of pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) groups. Meanwhile, the bands in the 400–700 and 970–1300 cm^{-1} regions are attributed to O–P–O bending and P–O stretching vibrations, respectively, which are typical of orthophosphate (PO_4^{3-}) groups [32]. All relevant vibrational data are summarized in Table S3. The coexistence of these characteristic phosphate and pyrophosphate signatures provides compelling evidence for the successful formation of the $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ structure, validating the expected chemical composition and bonding environment of the synthesized material. Thermogravimetric analysis (TGA) reveals a markedly lower residual carbon content in the optimized NFIPP03 sample (5.17%) compared to the undoped NFIPP00 (8.72%), as shown in Figure 2g. This reduction suggests improved carbon decomposition efficiency and an enhanced thermal stability. The specific surface area and pore structure of NFIPP00 and NFIPP03 were evaluated using N_2 adsorption–desorption measurements. As shown in Figure 2h, the optimized NFIPP03 exhibits a moderately higher Brunauer–Emmett–Teller (BET) specific surface area of 13.719 $\text{m}^2 \text{g}^{-1}$, compared to 10.860 $\text{m}^2 \text{g}^{-1}$ for NFIPP00. This increase in surface area is expected to enhance electrode–electrolyte interaction and provide more accessible active sites for Na^+ intercalation, contributing to improved electrochemical performance. The corresponding pore size distribution curves, shown in Figure 2i, reveal that NFIPP03 possesses a slightly larger average pore size than NFIPP00, which aligns well with the porous morphology observed in SEM images. These structural features facilitate efficient electrolyte infiltration, suggesting that NFIPP03 provides a more favorable environment for rapid Na^+ ion transport [33].

To understand the effect of the local electronic environment, EPR spectroscopy, M–T measurements, and two-probe conductivity analysis were performed. EPR spectroscopy was specifically employed to examine the electronic spin states and g-factor, offering insights into the behavior of unpaired electrons under an applied magnetic field. As illustrated in Figure 2j, EPR spectra exhibited notable shifts following elemental doping. The observed difference in g-factor ($\Delta g = 4.46 \times 10^{-3}$) between doped and undoped samples indicates that changes in angular momentum gained or lost by unpaired electrons can significantly alter the

g-value. The increased g-factor after In^{3+} -doping suggests an enhancement in the spin state of Fe, reflecting a modified local electronic configuration in the NFIPP03 sample. To further validate these observations, magnetization vs. temperature (M–T) measurements were conducted to evaluate the magnetic behavior of both samples. As depicted in Figure 2k, the plot of $1/\chi$ vs. T displayed a linear trend with lower slope for NFIPP03 compared to the NFIPP00, revealing that doping enhances the paramagnetic properties of the material, indicating increase in the Pauli paramagnetism of free electron spins within the Fe-centres [31, 34]. These findings are consistent with previous studies [35–37]. To gain a more comprehensive understanding of the electronic conductivity of the NFIPP series, two-point probe measurements were conducted. As depicted in Figure 2l, the average conductivities for NFIPP00, NFIPP01, NFIPP03, NFIPP05, NFIPP07, and NFIPP10 were determined to be 5.95×10^{-9} , 1.12×10^{-8} , 1.72×10^{-8} , 2.01×10^{-8} , 2.33×10^{-8} , and $3.42 \times 10^{-8} \text{ S cm}^{-1}$, respectively. This progressive enhancement in conductivity with increasing indium content, strongly suggests that In^{3+} doping enhances the electronic transport properties of the material, likely by facilitating charge delocalization or modifying the local electronic structure at Fe-sites. These findings align with previous studies demonstrating that indium doping enhances electrical conductivity in Fe-based materials. For instance, indium-doped LiFePO_4 cathodes have shown improved electrochemical performance due to increased electronic conductivity [38]. The elemental compositions and chemical state of the synthesized samples were further characterized using X-ray photoelectronic spectroscopy (XPS). The survey spectra of NFIPP00 and NFIPP03 (Figure 3a,b) clearly show the presence of Na 1s, Fe 2p, O 1s, P 2p, C 1s, and In 3d (only in NFIPP03), confirming successful indium incorporation. High-resolution deconvoluted spectra (Figure 3c–g for NFIPP03; Figure S1 for NFIPP00) provide deeper insights into the oxidation states of key elements. The Fe 2p spectrum confirms the coexistence of Fe^{3+} and Fe^{2+} in NFIPP03 (Figure 3c). The characteristic peaks at 711.2 (Fe $2p_{3/2}$) and 724.5 eV (Fe $2p_{1/2}$) are assigned to Fe^{2+} , while the peaks at 714.4 (Fe $2p_{3/2}$) and 727.6 eV (Fe $2p_{1/2}$) correspond to Fe^{3+} , accompanied by satellite peaks at 718.2 and 731.2 eV. Similar features are observed for NFIPP00 (Figure S1), indicating partial reduction of Fe^{3+} to Fe^{2+} during the reaction [39]. Similarly, the In 3d region (Figure 3d) reveals two distinct peaks at 445.8 and 453.0 eV, attributed to In $3d_{5/2}$ and In $3d_{3/2}$, respectively, confirming the presence of In^{3+} [31]. The C 1s spectra were deconvoluted to reveal three primary bonding environments (Figure 3e). A dominant peak at 284.6 eV corresponds to sp^2 -hybridized graphitic carbon ($\text{C}=\text{C}$), indicative of π -bonded delocalized electrons. Additional peaks at 285.8 and 288.7 eV are attributed to C–O and O–C=O species, respectively, suggesting the presence of surface-bound oxygenated functional groups [10, 40].

The surface morphology of NFIPP00 and NFIPP03 was examined via scanning electron microscopy (SEM), as shown in Figures S2 and S3. Both samples exhibit sponge-like porous structures formed after the high-temperature annealing process. These interconnected pores are expected to facilitate improved electrolyte penetration and enhance the interfacial contact between the electrolyte and cathode material, thereby promoting more efficient Na^+ insertion and extraction. Notably, no significant morphological differences were observed between the undoped and doped samples, indicating that the macroscopic morphology

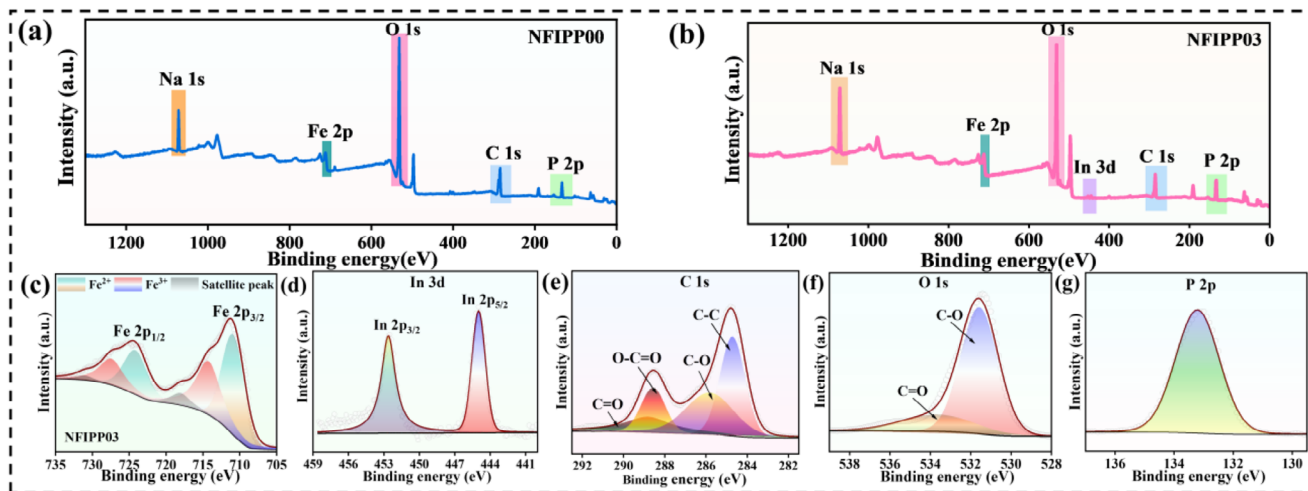


FIGURE 3 | (a,b) XPS survey scan of NFIPP00 & NFIPP03. (c-g) Deconvoluted spectrum of Fe2p, In3d, C 1s, O 1s, P 2p for NFIPP03.

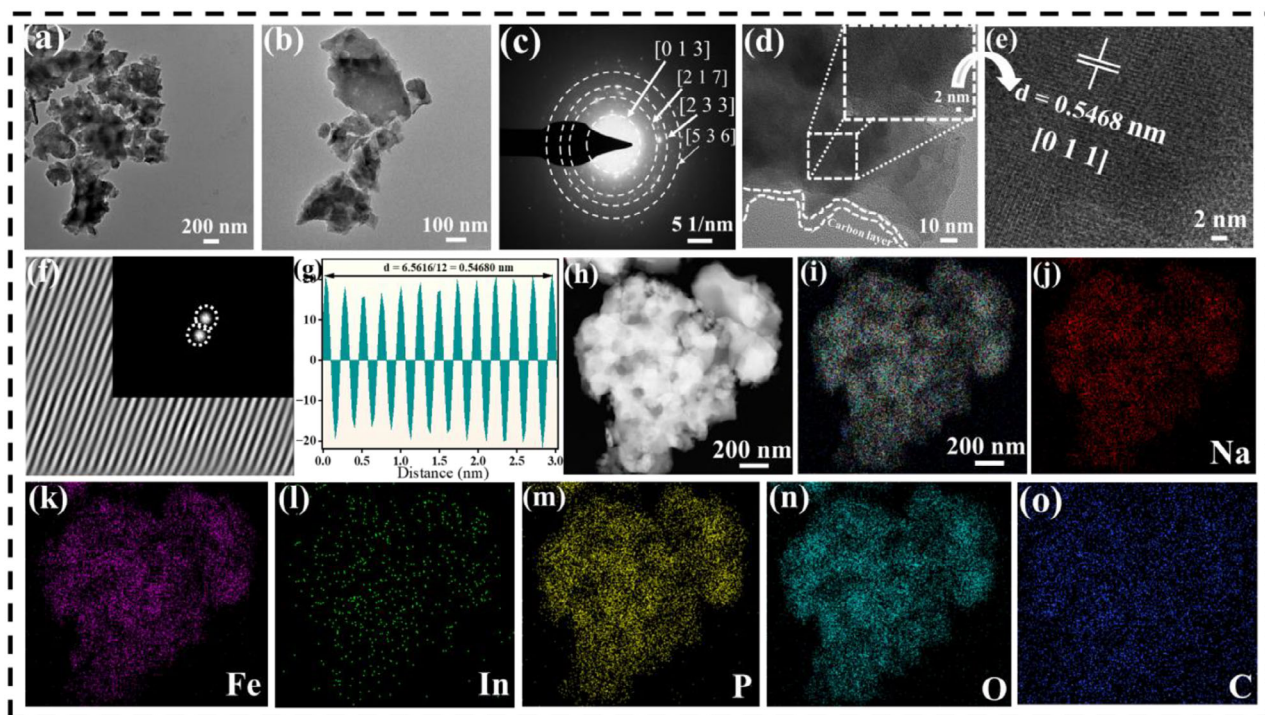


FIGURE 4 | (a,b) HRTEM images. (c) SAED patterns. (d) Lattice fringes. (e) d-spacing and (f,g) corresponding IFFT (h) HAADF image and (i-o) EDX elemental mapping for NFIPP03.

of the NFPP framework remains unaffected mainly by indium incorporation. High-resolution transmission electron microscopy (HR-TEM) images of NFIPP03 and NFIPP00, presented in Figure 4 and Figure S4 respectively, reveal well-defined lattice fringes along with a thin carbon coating, confirming the high crystallinity of both samples. The measured interplanar spacing for NFIPP03 is 0.547 nm, corresponding to the (011) plane, whereas NFIPP00 exhibits a spacing of 0.401 nm associated with the (112) plane. This increase in d-spacing for NFIPP03 upon In^{3+} doping is consistent with the lattice expansion observed in the Rietveld refinement results. The corresponding Fast Fourier Transform (FFT) patterns, shown in Figure 4f,g and Figure S4c,d, further validate the crystalline nature and lattice orientation of

the materials. Additionally, SEM-EDX and TEM-EDX elemental mapping confirm the uniform distribution of elements and verify the successful incorporation of indium into the NFIPP03 structure (Figure 4i-o), with no detectable indium observed in the undoped NFIPP00 sample (Figure S4h-l).

The chemical composition and stoichiometric integrity of the synthesized NFIPP framework were verified using ICP-OES. As summarized in Table S12, the experimental results demonstrate an exceptional correlation with the targeted molar ratios. When normalized to the phosphorus content ($p = 4.00$), the sodium content for both NFIPP00 (3.95) and NFIPP03 (3.93) shows nearly ideal agreement with the theoretical stoichiometry,

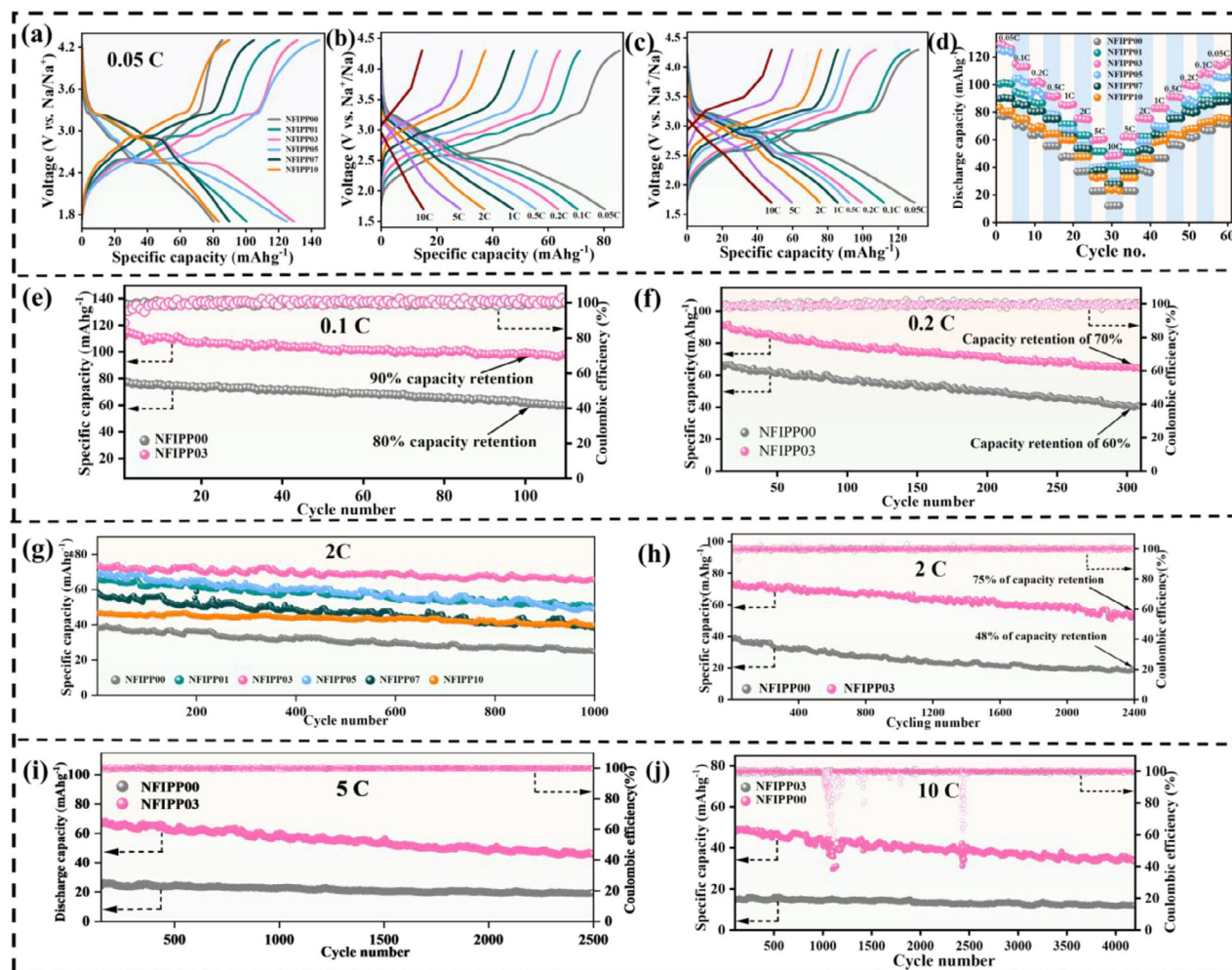


FIGURE 5 | Electrochemical performance of the NFIPP samples in the voltage range of 1.7–4.3 V vs. Na/Na⁺. (a) Charge–discharge profile of all NFIPP electrodes at a current rate of C/20. (b,c) GCD profiles of NFIPP00 and NFIPP03 at different C-rates. (d) Rate capability from C/20 to 10C for all samples. (e,f) Cycling performance at 0.1C & 0.2 C for NFIPP00 & NFIPP03. (g) Cycling stability at 2C for all NFIPP samples. (h) Extended cycling performance at 2C for NFIPP00 & NFIPP03. (i,j) Cycling stability at high current rate of 5 & 10C for NFIPP00 & NFIPP03.

confirming that the sodium-rich nature of the compound was successfully maintained throughout the high-temperature synthesis. Furthermore, the transition metal occupancy closely mirrors the anticipated 3:4 metal-to-phosphorus balance, with NFIPP00 and NFIPP03 yielding Fe ratios of 2.97 and 2.92, respectively. Most significantly, the quantified Indium content for the doped sample ($x = 0.031$) is in excellent agreement with the target doping level ($x = 0.030$). These findings validate the precision of the synthesis protocol and confirm that the In³⁺ ions have been accurately incorporated into the host polyanionic lattice, ensuring the structural and chemical fidelity required for reliable electrochemical investigations.

2.2 | Electrochemical Performance

To probe the electrochemical behavior of the In³⁺-substituted NFPP system, Na-half cells were tested over a voltage window of 1.7–4.3 V. The galvanostatic charge–discharge (GCD) profiles at 0.05 C for all NFIPP cathodes (Figure 5a) revealed a distinct performance enhancement upon indium doping. Among the series, NFIPP03 emerged as the most promising candidate, delivering

an outstanding specific capacity of 129.3 mAh g⁻¹, markedly outperforming NFIPP00 (80.3 mAh g⁻¹), NFIPP01 (100.4 mAh g⁻¹), NFIPP05 (124.1 mAh g⁻¹), NFIPP07 (89.8 mAh g⁻¹), and NFIPP10 (83.3 mAh g⁻¹). This pronounced capacity enhancement across all doped samples highlights the critical role of In³⁺ incorporation in boosting electrochemical performance. Interestingly, while low-level substitution proved beneficial and further increasing in the In³⁺ content beyond $x = 0.03$ (NFIPP03) led to a noticeable decline in specific capacity. This drop is likely due to the excessive occupation of electrochemically active Fe-sites by inactive In³⁺ ions, which may disrupt the redox kinetics and hinder ion transport pathways [41]. The GCD profiles of NFIPP00 and NFIPP03 at varying current rates (0.05–10 C), shown in Figure 5b,c, clearly illustrate their rate capabilities. A comparative rate performance of all NFIPP samples is summarized in Figure 5d and Table S4. Specifically, NFIPP03 demonstrated outstanding rate performance, delivering specific capacities of 129.3, 111.9, 102.4, 92, 85.6, 75.5, 60.5, and 48.7 mAh g⁻¹ at current rates of 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 C, respectively. In contrast, NFIPP00 exhibited considerably lower capacities under identical conditions. Upon recurring the current rate to 0.05 C, NFIPP03 retained 90% of its initial capacity (116.3 mAh g⁻¹), compared to 88.5% retention

(71.2 mAh g⁻¹) for NFIPP00 after 60 cycles highlighting the superior rate capability and cycling stability of the In-doped mixed phosphate-pyrophosphate system.

Further, NFIPP03 exhibited a specific capacity of 129.3 mAh g⁻¹ at 0.05 C, corresponding to an energy density of ~359 Wh kg⁻¹ substantially higher than NFIPP00 (~209 Wh kg⁻¹). After 100 charge-discharge cycles at 0.1 C, NFIPP03 retained nearly 90% of its initial capacity, compared to ~80% for NFIPP00 (Figure 5e). Even after 300 cycles, NFIPP03 maintained almost 60% of its capacity with nearly 100% coulombic efficiency (Figure S6a). At 0.2 C, NFIPP03 delivered 92.2 mAh g⁻¹ with 70% capacity retention after 300 cycles, outperforming NFIPP00, which retained only 60% (Figure 5f). Over 400 cycles, NFIPP03 continued to maintain stable cycling with less capacity decay (Figure S6b). Cycling at a high rate of 2 C for 1000 cycles (Figure 5g) revealed superior long-term stability of all doped samples relative to NFIPP00. Initial discharge capacities were 38.3 mAh g⁻¹ (NFIPP00), 65.8 mAh g⁻¹ (NFIPP01), 75.7 mAh g⁻¹ (NFIPP03), 68.8 mAh g⁻¹ (NFIPP05), 58.5 mAh g⁻¹ (NFIPP07), and 46.5 mAh g⁻¹ (NFIPP10), where NFIPP03 exhibited exceptional capacity retention of 90%. Extended cycling up to 2400 cycles at 2 C (Figure 5h) demonstrated showed excellent capacity retention of 75%. Furthermore, NFIPP03 endured up to 5000 cycles with minimum cycles with minimal capacity decay (Figure S6c).

To further validate the robustness of NFIPP03 in cycling stability, both the half-cells were tested under extreme high current rates. At 5 C, it delivered 68 mAh g⁻¹ exhibiting nearly 70% retention after 2500 cycles and maintained good cycling stability even after 5000 cycles (Figure 5i; Figure S6d). At 10 C, NFIPP03 retained 71% capacity after 4000 cycles (Figure 5j) and shows stable performance up to 9900 cycles (Figure S6e). Most impressively, at 20 C, it sustained up to 10 000 cycles (Figure S6f), emphasizing its outstanding cycling performance. These results demonstrate that moderate In³⁺-substitution (x = 0.03) substantially enhances both the rate performance and long-term stability of NFPP cathodes, making NFIPP03 a promising candidate for high-power NIB applications. To contextualize our results, we compared the electrochemical performance of this cathode material with that previously reported in the literature, as summarized in Table S11.

Cyclic voltammetry (CV) measurements were conducted for all NFIPP electrodes over a voltage range of 1.7–4.3 V vs. Na/Na⁺. All samples exhibited well-defined redox peaks, corresponding to the reversible Fe²⁺/Fe³⁺ redox couple, clearly indicating the redox activity associated with the Fe centers in the electrode material. The CV profiles of NFIPP00 and NFIPP03 recorded at a scan rate of 0.1 mV s⁻¹ exhibit three distinct redox peak pairs at 3.26/3.19, 2.95/2.85, and 2.66/2.49 V for NFIPP00, and at 3.24/3.21, 2.94/2.89, and 2.59/2.52 V for NFIPP03, respectively (Figure 6a,b), where 3.26/3.19 redox peaks are attributed to the insertion/extraction of Na1 (6-coordinate) and Na4 (6-coordinate) into/from NFPP structure [6]. The multiple redox potentials observed in the CV profiles correspond to the reversible insertion and extraction of Na⁺ ions at different crystallographic sites within the NFPP framework [42]. The CV curves for all NFIPP compositions, along with their peak separations (ΔV = V_{anodic} – V_{cathodic}), are presented in Figure S7 and are detailed in Table S5. Notably, NFIPP03 exhibits the smallest ΔV among all samples, indicating lower electrochemical polarization. Furthermore, all In³⁺-substituted

samples demonstrate reduced cell polarization compared to the undoped NFIPP00, highlighting the beneficial effect of indium doping in enhancing Na⁺ ion kinetics.

To further illustrate the reversibility of Na⁺ storage and electrode kinetics, differential capacity (dQ/dV vs. V) profiles were recorded over the first 200 cycles at a current rate of 0.1 C (Figure 6c). Remarkably, NFIPP03 maintained sharp and well-defined redox peaks with minimal peak shifts, even after prolonged cycling, indicating stable redox behavior and lower polarization relative to the undoped NFIPP00 electrode (Figure S8). Additionally, the electrochemical reversibility of the cathodes was evaluated by CV test at the same scan rate (ν = 0.1 mV s⁻¹) over the initial 5 cycles as depicted in Figure S9. Moreover, the CVs of NFIPP00 and NFIPP03 were recorded at various scan rates (0.1, 0.25, 0.5, 0.75, and 1.0 mV s⁻¹), shown in Figure 6d,e. Similarly, analysis for other doped compositions (NFIPP01, NFIPP05, NFIPP07 and NFIPP10) is presented in Figure S10. The linear correlation between peak currents (i_{pa}, i_{pc}) vs. the square root of scan rate (ν^{1/2}) for all the NFIPP samples investigated, as illustrated in Figure S11 with the corresponding slope values provided in the inset is summarized in Table S6. To determine the Na⁺ ion transport properties, the diffusion coefficient (D_{Na+}) was calculated using the Randles–Ševčík equation as given below [43–45]:

$$i_p = (2.69 \times 10^5) n^{\frac{1}{2}} A D_{Na+}^{\frac{1}{2}} C_{Na+} \nu^{\frac{1}{2}} \quad (1)$$

where i_p (mA) is the peak current, n is the number of electrons transferred per mole of reaction, A (1.13 cm²) is the surface area of the cathode, C_{Na+} (mol cm⁻³) is the sodium-ion concentration, and ν (mV s⁻¹) indicates the sweep rate. The D_{Na+} values for both anodic and cathodic peaks for all the NFIPP samples were estimated and illustrated in Figure 6f,g using the Equation (1). Among all compositions, NFIPP03 demonstrates the highest D_{Na+} values across all three redox peaks, with diffusion coefficients of 1.52 × 10⁻¹⁰/5.02 × 10⁻¹¹, 1.43 × 10⁻¹⁰/6.02 × 10⁻¹¹, and 1.86 × 10⁻¹¹/3.72 × 10⁻¹¹ cm² s⁻¹ for the anodic/cathodic processes, respectively, highlighting its superior Na⁺ diffusion kinetics. In contrast, the undoped NFIPP00 exhibits the lowest D_{Na+} values of 3.81 × 10⁻¹¹/7.52 ×

10⁻¹², 3.84 × 10⁻¹¹/6.25 × 10⁻¹³, and 4.12 × 10⁻¹³/4.14 × 10⁻¹² cm² s⁻¹ across the corresponding peaks. These results demonstrate the beneficial impact of In³⁺ doping on enhancing Na⁺ ion transport within the NFPP structure. All calculated D_{Na+} values are summarized in Table S7.

The reaction kinetics can be further described using the following relations [46, 31]:

$$i_p = a \nu^b \quad (2)$$

$$\log i_p = \log a + b \log \nu \quad (3)$$

$$i = k_1 \nu + k_2 \nu^{\frac{1}{2}} \quad (4)$$

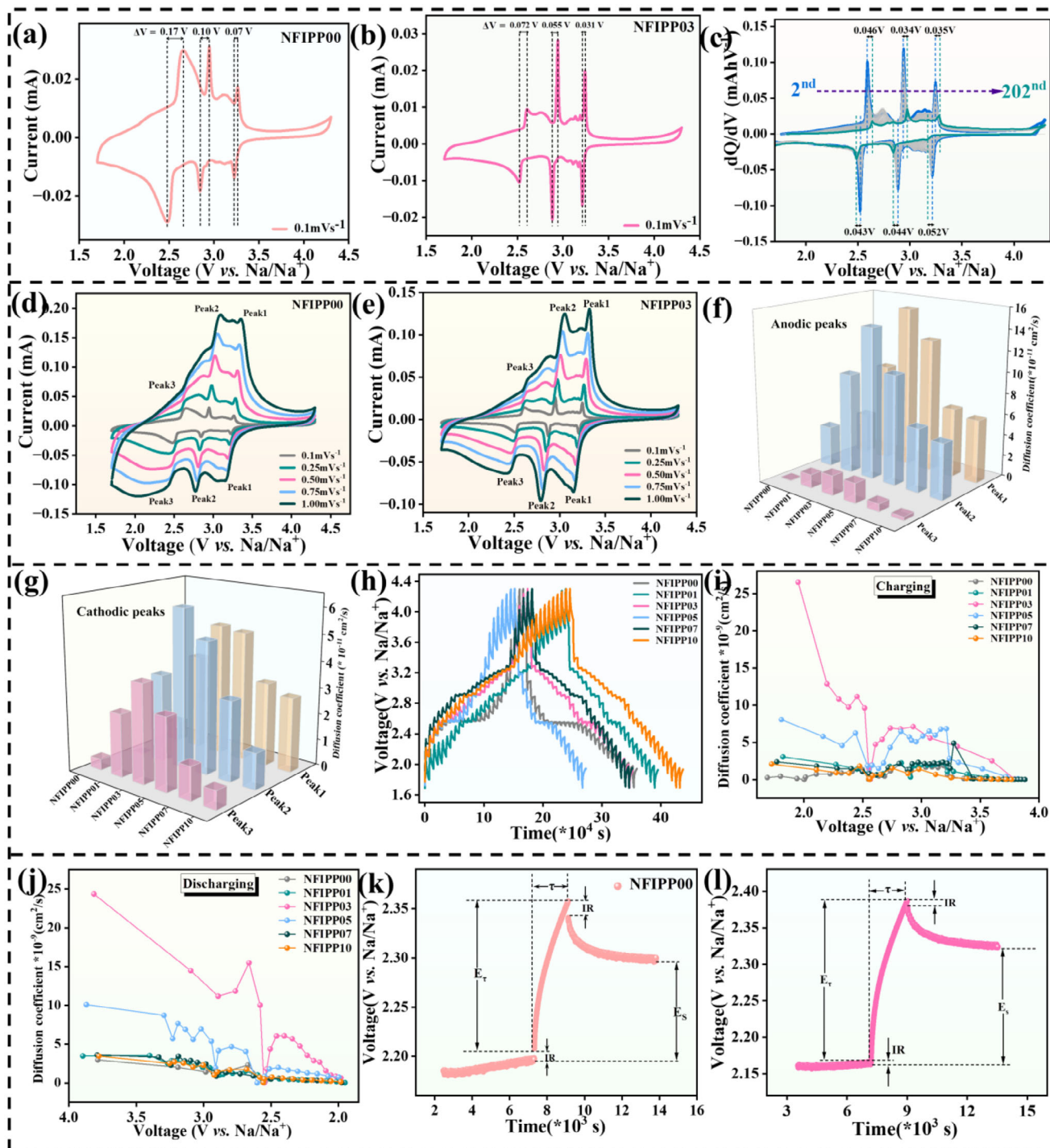


FIGURE 6 | (a,b) The CV curves recorded at 0.1 mV s^{-1} exhibits the peak separation of NFIPP00 & NFIPP03 respectively. (c) Differential capacity plot (dQ/dV) from second to the 200th cycles of NFIPP03. (d,e) CV profiles at different scan rates from 0.1 to 1.0 mV s^{-1} . (f,g) Na^+ diffusion coefficient from anodic and cathodic peaks respectively evaluated from CV test. (h) Galvanostatic intermittent titration technique (GITT) profiles and corresponding charge (i) and (j) discharge diffusion coefficients for all cathodes. (k,l) Single titration step for NFIPP00 and NFIPP03 respectively.

Equation (2) is the power law relation between the peak current (i_p , mA) and the sweep rate (v , mV s^{-1}). The linear fitting of $\log(i_p)$ and $\log(v)$, presented in Figure S12a–f (left column), yields a slope b as described in Equation (3). The b -value serves as a diagnostic parameter to interpret the charge storage mechanism, $b \approx 0.5$ signifies a diffusion-controlled process, whereas a $b \approx 1.0$ suggests surface-controlled (pseudo-capacitive) behavior.

When b lies between 0.5 and 1.0 , it indicates that both diffusion and surface-driven processes contribute to the charge storage kinetics [47]. In our case, the b -values calculated for all NFIPP samples (insets of Figure S12a–f, left column) consistently fall within this intermediate range, revealing that Na^+ storage occurs via a synergistic combination of diffusion-controlled intercalation and surface-controlled pseudo-capacitive mechanisms. The

relative contributions of diffusion-controlled and surface-driven (pseudo-capacitive) processes were quantitatively assessed using the Trasatti analysis [48], as described by Equation (4). In this equation, the current (i) at a given potential is expressed as a function of the scan rate (ν), where $k_1\nu$ denotes the capacitive contribution and $k_2\nu^{1/2}$ corresponds to the diffusion-controlled contribution, where with k_1 and k_2 are proportionality constants. This method enables a deconvolution of the total current into its capacitive and diffusion components. The capacitive vs. diffusion contributions were first evaluated at a scan rate of 0.1 mV s⁻¹ (Figure S12g–l, middle column), and then systematically analyzed across the full range of scan rates from 0.1 to 1.0 mV s⁻¹ (Figure S12m–r, right column). Significantly, NFIPP03 exhibited a significantly higher diffusion-controlled contribution compared to NFIPP00, suggesting enhanced Faradaic intercalation kinetics. This behavior not only facilitates more efficient Na⁺ storage but also contributes to improved structural integrity and long-term cycling stability.

To further elucidate the origin of the enhanced electrochemical performance resulting from In³⁺ substitution, the galvanostatic intermittent titration technique (GITT) was employed to estimate the Na⁺ ion diffusion coefficients (D_{Na+}) of the NFIPP samples. Prior to the GITT measurements, the cells were pre-cycled twice at a current rate of 0.1 C to ensure thermal equilibrium and stabilize the system for accurate diffusion analysis. The Na⁺ ion diffusion coefficient was subsequently calculated using the following Fick's second law of diffusion equation [49]:

$$D_{Na+} = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{A} \right)^2 \left[\frac{\Delta E_s}{\Delta E_\tau} \right]^2 \quad (5)$$

where τ is the applied pulse current time (in sec), and n_m represents the total number of moles of cathode material, V_m is the molar volume (in cm³ mol⁻¹), ΔE_s (in V), and ΔE_τ (in V) were extracted at each step from GITT experiment. The GITT profiles of all NFIPP cathodes, recorded over the voltage range of 1.7–4.3 V, are presented in Figure 6h. The corresponding Na⁺ ion diffusion coefficients (D_{Na+}), calculated using Equation (5), are shown in the charging and discharging profiles in Figure 6i,j, respectively. The variation in diffusion efficiency across different voltage regions is attributed to the sequential extraction and insertion of sodium ions from and into distinct crystallographic sites within the NFIPP framework [6]. Among all compositions, NFIPP03 exhibits the highest average D_{Na+} value of 5.36×10^{-9} cm² s⁻¹ during charging and 5.00×10^{-9} cm² s⁻¹ during discharging, significantly outperforming the undoped NFIPP00, which shows values of 0.61×10^{-9} cm² s⁻¹ (charging) and 0.84×10^{-9} cm² s⁻¹ (discharging), as detailed in Table S8. This remarkable enhancement in Na⁺ diffusion kinetics for NFIPP03 is primarily attributed to the broader ion diffusion pathways and increased sodium vacancy concentration induced by In³⁺ substitution. In addition, representative single titration steps for NFIPP03 and NFIPP00 are illustrated in Figure 6k,l, respectively, while those for the remaining NFIPP samples are provided in Figure S13. The significant enhancement in Na⁺ diffusion coefficients upon In³⁺ substitution can be attributed to two key factors—the creation of Na⁺ vacancies to compensate for charge imbalance introduced by trivalent cation doping, which facilitates more rapid ion migration, and a slight lattice expansion induced by the larger ionic radius of In³⁺ compared to Fe³⁺, thereby

broadening the diffusion pathways. Together, these effects lower the energy barriers for Na⁺ migration and contribute to the superior electrochemical kinetics observed in the In-doped NFIPP samples [50].

Furthermore, to gain deeper insights into the Na⁺ ion diffusion dynamics within the NFIPP cathodes, electrochemical impedance spectroscopy (EIS) was recorded. The raw EIS data are presented in Figure 7a, with the corresponding fitted circuit is shown in the inset. Additionally, the fitted curves for all NFIPP samples are displayed in Figure 7b. The Nyquist plots display a depressed semicircle in the high-to-medium frequency region, corresponding to the charge-transfer resistance (R_{ct}), followed by an inclined linear tail at lower frequencies, characteristic of the Warburg impedance (W), which reflects the Na⁺ ion diffusion process within the electrode material [21]. It is worth highlighting that the NFIPP03 cathode exhibits the lowest charge-transfer resistance (R_{ct}) value of 307.34 Ω among all the NFIPP samples, as shown in Figure 7c, along with the lowest series resistance (R_s) value, presented in Figure 7d. However, R_s remains unaffected mainly by In³⁺ substitution, indicating that the electrolyte and interfacial resistances are not significantly influenced by doping. In contrast, the undoped NFIPP00 displays the highest R_{ct} value of 1077.7 Ω among all cathodes. The fitted parameters are summarized in Table S9. The consistently lower R_{ct} values observed for NFIPP03 confirm its superior charge-transfer kinetics, which are in strong agreement with its outstanding long-term cycling stability. The relationship between the real part of impedance (Z') and the inverse square root of angular frequency ($\omega^{-1/2}$) in the low-frequency region is illustrated in Figure 7e. The Warburg factor (σ), which reflects ion diffusion resistance, is obtained from the slope of the linear fit of Z' vs. $\omega^{-1/2}$, based on the following equation [51]:

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2} \quad (6)$$

where Z' is the real impedance (Ω), R_s is the solution resistance (Ω), R_{ct} is the charge transfer resistance (Ω), and ω is the angular frequency (rad s⁻¹). In our study, NFIPP00 exhibits a steeper slope indicating a higher Warburg factor (σ), which corresponds to greater resistance for Na⁺ ion migration and hence lower diffusion capability compared to all other doped cathodes. In contrast, NFIPP03 shows the smallest σ , reflecting lower ionic resistance and enhanced Na⁺ diffusion [52]. Moreover, the Na⁺ diffusion coefficient derived from EIS measurements in the low-frequency region was calculated using the following equation [53]:

$$D_{Na+} = \left(\frac{R^2 T^2}{2n^4 F^4 A^2 C_{Na+}^2 \sigma^2} \right) \quad (7)$$

where D_{Na+} is the Na⁺ diffusion coefficient, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T represents the absolute temperature (298 K), F is the Faraday's constant (96500 C mol⁻¹), A is the contact area (cm²), n is the total number of electrons participated in the electrochemical reaction, C_{Na+} is the concentration of Na⁺ in the host material (cm³ mol⁻¹). Notably, the optimized NFIPP03 exhibits the highest Na⁺ diffusion coefficient (D_{Na+}) of 8.83×10^{-14} cm² s⁻¹, significantly outperforming the undoped NFIPP00, which shows a much lower value of 1.6×10^{-15} cm² s⁻¹,

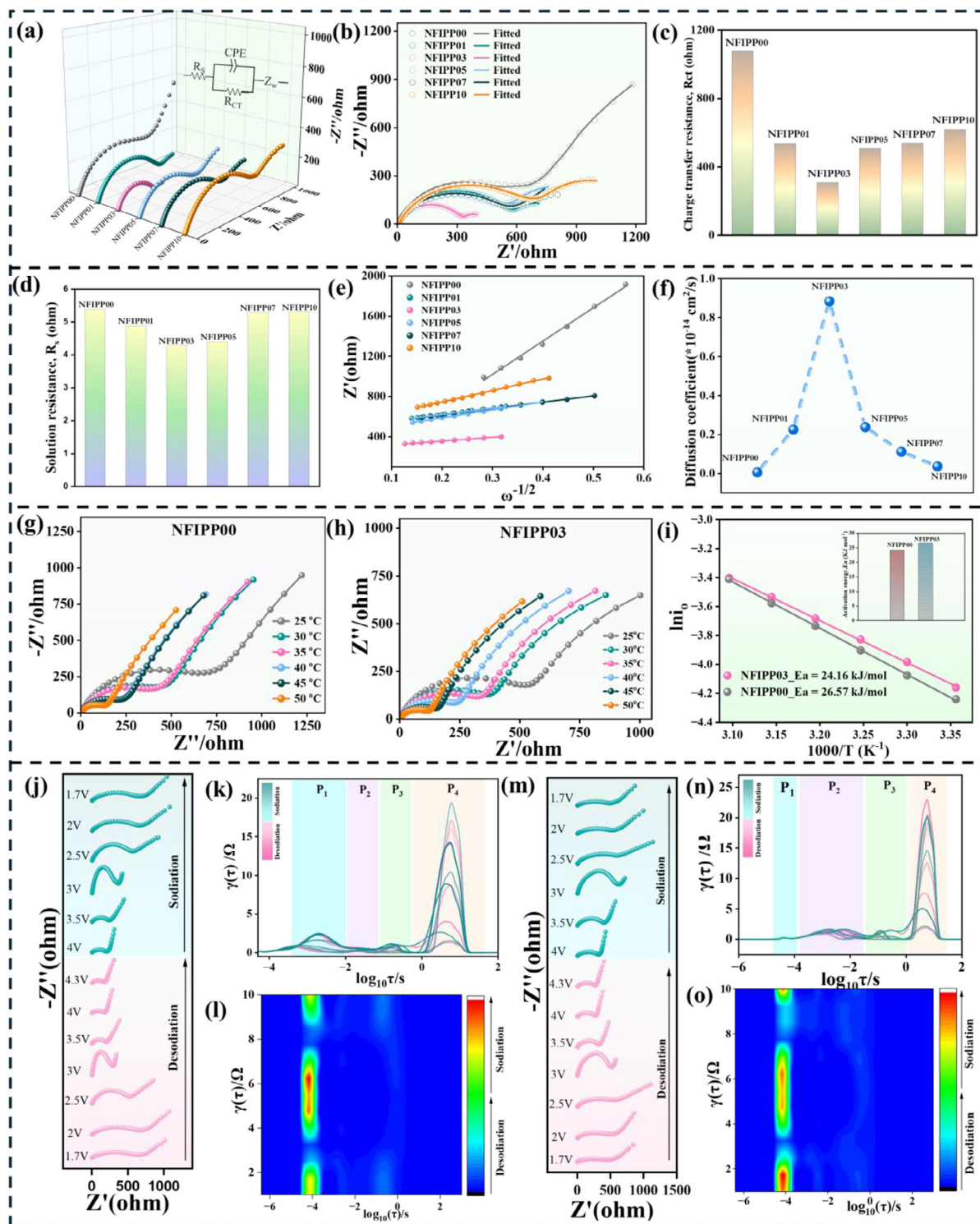


FIGURE 7 | (a) Nyquist plot and corresponding equivalent fitted circuit (inset) and fitted EIS spectrum (b) and corresponding R_s (c) and R_{ct} (d) values. (e) The plot Z_{re} vs. $\omega^{-1/2}$ obtained from the lower frequency data of the Nyquist plot. (f) Na⁺-diffusion coefficient evaluated using EIS test. (g) Arrhenius plots of NFIPP00 & NFIPP03. (h,i) Temperature-varied EIS plots of NFIPP00 & NFIPP03 recorded as 2.5 V. (j,m) In situ EIS profiles at different voltages (k,n) DRT curves (l,o) 2D DRT intensity variation graphs during charge/discharge for NFIPP00 and NFIPP03.

as illustrated in Figure 7f. The detailed D_{Na^+} values for all NFIPP samples are summarized in Table S10. This improved diffusion behavior aligns well with the superior electrochemical performance observed for NFIPP03. To evaluate the temperature dependence of Na⁺ transport kinetics, EIS measurements were

performed on both NFIPP00 and NFIPP03 across the range of 25°C–50°C, as shown in Figure 7g,h. With increasing temperature, a notable reduction in the semicircle diameter of the Nyquist plots was observed, indicating enhanced charge transfer kinetics and reduced interfacial resistance. This thermal behavior

suggests a strong temperature dependence of the Na⁺ diffusion process. The apparent activation energy for Na⁺ (de)insertion was subsequently calculated using the Butler–Volmer Equation (8) and the Arrhenius Equation (9):

$$i_0 = \left(\frac{RT}{nF} \right) \frac{1}{R_{ct}} \quad (8)$$

$$i_0 = A \exp \left(-\frac{E_a}{RT} \right) \quad (9)$$

$$\ln i_0 = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (10)$$

where i_0 is the exchange current density, R_{ct} is the charge-transfer resistance, T is the absolute temperature (K), R is the gas constant, n is the number of electrons involved, and F is Faraday's constant. The Arrhenius plot of $\log(i_0)$ vs. $1/T$ is presented in Figure 7i, and the activation energy (E_a) was determined from the slope of this plot, as shown in the inset. NFIPP03 demonstrated a lower activation energy of 24.16 kJ mol^{−1}, compared to 26.52 kJ mol^{−1} for NFIPP00, indicating that In³⁺ substitution effectively facilitates Na⁺ transport by lowering the energy barrier for ion migration and improves charge-transfer kinetics.

In situ-EIS measurements were conducted at multiple voltage points during charge–discharge cycling to investigate the electrochemical behavior of NFIPP00 and NFIPP03. This real-time monitoring approach enables precise tracking of internal resistance variations, offering valuable insights into the dynamic electrochemical processes within the electrode materials. Analysis of the Nyquist plots (Figure 7j,m) demonstrates distinct differences in charge transfer resistance (R_{ct}) and solution resistance (R_s) at various states of charge. Notably, NFIPP03 maintains consistently lower R_{ct} values than NFIPP00 throughout all voltage states, confirming improved charge transfer kinetics resulting from In³⁺ substitution, depicted in Figure S14. To disentangle the overlapping electrochemical processes present in the EIS spectra, the Distribution of Relaxation Times (DRT) technique was utilized. In contrast to conventional equivalent circuit modeling, DRT offers a model-independent approach that enables finer resolution of individual electrochemical processes based on their specific relaxation times [54, 55]. The DRT spectra for NFIPP00 and NFIPP03, as illustrated in Figure 7k,n, exhibit distinct peaks corresponding to different electrochemical phenomena. Through DRT analysis, the impedance components related to diffusion were successfully isolated, revealing two dominant relaxation time constants: one associated with interfacial diffusion ($\tau \approx 10^{-4}$ – 10^{-2} s) and another linked to bulk diffusion ($\tau \approx 10$ – 10^2 s) [56]. Notably, both interfacial and bulk impedance values in NFIPP03 are markedly reduced compared to NFIPP00, confirming that Na⁺ diffusion pathways have been effectively enhanced, thereby significantly lowering the ion migration resistance. To track the evolution of electrochemical behavior during charge–discharge cycling, a contour map was generated from the DRT spectra. This representation captures the intensity and progression of relaxation processes over time, offering a detailed perspective on the dynamic transformations within the electrode material [57]. For NFIPP03, the contour plot (Figure 7o) consistently shows lower and stable

relaxation times compared to NFIPP00 (Figure 7l) across cycles, indicating sustained ion transport and minimal kinetic degradation. Based on the comprehensive CV, GITT, and EIS analyses, it can be concluded that an optimal level of In³⁺ substitution within the NFPP lattice significantly enhances Na⁺ ion transport and mobility, thereby facilitating faster and more efficient electrochemical reactions during charge–discharge processes.

To elucidate the structural evolution of the cathode materials during electrochemical cycling, ex situ XRD was performed on both NFIPP00 and NFIPP03 samples at selected charge and discharge states [58]. For both compositions, the primary diffraction peaks corresponding to the mixed phosphate framework were retained throughout the cycling process, confirming robust structural stability. Ex situ XRD patterns collected before cycling, after full discharging and charging were compared to assess whether the original structure was restored, thereby indicating structural reversibility [59]. To ensure reliable results, coin cells were disassembled in an inert atmosphere, and electrodes were thoroughly washed with solvent to remove residual electrolyte salts before drying under vacuum at 60 °C. The XRD patterns in the 2θ range of 18–38°, as illustrated in Figure 8a,b, the diffraction peaks corresponding to the (4 0 0), (2 1 2), (0 1 3), (4 0 3), and (3 2 2) planes gradually shifted to lower 2θ values during discharge (Na⁺ insertion into the cathode) and returned to higher 2θ values upon charging (Na⁺ extraction from the cathode), ultimately regaining their initial positions. The corresponding voltage profile is presented in Figure 8c. Notably, for NFIPP00, a slight rightward shift in 2θ was observed after complete (de)sodiation, while NFIPP03 showed negligible 2θ deviation, highlighting its superior structural reversibility. This can be attributed to the substitution of In³⁺ at the Fe sites, which reinforces the lattice framework. Additionally, to probe the redox behavior of iron during cycling, ex situ XPS was conducted on optimized NFIPP03 samples at selected charge and discharge states. The Fe 2p spectra reveal that the oxidation state of Fe evolves reversibly with Na⁺ (de)insertion [60]. In Figure 8d, ex situ XPS measurements at various cell voltages reveal the evolution of the Fe oxidation state during cycling. At the fully discharged state (1.7 V), Fe is predominantly in the Fe²⁺ state as the charging potential gradually increases, spectral features corresponding to Fe³⁺ begin to emerge, and upon reaching 4.3 V, Fe²⁺ is fully oxidized to Fe³⁺. A distinct shift of the Fe 2p_{3/2} peak to higher binding energy is observed. Notably, at intermediate states including charged at 2.5 V and discharged at 3.5 V features corresponding to both Fe²⁺ and Fe³⁺ are observed, indicating the coexistence of mixed oxidation states during these stages of (de)sodiation.

To further elucidate the long-term structural stability of the cathode materials, ex situ TEM and ex situ XRD analyses were performed after 10,000 charge–discharge cycles at 10 °C for both the NFIPP00 and NFIPP03 samples, as summarized in Figure S16. The ex situ TEM images of NFIPP00 (Figure S16a–c) reveal noticeable microstructural degradation after prolonged cycling, including loss of well-defined lattice features, which is consistent with its comparatively inferior cycling stability. In contrast, the ex situ TEM images of NFIPP03 (Figure S16e–g) exhibit a more preserved morphology, and clear lattice fringes remain distinctly visible in the high-resolution TEM image (Figure S16h), indicating the retention of crystallinity even after extended

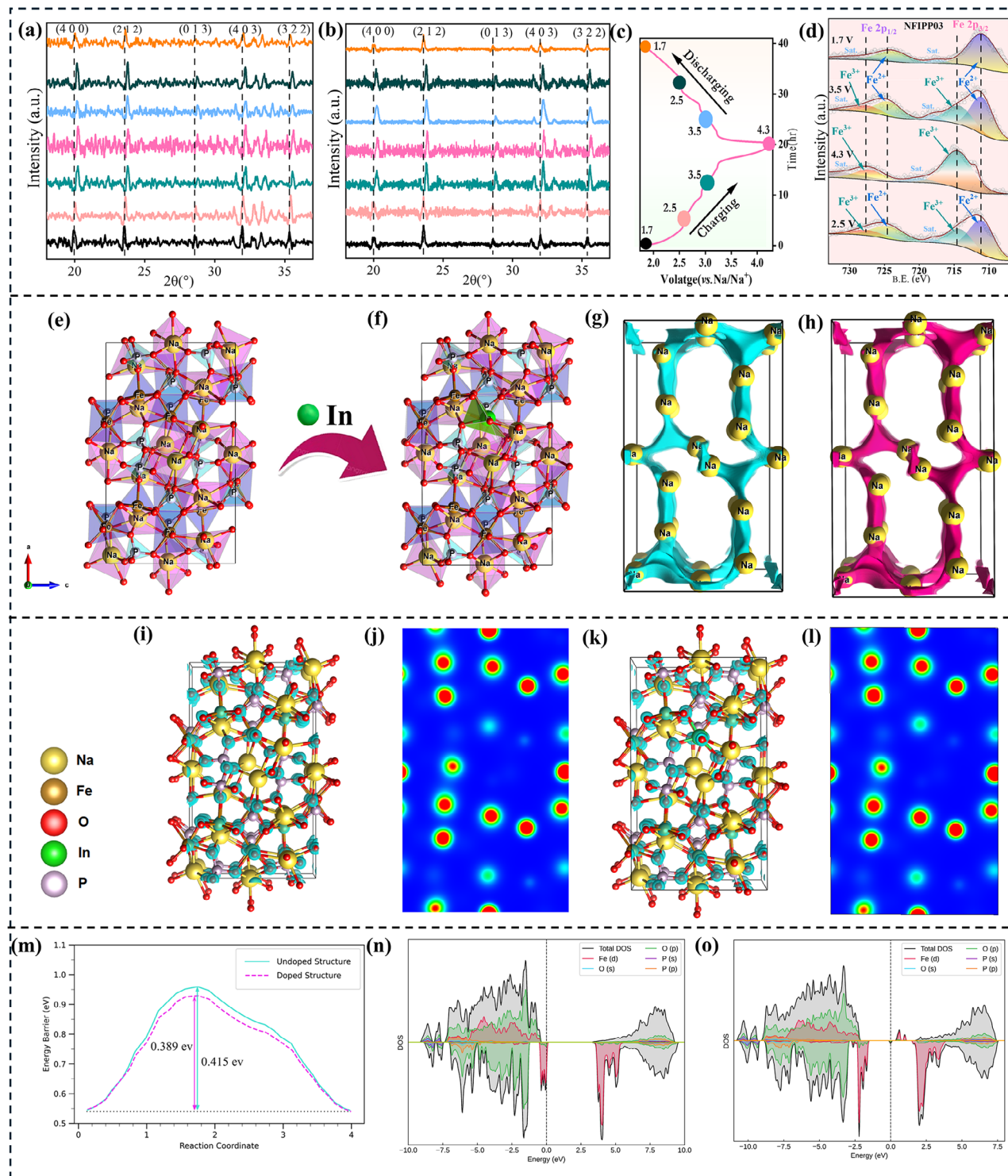


FIGURE 8 | (a) & (b) Ex situ XRD, (c) corresponding voltage profile of NFIPP00 & NFIPP03. (d) ex situ XPS of NFIPP03. (e) & (f) Estimated crystal structure and the calculated Na^+ diffusion pathways (k) & (l) in NFIPP00 and NFIPP03 structures respectively. Charge density distribution (i) & (k), corresponding 2D-contour plot (j) & (l) of NFIPP00 & NFIPP03. (m) Comparison of activation energy barriers of Na^+ in NFIPP00 and NFIPP03. Total/Projected Density of states (DOS) (n) & (o) of NFIPP00 and NFIPP03 respectively.

high-rate cycling. Furthermore, the selected area electron diffraction (SAED) pattern of NFIPP03 (Figure S16i) shows well-defined diffraction spots corresponding to the crystalline planes, providing additional evidence of the preserved long-range crystallinity after prolonged cycling.

The corresponding ex situ XRD patterns of NFIPP00 and NFIPP03 collected after 10,000 cycles are presented in Figure S16j. NFIPP03 maintains sharp and well-defined diffraction peaks characteristic of the mixed-polyanion framework compared to NFIPP00. These XRD results are in good agreement with the

ex situ TEM observations and further confirm the superior structural robustness of NFIPP03 during long-term cycling.

To place the electrochemical performance of the optimized NFIPP03 cathode in a broader context, a comparison with recently reported sodium iron-based phosphate cathode materials tested in half-cell configurations is provided [61–64]. Figure S16k compares the energy density and power density, highlighting that NFIPP03 delivers a competitive balance between high energy and high power. Additionally, Figure S16l summarizes the cycling stability performance in terms of C-rate and cycle number, demonstrating that NFIPP03 exhibits outstanding long-term durability compared with many reported cathodes [65–68]. These comparative results further underscore the promise of NFIPP03 as a high-performance and durable sodium-ion battery cathode material.

3 | Density Functional Theory Calculations

Density functional theory calculations were conducted to elucidate the atomic-scale phenomena responsible for the superior electrochemical characteristics observed in indium-substituted NFPP cathode materials. The computational frameworks (Figure 8e,f) successfully reproduced experimental lattice parameters for the undoped framework, with calculated values showing excellent agreement with X-ray diffraction measurements. Indium doping at the Fe2 crystallographic position was selected based on its energetically favorable nature compared to other sites [6], achieving a doping level of 4.17 atomic percent. This doping induces a marginal unit cell expansion of approximately 0.6%. This dimensional change reflects the larger ionic radius of In^{3+} (0.80 Å) relative to Fe^{2+} (0.78 Å). This modest volume increase demonstrates that the phosphate-pyrophosphate network can accommodate dopant atoms without significant distortion of the primary diffusion channels. Bond valence sum calculations reveal substantial modifications to the sodium-ion transport network upon the incorporation of indium. The 4.17% doped configuration (Figure 8h) exhibits significantly widened migration corridors compared to the pristine material (Figure 8g), establishing an enhanced 3D interconnected pathway system. The charge density distribution for both samples (Figure 8i,k) were evaluated to understand the effect of In^{3+} doping on charge distribution. A uniform charge distribution was observed in both cases, indicating that In^{3+} substitution helps maintain the structural integrity of the cathode. Additionally, we plotted corresponding 2D contour maps of the charge density distribution, represented in Figure 8j,l, to visually illustrate these changes in electronic environment, supporting the role of indium doping in stabilizing the lattice and facilitating efficient Na^+ migration. Critical migration routes, illustrated in Figure S15a,c, demonstrate measurably reduced activation barriers, one of which is directly compared between the pristine and 4.17 % doped systems, further highlighted in Figure 8m to illustrate this effect. Electronic structure investigations uncover dramatic alterations in the material's band characteristics. The pristine NFIPP00 compound exhibits semiconducting behavior with a substantial bandgap of 3.30 eV as depicted in the in Figure 8n, consistent with values reported in previous studies [21]. Indium doping at 4.17% concentration dramatically narrows this gap to 0.43 eV, as shown in Figure 8o, while higher substitution

levels (8.34%) further reduce the gap to 0.10 eV (Figure S15e) and the band structure depicted in Figure S15f demonstrating a systematic correlation between dopant concentration and electronic conductivity enhancement. Detailed analysis of the total and projected density of states reveals the emergence of new electronic states near the Fermi level. These states arise from orbital hybridization between Fe 3d and O 2p electrons near indium dopant sites. The introduction of these mid-gap states generates additional charge carriers, fundamentally altering the electronic transport properties and accounting for the observed reduction in bandgap. Additionally, the band structure (Figure S15b,d) shows the formation of new localized electronic states close to the Fermi level which result from doping and contribute to the improved electronic properties. The expansion and interconnection of sodium-ion diffusion channels, coupled with the improvement in electronic conductivity through bandgap reduction, synergistically contribute to the superior rate capability and energy density characteristics of the doped cathode material. These findings establish indium substitution as an effective strategy for optimizing both ionic and electronic transport properties in sodium-ion battery cathode materials.

4 | Conclusion

We present a novel Leidenfrost-assisted synthesis of In^{3+} -doped $\text{Na}_4\text{Fe}_{3-x}\text{In}_x(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ (NFIPP) cathodes as a scalable and cost-effective route to advanced NIB materials as a promising alternative to traditional synthesis methods. Indium doping induces lattice expansion, increases Na–O bond lengths and enhancing Na^+ diffusion and electronic conductivity. Comprehensive analyses confirm the structural stability and uniform dopant distribution, along with enhancement in spin state and electrical conductivity. The optimized NFIPP03 ($x = 0.03$) exhibits a high specific capacity of 129.34 mAh g^{-1} at 0.05 C, excellent rate performance, and outstanding cycling stability, retaining ~90% of its capacity after 1000 cycles at 2 C and demonstrating durability over 10 000 cycles at 20 C. Electrochemical and kinetic studies reveal significantly improved Na^+ transport and reduced charge-transfer resistance due to doping. This work demonstrates the potential of Leidenfrost synthesis for the scalable production of advanced mixed-polyanion cathodes, positioning NFIPP03 as a promising candidate for sustainable, large-scale sodium-ion energy storage.

5 | Experimental Section

Experimental details can be found in the Supporting Information.

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Conflicts of Interest

The authors declare no conflicts of interest.

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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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

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