Synthesis and Electrochemical Performance of xLiFePO$_4\cdot y$Li$_3$V$_2$(PO$_4$)$_3$ Composites

MA Ping-ping[1,2*], LIU Zhi-jian[1], XIA Jian-hua[1], CHEN Yu[2],

HU Pu[2], LU Zhi-chao[1], XIA Ding-guo[3]

（1. *China Iron and Steel Research Institute Group*, *Beijing* 100081, *China*；

2. *Beijing Central Press Union Technology Co LTD*., *Beijing* 100041, *China*；

3. *College of Engineering*, *Peking University*, *Beijing* 100871, *China*）

Abstract：　A series of xLiFePO$_4\cdot y$Li$_3$V$_2$(PO$_4$)$_3$ composites were systematically synthesized through solid state reactions by variations in the proportions of LiFePO$_4$ and Li$_3$V$_2$(PO$_4$)$_3$. The properties of the prepared compounds were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. The capacity of 162. 7 mAh·g^{-1} at 0. 2C rate was obtained with the relatively good cycle stability and good conductivity for 0. 95LiFePO$_4\cdot$0. 05Li$_3$V$_2$(PO$_4$)$_3$ due to more uniformed distributed and smaller particle sizes.

Key words：　lithium ion batteries；composite；doping；xLiFePO$_4\cdot y$Li$_3$V$_2$(PO$_4$)$_3$

CLC Number：　O646. 21　　　　　　　　　　　**Document Code**：　A

1　Introduction

Lithium ion batteries have been attracted more and more attention for high energy density and high working voltage. In commercial batteries, transition metal oxides with layered structure such as LiCoO$_2$ have been used as cathode materials extensively. However, the high costs, limited storage and toxicity prohibit its usage in large-scale applications. For the usage of batteries in hybrid electric vehicles, it requires better stability and more safety as mobile energy sources, but it is just the fatal to all layered structural compounds. In the search for substituting, phosphates such as LiFePO$_4$ have been recognized as promising positive electrodes because of their environmental benignity, low cost, high theoretical capacity of 170 mAh·g^{-1}[1]. The olivine structure belongs to a general family of "polyanion" compounds containing compact tetrahedral "anion" structural units

(XO_4)$^{n-}$ (X = P, S, As, Mo or W) with strong covalent bonding, networked to produce higher-coordination sites such as oxygen octahedral that supplies better thermal stability[2-3]. In the contrary, LiFePO$_4$ materials showed low electronic conductivity (10^{-9} ~ 10^{-10} S·cm^{-1}) and poor Li-ion diffusivity[2-3]. There are two effective ways which have been tried to improve the electronic conductivity and Li-ion diffusivity：one is to coat additions, such as conductive nanopowders or carbon black powders, onto the surface of the particles that could synthesize small sizes[4-7]；the other is to dope with some supervalent cations to improve the conductivity[2-3,8-10]. With the same problem, a NASICON-related structure α-Li$_3$V$_2$(PO$_4$)$_3$ exhibited a nearly theoretical capacity of 197 mAh·g^{-1}[10-13]. The LiFePO$_4$-based materials with the addition of Li$_3$V$_2$(PO$_4$)$_3$ showed a promising electronic conductivity[13-15]. By now, little attention has been paid to

systematically study the different characters of xLiFe-PO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ composites caused by the variety of proportion of LiFePO$_4$ and Li$_3$V$_2$(PO$_4$)$_3$ systematically. In this work an attempt was made to prepare a series of xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ and to investigate the effects of different contents of Li$_3$V$_2$(PO$_4$)$_3$ on the microstructure and electrochemical performance of the materials.

2　Experimental

Compounds of xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ were synthesized by solid state reactions. Stoichiometric amounts of LiOH·H$_2$O, FeC$_2$O$_4$·2H$_2$O, NH$_4$VO$_3$ and NH$_4$H$_2$PO$_4$ were ball milled in ethanol for 4 h. The precursors were mixed together and formed into powders by the spray-dry method. After transferred to a temperature-controlled tube furnace equipped with flowing nitrogen, these mixed powders were firstly pre-decomposed at the temperature of 350 ℃, subsequently calcined at 700 ℃ for 12 h, then cooled to room temperature. The pure LiFePO$_4$ and Li$_3$V$_2$(PO$_4$)$_3$ were synthesized by the same method.

The crystal structures of the prepared powders were investigated by X-ray diffraction (XRD) using a D8 X diffractometer (Bruker Co. Germany) with Cu K$_\alpha$ radiation from $2\theta = 10°$ to $70°$ at a step of $0.02°$. The morphology and composition of the samples were determined using a Hitachi S-4300 scanning electron microscope equipped with the energy dispersive spectrometer (EDS, Genesis Apex).

The electrodes consisted of 80% prepared powders, 10% carbon black powders, and 10% polyvinylidene fluoride in 1-methyl-2-pyrrolidinone solvent. After drying in an oven at 80 ℃ overnight, the electrodes were assembled into coin-type cells and then the cells were performed between 2.5～4.5 V. Glass fiber separators were placed between the electrodes and lithium metals which were used as the anodes.

3　Results and Discussion

3.1　Structural Analysis

The XRD patterns of all the prepared powders are given in Fig. 1. For the patterns with $y = 0$ and $y = 1.0$, pure LiFePO$_4$ and pure Li$_3$V$_2$(PO$_4$)$_3$ were

prepared without mixing their precursors. According to the sharp peaks in the patterns, both of them were well crystallized. There were no other peaks except an olivine phase with ordered orthorhombic structure belonging to the space group *Pnmb* with $y = 0.05$. The same result was also found by Yan[14] and Wu[18]. No obvious characteristic peaks of Li$_3$V$_2$(PO$_4$)$_3$ were seen in the sample of $y = 0.1$. The impurity of Li$_3$PO$_4$ observed was attributed to V^{3+} and Fe^{2+} doped in LiFePO$_4$ and Li$_3$V$_2$(PO$_4$)$_3$, respectively[19]. The characteristic peaks of Li$_3$V$_2$(PO$_4$)$_3$ became more apparent over $y = 0.2$ and still accompanied by the impurity Li$_3$PO$_4$.

Fig. 1　XRD patterns of xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ composites with different proportions of y
A. 2θ from $10°$ to $70°$; B. 2θ from $15°$ to $40°$

3.2　Morphological Examination

Small particle size and uniform size distribution would lead to promising electrochemical performance, cycle stability and high rate capacity[20]. Fig. 2 shows the SEM images of xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ com-

pounds. The particles with $y = 0.05$ (Fig. 2B) appeared well distributed with the similar shapes and size ranging $100 \sim 200$ nm. Moreover, the regular morphology and lack of agglomeration could improve the tap density[21].
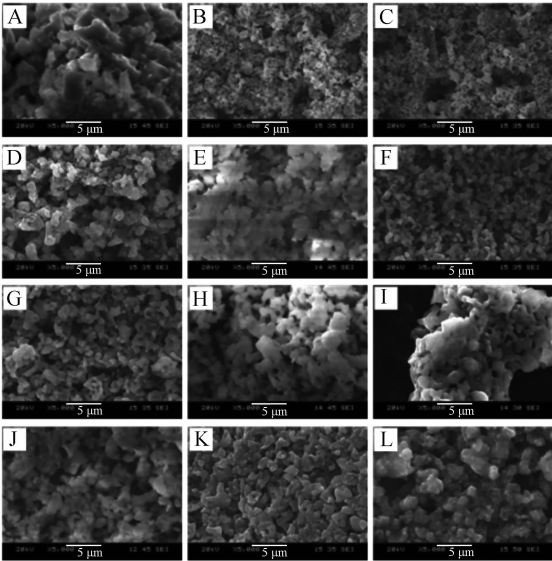

Fig. 2　SEM images of xLiFePO$_4$ · yLi$_3$V$_2$ (PO$_4$)$_3$ compounds with different proportions of y
A. $y = 0$; B. $y = 0.05$; C. $y = 0.1$; D. $y = 0.2$;
E. $y = 0.3$; F. $y = 0.4$; G. $y = 0.5$; H. $y = 0.6$;
I. $y = 0.7$; J. $y = 0.8$; K. $y = 0.9$; L. $y = 1.0$

Over $y = 0.5$ (Fig. 2G), all the morphologies were similar with the particle sizes being more than 200 nm. The particles agglomerated forming secondary particles, which are independent of different proportions. The particle sizes of pure LiFePO$_4$ (Fig. 2A) were smaller than those of pure Li$_3$V$_2$(PO$_4$)$_3$ (Fig. 2L) and the compounds more and more showed the characteristics of Li$_3$V$_2$(PO$_4$)$_3$ with the increasing of y in the proportion. This agreed well with the XRD results.

3.3　Electrochemical Properties

Fig. 3 compares the electrochemical performances of all xLiFePO$_4$· yLi$_3$V$_2$(PO$_4$)$_3$ compounds at 0.2C rate. The discharge capacity strongly depended on the proportions of y. In the case of the pure LiFePO$_4$ sample (Curve a), the discharge capacity was 151 mAh· g^{-1}, which is close to the theoretical capacity of 170 mAh·g^{-1}. It was found that two lithium ions were just

extracted at the voltages of 3.64 and 4.09 V (vs. Li/ Li$^+$) in the range of $2.5 \sim 4.2$ V[22]. The theoretical capacity of Li$_3$V$_2$(PO$_4$)$_3$ in the same potential range is 133 mAh·g^{-1}. The discharge capacity of the prepared pure Li$_3$V$_2$(PO$_4$)$_3$ was about 112 mAh·g^{-1} reaching 85% of the theoretical capacity with the standard potential plateaus 3.4 V for pure LiFePO$_4$ and 3.65, 3.7 and 4.1 V for pure Li$_3$V$_2$(PO$_4$)$_3$[23]. At $y = 0.05$ (Curve b) the best performance was observed with 162.7 mAh·g^{-1} at 0.2C rate, which might be contributed by the small particle sizes and well distributed particles (Fig. 2B). In addition, the proper proportions of x and y could form conductive phase that will not only impede the grain growth during sintering, but also give the particles more electronically conductive[16]. The capacity started to drop dramatically with the Li$_3$V$_2$(PO$_4$)$_3$ contents increased beyond 10%, that was partly due to the impurity of Li$_3$PO$_4$ as indicated by XRD (Fig. 1).

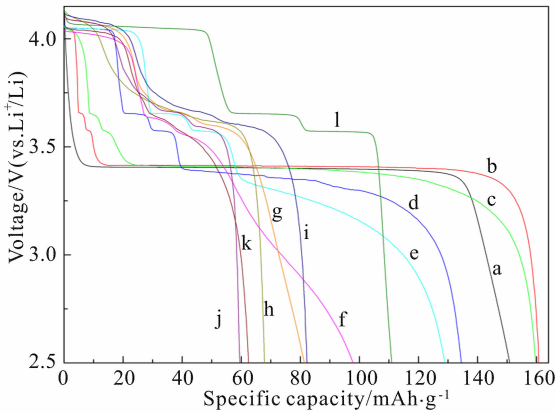Fig. 3　Discharge capacities of xLiFePO$_4$ · yLi$_3$V$_2$(PO$_4$)$_3$ compounds at 0.2C rate and room temperature
a. $y = 0$; b. $y = 0.05$; c. $y = 0.1$; d. $y = 0.2$;
e. $y = 0.3$; f. $y = 0.4$; g. $y = 0.5$; h. $y = 0.6$;
i. $y = 0.7$; j. $y = 0.8$; k. $y = 0.9$; l. $y = 1.0$

The discharge profiles of xLiFePO$_4$· yLi$_3$V$_2$ (PO$_4$)$_3$ compounds with various current densities at room temperature are presented in Fig. 4. The curve b ($y = 0.05$) exhibited better rate capability. The reversible capacities of 147.7, 122.3 and 87.4 mAh· g^{-1} were obtained at 1, 5 and 10C, respectively. To our knowledge, the electronic conductivity of the pure

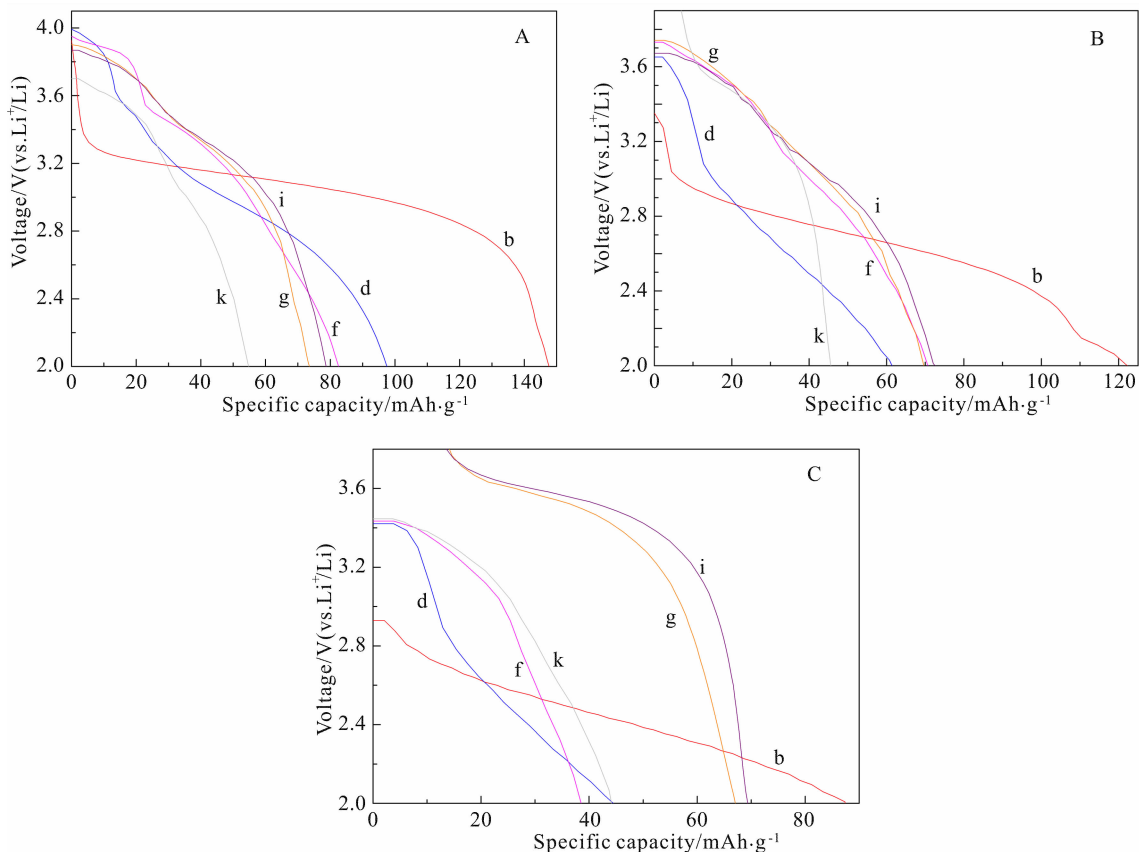Fig. 4   Capacities of $x\mathrm{LiFePO_4 \cdot} y\mathrm{Li_3V_2(PO_4)_3}$ compounds at different rates and room temperature
b. $y = 0.05$; d. $y = 0.2$; f. $y = 0.4$; g. $y = 0.5$; i. $y = 0.7$; k. $y = 0.9$
A. discharge at 1C; B. discharge at 5C; C. discharge at 10C

$\mathrm{LiFePO_4}$ is very low[2-9], however, the $0.95\mathrm{LiFePO_4 \cdot}$ $0.05\mathrm{Li_3V_2(PO_4)_3}$ compound behaved inspiringly well in the rate discharge capacity. This suggested that the smaller particle size and $\mathrm{Li_3PO_4}$ impurity might determine the electrochemical properties of $x\mathrm{LiFePO_4 \cdot}$ $y\mathrm{Li_3V_2(PO_4)_3}$ compounds. Yamada[24] and Chiang[25] reported that the particles with the same size had exhibited nearly similar electrochemical behaviors.

To further examine the cycle performance of 0.95 $\mathrm{LiFePO_4 \cdot 0.05Li_3V_2(PO_4)_3}$ compound, the long-term charge/discharge cycling tests at different current rates were performed and the results are given in Fig. 5. It is evident that almost no capacity fading was observed after 50 cycles.

Fig. 6A shows the TEM image of $0.95\mathrm{LiFePO_4 \cdot}$ $0.05\mathrm{Li_3V_2(PO_4)_3}$ composite. The particle sizes were about 200 nm, which is consistent with that observed from SEM. The EDS spectra obtained from the framed
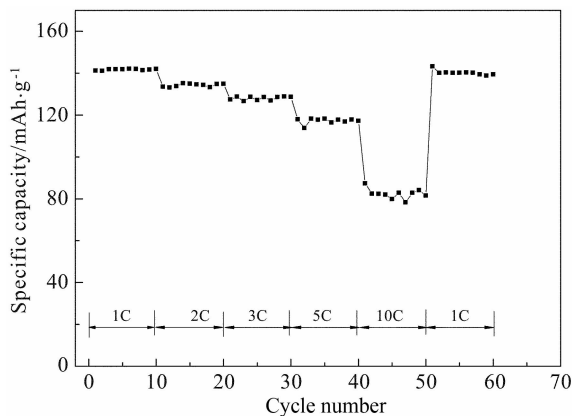

Fig. 5   Cycle life of $0.95\mathrm{LiFePO_4 \cdot 0.05Li_3V_2(PO_4)_3}$ compound at different rates

regions 1 and 2 in Fig. 6A are also shown in Fig. 6B and C, respectively. The existence of Fe, P and O elements only seen from Region 1 in Fig. 6A indicated the presence of $\mathrm{LiFePO_4}$. The appearance of V, P and O elements without Fe element in Fig. 6C confirmed the presence of $\mathrm{L_3V_2(PO_4)_3}$ in the composite.
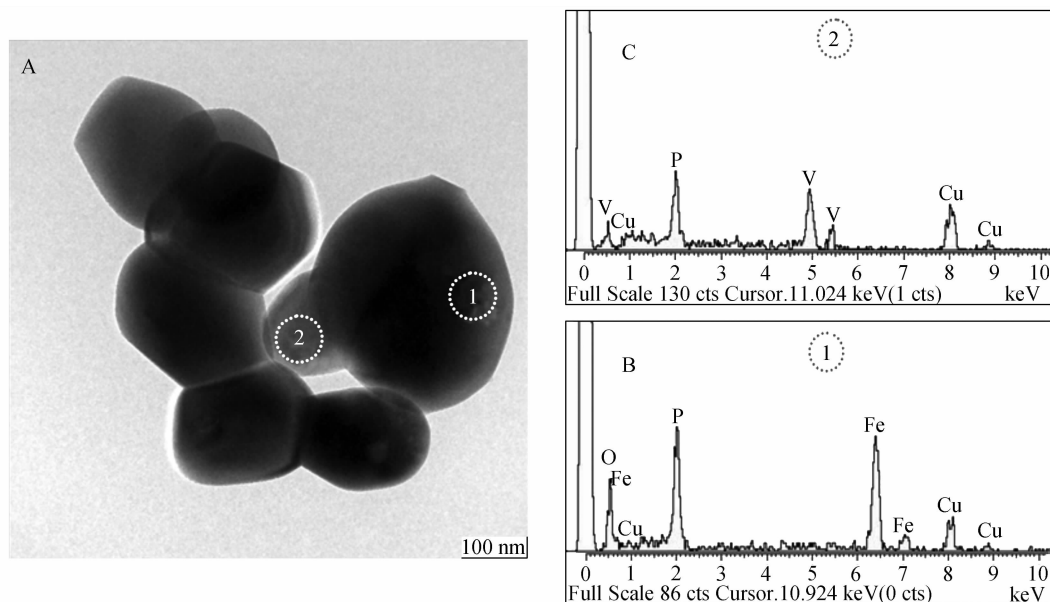
Fig. 6　TEM image of 0.95LiFePO$_4$·0.05Li$_3$V$_2$(PO$_4$)$_3$ composite (A) and EDS patterns of the framed regions (B,C) taken from A

4　Conclusions

The xLiFePO$_4$· yLi$_3$V$_2$(PO$_4$)$_3$ composites were systematically synthesized at 700 ℃ for 12 h in nitrogen atmosphere by solid state reactions using LiOH·H$_2$O, FeC$_2$O$_4$·2H$_2$O, NH$_4$VO$_3$ and NH$_4$H$_2$PO$_4$. The impurity of Li$_3$PO$_4$ occurred in the compounds over y = 0.1 and over y = 0.2, the characteristic peaks of Li$_3$V$_2$(PO$_4$)$_3$ became more obvious. The proper proportions of x and y were helpful to form conductive phase. The 0.95LiFePO$_4$·0.05Li$_3$V$_2$(PO$_4$)$_3$ compound showed more uniform distributed particles and smaller particle sizes than other compounds. The capacities of 162.7, 147.7, 122.3 and 87.4 mAh·g^{-1} were achieved at 0.2, 1, 5 and 10C rates, respectively.

References：

［1］　Padhi A K, Nanjundaswamy K S, Goodenough J B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries［J］. Journal of the Electrochemical Society, 1997, 144(4)：1188-1194.

［2］　Chung S Y, Bloking J T, Chiang Y M. Electronically conductive phospho-olivines as lithium storage electrodes［J］. Nature Materials, 2002, 1(2)：123-128.

［3］　Li T (李婷), Qian J F (钱江锋), Cao Y L (曹余良), et al. Electrochemical performance of Li$_{1-x}$M$_x$FePO$_4$ cathode materials synthesized by polymer pyrolysis poute

［J］. Journal of Electrochemistry (电化学), 2007, 13(2)：136-139.

［4］　Huang H, Yin S C, Nazar L F. Approaching theoretical capacity of LiFePO$_4$ at room temperature at high rates［J］. Electrochemical and Solid-State Letters, 2001, 4(1)：A170-A172.

［5］　Franger S, Cras F L, Bourbon C, et al. LiFePO$_4$ synthesis routes for enhanced electrochemical performance［J］. Electrochemical and Solid-State Letters, 2002, 5(10)：A231-A233.

［6］　Herle P S, Ellis B, Coombs N, et al. Nano-network electronic conduction in iron and nickel olivine phosphates［J］. Nature Materials, 2004, 3(3)：147-152.

［7］　Croce F, Epifanio A D, Hassoun J, et al. A novel concept for the synthesis of an improved LiFePO$_4$ lithium battery cathode［J］. Electrochemical and Solid-State Letters, 2002, 5(3)：A47-A50.

［8］　Park K S, Son J T, Chung H T, et al. Surface modification by silver coating for improving electrochemical properties of LiFePO$_4$［J］. Solid State Communications, 2004, 129(5)：311-314.

［9］　Yamada A, Chung S C. Crystal chemistry of the olivine-type Li(Mn$_y$Fe$_{1-y}$)PO$_4$ and (Mn$_y$Fe$_{1-y}$)PO$_4$ as possible 4 V cathode materials for lithium batteries［J］. Journal of the Electrochemical Society, 2001, 148(8)：A960-A967.

［10］　Wang G X, Bewlay S, Yao J, et al. Characterization of LiM$_x$Fe$_{1-x}$PO$_4$ (M = Mg, Zr, Ti) cathode materials prepared by the sol-gel method［J］. Electrochemical and

Solid-State Letters,2002,7(12):A503-A506.

[11] Ren M M,Zhou Z,Li Y Z,et al. Preparation and electrochemical studies of Fe-doped Li₃V₂(PO₄)₃ cathode materials for lithium-ion batteries[J]. Journal of Power Sources,2006,162(2):1357-1362.

[12] Barker J,Gover R K B,Burns P,et al. The effect of Al substitution on the electrochemical insertion properties of the lithium vanadium phosphate,Li₃V₂(PO₄)₃[J]. Journal of the Electrochemical Society,2007,154(4):A307-A313.

[13] Zheng J C,Li X H,Wang Z X. LiFePO₄ with enhanced performance synthesized by a novel synthetic route [J]. Journal of Power Sources,2008,184(2):574-577.

[14] Sun C S,Zhou Z,Xu Z G,et al. Improved high-rate charge/discharge performances of LiFePO₄ via V-doping[J]. Journal of Power Sources,2009,193(2):841-845.

[15] Liu K Y(刘开源),Huang J S(黄建书),Yang L(杨立). Effects of different carbon sources on performance of Li₃V₂(PO₄)₃/C composite cathode materials[J]. Journal of Electrochemistry(电化学),2010,16(1):30-34.

[16] Wang L N,Li Z C,Xu H J,et al. Studies of Li₃V₂(PO₄)₃ additives for the LiFePO₄ based Li ion batteries[J]. The Journal of Physical Chemistry C,2008,112(1):308-312.

[17] Yang M R,Ke W H,Wu S H. Improving electrochemical properties of lithium iron phosphate by addition of vanadium[J]. Journal of Power Sources,2007,165(2):646-650.

[18] Zhao T,Xu W,Ye Q,et al. Local structure of vanadium in doped LiFePO₄[J]. Journal of Synchrotron Radiation,2010,17:584-589.

[19] Zheng J C,Li X H,Wang Z X,et al. Novel synthesis of LiFePO₄-Li₃V₂(PO₄)₃ a composite cathode material by aqueous precipitation and lithiation[J]. Journal of Power Sources,2010,195(9):2935-2938.

[20] Bai Y(白莹),Yang J M(杨觉明),Qing C B(卿春波),et al. Electrochemical performances of C-coating and Co-doping LiFePO₄[J]. Journal of Electrochemistry(电化学),2011,17(3):334-338.

[21] Chen Y(陈宇),Wang Z L(王忠丽),Yu C Y(于春阳),et al. Electrochemical properties of Mo-doped LiFePO₄ cathode material[J]. Acta Physico-Chimica Sinica(物理化学学报),2008,24(8):1498-1502.

[22] Saidi M Y,Barker J,Huang H,et al. Electrochemical properties of lithium vanadium phosphate as a cathode material for lithium-ion batteries[J]. Electrochemical and Solid-State Letters,2002,5(7):A149-A151.

[23] Zheng J C,Li X H,Wang Z X,et al. Characteristics of xLiFePO₄·yLi₃V₂(PO₄)₃ electrodes for lithium batteries[J]. Ionics,2009,15(6):753-759.

[24] Yamada A,Koizumi H,Nishimura S,et al. Room-temperature miscibility gap in LiₓFePO₄[J]. Nature Materials,2006,5(5):357-360.

[25] Meethong N,Huang H Y,Speakman S A,et al. Strain accommodation during phase transformations in olivine-based cathodes as a materials selection criterion for high-power rechargeable batteries[J]. Advanced Functional Materials,2007,17(7):1115-1123.

自复合材料 xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ 的合成及电化学性能

马平平[1,2*]，刘志坚[1]，夏建华[1]，陈　宇[2]，胡　朴[2]，卢志超[1]，夏定国[3]

(1. 中国钢研科技集团公司, 北京 100081; 2. 北京中新联数码科技有限公司, 北京 100041;

3. 北京大学工学院, 北京 100871)

摘要：用固相法合成了不同比例的 xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$ 复合物. XRD、SEM 和电化学测试仪等分析方法表征了所有样品的特性. 结果表明，样品 0.95LiFePO$_4$·0.05Li$_3$V$_2$(PO$_4$)$_3$ 以 0.2C 的充放电倍率放电时具有 162.7 mAh·g^{-1} 的电化学容量. 同时该样品表现出了较其它样品更优异的循环稳定性和更良好的导电性能. 不同倍率下循环 60 周后，其容量保持率高达 98.7%. 颗粒细小的尺寸和均一的分布使得样品 0.95LiFePO$_4$·0.05Li$_3$V$_2$(PO$_4$)$_3$ 具有良好的电化学性能.

关键词：锂离子电池；复合物；掺杂；xLiFePO$_4$·yLi$_3$V$_2$(PO$_4$)$_3$