Effect of Vanadium Modification on Electrochemical Performance of LiFePO₄/C

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A series of vanadium doped LiFePO₄/C were synthesized by the carbothermal reduction method combining with balling technique. Results show that only a little of vanadium substitutes for iron site in the crystal lattice of olivine LiFePO₄ and impurity phases are detected when the vanadium content is over 0.5 mol %. LiVOPO₄, the first impurity phase, is discovered as vanadium content ranges from 1 mol % to 5 mol % and disappears at high doping level. Li₃V₂(PO₄)₃ and vanadium oxide are gained when vanadium content is over 5 mol %. The special charge/discharge capacity and rate capability are enhanced on a certain extent by vanadium doping and LiFe_{0.975}V_{0.025}PO₄ shows the most outstanding property among all samples. The improvement of electrochemical performance of LiFePO₄ mainly resulted from the formation of impurity phases, LiVOPO₄, instead of the vanadium doping into LiFePO₄ lattice. Thus, excellent electrochemical performance can be achieved by optimizing the content of vanadium.

Keywords: LiFePO₄, Composites, Vanadium doping, X-ray diffraction, Impurity phase.

INTRODUCTION

Increasing attention is shown to LiFePO₄ as the next-generation cathode material in lithium-ion batteries due to its non-toxicity, safety, stability, high capacity and the abundance of raw materials¹. But its low electrical (electronic and ionic) conductivity limits the electrochemical properties according to the charge/discharge rate capacity and operating temperature². Decreasing particle size^{3,4}, doping supervalence-ion^{5,6} and surface modification^{7,8} are the most normal and efficacious way to overcome the weakness. Among these approaches, doping supervalence-ion is a convenient and effective way to improve the electrochemical performance of LiFePO₄.

Vanadium is a particularly attractive element to be considered for modifying the LiFePO₄, because it might substitute on the Fe site forming a VO₆ group⁹ or on the tetrahedral P site forming a VO₄³⁻ group¹⁰ and it exists over a wide range of oxidation state forming various electrochemical active vanadium compounds, such as V₂O₅¹¹, VO₂¹², V₂O₃¹³, LiVPO₄F¹⁴, LiVOPO₄¹⁵, Li₃V₂(PO₄)₃¹⁶, which can join in the process of Li⁺ insertion and desertion. Sun *et al.*⁹ confirmed with Rietveld refinement that V-ion substituted Fe-ion in the LiFePO₄ matrix structure and the improvement of electrochemical property definitely owed to the vanadium doping. Omenya *et al.*¹⁶ reported that excessive vanadium could form impurity phase, Li₃V₂(PO₄)₃, at high doping level and the solid-solution limit

depended on the preparation method and heat-treatment temperature. Besides Li₃V₂(PO₄)₃, other impurities are also discovered. Zhang *et al.*¹⁷ found that two impurity phases co-existed, Li₃V₂(PO₄)₃ and LiVOPO₄, when vanadium content ranged from 5 mol % to 10 mol %. Ma *et al.*¹² discovered that the state and compound of vanadium changed with the doping level. V⁴⁺ substituted for Fe (LiFe_{1-x}V_xPO₄, 0 < x < 0.07) within the solid solubility, VO₂ distributed on the surface of the V-doped LiFePO₄ beyond the solid-solution limit and the formation of the secondary phase Li₃V₂(PO₄)₃ coexisted with the V-doped LiFePO₄ when vanadium content was over 11 mol %. Jin *et al.*¹³ stated that vanadium did not step into the crystal lattice and the improvement of electrochemical performance for the cathode eventually resulted from the co-coating of carbon and V₂O₃.

In this work, a series of vanadium doping LiFePO₄/C were synthesized with different levels. We demonstrated the existence of two impurity phases by XRD. Moreover, we researched the influence of vanadium compounds on electrochemical performance of LiFePO₄ and discuss the major factor on enhancing the electrochemical performance in our paper.

EXPERIMENTAL

Iron oxide (Fe₂O₃), lithium dihydrogen phosphate (LiH₂PO₄) and vanadium pentoxide (V₂O₅) with Li:Fe:V:P molar ratios of 1:1-x:x:1 (x = 0, 0.005, 0.01, 0.015, 0.025,

0.05, 0.1) were mixed with citric acid through a planetary balling process for 5 h, followed by heat-treatment at 700 °C for 12 h under pure nitrogen to obtain $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$. Excessive citric acid (5 wt %) as the carbon source was mixed with precursors by balling for 5 h. Subsequently, the mixtures were heated at 700 °C for 10 h in N_2 and the carbon coated $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$ were synthesized.

The crystallographic structural characterization was analyzed by X-ray diffraction (XRD, Rigaku D/max-2500/pc, CuK radiation) and X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, Al K α). The particle morphology and surface texture of samples were observed with field-emission scanning electron microscope (FE-SEM, S-4800).

The electrochemical performance of $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4/\text{C}$ cathode material was evaluated using columnar simulation cells. Active material powder (80 wt %) was mixed with acetylene black (10 wt %) and poly (vinylidene fluoride) binder (10 wt %) in N-methyl-2-pyrrolidone (NMP) to obtain slurry. The slurry was coated onto an aluminum foil and dried under vacuum at 120 °C for 12 h. Finally, the laminate was cut into round discs (1 cm in diameter) to be used as the working electrode. The electrolyte was 1 mol L⁻¹ LiPF_6 dissolved in the mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) with ratio of 1:1. Histogram cells were assembled in the glove box filled with argon gas. Charge-discharge tests were conducted on a battery test system (CT2001A, LAND, China) with cut-off voltages of 2.4 and 4.2 V (vs. Li/Li^+) at different current rates at room temperature. Cyclic voltammetry (CV) measurements were performed on an electrochemical working station (LK2005, LANLIKE, China) at a slow scanning rate of 0.1 mV s⁻¹ within a voltage range of 2.4–4.2 V. And the electrochemical impedance spectroscopy (EIS) was employed to characterize the interfacial resistance of cathode using a Chenhua CHI660A electrochemical workstation over the frequency range from 1 MHz to 0.01 Hz with amplitude of 10 mV ms⁻¹ at room temperature.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the as-prepared samples with different vanadium contents in the range of 0–10 mol % are shown in Fig. 1. It is revealed that the composition phases in $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4/\text{C}$ samples vary with the vanadium content. All diffraction peaks of pristine LiFePO_4/C powders and $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4/\text{C}$ with low vanadium content ($x = 0.005$) can be indexed with an ordered orthorhombic LiFePO_4 phase (Pnmb). No visible difference can be detected between the XRD patterns of two samples, indicating that V had doped into the host lattice. Impurity phase is formed when the vanadium content is over the solid solution limit and the peaks of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are distinctly detected in the high level vanadium-doped LiFePO_4/C samples ($x \geq 0.05$). But another impurity appears before the presence of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, which could be the lithium vanadium oxide or lithium vanadium phosphate and it disappears when the vanadium is over 5 mol % (Fig. 1b). Comparing the diffraction peaks of the impurity phase with the standard PDF card, it could be LiVOPO_4 . The result reveals that only little of vanadium step into the lattice and the formation of vanadium impurity changes with the doping level.

Fig. 1. XRD patterns of $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4/\text{C}$ ($x = 0, 0.005, 0.01, 0.015, 0.025, 0.05, 0.1$)

To prove our statement in further step, the selected $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4$ ($x = 0.025, 0.05, 0.1$) samples were dissolved by dilute hydrochloric acid, washed with deionized water and dried under vacuum to obtain the remainders. Fig. 2 shows the XRD patterns of the remainders which could be consisted of carbon and vanadium oxide. According to our analysis, the XRD patterns don't match to a certain compound, indicating that a series of complicated vanadium oxides coexist in the acid lysates. Although the composition can't be known definitely, the patterns can help us to conclude whether the same vanadium composition is formed in the selected samples. Compared with peaks of lysates, the components in sample a ($x = 0.025$) are different from sample b and c ($x = 0.05, 0.1$), demonstrating that the vanadium composition in $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4/\text{C}$ is different from the one in $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4/\text{C}$ and $\text{LiFe}_{0.9}\text{V}_{0.1}\text{PO}_4/\text{C}$, consistent to our former opinion. It is still not solved that why the vanadium phase is changed with the content. It is possible that the formation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ needs a stated vanadium content and energy. When the vanadium content doesn't reach the level or the surface energy is too high to obtain, an intermediate product, LiVOPO_4 , is formed and it transforms into $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ when the condition is proper. The structure transformation of LiVOPO_4 to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is successfully carried out by Kuo *et al.*¹⁸. The possible reaction mechanism is listed as follow¹⁹:

Fig. 2. XRD patterns of acid hydrolysis lystates from LiFe_(1-x)V_xPO₄ (x = 0.025, 0.05, 0.1)

The selected samples were applied by XPS to ensure the valence and state of vanadium in the LiFe_(1-x)V_xPO₄/C, which is shown in Fig. 3. The typical two-peak structure of V 2p XPS spectra are V 2p_{3/2} peak and V 2p_{1/2} peak. Compared the binding energy values of V 2p_{3/2} and V 2p_{1/2} in the two samples with the standard ones, the valences of vanadium in the two samples are both between 3⁺ - 4⁺, which means that V³⁺ and V⁴⁺ co-exist in the material. The presence of V⁴⁺ in the LiFe_{0.975}V_{0.025}PO₄ is due to LiVOPO₄. And the V⁴⁺ in LiFe_{0.9}V_{0.1}PO₄ maybe originate from kinds of vanadium composition with high valence and could not be analyzed by XRD, such as VO₂, gained by the decomposition of LiVOPO₄. They cannot be detected by XRD because of their low content and poor crystallization.

Fig. 4 is the FE-SEM images of the LiFe_(1-x)V_xPO₄ (x = 0, 0.025, 0.05, 0.1). Low level vanadium doping doesn't make apparent change on the morphology of LiFePO₄, that is to say, vanadium doping and the formation of LiVOPO₄ don't influence the crystal growing direction.

Electrochemical performance: The galvanostatic discharge curves measured at 1 C for LiFe_(1-x)V_xPO₄ samples are shown in Fig. 5. The first discharge capacity is enhanced

Fig. 3. XPS core level of V 2p for LiFe_{0.975}V_{0.025}PO₄ and LiFe_{0.9}V_{0.1}PO₄

by doping and vanadium content is found to have a dramatic effect on the capacity. V substitutes for Fe and locates into the crystal lattice when the vanadium content is low, which is beneficial to improve the electrochemical performance, as the first discharge capacity of LiFePO₄/C and LiFe_{0.995}V_{0.005}PO₄/C are 124.6 and 132.8 mAh g⁻¹, respectively. Impurity phases present by increasing the vanadium doping level and the different phase has different effect on the capacity ability. According to the result of XRD, LiVOPO₄ is formed when the vanadium content is below 5 mol % and LiFe_{0.975}V_{0.025}PO₄ shows excellent performance, whose first discharge capacity is up to 166.3 mAh g⁻¹. When the vanadium content is over 5 mol %, a secondary phase, Li₃V₂(PO₄)₃, appears and LiVOPO₄ absents. As seen in Fig. 5, not only a discharge plateaus at 3.35 V for intercalation of Li⁺ into LiFePO₄ but also three typical discharge plateaus around 3.57, 3.65 and 4.02 V for intercalation of two Li⁺ reversibly into Li₃V₂(PO₄)₃ based on the V³⁺/V⁴⁺ redox couple are distinctly observed in curves of the LiFe_{0.95}V_{0.05}PO₄/C and LiFe_{0.9}V_{0.1}PO₄/C, which matches well with the charge/discharge profiles of Li₃V₂(PO₄)₃/LiFePO₄ composites. The first discharge capacity of LiFe_{0.95}V_{0.05}PO₄/C and LiFe_{0.9}V_{0.1}PO₄/C are 158.4 and 136.1 mAh g⁻¹, respectively. Obviously, LiVOPO₄ is more efficient than Li₃V₂(PO₄)₃ to the improvement of electrochemistry performance of LiFePO₄. Because of the long heat-treating time and high

Fig. 4. SEM images of LiFePO₄/C (a), LiFe_{0.975}V_{0.025}PO₄/C (b) and LiFe_{0.95}V_{0.05}PO₄/C (c)

Fig. 5. Relationship between first discharge capacity and voltage measured at 1C for $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4$ ($x = 0, 0.005, 0.01, 0.015, 0.025, 0.05, 0.1$)

temperature, the solid-solution concentration is low and the impurity phases appear when the vanadium is only over 0.5 mol %. Thus, it can be concluded that the enhancement of the electrochemical performance should be mainly due to the existence of a small amount of impurity phase, especially LiVOPO_4 , rather than the doping of V in the host lattice.

To analyze the cyclic performance of the electrodes, selected samples are measured at different C rates and the results are shown in Fig. 6. The vanadium doped LiFePO_4 samples (2.5, 5 mol %) show better rate capacity than the pristine, especially at high C rate (5 C, 10 C). The transport of electrons from the particle surface to the current collector is the critical step, particularly at high current rate²⁰. And the vanadium composition can improve the graphite degree of carbon to increase the electron transportation. Thus, the promotion is obvious at high rate, owing to the effect of impurity phase on the electron transport on the particle surface. Although $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4$ still has an advantage over $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4$ at high rates, the discharge capacity of $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4$ goes downhill, due to the poor cyclic performance of LiVOPO_4 .

Cyclo-voltammogram profiles reflect not only the electrochemical properties of the active material but also the electrochemical activity of the entire electrode. The cycle

Fig. 6. Cycling performance of $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4$ measured from 1C to 10C

voltammograms for the selected samples with a scanning rate of 0.1 mA s^{-1} are shown in Fig. 7. Only one couple of anodic and cathodic peaks, corresponding to the phase transition process of LiFePO_4 and FePO_4 , are observed in the CV profiles of the pristine LiFePO_4/C and the $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4/\text{C}$ (Fig. 7a). Because of the low content of LiVOPO_4 in $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4/\text{C}$, no anodic or cathodic peak of Li^+ extraction/insertion reaction in LiVOPO_4 is found in the curve. With an increase in the vanadium concentration to 5 mol %, three additional reduction peaks, associating with reduction potentials of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, are detected in Fig. 7b. Compared with other samples, especially the pristine, $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4/\text{C}$ shows a higher peaks intensity and a smaller difference between the reduction and oxidation potentials (0.205 V), indicating that the electrode reaction has a higher rate constant and a better reversibility of the Li^+ extraction/insertion reactions. This is the reason why $\text{LiFe}_{0.975}\text{V}_{0.025}\text{PO}_4/\text{C}$ has the most excellent electrochemical property.

Fig. 7. CV profiles of $\text{LiFe}_{(1-x)}\text{V}_x\text{PO}_4$ at the scanning rate of 0.1 mA s^{-1} and in a potential window of 2.4-4.2 V (vs. Li^+/Li)

Fig. 8 shows the electrochemical impedance spectra (EIS) of the LiFePO_4/C and vanadium doped LiFePO_4/C electrode material after 5th cycle. EIS curves are composed of a depressed semicircle in high frequency region and a straight line in low frequency region. An intercept at the Z_{re} axis in the high frequency region corresponds to the ohmic resistance of

the electrolyte, followed by a semicircle in the middle frequency range, indicating the charge transfer resistance and a straight line in the low frequency region, related to the Warburg impedance due to the diffusion of the lithium-ion in the bulk of the electrode material. The impedance spectra can be described by the equivalent circuit presented in the inset picture, where R_s represents ohmic resistance, R_{ct} represents the charge transfer resistance, Z_w represents the Warburg impedance and the constant phase element CPE is placed to represent the double layer capacitance and passivation film capacitance²¹. The fitting results were analyzed by Zview-Impedance 2.80 software and R_{ct} values are listed in Table-1. The charge transfer resistance is related to complex reaction of charge transfer process between the electrolyte and the active materials²². Compared with the pristine, the impedance obviously decreases in the charge/discharge process with the appropriate amount of vanadium doping. The smaller charge transfer resistance indicates that lithium-ion and electron transfer are more feasible on the electrode and V-doping and impurity phases are benefit to overcome the restriction of kinetics in the charge/discharge process and improve the electrochemical activity of the material. But the improvement isn't continuous with the increasing vanadium doping level. The value of R_{ct} increases when vanadium content is over 2.5 mol %, which is consistent with the results of charge/discharge testing.

TABLE-1
IMPEDANCE PARAMETERS OF SAMPLES

Sample	$R_{ct}(\Omega)$	$j^0(\text{mA g}^{-1})$
LiFePO ₄ /C	927.8	27.7
LiFe _{0.98} V _{0.015} PO ₄ /C	559.5	45.9
LiFe _{0.975} V _{0.025} PO ₄ /C	264.5	97.1
LiFe _{0.95} V _{0.05} PO ₄ /C	470.3	54.6
LiFe _{0.9} V _{0.1} PO ₄ /C	804.7	31.9

The exchange current density (j^0) is a very important parameter of kinetics for electrochemical reaction and can measure the catalytic activity of electrodes. It is calculated using the following formula:

$$j^0 = \frac{R \cdot T}{n \cdot m \cdot R_{ct} \cdot F}$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (298 K), n is the charge transfer number per molecule during the intercalation which is 1 for LiFePO₄, m is the mass of active material and F is the Faraday's constant ($96,500 \text{ C mol}^{-1}$). The results are listed in Table-1 and the LiFe_{0.975}V_{0.025}PO₄/C exhibits a higher j^0 , 97.1 vs. 27.7 mA h g^{-1} , than pure LiFePO₄/C, implying that the catalytic activity and the reversibility of LiFe_{0.975}V_{0.025}PO₄/C electrode are improved by doping V. The improvement of electrochemical performance of electrodes results from the existence of impurity phases which accelerate the catalytic activity and electron transfer on the particle surface. And LiVOPO₄, as a impurity phase, shows more prominent influence on the charge/discharge capacity, compared with Li₃V₂(PO₄)₃. The EIS results indicate that doping with an appropriate amount of V-ion can improve the electrochemical activity of LiFePO₄/C composite.

Fig. 8. Electrochemical impedance spectra profile of samples and equivalent circuit

Conclusion

LiFePO₄/C doped with different vanadium content is successfully synthesized by the carbothermal reduction method. The XRD results indicate that only a little of vanadium substitutes the iron into the crystal lattice and the impurity phase exists when the vanadium content is over 0.5 mol %. The formation of impurity phase, LiVOPO₄ or Li₃V₂(PO₄)₃, depends on the doping level and has a dramatic effect on electrochemical performance. The valences of vanadium in LiFe_{0.975}V_{0.025}PO₄/C and LiFe_{0.9}V_{0.1}PO₄/C are both between 3⁺-4⁺, according to the XPS result. LiFePO₄/C doped with 2.5 mol % vanadium not only shows the best special capacity and rate capability, but also has higher ionic conductivity and reversibility of redox reaction, owing to the presence of LiVOPO₄. Therefore, the enhancement of the electrochemical performance should be mainly due to the existence of a small amount of impurity phase, especially LiVOPO₄, rather than the doping of vanadium in the host lattice.

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