$Li_3V_2(PO_4)_3$/C Composite Material with Porous Structure and Nano-carbon Webs Synthesized through Liquid Nitrogen Quenching

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$Li_3V_2(PO_4)_3$/C composite material with a porous structure and nano-carbon webs are synthesized through a chemical reduction–lithiation and liquid nitrogen quenching method. $Li_3V_2(PO_4)_3$/C sample was characterized by XRD, SEM, and TEM. X-ray diffraction results show $Li_3V_2(PO_4)_3$ is monoclinic with a space group of $P2_1/n$. SEM and TEM images indicate that the $Li_3V_2(PO_4)_3$ particles are about 200 nm in diameter, have porous structure, and are coated with nano-carbon webs. Electrochemical measurement results indicate that the $Li_3V_2(PO_4)_3$/C cathode exhibits high-rate characteristic and delivered a stable discharge capacity of 131.57 mA h g^{-1} at 0.1 C (14 mA g^{-1}), in the range of 2.6–4.5 V.

Since $LiFePO_4$ was proposed as cathode material for lithium-ion batteries, considerable studies have been performed on transition-metal polyanion materials based on PO_4^{3-}, such as $LiMnPO_4$, $LiCoPO_4$, $Li_3M_2(PO_4)_3$ (M = V and Fe) and $LiVPO_4F$, because of their high capacity and thermal stability.[1–8] Among these materials, the monoclinic $Li_3V_2(PO_4)_3$ is a highly promising competitor proposed as a cathode for higher voltage lithium-ion batteries because it possesses high reversible capacity, high operate voltage, and good ion mobility.[9–11] However, $Li_3V_2(PO_4)_3$ has low conductivity due to the polarization of the V–O bond. Carbon coating is an effective way to improve the performance of $Li_3V_2(PO_4)_3$.

To the best of our knowledge, cathode material (such as $LiFePO_4$) with porous structure shows better electrochemical performance compared to conventional structure.[12–14] The pore-containing nano-sized particles are wrapped by nano-carbon webs; the pores, when filled with liquid electrolyte, are responsible for easy ion exchange; the nano-carbon webs, on the other hand, serves for improving electronic conductivity.

In this paper, $Li_3V_2(PO_4)_3$/C composite with porous structure and nano-carbon webs has been synthesized by a compound technique "chemical reduction–lithiation and liquid nitrogen quenching (CLQ)," by using oxalic acid as the reducer as well as the carbon source; the physical properties and electrochemical performance of the sample are investigated.

Amorphous $Li_3V_2(PO_4)_3$ was prepared by chemical reduction and lithiation[15] between Li_2CO_3, V_2O_5, $NH_4H_2PO_4$, and oxalic acid (a nominal composition of Li:V:P = 3:2:3). The amorphous $Li_3V_2(PO_4)_3$ was first pressed into pellets; subsequently it was transferred to a quartz-tube; then the quartz-tube was sealed in argon atmosphere. Second the samples were fired at 650 °C for 12 h in a tube furnace; third the quartz-tubes with the sample were taken out of the furnace immediately and put into liquid nitrogen. Finally, the $Li_3V_2(PO_4)_3$/C was obtained by separating the sample from the fragile quartz pieces.

Structural and crystalline phase analyses of the products were taken from the powder X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu Kα radiation. The samples were observed by scanning electron microscopy (SEM, JEOL, JSM-5612LV) and a Tecnai G12 transmission electron microscope (TEM). Composition analysis of the elemental carbon in $Li_3V_2(PO_4)_3$/C was performed by C–S analysis equipment (Eltar, Germany).

The electrochemical characterization was performed using a CR2025 coin-type cell. Typical positive electrode loadings were in the range of 2–2.5 mg cm^{-2}, and an electrode diameter of 14 mm was used. For positive electrode fabrication, the prepared powders were mixed with 10% of carbon black and 10% poly(vinylidene 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 12 h. The test cell consisted of a positive electrode and lithium foil negative electrode separated by a porous polypropylene film and 1 mol L^{-1} $LiPF_6$ in EC, EMC, and DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. Electrochemical tests were carried out using an automatic galvanostatic charge–discharge unit and NEWARE battery cycler, between 2.6 and 4.5 V vs. Li/Li$^+$ electrode at ambient temperature.

$Li_3V_2(PO_4)_3$/C composite synthesized at 650 °C for 12 h through CLQ shows a series of diffraction peaks in its XRD pattern, as shown in Figure 1. The crystal structure is identified to be monoclinic $Li_3V_2(PO_4)_3$ structure indexed to $P2_1/n$ (ICDD 43-0526). No obvious impurities were detected in the XRD results. Carbon remaining in $Li_3V_2(PO_4)_3$/C composite material was not detected, which indicates the residual carbon is amorphous or the thickness of the residual carbon on the $Li_3V_2(PO_4)_3$/C powders is too thin.[16] The unit cell parameters obtained by least squares refinement based on a monoclinic structure using space group $P2_1/n$ are as follows: $a = 0.85766$, $b = 0.86862$, $c = 1.19067$ nm, $\beta = 90.52°$, and cell volume = 0.88703 nm^3, similar to the previous report.[17,18]

The particle morphology observed by SEM is shown in Figure 2a, and the average particle size is around 200 nm. All

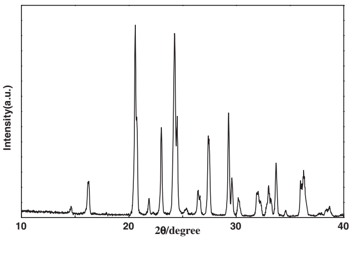

Figure 1. XRD pattern of the $Li_3V_2(PO_4)_3$/C composite.

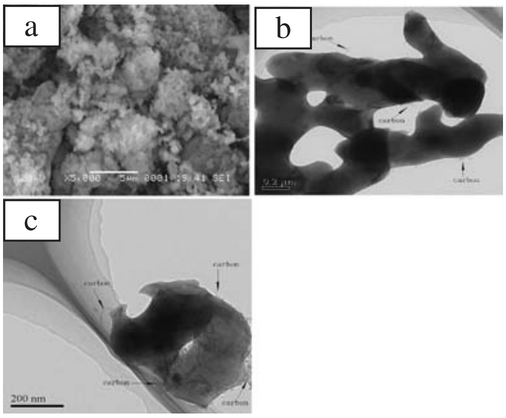

Figure 2. (a) SEM image of the synthesized $Li_3V_2(PO_4)_3/C$ composite; (b), (c) TEM images of the synthesized $Li_3V_2(PO_4)_3/C$ composite.

particles seem to be porous with nanometer pores. The amount of carbon in $Li_3V_2(PO_4)_3/C$ composite measured by C–S analysis equipment was about 0.5 wt %. However, it was difficult to distinguish carbon from $Li_3V_2(PO_4)_3$ powder via SEM. So we studied this composite further with TEM. As shown in Figures 2b and 2c, the $Li_3V_2(PO_4)_3$ particle has a porous structure, and the porous $Li_3V_2(PO_4)_3$ particle was wrapped with nano-carbon webs, the thickness of carbon webs is about 10–20 nm. We found that the morphology of this $Li_3V_2(PO_4)_3/C$ composite is different from previous reports, where $Li_3V_2(PO_4)_3$ and carbon could be identified as small particles.[15,18,19] According to our previous study,[15] the $Li_3V_2(PO_4)_3$ synthesized by chemical reduction and lithiation did not have this unique structure, So we think this porous structure and nano-carbon webs are attributed to the fast liquid nitrogen quenching. And the $Li_3V_2(PO_4)_3/C$ powders have larger surface areas ($25\,m^2\,g^{-1}$) than that ($10\,m^2\,g^{-1}$) synthesized previously.[15]

It was expected that this type of composite would be very effective in enhancing the electrochemical performance of $Li_3V_2(PO_4)_3$. Figure 3a shows the first charge/discharge curves of $Li/Li_3V_2(PO_4)_3/C$ cells at different rates. A discharge specific capacity of $131.57\,mA\,h\,g^{-1}$ at 0.1C was obtained, 99.6% of theoretical capacity ($132\,mA\,h\,g^{-1}$). Furthermore, the $Li_3V_2(PO_4)_3/C$ powder shows good performance at higher rate, as shown in Figures 3a and 3b. The initial discharge capacity values of $Li_3V_2(PO_4)_3$ at the rate of 1C, 2C, and 5C are about 123.48, 121.92, and $113.07\,mA\,h\,g^{-1}$, respectively. These results are better than Q. Q. Chen and X. C. Zhou[19,20] reported and are also better than the results we reported previously,[15] in which the $Li_3V_2(PO_4)_3/C$ obtained without fast liquid nitrogen quenching.

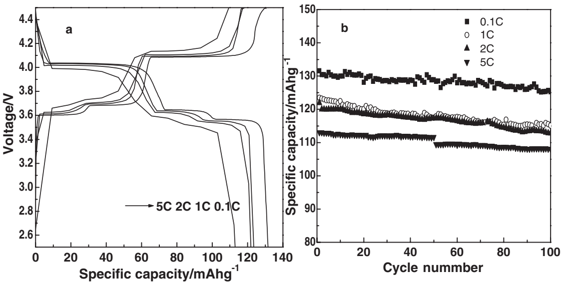

Figure 3. (a) Rate performance of $Li_3V_2(PO_4)_3/C$ synthesized at 650 °C for 12 h, (b) cycle performance of $Li_3V_2(PO_4)_3/C$ synthesized at 650 °C for 12 h.

The cycle life of the $Li_3V_2(PO_4)_3/C$ synthesized at 650 °C for 12 h at different C rates to a cutoff voltage between 2.6 and 4.5 V is shown in Figure 3b. The initial discharge capacity values of the $Li_3V_2(PO_4)_3$ at the rate 0.1C, 1C, 2C, and 5C are about 131.57, 123.48, 121.92, and $113.07\,mA\,h\,g^{-1}$, respectively, and after 100 cycles the corresponding discharge capacity values are about 125.30, 115.09, 112.77, and $108.11\,mA\,h\,g^{-1}$, respectively. The cell retains 95.23, 93.21, 92.49, and 95.61% of its initial discharge capacity. It also indicates that the cycle performances are better than $Li_3V_2(PO_4)_3/C$ synthesized without fast liquid nitrogen quenching, as we reported previously.[15] This relatively large capacity and high rate capability are due to the $Li_3V_2(PO_4)_3$ with a porous structure and coated with nano-carbon webs.

A new type of $Li_3V_2(PO_4)_3/C$ composite in which nano-carbon webs wrap porous $Li_3V_2(PO_4)_3$ particles was obtained through CLQ. The porous structure and nano-carbon webs are attributed to fast liquid nitrogen quenching. This porous structure helps the electrolyte to penetrate the $Li_3V_2(PO_4)_3$ material and promotes good electronic contact among the $Li_3V_2(PO_4)_3$ particles. The nano-carbon webs were very effective in improving the electronic conductivity of $Li_3V_2(PO_4)_3$. These characteristics of porous structure and nano-carbon webs largely enhanced the electrochemical properties of $Li_3V_2(PO_4)_3$ such as capacity and rate capability.

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