



# Preventing structural degradation from $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ to $\text{V}_2(\text{PO}_4)_3$ : F-doped $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode composite with stable lifetime for sodium ion batteries

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## HIGHLIGHTS

- F-doped  $\text{Na}_3\text{V}_2(\text{PO}_4)_3\text{-xF}_x/\text{C}$  samples are synthesized by solid-state reaction method.
- F-doping can restrain the structural degradation from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  to  $\text{V}_2(\text{PO}_4)_3$ .
- F-doping can decrease the particle size efficiently.
- Retention of F-0.07-NVP/C is 86% ( $97.8 \text{ mAh g}^{-1}$ ) after 1000 cycles at  $200 \text{ mA g}^{-1}$ .
- $D_{\text{Na}^+}$  of F-0.07-NVP/C is two orders of magnitude higher than NVP/C.

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## ABSTRACT

A prospective NASICON-type F-doped  $\text{Na}_3\text{V}_2(\text{PO}_4)_{2.93}\text{F}_{0.07}/\text{C}$  (F-0.07-NVP/C) composite is synthesized by a solid-state reaction method. F-doping can restrain the structural degradation from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  to  $\text{V}_2(\text{PO}_4)_3$  and enhance the structural stability. Meanwhile, it can decrease the particle size to diminish the pathway of  $\text{Na}^+$  diffusion, which can increase ionic conductivity efficiently. The kinetic behavior is significantly improved and it is beneficial to reinforcing the electrochemical performance of F-doping composites. Compared with Undoped-NVP/C sample, F-0.07-NVP/C composite delivers a  $113 \text{ mAh g}^{-1}$  discharge capacity at  $10 \text{ mA g}^{-1}$ , which is very close to the theoretical capacity ( $117 \text{ mAh g}^{-1}$ ). As for cycle performance, a reversible capacity of  $97.8 \text{ mAh g}^{-1}$  can be obtained and it retains 86% capacity after 1000 cycles at  $200 \text{ mA g}^{-1}$ . F-0.07-NVP/C composite presents the highest  $D_{\text{Na}^+}$  ( $2.62 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$ ), two orders of magnitude higher than the undoped sample ( $4.8 \times 10^{-17} \text{ cm}^2\text{s}^{-1}$ ). This outstanding electrochemical performance is ascribed to the synergetic effect from improved kinetic behavior and enhanced structural stability due to F-doping. Hence, the F-doped composite would be a promising cathode material in SIB for energy storage and conversion.

## 1. Introduction

Over the past few decades, there has been increased attention to the renewable energy devices based on electrochemical energy storage (EES) technology due to their high round-trip efficiency, and outstanding energy characteristics to meet the energy shortage challenge [1]. With the significant development of lithium-ion battery (LIB)

technologies, they have been playing important roles in various fields such as electric vehicles, portable computers and so on all over the world [2]. However, the inhomogeneous geographical distribution, extraordinarily limited storage content and rough recycling of lithium resources are obstacles for further large-scale production of LIB [3,4]. Therefore, it is of great significance to employ other energy storage systems as alternatives to LIB [5–7]. Recently, sodium ion batteries

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(SIBs) have become research hotspots as promoting energy systems to replace LIBs due to their abundant reserves and low cost [8–10]. However, there are still many challenges for the development of SIB because of the fundamental differences between sodium and lithium. The larger ionic radius of  $\text{Na}^+$  (0.98 Å vs.  $\text{Li}^+$  0.69 Å) will lead to slower ion diffusion and larger unit cell volume change upon  $\text{Na}^+$  deintercalation, which usually generates poor kinetic properties [11]. Accordingly, electrode materials with enough interstitial space for  $\text{Na}^+$  transportation are highly recommended [12].

Recently, sodium super ionic conductors (NASICON) cathode materials have been investigated for SIB due to their unique crystal structure [13–15]. NASICON-type sodium vanadium phosphate ( $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ) is one of the most prospective cathode materials for SIB. It has been proved that  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  can exhibit two voltage platforms at 1.6 V and 3.4 V vs.  $\text{Na}^+/\text{Na}$ , related to  $\text{V}^{3+}/\text{V}^{2+}$  and  $\text{V}^{4+}/\text{V}^{3+}$  redox couples with theoretical specific capacities of 58.8 and 117.6 mAh  $\text{g}^{-1}$  [16–18]. The framework composed of corner-sharing octahedral  $\text{VO}_6$  and tetrahedral  $\text{PO}_4$  generates excellent structure and thermal stability [19–21]. However, poor electrical conductivity and Na-ion diffusion mobility impede the improvement of electrochemical performance. Moreover, the moving disadvantage of large-size  $\text{Na}^+$  cannot be neglected when the intercalation/deintercalation of  $\text{Na}^+$  proceeds through the structure. Many studies have found that the significant volume change because of the accommodation of  $\text{Na}^+$  usually leads to structural degradation of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and subsequent capacity loss, resulting in poor rate and cyclic performance [14,22–24]. To cover the shortages, nano-crystallization [25–29], conductive layers-coating [30–34] and dopants introduction [35–40] can promote the kinetic performance in both LIB and SIB tremendously. Anion-doping is a feasible method to enhance the kinetics and cyclic stability, which is widely used in LIB [41–43]. However, the effects of anion substituting on the structure stability and electrochemical performance of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  composite have been rarely explored.

Fluorine doping is a significant approach to improve the electrochemical performance in various cathode materials in LIB field. In this work, we demonstrate that F-doped  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x/\text{C}$  composites can be promising cathode materials due to the advantages of favourable effects on electrochemical properties related to LIB. Compared to undoped  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample, the F-doped  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x/\text{C}$  composites show outstanding rate and cyclic performance, which results from superior structure stability and enhanced electrochemical properties. Moreover, the discovery of structural variation during intercalation/deintercalation for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cathode material has been thoroughly investigated for the first time.

## 2. Experimental

### 2.1. Material preparation

We adopted a convenient carbon-thermal reduction method to synthesize the  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x/\text{C}$  samples, where  $x = 0, 0.01, 0.04$  and  $0.07$ . Analytical purity  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NaF}$  and  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$  were used as starting materials. 5 wt% excess  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$  was added to ensure that the reducer was enough for the  $\text{V}^{3+}/\text{V}^{5+}$  reaction in order to keep the stoichiometric ratio. These materials were mixed together and ball-milled in pure ethanol in stoichiometric proportion for 12 h. Then the mixed slurry were dried off at 80°C for 12 h, followed by preheated treatment at 450°C for 4 h in an argon furnace. Subsequently, the mixture was heated at 700°C for 6 h in argon atmosphere. The prepared pristine and doped samples containing 1%, 4%, and 7% fluorine are abbreviated as Undoped-NVP/C, F-0.01- NVP/C, F-0.04- NVP/C and F-0.07- NVP/C.

### 2.2. Characterization

X-ray diffraction (XRD) measurements by X'pert Pro (PANalytical)

were employed to examine the crystal structure of samples. The particle morphology was observed by a Scanning Electron Microscopy (SEM, FEI Quanta FEG 250) and a Transmission Electron Microscopy (TEM, JEM 2100). Fourier transform infrared (FT-IR) absorption spectra were analyzed by an FTIR-spectrometer (Nicolet iS10, Thermo Scientific) at room temperature. The particle sizes were measured by a zeta size analyzer (Nano-ZS90, Malvern). Thermogravimetric Analysis (TGA, Mettler-Toledo) were employed to analyze the weight percentages of carbon in every sample, respectively.

### 2.3. Cell fabrication and electrochemical measurements

Electrochemical measurements of the prepared composites were conducted in 2016-type coin half-cells. The working electrodes including 70 wt% active material, 20 wt% acetylene black and 10 wt% binder (PVDF) were dissolved in N-Methyl-2-Pyrrolidone (NMP) solvent and then mixed uniformly in a ball mill. A clean aluminum foil was acted as a substrate and the final electrodes were vacuum dried at 120°C for 12 h. Sodium metal was used as the anode and the separator was Celgard 2400 membrane. 1 M  $\text{NaClO}_4$  in propylene carbonate (PC) with 2 vol% fluoroethylene carbonate (FEC) was applied as electrolyte. The loading mass of active species during the electrochemical evaluation is typically about 1.5–2.0 mg  $\text{cm}^{-2}$ , and the electrode footprint area is 2.01  $\text{cm}^{-1}$ . The electrochemical performance of cells were tested on a LAND CT2001A battery test system (Wuhan, China) in the voltage ranges of 2.3–4.2 V vs.  $\text{Na}/\text{Na}^+$  at room temperature. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were conducted by using a Versatile Multichannel Galvanostat 2/Z (VMP2, Princeton Applied Research). The amplitude is 5 mV and the frequency ranges between  $10^{-2}$  and  $10^5$  Hz for the EIS. The scan rate was 0.1  $\text{mV s}^{-1}$  and the voltage ranged between 2.3 V and 4.2 V for the CV. The electronic conductivity measurements were performed on a RTS-9 linear four-point probe system.

## 3. Results and discussion

In order to investigate the influence of F-doping on the crystal structure, XRD measurements were employed and the results are displayed in Fig. 2a. All the XRD patterns of  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x/\text{C}$  ( $x = 0, 0.01, 0.04$  and  $0.07$ ) samples can be indexed to R-3c space group and are in good agreement with the framework of a rhombohedral NASICON structure. The sharp peaks correspond to the high crystallinity for all samples. It is noteworthy that  $\text{NaVP}_2\text{O}_7$  is detected as impurity phase in all samples but  $\text{NaVO}_2$  is existed only in F-doping samples. The result of  $\text{NaVP}_2\text{O}_7$  is consistent with the research by Si et al. [33]. Moreover, the existence of  $\text{NaVO}_2$  in the F-doping samples is facilitated to the intercalation/deintercalation of  $\text{Na}^+$  because it has the layer structure for rapid migration of  $\text{Na}^+$  [44,45]. Our work indicates that the lattice parameters of samples decrease gradually with the content of F-doping, consistent with Zhong et al. [43]. The enlarged part indicates that the position of peak (024) shifts slightly to the larger angle gradually with the increase of F-doping content, which suggests that the F-doping samples have less lattice parameter and interplanar spacing. Table 1 shows the unit cell parameters calculated from the indexed patterns. With the increasing content of F-doping, the volume of  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x$  samples declines slightly, which indicates that F-

**Table 1**  
Unit cell parameters in the R-3c space group for  $\text{Na}_3\text{V}_2(\text{PO}_4)_{3-x}\text{F}_x$  samples.

Sample	a = b/Å	c/Å	Volume/Å <sup>3</sup>
Undoped-NVP/C	8.737 (7)	21.82 (3)	1442.72
F0.01-NVP/C	8.727 (6)	21.85 (3)	1441.23
F0.04-NVP/C	8.721 (9)	21.86 (4)	1440.27
F0.07-NVP/C	8.717 (8)	21.88 (4)	1439.38

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