Effect of Ti-doping on the electrochemical performance of sodium vanadium(III) phosphate

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Na3V2–,xTi,x(PO4)3 (x = 0.00, 0.05, 0.10, and 0.15) was successfully synthesized by a conventional solid-state route. The XRD results show that Ti is incorporated in the lattice of Na3V2(PO4)3 and the tetragonal structure has not been changed after doping. Among all the composites, the Na3V1.9Ti0.1(PO4)3 composite delivers the highest discharge capacity of 114.87 mA h g−1 at 0.1C and possesses a capacity retention of 96.23% after 20 cycles at 0.1C, demonstrating the better rate performance and cycle stability in the potential range of 2.0–3.8 V. Electrochemical impedance spectroscopy (EIS) results reveal that the Na3V1.9Ti0.1(PO4)3 composite has a lower charge transfer resistance and a higher Na-ion diffusion coefficient compared to other composites. The results indicate that Ti-doping in Na3V2(PO4)3 can effectively enhance the electrochemical performance of this tetragonal compound, especially at a high charge/discharge rate.

1 Introduction

Since the combustion of fossil fuels results in air pollution and increases the greenhouse effect, much attention has been focused on the exploitation of new energy sources. Development of new alternative energy storage systems with low cost, high safety and environmentally friendly electrode materials are critical to meet our rising energy demands and, in particular, to facilitate the adoption of renewable energy generation. Large-scale electric energy storage is a key enabler for the use of renewable energy.1 Lithium ion batteries with high energy and power densities have been considered as the best power sources for portable equipment today.2–4 LiFePO4, FePO4, LiMnP04, LiFeP04, LiNiP04, Li1/2V2(PO4)3, and LiCoO2 have been researched as cathode materials for Li-ion batteries.5–10 However, there is serious concern about the availability of lithium owing to the amount of lithium reserves in the earth, especially for large-scale applications.17–18 On this occasion, the eco-friendly sodium-ion batteries have become the focus in the field of energy and environment due to the abundance of sodium.17–19

In recent years, many electrode materials such as Na2CoO2,22 Na4.45MnO2,23 Na2V6O15,24 Na1–xNi1.5Mn0.5O2,25 NaNi1.5Mn1/3–x/3Co1/3O2,26 NaFePO4,27 NaFeSO4F,28 NaV1–xCr2xP04F,29 Na2FePO4F,30 Na3V2(PO4)3F31 Na2Ti3O7,32,33 and Na2CrH4O4 (ref. 34) have been extensively investigated for sodium ion batteries. Recently, NASICON (for Na+ superionic conductor)-type electrode materials that can generate large interstitial spaces, through which sodium ions can diffuse, have aroused much interest of many researchers.35–38

Na3V2(PO4)3 (NVP), which is a polyanionic material, has been greatly exploited37 for its several advantages: (1) good ionic mobility, (2) high theoretical specific capacity (117.6 mA h g−1), (3) two very flat and stable redox electric potentials (3.4 and 1.6 V vs. Na/Na+) based on the V3+/V5+ and V3+/V4+ redox couples, respectively. However, the stability of the structure of NVP also needs to be improved. It has been reported that transition metal doping is a useful way to improve the electrochemical performance of Li3V2(PO4)3.38 Several cations, such as Fe3+39 Cr3+,40 Mg2+,41 Co2+,41 and Ti4+41 can be doped at the V site in the LVP, resulting in improved utilization of materials, high rate capabilities, electric conductivity, and cyclic stability. In the present work, we investigate aliovalent substitution of VIII with TiIV in NVP. So far, no studies have been done to dope titanium in NVP. We examine the effect of low levels of Ti doping on the electrochemical performance of NVP. The addition of titanium did not influence the structure of NVP, but the particle size was reduced and the electrical conductivity was improved, resulting in high rate capability.

2 Experiment

2.1 Synthesis

The Na3V2–,xTi,x(PO4)3 (x = 0.00, 0.05, 0.10, 0.15) composites were synthesized by a conventional solid-state route. NaH2PO4·2H2O and V2O5 were used as the starting materials and ethanediolic acid was used as the reductant. In a typical synthesis process, V2O5, NaH2PO4·2H2O, nano-size TiO2, and H2C2O4 (in the appropriate amount) were mixed and ball-milled with alcohol media in a container of a planetary ball-mill at
300 rpm for 5 h. After ball-milling, the obtained mixture was dried at 75 °C, then calcinated at 400 °C for 4 h and heated up to 750 °C and held there for 10 h in an atmosphere-controlled furnace under argon. The heating rate was 5 °C min⁻¹. The Na₃V₄₋ₓTiₓ(PO₄)₃ (x = 0.00, 0.05, 0.10, 0.15) composites was obtained.

2.2 Material characterization
Thermogravimetric (TG/DSC) analysis of the mixture was measured on a SDT Q600 TG-DTA apparatus at temperature between 25 and 900 °C at a heating rate of 5 °C min⁻¹ under argon flow. The powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) measurement using Cu Kα radiation was employed to identify the crystalline phases of the synthesized composites. XRD Rietveld refinement was analyzed by software (MAUD). The morphologies and chemical compositions of the composites were observed by scanning electron microscopy (SEM, JEOL, JSM-5600LV, Japan) and a energy dispersive X-ray (EDX) detector.

2.3 Electrochemical performance tests
The cathodes used for the electrochemical tests consisted of 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF), which was used as the binder. N-Methyl-2-pyrrolidone (NMP) was used as a solvent and an aluminum foil as a current collector (~2.0 mg cm⁻²). It was dried in a vacuum oven at 120 °C for 4 h. Electrodes of the desired size were then punched out from the dried slurry. Electrochemical cells were assembled in a glove box filled with high-purity argon; pure sodium foil was used as the counter electrode. The electrolyte solution was 1 M NaClO₄ (EC:DEC) (1% VC) soaked in glass fiber separators (GF/D-Whatman). The test cells were galvanostatically cycled between 2.0 and 3.5 V. Na⁺/Na at various C-rates based on the theoretical capacity of 118 mA h g⁻¹. The cyclic voltammetry (CV) profiles were recorded with a LK2005A electrochemical workstation (Lanlike Co., China). Electrochemistry impedance spectroscopy (EIS) was measured with an electrochemical workstation (CHI 660D) by applying an AC voltage of 5 mV in the frequency range from 100 kHz to 0.04 Hz.

Fig. 1 The TGA curve of Na₃V₁.₉Ti₀.₁(PO₄)₃.

Fig. 2 (a) XRD patterns of Na₃V₄₋ₓTiₓ(PO₄)₃ (x = 0.00, 0.05, 0.10, 0.15) with various doping amount, (b) the XPS spectra of Ti 2p (Na₃V₁.₉-Ti₀.₁(PO₄)₃), (c) the XPS spectra of V 2p (Na₃V₂(PO₄)₃ and Na₃V₁.₉Ti₀.₁(PO₄)₃).
3 Results and discussion

Fig. 1 shows the TGA curve of Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$. The TGA test was taken in the oxygen. It was observed that the carbon content in the Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ was 5.35%.

XRD patterns of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00$, $0.05$, $0.10$, $0.15$) with various amounts of Ti doping are shown in Fig. 2a. All the peaks are indexed to a single phase of tetragonal crystal type.

### Table 1

|                | a (Å)  | c (Å)  | Vol. (Å$^3$) | $R_w$ (%) |
|----------------|--------|--------|--------------|-----------|
| Na$_3$V$_2$(PO$_4$)$_3$ | 8.72436 | 21.80602 | 1659.8       | 9.9       |
| Na$_3$V$_{1.95}$Ti$_{0.05}$(PO$_4$)$_3$ | 8.72275 | 21.80401 | 1659.0       | 11.7      |
| Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ | 8.71929 | 21.80088 | 1657.4       | 10.2      |
| Na$_3$V$_{1.85}$Ti$_{0.15}$(PO$_4$)$_3$ | 8.72137 | 21.80135 | 1658.3       | 11.4      |

Fig. 3 Refinement XRD profiles for Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$: (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$.

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Fig. 4 SEM images of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$: (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$. 
Na$_3$V$_2$(PO$_4$)$_3$, which is consistent with the references. It is clear that no impurity peaks such as Ti-doped composites are detected, indicating that the as-prepared composites are pure phase and the structure is unchanged after Ti doping. These sharp peaks in the patterns suggest good crystallinity of the powders.

The XPS spectra of Ti 2p (Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$) was shown in Fig. 2b. The binding energy of Ti in the picture to be 459.7 eV, matched well with some previous work, which indicates the valence of Ti in Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ is +4. The XPS spectra of V 2p (Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$) was shown in Fig. 2c. It is obviously that the binding energy of V in Ti-doping sample (Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$) is 516.79 eV and the binding energy of V in Na$_3$V$_2$(PO$_4$)$_3$ is 516.89 eV, which means that the doping of titanium reduces the valence of V. The result means that Ti is doped in the V site.

Fig. 3 show the refined XRD data for Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$). The calculated pattern matched well with the PDF standard card. The refined lattice parameters and atomic coordination are listed in Table 1. The $R_w$ of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) were 9.9%, 11.7%, 10.2% and 11.4%, respectively. The decrease of cell volume can be attributed to the insertion of Ti, which is consistent with the previous result. As can be seen in Table 1 that the Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ had the smallest volumes. This indicates that the Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ composites had smallest particle size.

Fig. 5 EDX images of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$. (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.15$. 

Na$_3$V$_2$(PO$_4$)$_3$, which is consistent with the references. It is clear that no impurity peaks such as Ti-doped composites are detected, indicating that the as-prepared composites are pure phase and the structure is unchanged after Ti doping. These sharp peaks in the patterns suggest good crystallinity of the powders.
The rise of Ti concentrations, indicating that the Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ component elements in the composites. It can be seen in Fig. 5 that the primary particles are in nanoscale and agglomerated to form secondary particles, showing similar irregular granular shapes. The results indicate a more homogeneous distribution of Ti-doping composites than the pristine one.

Fig. 5 shows the SEM images of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) composites. EDX was used to investigate the existed element Ti is existed in Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$, showing similar irregular granular shapes. The results indicate that the Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ composite is successfully synthesized.

Fig. 6 shows the initial charge–discharge voltage profiles of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) at a current rate of 0.1C in the potential range of 2.0–3.8 V. The curves indicate that two Na ions were extracted from/inserted into Na$_3$V$_x$(PO$_4$)$_3$ per formula unit during the charging/discharging processes, which lasted for 10 h. It can be seen from Fig. 6 that the charge curves for all cathodes exhibited a plateau at approximately 3.4 V and so did the corresponding discharge curves; these were attributed to the two-phase transitions occurring during the electrochemical reaction, which was agreed well with the CV curves as showed in Fig. 7. The initial discharge capacity of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ composites ($x = 0.00, x = 0.05, x = 0.10, x = 0.15$) are 102.58 mA h g$^{-1}$, 107.63 mA h g$^{-1}$, 114.87 mA h g$^{-1}$ and 111.95 mA h g$^{-1}$, respectively. The coulombic efficiency of the initial cycle is about 94.9%, 96.7%, 98.9% and 97.8%, respectively. As can be seen from Fig. 6 that the capacities of Ti-doped Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) are higher than pristine Na$_3$V$_x$(PO$_4$)$_3$. In addition, the voltage difference of Ti-doped Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ is smaller than that of pristine Na$_3$V$_x$(PO$_4$)$_3$, resulting from the lower electrode polarization. It is clearly seen from Table 3 that Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ exhibits the lowest polarization potential of 0.03 V with the best electrochemical performance and the highest initial discharge capacity, indicating that Ti-doping does not block the tunnels of Na ions and probably increases the charge and discharge capacities and charge–discharge efficiency.

CV measurement was carried out at a scan rate of 0.1 mV s$^{-1}$ to provide more information about the electrochemical properties, the second voltammograms (CV) of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) samples in the voltage range of 2.0–3.8 V are presented in Fig. 7. It can be observed that the CV curves are very similar. There are one oxidation peak and one reduction peak, corresponding to the relative Na$^+$ ion extraction and reinsertion. However, the Na$^+$ ion extraction and insertion processes for Ti doped samples are more stable, which is ascribed to relatively sharper peaks. Moreover, the Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ sample present the smallest potential differences between anodic and cathodic peaks, which is consistent with the result in charge–discharge voltage profiles, indicating the good reversibility of the Na$^+$ extraction/re-insertion and lower ohmic resistance in the electrode.

As shown in Fig. 8, five current densities, i.e. 0.1C, 0.5C, 1C, 2C and 5C, are employed to evaluate the rate capability of Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) (charging current density is 0.1C). It can be observed that the profiles reveal a large plateau at 3.4 V for discharge and the rate performance of the composites is highly affected by the Ti-doped content. Increasing Ti-doping amount first led to the enhancement of rate capability. It can be seen in Fig. 8 that Ti-doping samples show better rate performance than pristine Na$_3$V$_2$(PO$_4$)$_3$. Moreover, Na$_3$V$_{1.5}$Ti$_{0.1}$(PO$_4$)$_3$ shows the best rate performance, delivering a capacity of 114.87 mA h g$^{-1}$, 113.75 mA h g$^{-1}$,
111.07 mA h g\(^{-1}\), 106.67 mA h g\(^{-1}\), and 98.63 mA h g\(^{-1}\). Moreover, the discharge voltage plateau of Na\(_3\)V\(_{1.9}\)Ti\(_{0.1}\)(PO\(_4\))\(_3\) is still higher than 3.3 V at 5C rate, indicating that Na\(_3\)V\(_{1.9}\)Ti\(_{0.1}\)(PO\(_4\))\(_3\) has a lower polarization. The results prove that Ti-doping can enhance the electrochemical performance.

All the Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.00, 0.05, 0.10, 0.15\)) samples were cycled at five current densities (0.1, 0.5, 1, 2, and 5C) between 2.0 and 3.8 V, and the results are shown in Fig. 9a. Each current density was tested for 5 cycles. It can be observed that the Ti-doping samples show a better rate performance than pristine Na\(_3\)V\(_2\)(PO\(_4\))\(_3\). Even so, a further increase of the titanium content was not as advantageous as for the former samples. Moreover, the rate performance of Na\(_3\)V\(_{1.9}\)Ti\(_{0.1}\)(PO\(_4\))\(_3\) demonstrates the best among all samples, and it keeps a 97.02% at all rates, higher than that of the others. The sample with suitable Ti-doping content (\(x = 0.10\)) shows the best rate performance compared with other samples. The results proved that Ti-doping can improve the rate performance of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\).

Fig. 9b shows the cycling performance of Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.00, 0.05, 0.10, 0.15\)) electrodes at 0.5C. As can be seen from Fig. 9b that the Ti-doping samples, expect Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.05\)), show a better cycling performance than pristine Na\(_3\)V\(_2\)(PO\(_4\))\(_3\). The discharge capacity of Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) composites (\(x = 0.00, x = 0.05, x = 0.10, x = 0.15\)) are 101.83 mA h g\(^{-1}\), 106.02 mA h g\(^{-1}\), 113.75 mA h g\(^{-1}\) and 110.59 mA h g\(^{-1}\), respectively, and 94.59%, 93.44%, 96.70% and 95.25% remained after 100 cycles in the range of 2.0–3.8 V at 0.5C. The results indicate that suitable Ti-doping content (\(x = 0.10, x = 0.15\)) can enhance the cycling performance of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\).

Fig. 8 The discharge curves of Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.00, 0.05, 0.10, 0.15\)) at various rates. (a) \(x = 0.00\), (b) \(x = 0.05\), (c) \(x = 0.10\), (d) \(x = 0.15\).

Fig. 9 (a) Discharge capacities of Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.00, 0.05, 0.10, 0.15\)) samples at current densities of 0.1C, 0.5C, 1C, 2C and 5C in the voltage range of 2.0–3.8 V. (b) cycling performance of Na\(_3\)V\(_{2-x}\) Ti\(_x\)(PO\(_4\))\(_3\) (\(x = 0.00, 0.05, 0.10, 0.15\)) electrodes at 0.5C.
samples with Ti-doping can increase the charge transfer speed of the Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ results in its best electrochemical performance among all the samples. The results indicate that the electrochemical property of Na$_3$V$_2$(PO$_4$)$_3$ composites can be improved by an appropriate amount of Ti ion doping.

### 4 Conclusion

The Na$_3$V$_{2-x}$Ti$_x$(PO$_4$)$_3$ ($x = 0.00, 0.05, 0.10, 0.15$) was successfully synthesized by a conventional solid state route. Based on the XRD refinement results, Ti has incorporated into the lattice of Na$_3$V$_2$(PO$_4$)$_3$. The amount of Ti doping has an important impact on electrochemical performance. In the electrochemical test, Na$_3$V$_{1.9}$Ti$_{0.1}$(PO$_4$)$_3$ exhibits the best specific capacity of 114.87 mAh g$^{-1}$ at 0.1C in the potential range of 2.0–3.8 V and possessing the capacity retention of 96.70% after 100 cycles at 0.5C. The Ti-added Na$_3$V$_2$(PO$_4$)$_3$ composites also show higher rate capability and cycle performance compared with the pristine Na$_3$V$_2$(PO$_4$)$_3$. The results of CV and EIS revealed that the doping titanium at an appropriate amount could increase the diffusion coefficient of sodium ions and result in the improvement of the reversibility of the materials. The results indicate that the Ti doping is an effective approach to achieve excellent electrochemical performance for the sodium ion pyrophosphate.

### Conflicts of interest

There are no conflicts to declare.

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