

## $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ 和 $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ 的结构和电化学性能的比较研究

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**摘要:** 采用溶胶-凝胶法合成了锂离子正极材料  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  (LVP/C) 及  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ , 并用 XRD、循环伏安及交流阻抗等方法, 研究了大量 Na<sup>+</sup> 掺杂对材料结构和电化学性能影响。结果表明, 大量钠离子的掺杂会使 LVP 结构由单斜向菱方转变。掺杂化合物  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  在 0.5 C 充电 1 C 放电时, 首次放电容量为  $118 \text{ mAh} \cdot \text{g}^{-1}$ , 50 次循环后容量保持率为 92.4%, 并发现与单斜 LVP 存在多个放电平台不同,  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  仅在 3.7 V 处有一个放电平台。

**关键词:** 锂离子电池; 正极材料; 磷酸钒锂; 溶胶凝胶法; 钠掺杂; 晶体结构

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## A Comparative Structural and Electrochemical Study of Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and Rhombohedral $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$

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**Abstract:** A lithium-ion battery cathode material,  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ , was prepared by the sol-gel method and characterized by X-ray diffraction (XRD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). As a control,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  (LVP/C) was also prepared and studied. The effect of sodium-ion doping on the structure and electrochemical properties was studied. The XRD pattern of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  indicates that the monoclinic structure of  $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$  has transformed into a rhombohedral structure because of large amount of sodium-ion doping. For  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ , a specific discharge capacity of  $118 \text{ mAh} \cdot \text{g}^{-1}$  is achieved at a 0.5 C charge rate and 1 C discharge rate, and a 92.4% retention rate of the initial capacity is obtained after 50 cycles. Different from monoclinic LVP, there is only one discharge plateau at 3.7 V in the charge/discharge voltage profile of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ .

**Key words:** lithium-ion battery; cathode material; lithium vanadium phosphate; sol-gel preparation; Na-doping; crystal structure

With the development of hybrid electric vehicles (HEVs) and electric vehicles (EVs), high energy density Li-ion batteries will be in great demand, thus leading to the investigation in high energy density materials<sup>[1]</sup>. Lithium conducting phosphate materials such as  $\text{LiFePO}_4$  and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  have shown remar-

kable electrochemical and thermal stability and a wide working temperature range<sup>[2-3]</sup>, therefore they are considered as highly promising cathode materials for high power Li-ion batteries.

Compared with  $\text{LiFePO}_4$  (LFP),  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (LVP) has better safety performance, a larger ionic diffusion

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coefficient and a higher energy density<sup>[3-5]</sup>. Therefore, LVP is considered as a better cathode material than LFP<sup>[6-7]</sup>. However, LVP has low electrode conductivity and poor rate performance as a result of its low electronic conductivity<sup>[8-10]</sup>, which restricts its practical application as a cathode material for Li-ion batteries. To solve this problem, many studies have been carried out through coating with carbon<sup>[8-12]</sup> and doping with other metals (*i.e.* Nb, Fe, Al, Mg, K, Sc, Zr, Cr, *etc.*)<sup>[13-19]</sup>. However, studies on another disadvantage of LVP, the non-flat voltage characteristics (3 plateaus at 3.5~3.6, 3.6~3.7 and 4.0~4.1 V corresponding to the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple<sup>[20]</sup>), have been scarcely carried out. Based on the study of Mineo Sato et al.<sup>[18]</sup>, the disappearance of the two-plateau boundary in the charge/discharge curves come from the stabilized orthorhombic phase of LVP at room temperature by substituting Zr for V sites with the molar fraction beyond 0.05. Therefore, one hypothetical way to smooth charge/discharge curves may be proposed: to stabilize the rhombohedral or the orthorhombic phase.

In this paper, LVP doped with a large amount of Na was prepared by the sol-gel method. The effects of Na-doping on the structure and electrochemical properties were investigated as well.

## 1 Experimental

### 1.1 Synthesis and characterization of samples

A  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  sample was prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$  (AR), NaOH (AR),  $\text{NH}_4\text{VO}_3$  (AR),  $\text{NH}_4\text{H}_2\text{PO}_3$  (AR) and citric acid (AR) at a molar ratio of 2.5:0.5:2:3:6. The added citric acid acted as a carbon source that not only can reduce  $\text{V}^{5+}$  to  $\text{V}^{3+}$  but also can form a continuous network structure of carbon for electronic conduction. These raw materials were dissolved in 100 mL distilled water, and then the mixture was heated under continuous stirring at 80 °C until the precursor was obtained. The obtained gel was dried in a vacuum oven at 110 °C, and then the obtained powder sample was ground, pelletized and heated at 350 °C in a furnace under flowing argon gas for 4 h to decompose the organic constituents. The sample was then crushed, subsequently heated at 600 °C and kept for 12 h under

a stream of argon gas. The sample was taken out after it was cooled down to room temperature, and then ground in an agate mortar for later use. As a control, an undoped  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample was also prepared through the same procedure except the addition of NaOH (AR).

The crystal morphology of the samples was confirmed by XRD using a D/max-rB X-ray diffractometer (Rigaku, Japan) with Cu  $K\alpha$  radiation ( $\lambda=0.154\ 178\ \text{nm}$ ), a voltage of 45 kV, a current of 50 mA, a scan rate of  $4^\circ\cdot\text{min}^{-1}$  and  $2\theta$  from  $10^\circ$  to  $90^\circ$ .

### 1.2 Assembly of cells and electrochemical measurements

The cathode slurry was prepared by mixing one of the synthesized powders with acetylene black and polyvinylidene fluoride (PVDF) at a mass ratio of 80:10:10 in *n*-methyl-2 pyrrolidone (NMP). Then the cathode slurry was coated on aluminum foil with a thickness of 20  $\mu\text{m}$ . The cathode electrodes were roll-pressed at a pressure of 5 MPa after being dried at 110 °C under vacuum for 12 h. It was then cut into a wafer (15 mm in diameter). A typical cathode electrode was 8.5~9.5 mg in weight and 0.1 mm thick. The anode was lithium metal foil of about 0.30 mm thick. Celgard 2400 with a thickness of about 0.02 mm was used as a separator.  $\text{LiPF}_6$  of  $1\ \text{mol}\cdot\text{L}^{-1}$  in a mixture of EC, DMC and DEC (a volume ratio of 1:1:1) was used as the electrolyte. CR2025-type coin cells were assembled in a glove box filled with high-purity argon.

The coin cells were galvanostatically charged at 0.5 C and discharged at 1 C over a voltage range of 3.0~4.3 V using a multichannel battery test system. The cyclic voltammetry (CV) test was carried out on a CHI-750d electrochemical work station with a voltage between 3.0 and 4.3 V. CHI-750d were also used in the electrochemical impedance spectroscopy (EIS) test with a frequency range from 0.1 to 10 kHz. All experiments were carried out at a temperature of  $(25\pm0.5)^\circ\text{C}$ .

## 2 Results and discussion

### 2.1 Sample characterization

XRD analyses were conducted to examine the

crystal structure changes during the process of sodium-ion doping to prepare  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$ . As shown in Fig. 1, LVP has an orderly monoclinic structure with space group  $P2_1/n$ <sup>[6]</sup>, whereas,  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$  has a rhombohedral structure with space group  $R\bar{3}$ <sup>[21]</sup>, and the change in structure was a result of large-dose doping of  $\text{Na}^+$ . However, diffraction peaks related to monoclinic LVP are detected (as masked in Fig.1) in the XRD pattern for  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$ , indicating that the synthesized powders are composed of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$  and LVP phases. Based on the XRD patterns, there is no evidence of diffraction peaks from carbon, which indicates that the residual carbon has an amorphous structure and/or the residual carbon layer on the LVP/C particles is too thin to be detected by powder XRD<sup>[22]</sup>.

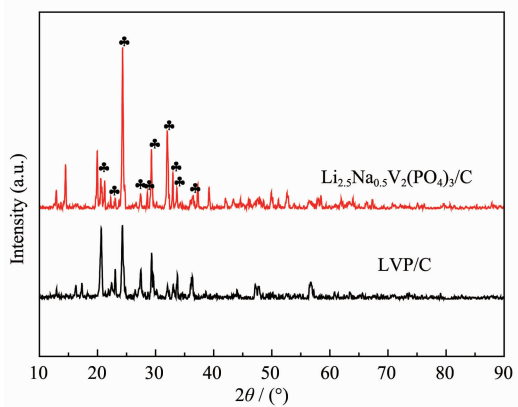


Fig.1 XRD patterns of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and LVP/C

## 2.2 Electrochemical properties of samples

A charge/discharge test was carried out to characterize electrochemical performance of the LVP/C and  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  systems at a 0.5 C charge rate and a 1C discharge rate (here, the 1C rate corresponds to a current rate of  $133 \text{ mA} \cdot \text{g}^{-1}$ ), and the result is shown in Fig.2 (a). During the discharge process of LVP/C, three plateaus can be observed at 4.08, 3.63, and 3.55 V, which correspond to a sequence of transitions between the single phase of  $\text{Li}_x\text{V}_2(\text{PO}_4)_3$  ( $x=1.0, 2.0, 2.5, 3.0$ ). The removal of Li-ions from the stable tetrahedral sites causes a single-step (4.10 V), this step corresponds to the phase transition from  $\text{Li}_{1.0}\text{V}_2(\text{PO}_4)_3$  to  $\text{Li}_{2.0}\text{V}_2(\text{PO}_4)_3$ . Then the existence of an ordered phase  $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$  at a mixed  $\text{V}^{3+}/\text{V}^{4+}$  state results in two steps (3.60 and 3.65 V), which are associated with the changing process from

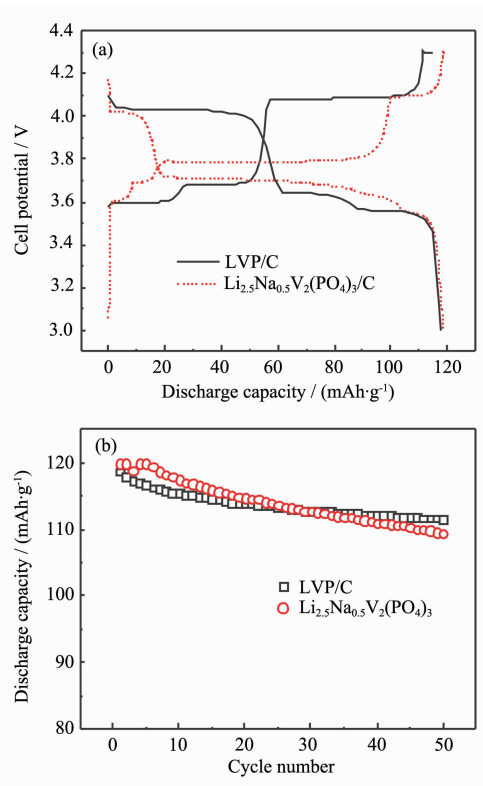


Fig.2 (a) Initial charge/discharge curves and (b) cycle performance of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and LVP/C at a 0.5C charge rate and a 1C discharge rate

$\text{Li}_{2.0}\text{V}_2(\text{PO}_4)_3$  to  $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$  and  $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$  to  $\text{Li}_{3.0}\text{V}_2(\text{PO}_4)_3$ , respectively<sup>[19]</sup>. By comparison, during the discharge process of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ , only two plateaus can be noted, which could be accounted by the disappearance of the multiphase transition accompanied with a too large amount of  $\text{Na}^+$  doping. Based on the XRD analysis and the discharge profile of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ , the first step with an average voltage at around 4.0 V can be ascribed to the insertion of  $\text{Li}^+$  in the  $\text{Li}_x\text{V}_2(\text{PO}_4)_3$  system, corresponding to the process from  $\text{Li}_{1.0}\text{V}_2(\text{PO}_4)_3$  to  $\text{Li}_{2.0}\text{V}_2(\text{PO}_4)_3$ , the second step with an average voltage at around 3.7 V is the discharge results of transformation of  $\text{Li}_x\text{V}_2(\text{PO}_4)_3$  and  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$ , where  $x=2, 2.5$ , and 3. In addition, the subsequent discharge curves of  $\text{Na}^+$ -doped LVP display a clear discharge plateau at 3.7 V. This value is comparable to 3.8 V for the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple found for  $\text{Li}_{3-x}\text{FeV}(\text{PO}_4)_3$  under the same condition<sup>[21]</sup>, which means that the replacement of  $\text{Li}^+$  by  $\text{Na}^+$  in the lattice has little influence on the energy of the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple.

The results of charge/discharge cycles in a range of 3.0~4.3 V at room temperature are shown in Fig.2(b) for both LVP/C and  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ . As seen in the Fig. 3, in the LVP/C system, the discharge capacities for 1<sup>st</sup> and 50<sup>th</sup> cycle are  $118 \text{ mAh} \cdot \text{g}^{-1}$  and  $111 \text{ mAh} \cdot \text{g}^{-1}$ , respectively, so the discharge capacity retention rate is 94.1%; in the  $\text{Na}^+$  doping LVP/C system, the discharge capacities for 1<sup>st</sup> and 50<sup>th</sup> cycle are  $118 \text{ mAh} \cdot \text{g}^{-1}$  and  $109 \text{ mAh} \cdot \text{g}^{-1}$ , respectively, so the discharge capacity retention rate is 92.4%. The decrease in the capacity retention rate could be accounted for by a too large amount of Na-doping, which has induced the structure changes and may cause the phase instability.

The CV curves were recorded for the  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and LVP/C systems in a potential range 3.0~4.3 V at a slow scan rate of  $0.1 \text{ mV} \cdot \text{s}^{-1}$  and the obtained cyclic voltammograms are shown in Fig.3. Three reduction peaks can be observed in the cyclic voltammograms for LVP/C, whereas only two reduction peaks can be observed in the cyclic voltammograms for  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ . The results are in good agreement with the charge/discharge curves shown in Fig.2(a). The multiple reduction peaks become one peak accompanied with the monoclinic structure changing to a rhombohedral structure, which results in transformation of a multi-phase reaction mechanism to a single-phase reaction mechanism during the charge/discharge process. In theory, the phase transition process may lead to the formation of new interfaces and hinder the diffusion of lithium ions (the more complicated phase transition process, the more difficult diffusion of lithium ions)<sup>[13]</sup>. Therefore, the lithium ion

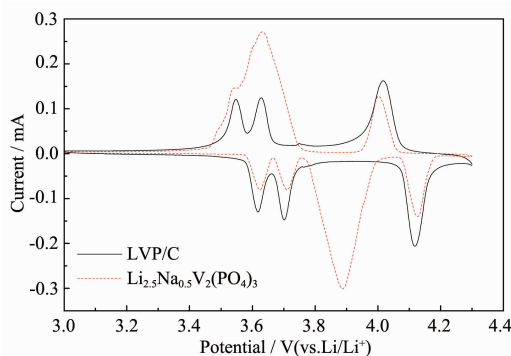


Fig.3 Cyclic voltammograms for  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and LVP/C

diffusion and the cycling performance should have been effectively improved with the multi-phase reaction mechanism transforming to a single-phase reaction mechanism. However, the lattice distortion caused by the existence of a too large amount of  $\text{Na}^+$  can lead to a slight decrease of cycling performance, which resembles that of other metal ion doping<sup>[14,19]</sup>.

The electrochemical kinetic properties of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  were also investigated by EIS at the open circuit voltage (OCV) state. As shown in Fig.4, the charge transfer resistance of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  decreased significantly with the replacement of  $\text{Li}^+$  by  $\text{Na}^+$ .

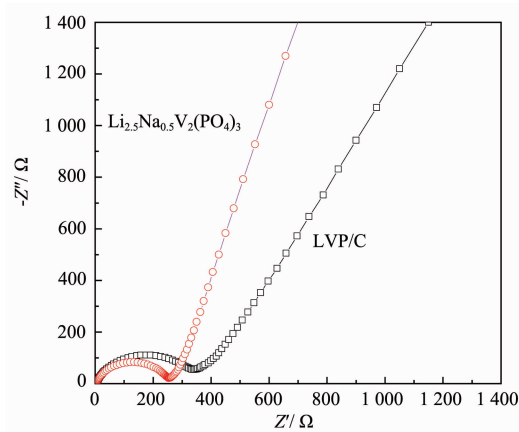


Fig.4 Nyquist plots of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  and LVP/C

### 3 Conclusions

A lithium-ion battery cathode material  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  was prepared by using the sol-gel method with  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and citric acid as raw materials. The XRD patterns indicate that the monoclinic structure of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has changed into a rhombohedral structure with the replacement of half  $\text{Li}^+$  by  $\text{Na}^+$ ; There is a clear and flat discharge plateau at 3.7 V in the charge /discharge voltage profile of the Na-doped LVP/C, which could be attributed to  $\text{Na}^+$  doping. At a discharge rate of 1C, the discharge specific capacity of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  is  $118 \text{ mAh} \cdot \text{g}^{-1}$  in the first cycle and a 92.4% capacity retention rate can still be held after 50 cycles. The Na-doping might have caused changes in the structure of LVP and made the discharge plateau smoother, which makes  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3/\text{C}$  a good potential

cathode material for lithium ion batteries. However, the structure change of the material leads to a slight decrease in the capacity retention rate. Studies on stabilizing the rhombohedral structure and phase stability of  $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$  will be the focus of our future work.

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