Detailed investigation of Na$_{2.24}$FePO$_4$CO$_3$ as a cathode material for Na-ion batteries

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Na-ion batteries are gaining an increased recognition as the next generation low cost energy storage devices. Here, we present a characterization of Na$_3$FePO$_4$CO$_3$ nanoplates as a novel cathode material for sodium ion batteries. First-principles calculations reveal that there are two paths for Na ion migration along b and c axis. In-situ and ex-situ Fe K-edge X-ray absorption near edge structure (XANES) point out that in Na$_3$FePO$_4$CO$_3$ both Fe$^{2+}$/Fe$^{3+}$ and Fe$^{3+}$/Fe$^{4+}$ redox couples are electrochemically active, suggesting also the existence of a two-electron intercalation reaction. Ex-situ X-ray powder diffraction data demonstrates that the crystalline structure of Na$_3$FePO$_4$CO$_3$ remains stable during the charging/discharging process within the range 2.0–4.55 V.

Lithium ion batteries (LIBs) represent a real technological advancement in energy storage systems (ESSs), with many applications in our daily life: laptops, cameras, mobile phones, etc. However, due to the increasing demand of Li for applications in large facilities, the lack of Li resources is a serious drawback. Compared with LIBs, sodium ion batteries (SIBs) appear more appropriate for ESSs because of the abundance of sodium natural resources, its better economic efficiency and the lower cost of raw materials. In addition, because of sodium’s lower potential for intercalation materials, the electrolyte offers more choices. Compared to standard H electrode, they are $-2.71$ V for Na$^+$/Na and $-3.02$ V for Li$^+$/Li, respectively.

Among the investigated cathode materials for SIBs, polyanionic materials attract a large attention, because the main structure contains strong covalent bonds of polyanion characterized by a good thermal stability, which imply improved safety characteristics for these batteries. Carbonophosphates ($A_3$MPO$_4$CO$_3$) introduced by Ceder’s team are a good reference for these systems. Theoretical works suggested that the $A_3$MPO$_4$CO$_3$ structure can be better deintercalated with more than one Na from crystalline structure, pointing out the existence of a two-electrons reaction. Chen et al. successfully synthesized Na$_3$MnPO$_4$CO$_3$, and with ex-situ solid state NMR experiments, they showed that both Mn$^{2+}$/Mn$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ redox couples are electrochemically active. Actually, the two electrons reaction mechanism implies that electrode materials may have a high specific capacity. However, their effective specific capacity was not good enough, especially at high rates. There are still few reports discussing the factors limiting the capacity or the cycle life. As a consequence, it is still a great challenge enhancing both rate capability and cyclability of Na$_3$MnPO$_4$CO$_3$ cathode materials.

In the present work, we used a modified hydrothermal method to synthesize Na$_3$FePO$_4$CO$_3$ nanoplates. The structural evolution of this compound was carried out by combining a DFT computation with in-situ and ex-situ XAS as well as XRD experiments. When used as cathode materials in Na ion batteries, both Fe$^{2+}$/Fe$^{3+}$ and Fe$^{3+}$/Fe$^{4+}$ redox are electrochemically active and the crystalline structure remains stable during charging/discharging process. However, when compared with previous works, the as-prepared Na$_3$FePO$_4$CO$_3$ system shows better electrochemical properties in terms of both high-rate charge/discharge performance and cyclability.

**Results**

**Geometrical structure and possible Na$^+$ transfer paths.** Figure 1a displays the XRD pattern of the synthesized sample. Diffraction peaks are in good agreement with the standard p21/m space group Na$_3$FePO$_4$CO$_3$ (PDF#35-0678). Diffraction features due to impurity were not detected, meanwhile, the strong intensity also suggests a high...
crystallinity of the as-prepared sample. The Rietveld refinement result points out that the accurate molecular formula is $\text{Na}_3-x\text{FePO}_4\text{CO}_3$ with $a = 8.948334$ Å, $b = 5.167109$ Å, $c = 6.593195$ Å, $\beta = 90.16091$ and $V = 304.8485$ Å$^3$, as listed in table S1.

Comparison of the white line energy at the Fe K edge among as-prepared Na$_3$FePO$_4$CO$_3$, FeO and Fe$_2$O$_3$ standards supports the existence of a mixed valence between Fe$^{2+}$ and Fe$^{3+}$ configurations (see figure S1). The Mössbauer spectroscopy experiment performed on as-prepared products suggests rewriting the exact formula as Na$_{2.24}$FePO$_4$CO$_3$, (see figure S8). However, as proposed in a previous work$^{31}$, the crystal structure of the Na$_3$FePO$_4$CO$_3$ is isostructural to Na$_3$MnPO$_4$CO$_3$ (see figure 1b–d) with a main framework composed of distorted FeO$_6$ octahedra, PO$_4$ tetrahedra and CO$_3$ plane triangles. These groups are connected with each other, forming a two dimensional chain in the (010) plane (see figure 1c). Two different sites (4f and 2e) are present in the crystal for the sodium atoms, named Na1 and Na2, and surrounded by 7 and 6 O atoms, respectively. A first-principles calculation showed that the band gap of the as-prepared Na$_3$FePO$_4$CO$_3$ is 3.4 eV, smaller than the value of 3.7 eV of the LiFePO$_4$ $^{36}$. The electron density around the Fermi level demonstrates also that Na$_3$FePO$_4$CO$_3$ compounds may have a good electronic conductivity (see figure 2a). From figure 2b and 2c, we show also that there are two-dimensional channels along b and c axis to insert Na atoms (Na1-Na2-Na1, Na1-Na1-Na2-Na1), in agreement with a previous report$^{36}$. The energy barriers of two most ideal Na diffusion paths are 0.6 and 0.7 eV (see in table S2), respectively. Both are much higher than the energy barrier of LiFePO$_4$ (0.3 eV)$^{37}$, pointing out the low ionic conductivity of the Na$_3$FePO$_4$CO$_3$. As a consequence, it is mandatory synthesizing highly oriented nanomaterials along b or c axis to obtain excellent electrochemical performances.

Morphology and thermostability characterization of Na$_3$FePO$_4$ CO$_3$. The morphology and size of as-prepared Na$_3$FePO$_4$CO$_3$ products were characterized by transmission electron microscopy (TEM). As shown in figure 3a, TEM images display a plate-like morphology with a width in the range of 100–200 nm and a thickness of ~50 nm. The Brunauer-Emmet-Teller (BET) characterization (see figure S3) demonstrates that the surface area is as high as 46 m$^2$/g and the selected area electron diffraction (SAED) pattern reveals that the exposed planes of Na$_3$FePO$_4$CO$_3$ nanoparticles have the (001) orientation. As mentioned above, the [001] direction is also one of the Na ion diffusion paths, so that this preferred orientation enhances the Na ion transfer capabilities that results also in a better rate capability.

Figure 3d shows the thermal gravimetric (TG) and differential thermal analysis (DTA) of Na$_3$FePO$_4$CO$_3$ nanoparticles. Data points
out that the material did not experience any thermal decomposition up to 550°C. Moreover, CO₂, rather than other flammable gases, would be released even at the decomposition temperature of 550°C. This behavior ensures the safety of SIBs and guarantees the high thermal stability of this cathode candidate, an additional important feature that makes it a suitable cathode material for ESSs.

**Electrochemical characterization of the Na₃FePO₄CO₃.** The electrochemical behaviour of the Na₃FePO₄CO₃ has been tested with the galvanostatic discharge-charge technique. Figure 4a showed a discharge profile with different cycles at the current density of 10 mA g⁻¹ at 20°C (100 mA g⁻¹ was defined as 1 C). The long plateau at 2.7 V in the first discharge curve is attributed to the reduction of Fe³⁺ to Fe²⁺. The first discharge capacity can deliver 121 mAh g⁻¹. After 50 cycles of test, the capacity still shows a reversible capacity of 96 mAh g⁻¹ with a columbic efficiency 99%, that represents a really good stability.

Figure 5 shows the first three cyclic voltammogram (CV) curves of the electrodes recorded for the Na₃FePO₄CO₃ at the scan rate of 0.1 mVs⁻¹ at 20°C. The sample shows a strong peak at around 2.7 V in the first anodic scan that corresponds to a reduction from Fe⁵⁺ to Fe⁴⁺ while the broad peaks at ~4.2 V could be associated to the transition from Fe⁵⁺ to Fe⁶⁺. In the cathodic scan, two oxidation peaks also occur, accordingly. The two couples of redox features are similar to those of the Li₂FeSiO₄ data 39–40, which have been recognized as electrochemically active Fe³⁺/Fe⁴⁺ and Fe⁴⁺/Fe⁵⁺ redox. The latter also implies the existence of a possible two electrons reaction path in the Na₃FePO₄CO₃.

Regarding Na₃FePO₄CO₃ nanoplates, another fundamental improvement is its rate capability. As shown in Figure 4d, the as-prepared Na₃FePO₄CO₃ nanoplates showed the highest rate capability among the samples previously reported 35. Even at the current density of 200 mA g⁻¹, Na₃FePO₄CO₃ nanoplates still exhibit a favourable specific capacity of 58 mAh g⁻¹. Moreover, the Na₃FePO₄ CO₃ at 10 mA g⁻¹ can recover the initial reversible specific capacity after the high rate measurements, implying their good reversibility.

**Discussion**

In order to get a deeper understanding of the charge/discharge mechanism and of the structural evolution of the two electrons process, electrochemical tests at different cutoff voltages, in-situ XANES, ex-situ XRD and XANES measurements were carried out. As shown in figure 6, two charge potentials around 2.7 and 4.2 V appear when it is charged to 4.55 V, while we observed only one charge potential for the other charged to 3.8 V. On the other hand, the discharge capacity delivered with 3.8 V cutoff potential was obvious lower than the one charged to 4.55 V. All the different electrochemical performances suggest that further Na⁺ can be extracted working with a higher voltage. In other words, the Fe³⁺/Fe⁴⁺ redox can only be active in a higher potential. A similar situation is found in another polyanionic Li₂FeSiO₄ system reported by Yang’s team 39. In-situ XANES spectroscopy and ex-situ XRD were applied to further confirm the occurrence of the two electrons process. The K edge XANES spectroscopy of 3d transition metals originates from an electron excitation from a core level 1s to 4p unoccupied states 41. Since it is driven by high order correlation functions beyond the pair correlation one, it can be considered a fingerprint of the local geometry around the absorption atoms 42–43. Moreover, the absorption energy is related to the effective electrons of absorption atoms, so that assuming the same coordination, the energy position shifts to higher level for an increased oxidation state of the absorption atoms. We

![Figure 2](https://www.nature.com/scientificreports)

**Figure 2** The calculated density of state (DOS) and the Na⁺ transfer paths in the Na₃FePO₄CO₃. (a) The DOS of pure Na₃FePO₄CO₃ with GGA + U. The Fermi level is set as a reference; (b) one of the most probable Na diffusion pathways for the Na₃FePO₄CO₃ is along the b axis. Its calculated energy barrier is just 0.642 eV; (c) another possible Na diffusion pathway is along the c axis with an energy barrier of 0.716 eV. Dark yellow spheres are 4f Na atoms, light yellow the 2a Na, while solid and dot black lines are the outwards and the inwards diffusion pathways among Na atoms.
may then use the shift of the energy position of a XANES spectrum to establish and monitor the change of the valence state. From in-situ XANES spectroscopy showed in figure 7a, we found that both the edge shape and position of the pre-edge do not change, while the energy position shifts to higher energy when charged to 4.55 V. Compared with the reference samples FeO and Fe₂O₃, we may claim that the Fe valence state can be increased to a valence higher than 3⁺ (see figure 7a). On the contrary, for ex-situ experiments, after increasing to 3⁺, figure 7b showed that the Fe valence state remains constant. Because of the instability of the Fe⁴⁺ it is easy to understand that the Fe⁴⁺ configuration obtained by the electrochemical reaction can be reduced to Fe³⁺ in air. Therefore, the edge energy position does not shift. Regarding the pre-edge position, we are still unable to fully explain its behavior due to its complexity. However, combined with data available in the literature, it is reasonable to consider that the Fe⁴⁺/Fe³⁺ redox couple is active.

Ex-situ XRD patterns taken with a current of 10 mA/g at different charging/discharging potentials are shown in figure 8. No obvious changes are detectable in the diffraction features of XRD patterns during the Na ion insertion/de-insertion process, suggesting that the charging/discharging is a sing-phase process. The strong intensity of the diffraction peaks indicates also that the cathode material has a stable crystalline structure during the entire charging/discharging process.

The good electrochemical performance of the Na₃FePO₄CO₃ nanoplates can be due to: a) a preferred orientation that guarantees a high electrical conductivity of the overall electrode, an improved specific capacity, a good cycling performance and a high rate capability; b) an existing electrochemical active Fe⁴⁺/Fe³⁺ redox couple that offers the possibility to obtain a high capacity. As a consequence, the unique characterization of the as-prepared Na₃FePO₄CO₃ nanoplates provides a good electrochemical performance when applied to SIBs.

In summary, a simple modified hydrothermal method has been setup to synthesize Na₃FePO₄CO₃ nanoplates. A full characterization by SEM, TEM and SEAD revealed that the nanoplate size ranges from 100 to 200 nm with a thickness of about 50 nm. A preferred orientation on the (001) plane has been identified. Moreover, the capacity of Na₃FePO₄CO₃ nanoplates stabilized at 96 mA/h/g with a current density of 10 mA/g after 50 cycles. Finally, in-situ and
ex-situ XANES spectroscopy at the Fe K edge provided a direct evidence of the existence of an electrochemical active $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox. To our knowledge, this is the first systematic evidence of a clear capacity contribution due to $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couples. The successful tests performed with the carbonophosphates suggested also that when optimized, polyanion materials could become reliable high-performance and low-cost electrode materials for the next generation of SIBs.

**Methods**

**Computational method.** Density functional theory (DFT) calculation was performed using the plane-wave based Vienna ab initio simulation package (VASP)
Figure 7 | In-situ and ex-situ XANES spectroscopy characterization. (a) In-situ Fe K edge XANES spectroscopy for different charging potentials showing the shift of the edge that probes the Fe valence change. Comparison with the reference samples FeO and Fe$_2$O$_3$ data points out that the valence may reach a value higher than 3$^+$ in the charging process; (b) ex-situ Fe K edge XANES spectroscopy for samples exposed to air. No Fe$^{4+}$ contributions is detected looking at the energy shift.

Figure 8 | XRD characteristics. (a–b) Ex-situ XRD patterns analysis of Na$_3$FePO$_4$CO$_3$ nanoplates during (a) charge and (b) discharge procedures. No structural transformations take place at different potentials during the first cycle. The strong intensity of the diffraction peaks indicates that the cathode material maintains a good crystalline structure during the entire charging/discharging process.
with the generalized gradient approximation (GGA) and exchange correlation functional parameterized by Perdew-Burke-Ernzerhof (PBE). The U parameter for the transition metal Fe is 4.0 eV while the energy cutoff was set to 600 eV for all computations.

**Synthesis of the Na3FePO4CO3**

Na3FePO4CO3 nanoparticles were prepared by a modified hydrothermal method. 4 mmol FeSO4·7H2O and 50 mg citric acid were dissolved in 10 ml water and sodium hydroxide (1 M) solution (volume ratio: H2O/NaOH = 3:1) to form a clear solution A. After 4 mmol (NH4)2HPO4 and 4 g Na2CO3 were dissolved in 20 ml H2O/EG mixed solution (volume ratio: H2O/EG = 3:1) to form a clear solution B. After a vigorous stirring, the solution A was dropped wisely in the solution B and this mixture was kept stirring for half hour. After that, the mixture products were transferred inside a 40 ml stainless steel autoclave and heated at 180°C for 70 hours. The final products were washed five times by distilled water and dried at 80°C in a vacuum oven overnight.

**Material characterization.** XRD experiments were carried out using an X-ray diffractometer (Bruker D8 Advance) equipped with a Cu Ka radiation (λ = 1.5406 Å). For the Rietveld refinement analysis we scanned over a range of 8° from 120° at step of 0.02° for 8 s and data were analyzed using the TOPAS software. Ex-situ XRD data at different voltages during the charging and discharging procedure were collected in a conventional way. To get the desired electrodes, the coin cells, which were charged/discharged to the desired cutoff voltages, needs to be disassembled by an electric criming machine (MTI Co.). Finally, the disassembled electrodes were washed with dimethyl carbonate (DMC), and dried by a hair dryer. SEM images recorded by a JEOL 4800 SEM show the sample morphology. TEM images and SAED patterns were acquired with a JEM2100F HRTEM. The thermal stability of the samples was evaluated at a heating rate of 5°C/min from RT to 1000°C in air with a TG/DTA thermo-gravimetric analyzer. Fe K edge XANES spectra were recorded at the 1W2 beamline of the Beijing synchrotron radiation facility (BSRF) and at the 14W1 beamline of the Shanghai synchrotron radiation facility (SSRF). For in-situ XAS experiment, coin cells were disassembled in an Ar-filled glove box to take out at first the positive electrode material. To remove the influence of the electrolyte, we cleaned them by DMC solutions. After drying, the positive electrode materials were sealed by a 3 M sellotape in an atmosphere of Ar.

**Electrochemical characterization.** The NaFePO4CO3 nanoparticle samples were mixed with carbon (super P) and a Poly tetra fluoro ethylene (PTFE) binder to form a slurry at the weight ratio of 6:3:1. The mixture was rolled in a thin sheet of uniform thickness (about 40–60 μm). After it was cut in appropriate sections before drying them in a vacuum oven at 120°C for 12 h. The cells were then assembled in an Ar-filled glove box. Metallic Navas were used as anode for LIBs tests. A high potential electrolyte (purchased from the Beijing Institute of Chemical reagents) with 1 M NaClO4 was used as the electrolyte for LIBs. A separator (whatman) was used for LIB and the charging-discharging performance under different current density was characterized with a cutoff potential in the range 2.0–4.5 V. The cyclic voltammogram was achieved at the scan rate of 0.1 mV/s.

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Author contributions
D.X. and Z.W. designed the experiments. W.H., B.L., J.M. and S.T. performed experiments and data analysis. J.Z., W.H., W.C. and Z.W. performed the calculations. D.X. and Z.W. led the whole work and the analysis. W.H., D.X. and Z.W. wrote the text.

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