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Synthesis and Electrochemical Properties of Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Cathode Materials for Lithium-ion Batteries

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Abstract: Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ were prepared by a carbothermal reduction(CTR) process. The properties of the Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ were investigated by X-ray diffraction (XRD), scanning electron microscopic (SEM), and electrochemical measurements. Results show that the Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has the same monoclinic structure as the undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and the particle size of Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is smaller than that of the undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and the smallest particle size is only about 1 μm . The Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples were investigated on the Li extraction/insertion performances through charge/discharge, cyclic voltammogram (CV), and electrochemical impedance spectra(EIS). The optimal doping content of Cr was that $x=0.04$ in the $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ samples to achieve high discharge capacity and good cyclic stability. The electrode reaction reversibility was enhanced, and the charge transfer resistance was decreased through the Cr-doping. The improved electrochemical performances of the Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials are attributed to the addition of Cr^{3+} ion by stabilizing the monoclinic structure.

Key words: lithium ion batteries; cathode material; $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; Cr-doping; carbothermal reduction method; cyclic voltammogram (CV)

1 Introduction

Since lithium iron phosphate, one kind of lithiated transition metal polyanion material based on PO_4^{3-} , was firstly reported as a cathode material for lithium-ion batteries by Padhi *et al* in 1997^[1], the framework materials based on the phosphate polyanion have recently been identified as potential electroactive materials for lithium and lithium ion batteries applications. Some other transition metal phosphate polyanion insertion hosts such as LiMnPO_4 ^[2], $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ ^[3,4], LiVPO_4F ^[4-10] and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ^[11-15] have received some recent attention because of their stable framework, relatively high voltage, good lithium ion transport and large theoretic capacity. With relatively high capacity and suitable operating voltage for the present commercial electrolyte system, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is considered to be one of the most promising cathode materials

among the above-mentioned phosphate polyanion hosts. Unfortunately, an unacceptable fade of capacity makes it difficult to utilize $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrodes fully in lithium cells^[14,15] unless modifications are made to the material to ameliorate the long-term cyclic ability. Recently, it was found that doping could improve the cyclic ability of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material. In this article, the Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by a carbothermal reduction(CTR) process was prepared, and the Cr-doping effects on the electrochemical performances of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material were investigated.

2 Experimental

$\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ ($x=0.00, 0.02, 0.04, 0.06$) cathode materials were prepared by a carbothermal reduction(CTR) method. In the first step, stoichiometric mixture of Cr_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ was thoroughly ground and then calcined at 900 °C for 6 h to get CrPO_4 . Then, stoichiometric mixture of V_2O_5 , CrPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, acetylene black and $\text{LiOH} \cdot \text{H}_2\text{O}$ was thoroughly ground and then calcined at 750 °C for 10 h under an inert at-

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mosphere to obtain the $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ product. The undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was also prepared for comparison through the same procedure without the addition of CrPO_4 .

The powder X-ray diffraction (XRD, XPert-Pro) measurement using CuK_α radiation was employed and recorded at room temperature to identify the crystalline phase of the synthesized materials. The particle size and morphology of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders were observed by scanning electron microscope (JEOL, GSM-6380LV) with an accelerating voltage of 15 kV.

The electrochemical characterizations were performed using CR2025 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10 wt% of carbon black and 10 wt% of polyvinylidene fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 120 °C for 10 h in vacuum. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 mol·L⁻¹ LiPF_6 in EC : EMC : DMC (1 : 1 : 1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 3.0-4.2 V versus Li/Li^+ electrode at room temperature. Cyclic voltammograms were tested in the three-electrode system using metallic foils as both counter and reference electrode at a scanning rate of 0.1 mV/s in the voltage ranges of 3.0-4.4 V. EIS experiments were performed with a 5 mV voltage magnitude in the range of 10 kHz to 10 mHz.

3 Results and Discussion

Fig.1 shows the XRD patterns of the undoped and Cr-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials. It illustrates that all samples were pure single phase with the monoclinic structure(space group $\text{P2}_1/\text{n}$). and no other phases were detected in the XRD patterns, indicating that Cr was completely doped into the crystal lattice of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Since the radius of Cr^{3+} (0.064 nm) is smaller than that of V^{3+} (0.074 nm) ions, Cr^{3+} ions may be located at the position of V^{3+} ions in the crystal lattice. Therefore, Cr doping does not change the basic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystal structure.

The micrograph for a series of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ samples were given in Fig.2, where a small change in the morphology of particles by Cr doping can be identified. When the Cr doping content x is 0.00, 0.02, 0.06, the slightly agglomerated and inhomogenous particles are formed. The particle size of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ exhibited

quite homogenous and the average size is about 1 μm when x is 0.04. It indicates that the appropriate Cr^{3+} ion dopant can make the particle size of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ smaller. It is well known that the charge and discharge of lithium-ion batteries are conducted by the movement of Li^+ ions in and out of the electrode materials. Since small particle size indicates short diffusion length of Li^+ ions, small particles will have an advantage in the rate capabilities of a battery.

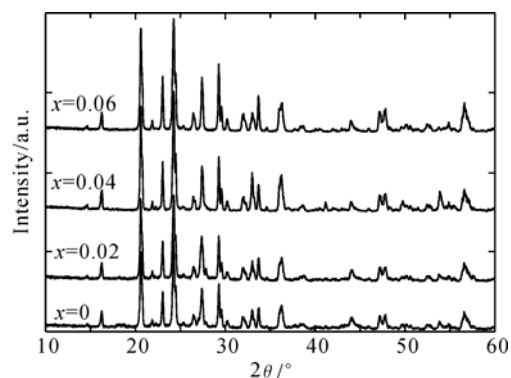


Fig.1 XRD patterns of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$

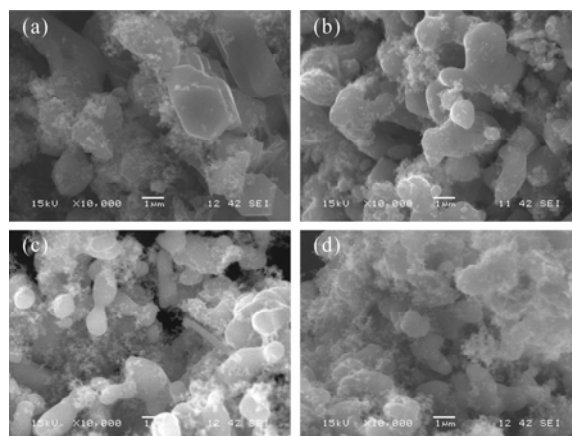
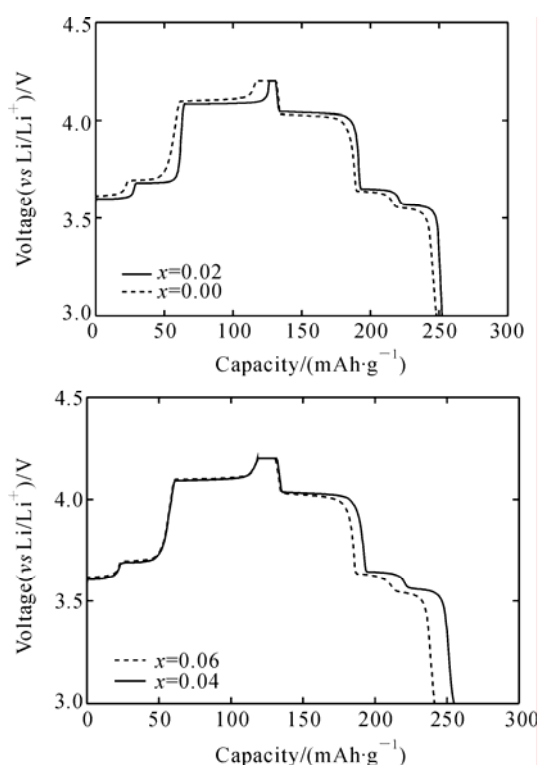


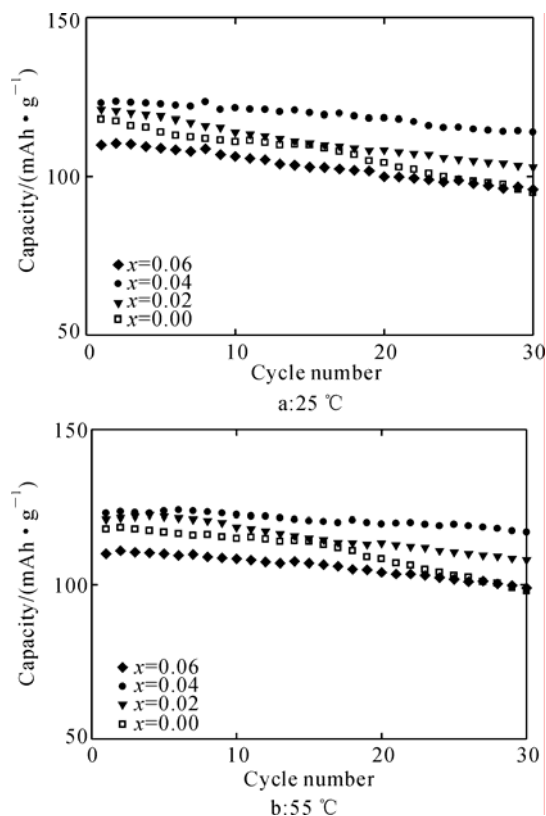
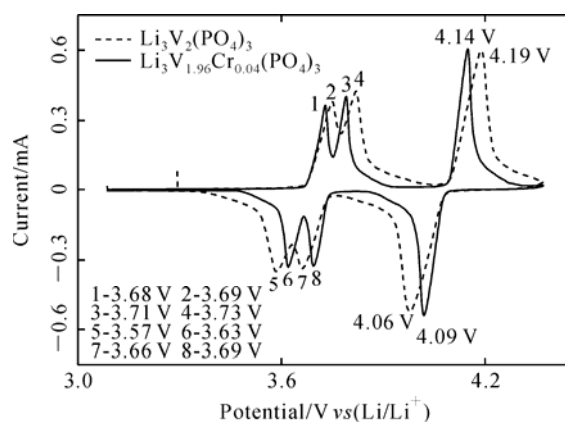
Fig.2 SEM images of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$:
(a) $x=0.00$; (b) $x=0.02$; (c) $x=0.04$; (d) $x=0.06$

Fig.3 shows the first charge-discharge curves of $\text{Li}/\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ cells at the rate of 0.5 C in the voltage range of 3.0-4.2 V at room temperature. As seen in Fig.3, it is clear that the initial charge capacities for $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ with $x=0.00, 0.02, 0.04$ and 0.06 are about 130, 131, 132, 131 $\text{mAh}\cdot\text{g}^{-1}$, and the discharge capacities are about 118, 121, 123, 110 $\text{mAh}\cdot\text{g}^{-1}$, respectively. The corresponding coulombic efficiency is 90.77%, 92.37%, 93.18% and 83.97%, respectively. It is clearly seen that the electrode reaction reversibility is enhanced considerably when the Cr doping content x is 0.04. This is because the homogenous particle of $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ leads to a uniform depth of charge (DOC) of each particle, which increases the utilization of the material. Accordingly, the coulombic efficiency is increased.

Fig.3 First charge-discharge curves of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$

The electrochemical cycling performance of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ samples tested at 25 °C is shown in Fig.4(a), in which the initial discharge capacity of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ with $x=0.00, 0.02, 0.04$ and 0.06 were 118, 121, 123, 110 $\text{mAh}\cdot\text{g}^{-1}$, with the capacity loss of 19.49%, 14.88%, 7.32% and 12.72% after 30 cycles, respectively. The electrochemical cycling performance was also tested at an elevated temperature (55 °C). As seen in Fig.4(b), all samples showed improved discharge capacity as well as capacity retention at 25 °C. The capacity loss of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ with $x=0.00, 0.02, 0.04$ and 0.06 was reduced to 16.95%, 10.74%, 4.88% and 10.00%, respectively. Obviously, the electrochemical performance of all $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ samples was improved at 55 °C, which may be attributed to the increased conductivity at the elevated temperatures. From the above results, it is clear that the $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ had the best electrochemical performance both at 25 and 55 °C.

It is noted that the repeated Li ion extraction/insertion from/into $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was accompanied by $\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ redox reactions, which may lead to the structural instability and the phase change because of the relatively large volume variation upon cycling. Since the radius of V^{3+} is 0.074 nm, and the radius of Cr^{3+} ions is 0.064 nm, the existence of Cr would counteract the volume shrinking/swelling during the Li^+ ions reversible extraction/insertion, and then increase the stability of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase in the long-term charge/discharge cycles. Therefore, the cyclic performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ could be apparently improved through the doping of a certain amount of Cr^{3+} ions.

Fig.4 Electrochemical cycling performance of $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ Fig.5 CV curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ electrodes in the first cycle

The initial cyclic voltammogram (CV) curves for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ electrodes at a scanning rate of 0.1 mV/s are shown in Fig.5. Both curves of the electrodes showed a similar profile, which indicated that the reaction mechanism was not changed during the lithium extraction/insertion process for the doped electrode, while all redox peaks were shifted after the Cr doping. As shown in Fig.5, three oxidation peaks of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was observed at around 3.69, 3.73, and 4.19 V, coupled with three reduction peaks at 3.57, 3.66 and 4.06 V, respectively. In the case of $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ electrode, the oxidation peaks shifted down to 3.68, 3.71, and 4.14 V, while the reduced peaks shifted up to at 3.63, 3.69 and 4.09 V, respectively. Namely, the potential difference for all three redox couples of $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ was reduced, which indicates that the reversibility of the electrode reaction could be enhanced by Cr-doping.

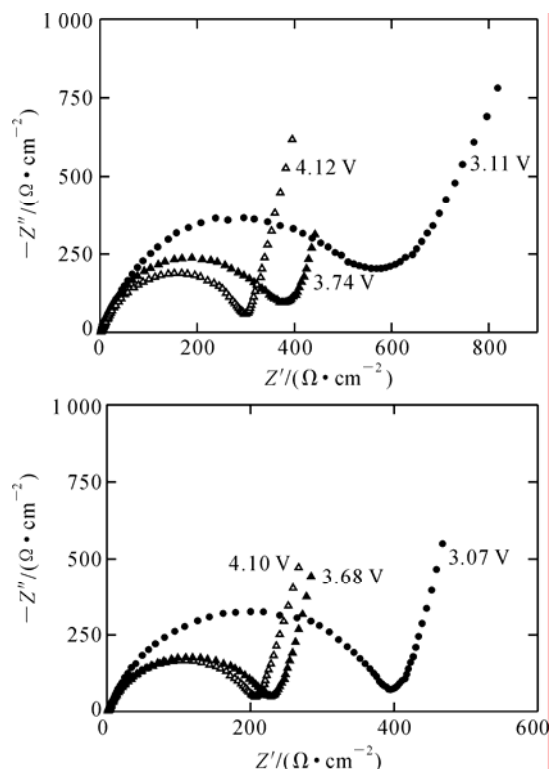


Fig.6 Nyquist plots for the EIS of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ at different charge states

The electrochemical impedance spectra of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ electrodes materials were measured at different charging states. The typical Nyquist plots of EIS are presented in Fig.6 for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$. Similar EIS patterns were observed for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ systems. A semicircle was observed to center on the real axis at the high frequency range. In the low frequency range, a straight line at 45° to the real axis corresponds to the Warburg impedance. The high frequency semicircle is related to the charge-transfer resistance (R_{ct}) and the double-layer capacitance. The low frequency tails resulted from the diffusion of lithium ions in the bulk active mass. In the case of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the diameter of the semicircle significantly depends on the potential during charging, indicating that the film formation process is dependent on the lithium ion content. On the other hand, the charge transfer resistance, R_{ct} , shows a greater dependence on the lithium insertion and extraction levels. In the highly charged states, the sample was found to give lower R_{ct} values. Comparing the diameter of the semicircle of the above two system, it can be found that $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ showed lower R_{ct} value than $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, indicating that the Cr-doping may cause some defects in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ system, which increase the electronic conductivity and improve the Li^+ kinetic behavior.

4 Conclusion

$\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ cathode materials were successfully prepared by a carbothermal reduction (CTR) process. XRD studies show that $\text{Li}_3\text{V}_{2-x}\text{Cr}_x(\text{PO}_4)_3$ ($x=0.02, 0.04, 0.06$) has

the same monoclinic structure (space group $\text{P}2_1/n$) as the undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. SEM images are quite homogeneous with smaller particles when x is 0.04. The cyclability curves establish the possibility of structural stability of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ through Cr doping. The cyclic voltammetry discloses the enhanced reversibility of $\text{Li}_3\text{V}_{1.96}\text{Cr}_{0.04}(\text{PO}_4)_3$ as compared with the undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. In summary, the demonstrated performance of the synthesized Cr-doping $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material offers some properties favorable for their commercial application.

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