doi:10.1246/cl.2011.1087

Preparation and Electrochemical Performance of $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ Cathode Material

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$LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ was prepared via solid-state carbothermal reaction (CTR). F and V codoping did not alter the olivine structure of $LiFePO_4$ but reduced the particle size and improved the Li^+ diffusion coefficient. The cells based on this material showed higher discharge capacity, working voltage, rate capability, and better cyclic performance than that of undoped and F-doped materials.

Olivine-type $LiFePO_4$ is a promising cathode material for lithium-ion batteries due to low toxicity, low cost, high safety, and excellent reversibility.[1] However, the low electronic and ionic conductivities of pristine $LiFePO_4$ have been a barrier for its commercial application. To solve this problem, carbon coating and ion doping have been attempted. Carbon coating was an effective approach to improve the electronic conductivity of $LiFePO_4$.[2] Its disadvantage was the decrease of tap density of the material. So ion doping, such as Li or Fe sites occupied by Cr,[3] Mn,[4] and V,[5] was developed and was regarded as a good method of enhancing the conductivity. Recently, F substitution for PO_4^{3+} polyanion has given satisfactory results in enhancing the electrochemical performance.[6] However, fewer reports on the F–V codoping have been issued. In this study, $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ was prepared by a solid-state carbothermal reaction (CTR), and the effect of F and V codoping on the structure and electrochemical performance has also been discussed.

Stoichiometric amounts of Li_2CO_3, $(NH_4)_2HPO_4$, Fe_2O_3 with and without NH_4F, V_2O_5, together with 5 wt% of soluble starch were used as raw materials. The preparation is seen in ref 2. Finally, $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ (sample A), $LiFe(PO_4)_{0.95}F_{0.15}/C$ (sample B), and $LiFePO_4/C$ (sample C) were obtained, carbon content of which were about 2.49, 2.51, and 2.55 wt%, respectively, determined by thermogravimetric analysis. Electrochemical performance of the products was evaluated by constant current charge–discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) at room temperature. The working electrode (area: 575.20 mm^2, thickness: ca. 0.10 mm, mixture mass: 5.1 mg) consisted of as-synthesized products, acetylene black, and poly(tetrafluoroethylene) (PTFE) binder with a weight ratio of 80:15:5. The assembly of coin-type cells was similar to ref 2. The cells were charged and discharged at 0.1, 1, and 5 C rates in 2.5–4.2 V. The scan rate of CV was 1 mV s^{-1} in 2.5–4.2 V while the amplitude of EIS was 5 mV in the frequency range of 10^{-2}–10^5 Hz.

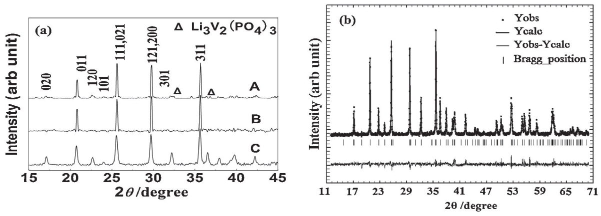

Figure 1. (a) XRD patterns of three samples and (b) Rietveld refinement of sample A.

Table 1. The lattice parameters and refinement factors of three samples

Samples	a/Å	b/Å	c/Å	Vol./Å^3	R_p/%	R_{wp}/%
A	10.26041	5.98003	4.68892	287.70	8.23	6.80
B	10.30395	5.98431	4.69241	289.34	11.20	8.68
C	10.32899	6.00538	4.69692	291.35	5.73	3.12

Figure 1a shows the XRD patterns of the samples. The diffraction lines of the products were indexed well in the orthorhombic *Pnma* space group (JCPDS 40-1499). Some impurities such as $Li_3V_2(PO_4)_3$ were detected in sample A, but no obvious impurity was found in the other two samples. Some peaks of the doped $LiFePO_4$, such as peaks (101) and (301), became weak or even disappeared, and their positions shifted slightly to the higher 2θ angles. This is different from other literature.[5–7] It may be related to the differences of dopant content and iron source. The lattice parameters and refinement factors of the materials are shown in Table 1, and Figure 1b presents the Rietveld refinement of sample A. It is noted that sample A had the smallest b and volume values, which benefitted the motion of Li^+ in the bulk $LiFePO_4$. Above all results suggest that F and V elements have been successfully incorporated into the $LiFePO_4$ lattices.

In order to further study the morphology of the doped materials, SEM and EDX analysis were performed, and the results are shown in Figure 2. It can be seen that two doped samples were sphere-like and that their particle size was about 200–500 nm (Figures 2a and 2b). The smaller particle size of $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ can shorten the pathway of Li^+ ion migration so that it can improve the ionic conductivity, resulting in a good electrochemical properties. The Fe, P, O, C, F with and without V elements were detected by EDX analysis on the surface of the products, and their contents (error <0.95%) are presented in Figures 2c and 2d. These data indicate that the F and V elements were introduced into the $LiFePO_4/C$ material. Unfortunately, the sites of F and V doping are still not precisely clear, but the effect on the electrochemical performance of the $LiFePO_4/C$ cathode material is obvious.

Figure 3 presents the charge–discharge profiles of three samples and cyclic performance of $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$

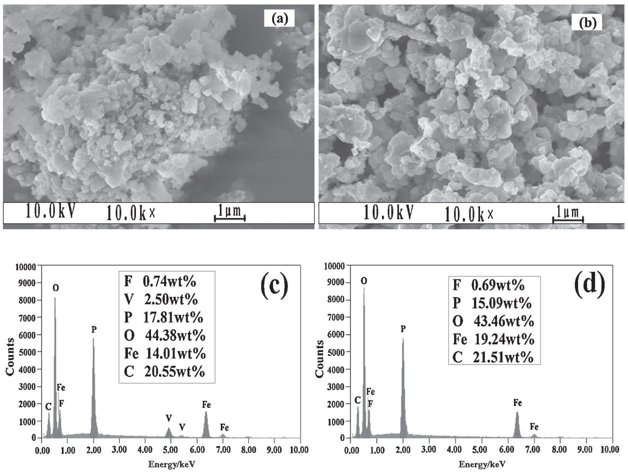

Figure 2. SEM images of $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ (a), $LiFe(PO_4)_{0.95}F_{0.15}/C$ (b), and corresponding EDX in (c) and (d).

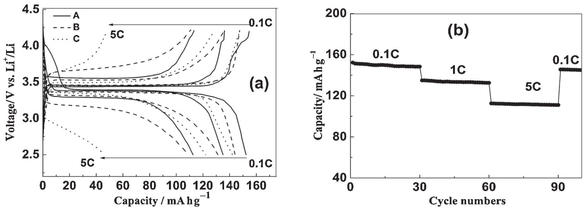

Figure 3. (a) Charge–discharge curves of three materials and (b) cyclic performance of sample A at 0.1, 1, and 5 C rates.

(sample A) under 0.1, 1, and 5 C rates. The sample A had a best discharge capacity of 152.3, 135, 112.6 mA h g^{-1} at 0.1, 1, and 5 C rates among the samples (Figure 3a). What is more, it had the higher discharge voltage of 3.394 (0.1 C), 3.382 (1 C), and 3.293 V (5 C), compared to 3.365 (0.1 C), 3.311 (1 C), and 3.17 V (5 C) for $LiFe(PO_4)_{0.95}F_{0.15}/C$ (sample B) and 3.371 (0.1 C), 3.292 (1 C), and 2.850 V (5 C) for $LiFePO_4/C$ (sample C). It should be noted that the V element offered a short voltage plateau at about 3.8 V under 0.1 C due to the appearance of $Li_3V_2(PO_4)_3$. In addition, sample A had a good cyclic performance (Figure 3b). Its capacity retention rates up to 30 cycles at different rates were 97.4% (0.1 C), 98.2% (1 C), and 98.6% (5 C). After heavy load (e.g., 5 C), it still delivered a capacity of 145.6 mA h g^{-1} at 0.1 C. All of these data indicate that F and V codoping improves the electrochemical performance of $LiFePO_4$ cathode material and decreases the polarization of the electrode.

Figure 4a shows the CV curves of three samples. All materials have similar CV curves with a couple of redox peaks. The redox peak of sample A was centered at 3.597/3.307 V, while 3.658/3.276, 3.752/3.227 V for sample B and C, respectively. Obviously, sample A shows narrower peak separation and sharper peaks than the others. This indicates an easier lithiation and delithiation in the F and V codoped materials. Besides, F and V codoping gave one pair of redox peak at ca. 4.06 V and two reduced peaks at 3.57 and 3.65 V due to the production of $Li_3V_2(PO_4)_3$ compounds. This is good for the high voltage plateau.

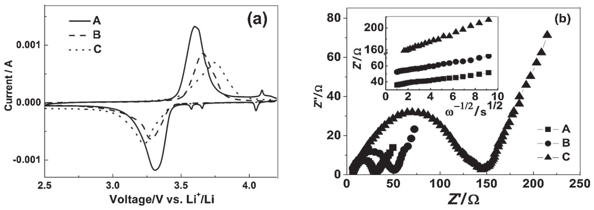

Figure 4. (a) CV curves and (b) EIS spectra of three materials.

The EIS of the samples was performed on a CHI660B electrochemical analysis instrument using two electrode configuration (lithium electrode was used as counter and reference electrode). Results are presented in Figure 4b. It is well known that charge-transfer resistance (R_{ct}) and lithium diffusion kinetics control the electrochemical behavior of $LiFePO_4$. The lithium ion diffusion coefficient (D) can be obtained by the low frequency straight line in Figure 4b according to the following equations:[8]

$$D = R^2T^2/2A^2n^4F^4C^2\sigma^2 \tag{1}$$

$$Z' = R_e + R_{ct} + \sigma\omega^{-1/2} \tag{2}$$

Where R, T, F, n, and C (1 M Li^+ concentration in electrolyte) are constant, A is the BET surface area of the materials, and R_e is electrolyte resistance. σ can be calculated from the plots of Z' against $\omega^{-1/2}$ (inset in Figure 4b). The D values of sample A was 1.53×10^{-12} cm^2 S^{-1}, while 9.54×10^{-13} and 9.18×10^{-14} cm^2 S^{-1} for sample B and C, respectively. The R_{ct} value of the former (about 24 Ω) is smaller than the latter (about 44 and 140 Ω). Obviously, F and V codoping helped to decrease the R_{ct} value and to make the motion of Li^+ fast, which benefited the electrochemical performance of $LiFePO_4$.

In summary, $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ (sample A) was prepared by a solid-state carbothermal reaction. F and V codoping does not change the olivine structure of $LiFePO_4$ but reduces the particle size. $LiFe_{0.9}V_{0.1}(PO_4)_{0.95}F_{0.15}/C$ delivers 152.3, 135, and 112.6 mA h g^{-1} at 0.1, 1, and 5 C rates and owns a D values of 1.53×10^{-12} cm^2 S^{-1}, which is higher than that of undoped and F-doped materials. Furthermore, it also has a higher working voltage and better cyclic performance. All these improvements on the electrochemical performance of the $LiFePO_4$ cathode material can be attributed to the effective F and V codoping.

References

1 A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **1997**, *144*, 1188.
2 M. Pan, Z. Zhou, *Mater. Lett.* **2011**, *65*, 1131.
3 S. Shi, L. Liu, C. Ouyang, D.-s. Wang, Z. Wang, L. Chen, X. Huang, *Phys. Rev. B* **2003**, *68*, 195108.
4 Y. Wang, D. Zhang, X. Yu, R. Cai, Z. Shao, X.-Z. Liao, Z.-F. Ma, *J. Alloys Compd.* **2010**, *492*, 675.
5 J. Ma, B. Li, H. Du, C. Xu, F. Kang, *J. Electrochem. Soc.* **2011**, *158*, A26.
6 X.-Z. Liao, Y.-S. He, Z.-F. Ma, X.-M. Zhang, L. Wang, *J. Power Sources* **2007**, *174*, 720.
7 L. Yang, L. Jiao, Y. Miao, H. Yuan, *J. Solid State Electrochem.* **2010**, *14*, 1001.
8 S. Zhang, C. Deng, B. L. Fu, S. Y. Yang, L. Ma, *J. Electroanal. Chem.* **2010**, *644*, 150.