The structural origin of enhanced stability of $\text{Na}_{3.32}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$ cathode for Na-ion batteries

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ABSTRACT

The storage of renewable energy depends largely on sustainable technologies such as sodium-ion batteries with high safety, long lifespan, low cost, and non-toxicity. Pyrophosphate $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ cathode could meet this requirement, however, its structural stability needs to be further enhanced for practical purposes. To overcome this problem, Na-deficient $\text{Na}_{3.32}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$ with exceptional stability is prepared by Ca selective doping in this work. *In operando* synchrotron-based X-ray diffraction (SXRD) and *in situ* X-ray absorption near edge spectroscopy (XANES) results reveal that the prepared $\text{Na}_{3.32}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$ is a single-phase solid-solution reaction with high reversibility. A strong correlation between the voltage curve and lattice parameters is deciphered for the first time. Additionally, the atomic-doping-engineering strategy could significantly enhance the thermal and electrochemical stability of the electrode materials, contributing to their good structural reversibility and enhanced operational safety. Specifically, after 1000 cycles at 1 C, the Ca doped electrode achieves a high capacity retention of 81.7%, which is much better than that of the un-doped electrode (15.5%). Our work may pave a new avenue for designing safe and low-cost cathode materials for battery applications with long cycle life.

1. Introduction

Due to growing energy shortages, the sustainable storage of new energy sources in large electric energy storage systems (EESs) has been a key issue worldwide [1–3]. The scale of EES equipped with an energy generator far exceeds that of hybrid electric vehicles (HEV) or electric vehicles (EV). Therefore, cost effectiveness and operational safety become the paramount preconditions. Inexpensive sodium ion battery (SIB) is resource-rich, nontoxic, safe, and is one of the best choices for EESs [4–6]. Because of the larger radius ($r_{\text{Na}^+} = 1.02 \text{ \AA} > r_{\text{Li}^+} = 0.76 \text{ \AA}$)

and the higher molar mass ($M_{\text{Na}} = 22.99 \text{ g mol}^{-1} > M_{\text{Li}} = 6.94 \text{ g mol}^{-1}$) [7], more energy is needed to overcome the diffusion barrier of Na^+ in the host, which makes it much difficult to find a suitable host material. So far, the development of new battery technology remains a serious challenge. Numerous attempts have been made to discover the suitable electrode materials, such as NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ [8,9], $\text{Na}_{1-\delta}\text{Ni}_x\text{Mn}_{1-x}\text{O}_2$ [10,11], $\text{Na}_{2-y}\text{M}_x\text{Fe}(\text{CN})_6 \cdot z\text{H}_2\text{O}$ [12,13], and $\text{Na}_4\text{M}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ($\text{M} = \text{Co}, \text{Mn}, \text{and Ni}$, $0 < \delta < 1$, $0 < x < 1$, $0 < y < 2$) [14,15]. Nevertheless, their safety, cost, sustainability, and/or performance are the obstacles for large-scale application.

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Recently, strategic research gradually shifts from the oxides to Fe-based polyanionic compounds. Unfortunately, the reported compounds (NaFePO_4 , $\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_2\text{FeSiO}_4$, NaFeSO_4F , and $\text{Na}_{2+2x}\text{Fe}_{2-2x}(\text{SO}_4)_3$) are severely restricted by adverse structure or climate adaptation or thermal stability [16–20]. Especially $(\text{SO}_4)^{2-}$ and F^- anions are prone to thermal decomposition (350–400 °C) and/or moisture attack [20]. Exposure of PO_4 -based systems to high-temperature (500–550 °C) could cause O_2 evolution forming the pyrophosphate $[\text{P}_2\text{O}_7]$ or $(\text{PO}_{4-x})_2$ anions. Thus, the advantages of the earth-abundant $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple and the thermo-stable pyrophosphate $(\text{P}_2\text{O}_7)^{4-}$ anion can be preferentially deployed to design advanced cathode materials for SIBs [21]. In 2013, Hwang et al. first reported the promising $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ with a theoretical capacity of around 117 mAh g⁻¹ and a potential of 3.0 V [22]. However, this material suffers from structural instability during long-term electrochemical cycling and potential drop upon charging. So far, most studies on $\text{Na}_{4-x}\text{Fe}_{2+\alpha/2}(\text{P}_2\text{O}_7)_2$ ($2/3 \leq \alpha \leq 7/8$) have mainly focused on carbon wrapping [23–25]. And the changes made in the above work are basically outside the particles or smaller particles, and therefore hardly involve the crystal structure itself. Herein, our work is committed to improving both of the electrochemical and thermal performance, and giving a comprehensive mechanism understanding on the effects of cation doping in $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ (represented as NFPO) system, which is important for the large-scale application but has not been explored. Therefore, exploration of the (de)sodiation mechanism and thermal stability of $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ cathodes upon cycling is urgently required.

Cations doped with Mg^{2+} , Mn^{2+} , and Ni^{2+} , have shown enhanced electrochemical performance in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, but the thermal stability study was not reported in the literature [26–28]. Considering that Ca^{2+} doping is not only cost-effective, non-toxic and natural-abundant, but also chemically and thermally stable due to the robust bonding between Ca^{2+} and PO_4^{4-} [29]. Besides, the incorporation of Ca^{2+} would expand lattice volume, widen space and facilitate the diffusion of Na^+ ions [30]. Hence, different amounts of Ca are site-selectively introduced into $\text{Na}_{3.32}\text{Fe}_{2.34-x}\text{Ca}_x(\text{P}_2\text{O}_7)_2$ to stabilize the framework in this work. And the optimized sample is $\text{Na}_{3.32}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$ (represented as NFPO-Ca). The intrinsic correlation of crystal structure and electrochemical characteristics of NFPO-Ca, e.g. Na vacancies, structural evolution, cycling stability, lattice parameters, and voltage plateaus, is systematically investigated via *in situ* synchrotron-based X-ray diffraction (SXRD) and *in situ* X-ray absorption near edge spectroscopy (XANES). The results demonstrate that the (de)sodiation mechanism of NFPO-Ca is a solid-solution reaction. The enhanced structural stability of NFPO-Ca is uncovered by *in situ* high-temperature X-ray powder

diffraction (XRD), which is beneficial for eliminating the influence of the sodium defect in NFPO-Ca during long-term cycling. Finally, the natural-abundant constitute of Na-Fe-Ca-P-O, stable pyrophosphate $(\text{P}_2\text{O}_7)^{4-}$ anion, and Ca site-selective doping establish NFPO-Ca as a safe cathode candidate for large-scale economic SIBs system.

2. Results and discussions

2.1. Crystal structure

The high-resolution SXRD patterns of both, NFPO and NFPO-Ca, are indexed to a triclinic structure with $P1$ space group (JCPDS No. 83–0225) [23], as can be seen in Fig. S1a. Rietveld refinement was performed using the $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ model, and a good match between the patterns (calculated and observed) in both samples indicates a satisfactory fit. As shown in Fig. 1a, compared with NFPO, almost all reflections in NFPO-Ca move to a lower angle, suggesting a larger unit-cell volume of NFPO-Ca. Rietveld refinement results show that the lattice parameters of the NFPO compound are $a = 6.4126$ Å, $b = 9.3950$ Å, $c = 10.9809$ Å, and $V = 569.9982$ Å³, respectively, which are smaller than those of NFPO-Ca ($a = 6.4536$ Å, $b = 9.4068$ Å, $c = 11.0184$ Å, and $V = 575.9994$ Å³). The reason can be ascribed to the lattice expansion with the larger Ca^{2+} substitution ($r_{\text{Ca}^{2+}} = 1.0$ Å $>$ $r_{\text{Fe}^{2+}} = 0.78$ Å) [31,32]. The other refined parameters are compared and summarized in Table S1. In addition, the refined result suggests that Ca is site-selectively doping in Fe2 site (Fig. S1b). Fig. 1c shows that the polyhedral units in the NFPO and NFPO-Ca frameworks are similar. FeO_6 octahedra, FeO_4 tetrahedron, and P_2O_7 group together create the large Na-ion diffusion channels and interstitial spaces. Part of the Na4 sites along the a -axis is occupied by Fe1 atoms, which is called an anti-site defect [31]. In order to further understand the Na^+ diffusion channels, a bond valence (BV) method was used to elucidate the possible Na^+ diffusion pathways in each structure [33]. Both samples show that sodium ions preferentially diffuse via two one-dimensional conduction channels (Fig. 1c). The pathway 1 ($\text{Na}_2 \rightarrow \text{Na}_3 \rightarrow \text{Na}_2$) and pathway 2 ($\text{Na}_1 \rightarrow \text{Na}_3 \rightarrow \text{Na}_1$) are consistent with the previous theoretical calculations reported by Chen *et al.* [23]. These two pathways can provide sufficient space for effective and rapid diffusion of Na-ion. The Mössbauer spectrum of NFPO and NFPO-Ca in Fig. 1b were fitted with four doublets, implying four different crystallographic Fe^{2+} sites: Fe1 (occupying Na4 site), Fe4 site (FeO_4 , both corner- and corner-sharing mode), Fe2 sites (FeO_6 , corner-sharing mode), and Fe3 site (FeO_6 , both corner- and edge-sharing modes), as the displayed crystal structure in Fig. 1c. The Fe atoms in two outer doublets are considered to locate in

Fig. 1. Structural analysis of NFPO and NFPO-Ca. a) Rietveld refinement against the powder SXRD patterns ($\lambda = 0.4931$ Å) demonstrating Ca site-selective doping in Fe2 site; b) Four different Fe sites evidenced by four fitted Fe^{2+} -doublets (yellow, green, blue and purple areas) and Fe^{3+} species (red areas) in Mössbauer spectrum of two samples, showing the reduction in FeO_6 (green) of NFPO-Ca; c) Crystal structure of NFPO and NFPO-Ca with different polyhedrons FeO_6 (green), FeO_4 (green), and PO_4 (purple), displaying two similar possible pathways of sodium-ions in respective crystal structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

two different octahedral environments (FeO_6 octahedra) [31]. In these two compounds, although the structural isomorphism is retained, NFPO-Ca still causes a decrease in the green doublet area. The reduction of FeO_6 (green area) indicates that Ca preferentially occupies its Fe site [31]. Furthermore, there are two different Fe sites (Fe2 and Fe3) in their respective FeO_6 octahedra, and which Fe site could be occupied by Ca depends on the connection between P_2O_7 and FeO_6 . The crystal structures show that Fe3 octahedron connects P_2O_7 unit through the corner- and edge-sharing configuration, but Fe2 octahedron has only corner-sharing mode. The latter combination has smaller stereo hindrance, so Ca is more likely to occupy Fe2 site. This result is in good agreement with the refinement results, see Fig. S1b. According to the values of isomer shift (IS) and quadruple splitting (QS) (Table S2), the Fe^{2+} percentage of two compounds in a high-spin state is about 88%. More importantly, it is further disclosed that the appearance of trivalent Fe (Fe^{3+}) in the original structures is caused by inherent Na vacancies to maintain the electrical neutrality.

As shown in Fig. S2a, b, both compounds are composed of particles with micro-size and irregular granular shape, and a larger average particle size is obtained in NFPO-Ca. The high-resolution transmission electron microscopy (HRTEM) images with obvious lattice fringes are displayed in NFPO and NFPO-Ca compounds (Fig. S2c, d). The clear lattice fringes of (0 0 1) plane in NFPO and (0 1 1) plane in NFPO-Ca correspond to the interplanar spacing of around 0.751(2) nm and 0.826(2) nm, respectively. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) results in Table S3 demonstrate that the elemental ratio of Na, Fe, and Ca is in good according with the desired value (Na : Fe : Ca = 3.32 : 2.01 : 0.23). The EDS-mapping images show a uniform distribution of elements Na, Fe, P, O, Ca, C, N (Fig. S2g). X-ray photoelectron spectroscopy (XPS) (Fig. S3b) illustrates two distinct peaks at ~ 710.1 and ~ 723.8 eV along with their satellite peaks. They are ascribed to the $2p_{3/2}$ and $2p_{1/2}$ orbitals of Fe^{2+} in both powders [24], clarifying that Ca^{2+} incorporation does not affect the valence of Fe^{2+} , as demonstrated in the Mössbauer spectrum. Moreover, *in situ* XANES characterization also confirms that +2 is the main valence of Fe in NFPO-Ca electrode before charging, which will be discussed later. The

observation of spin-orbital of Ca 2p (at around 347.2 eV and 350.9 eV) directly confirms its successful presence in $\text{Na}_{3.32}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ (Fig. S3d) [34]. Moreover, no obvious differences in binding energy are found in the spectra of Na 1s and P 2p (Fig. S3e,f), which indicates that the bonding of Na and P in two compounds are similar. Fourier transform infrared (FT-IR) spectroscopy shows similar stretching and bending modes of $(\text{P}_2\text{O}_7)^{4-}$ ligands in both compounds (Fig. S4a). The main characteristic vibration of $(\text{P}_2\text{O}_7)^{4-}$ group is between 1300 and 400 cm^{-1} , with a narrow but multiple vibration modes [35]. Accordingly, three distinct band regions are assigned to the vibrations of P–O (950–1300 cm^{-1}), P–O–P (700–958 cm^{-1}), and O–P–O (400–680 cm^{-1}). Raman spectrum exhibits two predominant vibrational bands at approximately 1350 cm^{-1} (D band) and 1580 cm^{-1} (G bands) (carbon specie is from the decomposition oxalate) in Fig. S4b [35]. The intensity ratio (I_D/I_G) of D band and G band in NFPO and NFPO-Ca are 1.10 and 1.00, respectively, indicating a relatively high graphitization degree in NFPO-Ca. Overall, Ca incorporation does not cause difference in terms of Na bonding, Fe valence, and $(\text{P}_2\text{O}_7)^{4-}$ group.

2.2. Electrochemical properties

The galvanostatic charge and discharge profiles of NFPO and NFPO-Ca were tested at 1.5–4.15 V ($1\text{ C} = 110\text{ mA g}^{-1}$). Two phenomena should be noticed when comparing the electrochemical behaviors. One is the potential drop (Fig. 2a and Fig. S5a) between the first and subsequent charged curves; the other is the whole or partial absence of plateau at around 2.5 V (Fig. 2a and Fig. S5a). Potential drop in NFPO could originate from Fe irreversibly migrating and occupying the empty Na sites in the first charge. Such behavior alters the site occupancies of Na and Fe, leading to a lower voltage in subsequent cycles [36]. Similar cases also occurred in many Fe-based polyanionic materials, like $\text{Li}_2\text{FeP}_2\text{O}_7$ (0.07 V drop) and $\text{Li}_2\text{FeSiO}_4$ (0.3 V drop). Li/Fe structural disorder or phase transition during the first charged state is responsible for their potential drops [36]. However, the reason for the absence of 2.5 V plateau in this pyrophosphate material is not clear. To bring new insight, the cell test was started with the pre-discharge step (Fig. 2b and

Fig. 2. Electrochemical performance of NFPO and NFPO-Ca electrodes. a, b) Galvanostatic charge and discharge profiles of NFPO-Ca at 0.1 C between 1.5 V and 4.15 V, starting a) without and b) with pre-discharge; c) Cycling performance of two cathodes at 1 C.

Fig. S5a). The results show that the discharge capacity during the pre-discharge is around 10 mAh g^{-1} . Furthermore, the charging curves clearly deliver a complete plateau at 2.5 V in all cycles. The pre-discharge serves to first fill the initial Na vacancies, thereby eliminating the influence of Na vacancy defects in subsequent cycles [37].

Obviously, eliminating the Na vacancies in the original structure could restore the 2.5 V plateau and avoid the potential drop (Fig. 2b and Fig. S5a). These Na vacancies should be interpreted as the spontaneous extraction of Na^+ under the condition that the composite reacts with moisture in the atmosphere. And this reaction tends to occur when the target product is obtained by ball-milling and annealing treatment [37]. To further understand the effect of Ca substitution, the differential plot of galvanostatic test (dQ/dV) is depicted in Fig. S5d. In addition, the marked areas in dQ/dV profiles are enlarged (Fig. S5e). A smaller voltage drop in NFPO-Ca ($\Delta V = 0.011 \text{ V}$) than NFPO ($\Delta V = 0.025 \text{ V}$) indicates its superior structural stability and better reversibility during cycles. Interestingly, dQ/dV profiles between two samples are also different. Compared to NFPO, the 2.5 V plateau in NFPO-Ca remains almost unchanged, while the 3.0 V plateau evidently splits into two peaks at around 2.9 V and 3.12 V. The single-phase reaction in NFPO was reported [23], whereas the electrochemical behavior in NFPO-Ca seems to induce a phase transition at 3.0 V. *In situ* SXRD was conducted to further understand its reaction mechanism, see the discussion below.

The rate capabilities of two electrodes are shown in Fig. S5b, the initial discharge capacities of NFPO and NFPO-Ca exhibit about 81 and 100 mAh g^{-1} at 0.1 C, respectively. And even at 20 C, NFPO-Ca can still deliver 56 mAh g^{-1} , which is about two times higher than NFPO (29 mAh g^{-1}). Superior rate capability curves of NFPO-Ca than those of NFPO are presented in Fig. S6. Clearly, the inert Ca^{2+} doping benefits the rate capabilities without the expense of initial capacity fade. The better rate performance in NFPO-Ca can be ascribed to the enhanced charge transfer capability in NFPO-Ca. As shown in the EIS result (Fig. S7 and Table S5), for the fresh electrodes, NFPO-Ca shows a smaller R_{ct} value (130.5Ω) than NFPO (215.9Ω). This result suggests an improved electronic conductivity and enhanced electrochemical reaction kinetics in NFPO-Ca. Moreover, Ca substitution can also enhance Na^+ diffusion capability due to an expanding lattice volume (see GITT results below). These favorable characteristics contribute to a better rate performance in the NFPO-Ca cathode. Notably, when cycling at 1 C (Fig. 2c), compared to NFPO, NFPO-Ca shows remarkable improvement in the cycling stability, with an impressive capacity retention of 81.7% over 1000 cycles and high Coulombic efficiencies ($>99\%$) for all cycles. By contrast, the NFPO electrode exhibits much lower capacity retention of 15.5% at the end of 1000 cycles. To get more prolonged cycling information, the electrodes are tested over 2000 cycles at 5 C, showing that the capacity retention of NFPO-Ca (82.4%) is higher than that of NFPO (49.1%) in Fig. S5f. High temperature cycling is also an indispensable concern to evaluate the structural stability and operational safety. At 50°C , the cycling durability of NFPO-Ca is significantly improved compared to NFPO (Fig. S5c). In detail, the NFPO-Ca cathode clearly shows high capacity retention of 91.9% over 200 cycles, while the capacity of NFPO after 120 cycles dramatically decreases. Here, the delivered capacity at 1 C is higher than the one evaluated at ambient temperature, illustrating that NFPO is a thermo-sensitive material. But its structure could be effectively stabilized with Ca doping, which is further verified by studying the thermal behaviors of the charged electrodes using *in situ* high-temperature XRD, see below.

To further comprehend the practicability, the pyrophosphate NFPO-Ca electrode was fabricated into full cells using our home-made anode compound (NTO) as the counterpart (Fig. S5g-j) [38]. The NTO anode consists of two compounds, including $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The full cell NFPO-Ca//NTO delivers a reversible capacity of $\sim 80 \text{ mAh g}^{-1}$ with an operating voltage of $\sim 2.3 \text{ V}$ at 0.1 C (based on the NFPO-Ca cathode mass). After 200 cycles at 2 C, the full cell achieves the capacity retention of up to $\sim 76\%$ and a high Coulombic efficiency of above 99%.

Based on the high safety and sustainability of pyrophosphate, it could be expected to be a suitable alternative in future energy storage.

2.3. Reversibility and Na-ion dynamics

To explore the reversibility of electrodes with/without doping ion, cyclic voltammetry (CV) measurements were conducted at multiple scan rates. Two electrodes distinctly display two pairs of redox peaks, corresponding to the successive electrochemical reaction processes (Fig. S9). As the scan rate increases, the cathodic peaks in both electrodes consistently shift toward higher potentials and the anodic peaks shift oppositely. However, compared to the NFPO electrode, the potential difference of the NFPO-Ca electrode is lower, and its CV curve is more symmetrical. This phenomenon suggests smaller potential polarization and higher electrochemical reversibility in NFPO-Ca. Sodium ion diffusion coefficients (D_{Na^+}) are calculated from the initial GITT profiles (Fig. S10a,b). Overall, the variation trends of D_{Na^+} in both compounds are similar, consistent with reported results [23]. Basically, D_{Na^+} values show a continuous drop during charging, and a visible fluctuation of diffusion coefficients during discharging (Fig. S10e,f). The inserts of Fig. S10e and f are the magnifications of D_{Na^+} between 2.8 and 3.4 V, which clearly reveal the distinction of D_{Na^+} values in two samples. In NFPO-Ca, D_{Na^+} values vary from 10^{-10} to $10^{-14} \text{ cm}^2 \text{ s}^{-1}$, which are basically higher than those in NFPO as a whole. Hence, better electrochemical properties could be expected by rationally designing the structure with doping ions.

2.4. Operational risk evaluation

A charged cathode during battery operation may cause potential safety risk, such as overheating, self-decomposition, and oxygen evolution. The key to knowing the operational safety of any cathode is to study the thermal behavior of the charged cathode [39,40]. *In situ* high-temperature XRD patterns (Fig. 3a) shows that the triclinic reflections in the XRD diffraction patterns of the highly charged NFPO ($\text{Na}_{3.32-x}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$, $0 < x \leq 1$) can be retained up to 400°C . New reflections such as $\bar{1}01$, $\bar{2}12$ and 022 indexing to $\alpha\text{-NaFeP}_2\text{O}_7$ appear at around 450°C [40]. Further heating to 600°C , the starting component $\text{Na}_{3.32-x}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ gradually converts to $\alpha\text{-NaFeP}_2\text{O}_7$. This observation demonstrates that at temperatures $\geq 450^\circ\text{C}$, the desodiated $\text{Na}_{3.32-x}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ cathode experiences an irreversible transition from triclinic phase (P1) to monoclinic phase (P2₁/c) (Fig. 3b), as shown in the following equation:

Excitingly, the phase transition in the charged NFPO-Ca ($\text{Na}_{3.32-x}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$, $0 < x \leq 1$) occurs at a higher temperature of around 500°C , as shown in Fig. 3a. This result provides direct evidence that NFPO-Ca has better thermal stability than NFPO, which in turn reflects the structural superiority of NFPO-Ca as the reason for its long cycle life. Unlike the $(\text{PO}_4)^{3-}$ anions, $(\text{P}_2\text{O}_7)^{4-}$ anions will not thermally decompose and/or release oxygen until 600°C , demonstrating better safety than phosphate $(\text{PO}_4)^{3-}$ anions [40]. With the incorporation of Ca, the thermal stability of NFPO-Ca was enhanced. These two factors establish NFPO-Ca as a safe cathode candidate for future economic sodium-ion batteries. The safety advantage of NFPO-Ca can outperform other cathodes (see Table 1).

3. Mechanisms on structural stability in NFPO-Ca

3.1. Mechanism of sodium-ion storage

Phase evolutions can be identified by CV curves at low scan rates

Fig. 3. Thermal stability and phase evolution. a) *In situ* high-temperature XRD patterns of two charged cathodes, showing the phase transition from triclinic phase to monoclinic NaFeP_2O_7 occurring at higher temperature in NFPO-Ca; b) Structural crystals before and after phase transition with $\text{FeO}_6/\text{FeO}_4$ polyhedral (green) and PO_4 tetrahedra (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Phase transition temperatures comparison between present study and previously reported systems.

Electrode Material	Transition temperature (°C)	Charged State (V)	Reference No.
$\text{Na}_{3.32-x}\text{Fe}_{2.11}\text{Ca}_{0.23}(\text{P}_2\text{O}_7)_2$ ($0 < x \leq 1$)	500	4.15	Present study
$\text{Na}_{3.32-x}\text{Fe}_{2.34}(\text{P}_2\text{O}_7)_2$ ($0 < x \leq 1$)	450	4.15	Present study
$\text{Na}_{1.6}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($\delta \cong 0.67$)	100	4.3	[29]
Li_xFePO_4 ($0 \leq x \leq 1$)	250–390	Oxidized by NO_2BF_4	[41]
$\text{Li}_{0.33}\text{Ni}_{0.5+x}\text{Co}_{0.2}\text{Mn}_{0.3-x}\text{O}_2$ ($x = 0, 0.1, 0.2$)	215, 190, 169	~4.34, 4.21, 4.15	[42]
$\text{P2-Na}_x\text{CoO}_2$	100	4.3	[43]

[44]. When lowering the scan rate to 0.05 mV s^{-1} , NFPO-Ca exhibits a stronger peak splitting at 3.0 V (Fig. S11a). This redox reaction is more likely to be identified as two-phase reaction based on previous reports [44]. While Chen *et al.* reported the formation of solid solution phase in $\text{Na}_{3.42}\text{Fe}_{2.32}(\text{P}_2\text{O}_7)_2$ [23]. In addition, it still remains unclear whether the absence of the 2.5 V plateau affects the structural stability. Hence, to determine the phase evolution and charge compensation mechanism of NFPO-Ca, *in situ* SXR and *in situ* XANES were performed at MS beamline, (Swiss Light Source, Switzerland), and at P64 beamline (PETRA III,

Germany), respectively.

The *in situ* SXR patterns are displayed in Fig. 4a. The structural evolution of NFPO-Ca mainly presents as apparent reflections shift, and no reflections disappear or new reflections occur during the first cycle. These results reveal that NFPO-Ca experiences a single-phase transition in the process of sodium-ions intercalation and de-intercalation. During charging, the pair of reflections $\bar{1}02/122$ tends to merge and split again at approximately 3.0 V and 3.25 V, respectively, and *vice versa* during discharging. The positions of the reflections merging and splitting are basically consistent with the splitting potentials at the CV curve and the dQ/dV profile. Peak splitting might be ascribed to the respective voltage locations of different Fe sites. The octahedral FeO_6 (Fe2 site) with edge-sharing configuration generates a higher potential at 3.12 V compared to the corner-sharing mode [19,31]. Furthermore, clear structural evolution ($2\theta = 9.4 \sim 11.8^\circ$) occurs continuously and can be reversibly back to the original phase in a cycle, as reflected by *in situ* SXR pattern in Fig. S11b. Regarding the whole process, including the first cycle, and the second charge segment, a good preservation of crystal structure is evident, which indicates an excellent reversible sodium-ion intercalation/de-intercalation process. The continuous symmetrical peak evolution could be attributed to the continuous changes in lattice parameters during cycling, see the later section. Moreover, this symmetrical transition indicates a small structural distortion, implying a stable framework of NFPO-Ca. In addition, the *in situ* SXR pattern of the second charge at around 2.5 V shows a good recovery to the original state. This observation reveals that the absence of the 2.5 V plateau does not affect

Fig. 4. Structural evolution of NFPO-Ca during electrochemical (de)intercalation of Na^+ . a) *In situ* high-resolution SXRD patterns of NFPO-Ca collected at 0.1 C in the range of 1.50 – 4.15 V (wavelength $\lambda = 0.4931 \text{ \AA}$); b) Voltage – composition profiles of NFPO-Ca, showing the reversible Na^+ (de)intercalation; c) *In situ* XANES spectra of the Fe K-edge for NFPO-Ca investigated by manifesting the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox activity.

the structural stability of the solid-solution framework. These *in situ* SXRD patterns consist of more than 300 data sets that track a clear and continuous process of the ongoing reaction in NFPO-Ca. And the *ex situ* XRD pattern of NFPO-Ca also shows no obvious change after 5 and 20 cycles (Fig. S12). Therefore, it can be believed that the sodium-ion storage mechanism in NFPO-Ca is still a solid-solution reaction, similar to that in NFPO. Furthermore, the absence of the plateau at 2.5 V does not affect its structural superiority.

The pyrophosphate NFPO-Ca material shows a reversible sodium-(de)intercalation process involving $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox activity, mainly centering at around 3.0 V (vs. Na/Na^+ , Fig. 4b). The sloped voltage curve in Fig. 4b also illustrates a single-phase redox mechanism. Except for the first charge profile, a very narrow sloped voltage gap is observed between the charging and discharging stages in NFPO-Ca. This indicates that NFPO-Ca is a good host framework for reversible Na^+ (de)insertion. The difference from the first charge may be due to the irreversible local structure change upon Na-ion extraction. *In situ* XANES spectroscopy provides the possibility to understand the valence state changes in Fe in ongoing reactions. As shown in Fig. 4c, for the charge, the Fe K-edge spectra of NFPO-Ca gradually shifts to a higher energy, illustrating the reaction of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ [45]. Regarding the discharge, it basically returns to the lower energy position of Fe K-edge in the original path. The difference in the shape of K-edge spectra between charging and discharging can be ascribed as the changes of local structure [46]. It is worth noting that the valence state of Fe ions increases rapidly from $\sim +2$ to $\sim +3$ when the voltage increases from $\sim 2.85 \text{ V}$ to $\sim 3.25 \text{ V}$. This indicates that the repulsive force between Fe(III) cations is strongly related to the potential at 3.12 V.

3.2. Lattice parameters variation during the cycle

As presented in Fig. 5a and Fig. S13, the symmetrical evolution of *in situ* SXRD reflections indicates the symmetric variation of cell parameters in NFPO-Ca. The value of lattice parameter a evolves in a “V” shape, where the initial a value ($\sim 6.461 \text{ \AA}$) continuously reduces to $\sim 6.351 \text{ \AA}$ during charging, and returns to the original state in the reverse direction during discharging. Similar evolution trends are also observed in the parameters α and β (Fig. S13). The values of α and β start from $\sim 64.5^\circ$ and $\sim 85.7^\circ$, and end at $\sim 62.7^\circ$ and $\sim 83.3^\circ$ in the charged state. The c -value curve basically appears as “M” shape, first rising to $\sim 11.075 \text{ \AA}$ and then falling to $11.060 \text{ \AA}$. A symmetrical distribution of c value during discharging is displayed, thus forming an “M” shape. In contrast, the trajectory of γ value exhibits a distorted “W” shape, with a minimum value of $\sim 72.4^\circ$ at the boundary between charge and discharge.

Very interestingly, for the first time, it is deciphered that the fluctuant b values are closely correlated to the voltage curves. Furthermore, b value also corresponds to the Na content or specific capacity in the NFPO-Ca cathode during cycling. During charging, a segment with peak value of b ($\sim 9.428 \text{ \AA}$) appears in the range of $2.9 \text{ V} \sim 3.12 \text{ V}$. This voltage region closely matches the locations of the two split voltage peaks in the dQ/dV plot of NFPO-Ca (Fig. S5d). Before and after this segment, the initial b value ($9.405 \text{ \AA}$) first increases to the plateau value, and then drops to its trough value ($\sim 9.418 \text{ \AA}$) at $\sim 3.5 \text{ V}$. After that, the b value again increases rapidly, peaking at $9.447 \text{ \AA}$ at the end of charging. During discharging, the b value shifts back in a reversible way. At the beginning, the value of b drops rapidly and reaches a plateau ($b \approx 9.424 \text{ \AA}$), where the voltage range ($3.11 \sim 2.95 \text{ V}$) approximately corresponds to the position of the two split peaks (Fig. S5d). Thereafter, b increases to a peak value ($\sim 9.431 \text{ \AA}$) at 2.9 V and then rapidly drops to its minimum value at the end of the first discharge. Overall, the path of b

Fig. 5. Lattice parameters variations vs diffraction pattern number as gained from Rietveld refinement results. a) The changes in lattice parameters a , b , c , and unit-cell volume (V) together with the charge and discharge profiles (error bar is less than 2%); b) structural models at (1) pristine state (2.7 V), (2) charged state (4.15 V), (3) discharged state (2.7 V), and (4) discharged state (1.5 V).

value during charging/discharging looks like “multiple rolling hills”. The b value is highly correlated to the voltage curve, and the effect of b value could be further extended to the winding Na-diffusion path that roughly parallel to the bc plane and b -axis, as reflected by the fluctuation of D_{Na+} in Fig. S10e, f and previous report [23]. Another aspect to note is that the symmetry of the b -value curve is not as good as other curves (a , c , α , β , γ , and V). The reason could be a small amount of Fe migrating to the sodium site, altering the electrostatic repulsion force during charging. This change therefore causes a slight change in the sodium-ion diffusion paths and the lattice parameter b is more sensitive to this change. The calculated volume changes (ΔV) during the first charge and discharge are only 2.5% and 3.0%. Since the cut-off voltage of 1.5 V during discharge is lower than the open-circuit voltage (OCV) above 2.5 V, which means that more sodium ions would be inserted back to the framework. Therefore, the volume shrinkage ($\Delta V = 2.5\%$) during charging is lower than the volume expansion ($\Delta V = 3.0\%$) during discharging. In short, such a small change in the sodium (de)intercalation in the framework could contribute to a long cycle life of NFPO-Ca.

Figure 5b shows four typical structural models with different states, which can be representative for a typical solid solution reaction during the first cycle. Na vacancy, which is also found in the pristine state at ~2.7 V, could be used to indicate the capacity/voltage plateau. Upon charging, Na vacancy is increasing to the maximum at 4.15 V and the bond length of Fe-O (R_{Fe-O}) reaches the smallest value. Obviously, similar values of Na vacancy and R_{Fe-O} can be seen when NFPO-Ca discharges to 2.7 V. With further discharge to 1.5 V, more Na ions are inserted and the R_{Fe-O} value becomes larger. The change in R_{Fe-O} value is supposed to be related to the variation of Fe valence and Na vacancy. The strong correlation between Na vacancy and lattice parameter b can be ascribed to Na-ion diffusion pathway (*i.e.* parallel to the b -axis).

4. Conclusion

Through Ca site-selective doping, a superior thermal and electrochemical stability has been achieved in NFPO-Ca. The structural superiority offered by Ca doping contributes to a long cycle life, where NFPO-Ca delivers capacity retentions of 81.7% after 1000 cycles at 1 C. Both the charged state electrodes have undergone a thermal phase transition from triclinic ($P1$) to monoclinic ($P2_1/c$) phase, but the charged $Na_{3.32}$ -

$xFe_{2.11}Ca_{0.23}(P_2O_7)_2$ ($0 < x \leq 1$) has better thermal stability than the pristine material.

Furthermore, the complementary relationship between structure, safety, and electrochemical performance of these cathode materials are investigated in detail. The redox mechanism of NFPO-Ca is found to be an ideal solid-solution process. Interestingly, the voltage curve is highly correlated to the variable lattice parameter b value, as reflected by the potential plateaus corresponding to different b value regions. More importantly, the lattice parameter b can also be used as a sensitive indicator of Na content or specific capacity in the electrode materials during cycling. This underlying regulation of b -value and voltage plateau as well as Na content may provide an opportunity to understand the changes in voltage plateaus and specific capacities associated with other systems and the rationale behind. This work pioneers an effective strategy for designing electrode materials that could be extended to other energy materials to prolong battery life and improve operational safety.

CRediT authorship contribution statement

Yumei Liu conceived the idea and oversaw the project. Zhenguo Wu, Sylvio Indris, Weibo Hua interpreted and discussed the data. The experimental data were measured and analysed by Yumei Liu, Sylvio Indris, Weibo Hua, Nicola P. M. Casati, Akhil Tayal, Mariyam Susana Dewi Darma, Gongke Wang, Yuxia Liu, Chunjin Wu, Yao Xiao, Benhe Zhong, and Xiaodong Guo. Yumei Liu, Weibo Hua, and Xiaodong Guo wrote the article. All authors contributed to critical review of the manuscript and have given approval to this final draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2020.105417](https://doi.org/10.1016/j.nanoen.2020.105417).

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