

Effects of Carbon Coating on the Structure, Morphology and Electrochemical Performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Cathode Material Prepared by Solid State Method

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$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material was prepared by a solid-state method with sucrose as carbon source. The effects of carbon coating on the structure, morphology and electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ were investigated. Both the pristine and the carbon coated materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electroscopy (TEM) and electrochemical tests. Both samples have similar XRD patterns without extra reflections, which indicates that carbon coating doesn't affect the structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. SEM and TEM images confirm that a thin carbon layer is formed on the surface of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles. Electrochemical testing results reveals that $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ has better rate capability and higher discharge capacity than the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Indicated by the EIS results, the improvements can be attributed to the increased conductivity and charge transfer capability induced by carbon coating.

Keywords: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; carbon coating; cathode material; lithium ion battery

1. INTRODUCTION

The need for large-scale batteries impels the development of new materials for lithium ion batteries. Recently, lithium transition metal phosphates such as LiFePO_4 , LiMnPO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have been extensively studied [1-5]. In comparison with the conventional lithium transition metal oxides (e.g. LiCoO_2), the phosphate based materials exhibit many advantages such as low cost, nontoxicity, better thermal stability, et al. Especially, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can reversibly extract and insert two

lithium ions based on the V^{3+}/V^{4+} redox. All the three lithium ions can be completely extracted when it was charged to a higher voltage of 4.8 V, which results in a high theoretical capacity of $197 \text{ mAh}\cdot\text{g}^{-1}$. Therefore, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has been proposed as a highly promising cathode material for lithium ion batteries [6-9].

However, the major drawback of the phosphates and the ployanion materials is the low conductivity and poor ionic mobility [10-13]. The inherent conducting properties greatly affect its electrochemical performance and inhibit the further use in commercial applications. Fortunately, this problem can be largely solved by coating the particles with a thin conductive layer. Many conductive materials have been employed to build conductive layer for the phosphates [14-16]. Among these conductive materials, carbon is characterized by the fast electron transport and regarded as the excellent coating material [17-20]. Therefore, it is expected to build carbon coating on the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles for superior electrochemical performance.

X. H. Rui et al prepared carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by a solid state reaction process with different carbon sources of citric acid, glucose, PVDF and starch. The largest reversible capacity of $118 \text{ mAh}\cdot\text{g}^{-1}$ in the voltage region of 3.0-4.3 V is obtained for the sample with the citric acid as carbon source [21]. L. Wang et al prepared carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by a wet coordination method, and the material exhibits discharge capacity of $128 \text{ mAh}\cdot\text{g}^{-1}$ between 3.3 and 4.3 V and good reversible performance under a current density of $95 \text{ mA}\cdot\text{g}^{-1}$ [22]. M. M. Ren et al prepared core-shell $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite via a sol-gel route followed by hydrothermal treatment. Both enhanced electrochemical Li ion intercalation performance and electrical conductance are observed for the composite compared with the pure $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [23]. In this study, we investigated the impacts of carbon coating on the physical and electrochemical characteristics of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was prepared by solid state method with sucrose as carbon source, and both pristine and the carbon coating $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ materials were characterized and compared in detail.

2. EXPERIMENTAL

The pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was prepared by a solid-state method. Stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$, NH_4VO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ was mixed with oxalic acid and acetone, and the mixture was put into a high speed planetary mill. The milling lasted for several hours and then the resulting powder was collected and dried under vacuum. The mixture was then grounded and calcinated at 800°C for 8h in flowing argon. The carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was prepared by mixing the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with desired amount of sucrose, and then mixture was calcinated at 800°C for 4h in flowing argon to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$.

Powder X-ray diffraction (XRD, Bruker D8/Germany) employing $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of the samples. The morphology was observed with a field emission scanning electron microscope (SEM, HITACHI S-4800). The surface of the sample was observed with a transmission electron microscopy (TEM, JEOS-2010 PHILIPS). The coin cells were prepared as described in Ref. [24]. The composite electrode was made from a mixture of the active material, acetylene black, and Polyvinylidene Fluoride in a weight ratio of 80:10:10. The $1 \text{ mol}\cdot\text{L}^{-1}$ LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) was used as the

electrolyte. Galvanostatic charge-discharge measurements were performed in a potential range of 3.0-4.8 V at ambient temperature. The electrochemical impedance measurements were carried out with a CHI 660 C instrument.

3. RESULTS AND DISCUSSION

The XRD patterns of the pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples are shown in Figure 1. Both of the samples exhibit single phase structures based on monoclinic unit cell in space group $P2_1/n$. There is no peaks indexed to carbon was observed for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, which may be attributed to the amorphous state of carbon coating. The lattice parameters of both samples were calculated and the results are shown in Table 1. The cell parameters of both samples were close to each other within experimental errors, which confirms that carbon coating doesn't affect the structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

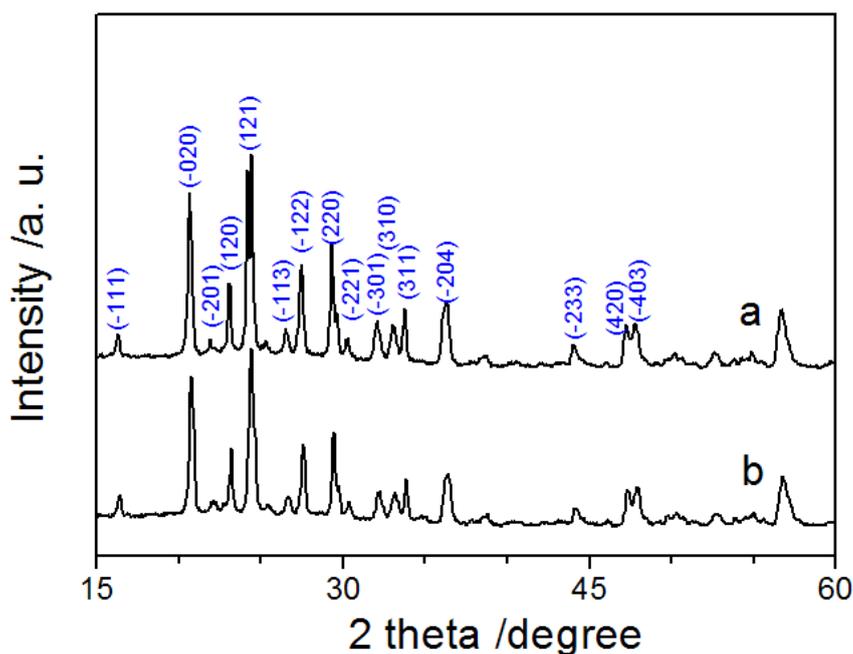


Figure 1. XRD pattern of the pristine (a) and carbon coated (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Table 1. Lattice parameters of the pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Sample	a (Å)	b (Å)	c (Å)	β
Pristine	8.5471	8.5732	11.9701	90.3450
Carbon coating	8.5483	8.5744	11.9689	90.3395

The SEM images of the pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples were shown in Figure 2 (a)-(d). Both samples composed of agglomerated primary particles with the size of about 5 μm . The

smooth particles with clear surfaces were observed for the pristine sample. However, the surfaces of the particles became coarse after carbon coating. In the SEM images, the carbon phase was not observed as a separate morphological feature. In order to characterize the carbon phase, the TEM observation was carried out on the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and the results are shown in Figure 3. A thin surface layer is observed for carbon coated sample, which confirms the presence of carbon layer on the surface of particles.

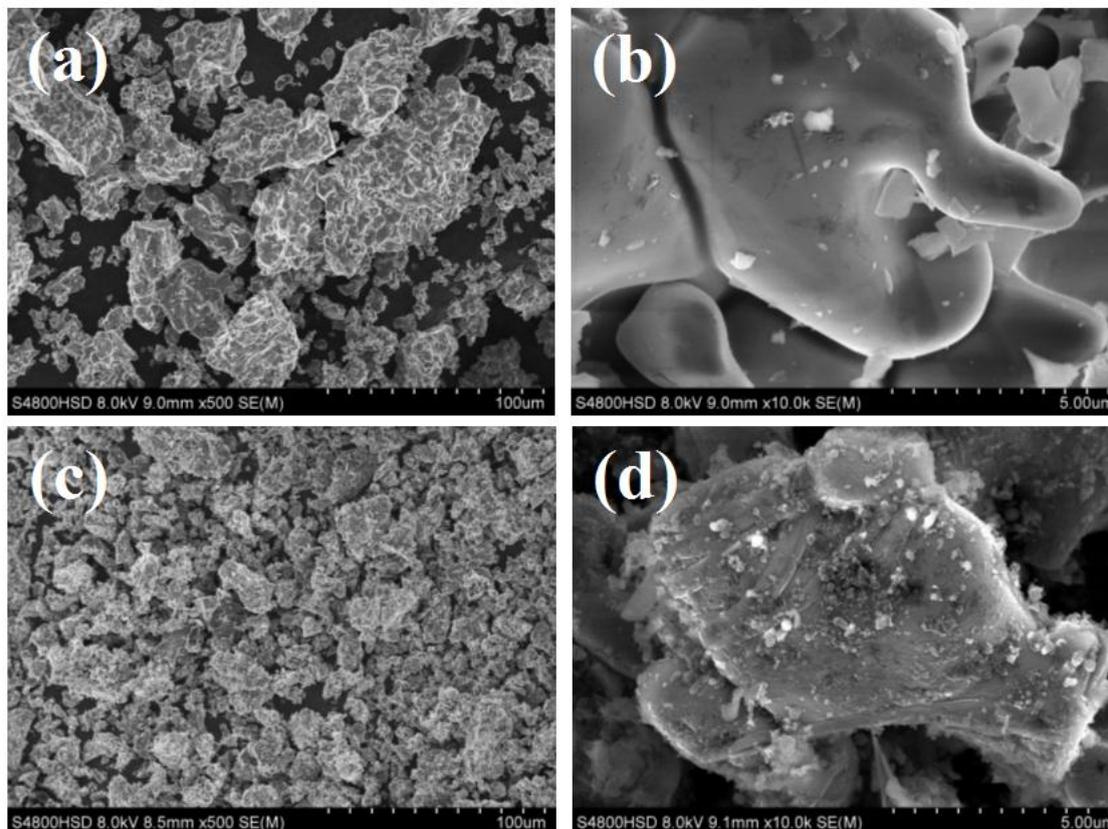


Figure 2. SEM images of the pristine (a,b) and carbon coated (c,d) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in different magnitude

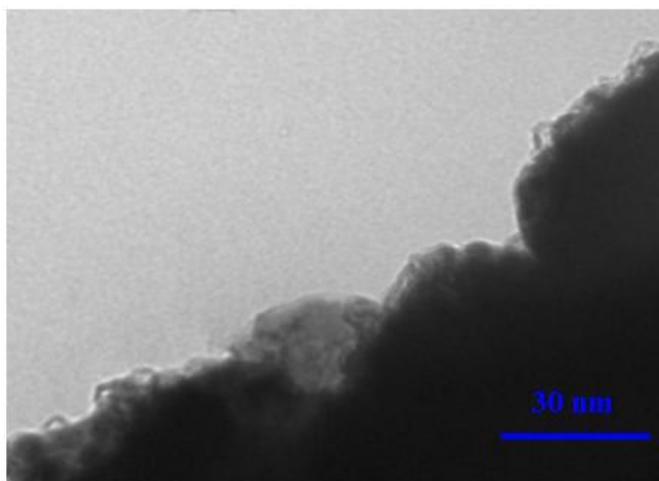


Figure 3. TEM image of carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Figure 4 shows the initial charge/discharge curves of the pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples at the 0.2 C rate in the voltage range of 3.0 V-4.8 V. For the carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, four plateaus at around 3.63, 3.70, 4.10 and 4.50 are observed in the charge curve, which corresponds to a sequence of phase transition processes between the single phases $\text{Li}_x\text{V}_2(\text{PO}_4)_3$. The first lithium ion is extracted in two steps, 3.63 V and 3.70 V, which is because of the presence of an ordered phase $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$. Subsequently, the second lithium ion is extracted in one single plateau of 4.10 V to form $\text{Li}_{1.0}\text{V}_2(\text{PO}_4)_3$. These initial three plateaus are related to the two lithium ions extraction which associated with the $\text{V}^{3+}/\text{V}^{4+}$ redox couple. Finally, the third lithium ion is removed in the plateau of 4.50 V, which indicates that one switches from the $\text{V}^{3+}/\text{V}^{4+}$ redox couple to the $\text{V}^{4+}/\text{V}^{5+}$ redox couple. However, for the pristine sample, all the plateaus become indistinguishable and the initial two plateaus combined to one slope. The lower capacity and decreased plateaus of the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ indicate its poor electrochemical performance than the carbon coated one. Therefore, the result indicates that carbon coating improved the electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in the initial cycle.

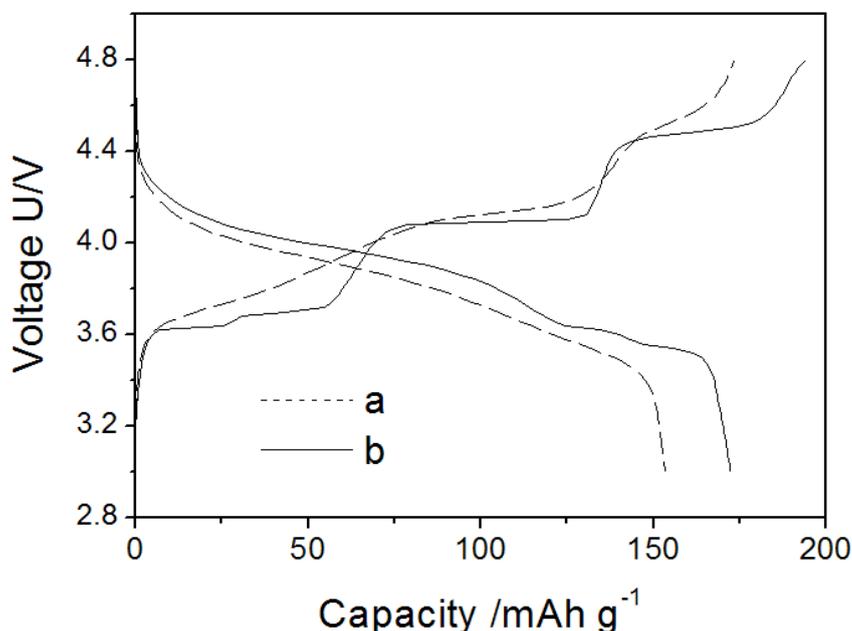


Figure 4. Initial charge/discharge curves of the pristine (a) and carbon coated (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

The electrochemical impedance spectroscopy of the pristine and carbon coated samples were compared in Figure 5. Both samples exhibit a semicircle at the high frequency, which corresponds to charge transfer resistance; and a sloping line at the low frequency, which corresponds to the solid-state diffusion resistance. The carbon coated sample exhibits much smaller high frequency semicircle than the pristine one, which indicates its lower charge transfer resistance than the pristine sample. The decreased charge transfer resistance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is associated with the conductive carbon coating layer, which forms a high conductive layer on the particle surface and increases the conductivity of the

electrode material. Therefore, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ sample exhibits improved electrochemical kinetic and enhanced electrochemical property.

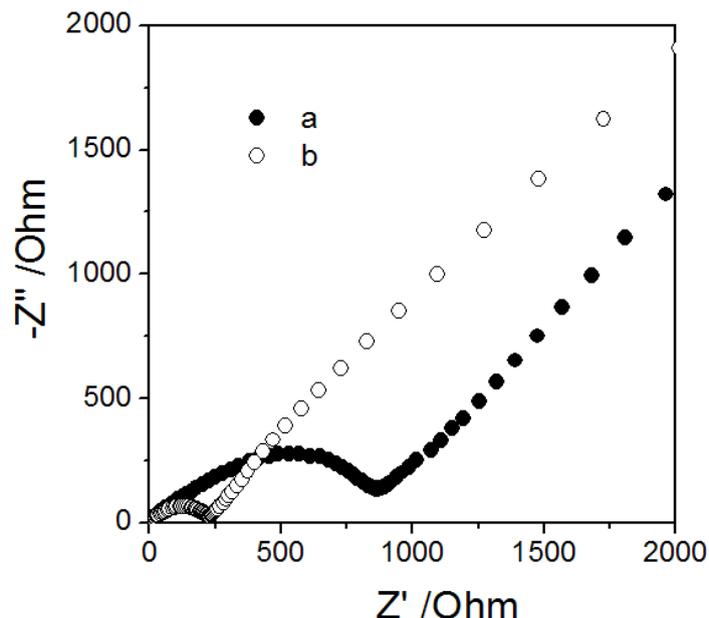


Figure 5. EIS spectroscopy of the pristine (a) and carbon coated (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Figure 6 shows the rate capability of both samples. Both cells were charge/discharged at different current densities, i. e. 0.2 C, 0.5 C, 1 C and 2 C in the voltage range of 3.0 and 4.8 V. The discharge capacity of each sample declines with an increase in current density. When the same current density is applied, the carbon coated sample exhibits larger capacity than the pristine one. The result indicated that the carbon coating enhanced the rate capability of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The improvement may be associated with the decreased charge transfer resistance, increased conductivity and enhanced electrochemical kinetic induced by conductive carbon coating.

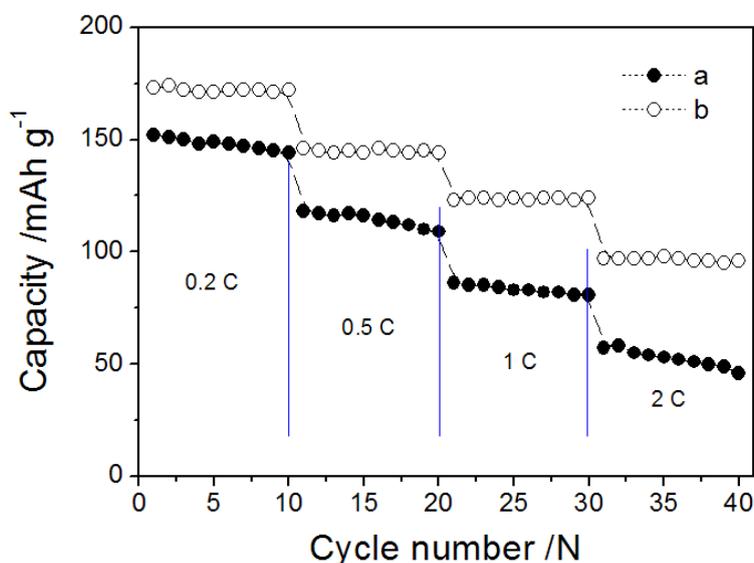


Figure 6. Rate capability of of the pristine (a) and carbon coated (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

4. CONCLUSIONS

The pristine and carbon coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ materials was prepared by solid state method and their physicochemical characteristics were compared in detail. XRD results show that both samples have similar structure and lattice parameters, which indicates that carbon coating doesn't affect the structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. SEM images show that the carbon coated sample has much coarse surface than the pristine one. TEM observation confirms the thin carbon layer exists on the surface of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles. Electrochemical testing results reveal that improved charge/discharge capacities and high rate capability are obtained for the carbon coated sample compared with the pristine one. Indicated by the EIS results, the improvements can be attributed to the decreased charge transfer resistance and enhanced conductivity induced by carbon coating.

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