Studies of V doping for the LiFePO$_4$-based Li Ion batteries

Ning Hua [a,b,c], Chenyun Wang [a,b,c], Xueya Kang [b,c,*], Tuerdi Wumair [b,c], Ying Han [b,c]

[a] Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] Xinjiang Key Laboratory of Electronic Information Materials and Devices, Urumqi, Xinjiang 830011, China

ARTICLE INFO

ABSTRACT

Alien atom doping has been adopted to modify the electrochemical performance of olivine type LiFePO$_4$ for cathode material. Here, we report that vanadium-doping can improve the performance of LiFePO$_4$/C immensely. LiFePO$_4$/C and V-doped LiFePO$_4$/C cathode materials were first synthesized by carbothermal reduction method. Physico-chemical characterizations were done by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Electrochemical behavior of the cathode materials was analyzed using cyclic voltammetry (CV) and galvanostatic measurements. ICP and XRD analyses indicated that V ions were sufficiently doped in LiFePO$_4$ and did not alter its crystal structure and exhibited the variation of lattice parameters with the doped degree. From the CV, the V ion doping affected the Li$^+$ ionic diffusion coefficient during both the delithiation and lithiation processes and it became larger with an appropriate amount doping. From the results, it is noted that vanadium ions doping can improve performance of LiFePO$_4$, especially on the aspect of stable cycle-life at higher C rate.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

For their great potential to be used as power sources for electric vehicles and hybrid electric vehicles, lithium ion batteries have captured a large share of the rechargeable battery market. The cathode material is a crucial factor of performance and safety of Li ion batteries, which has the greatest potential for improvement. As a result, phosphate-based materials have attracted considerable interest as a promising new class of cathode materials. Among them, the LiFePO$_4$ with olivine structure are particularly in the center of attention [1,2]. The main advantages of LiFePO$_4$ are high theoretical capacity (170 mAh g^{-1}), low cost, excellent cycling stability, low toxicity and environmentally benign nature [3–5]. However, there are still some drawbacks of this material, such as poor electronic conductivity and low Li ion motion ability [2,6,7], which are in need to be improved before its commercial applications. The ways of doping supervalent cations, synthesis of nanocrystalline grains and electronic conductive carbon coating have been regarded as effective methods to enhance its electronic conductivity and Li-ion diffusivity rate [8–12].

Meanwhile, various synthesis routes have been proposed to prepare LiFePO$_4$ for enhancing its ionic/electronic conductivity by optimization of particles with suitable preparation procedures. Besides the traditional solid-state reaction synthesis routine, alternative synthesis processes including sol–gel preparation [13,14], co-precipitation [15,16], microwave processes [17], hydrothermal reaction [18,19], vapor deposition procedure [20], etc. have been developed continually. However, many obstacles have been encountered for synthesis methods reported from a laboratory process to large-scale manufacture because of the complicated synthesis techniques, the hard-controlled synthesis situation and the relatively high cost Fe(II). Some reported methods were not fit for the large-scale manufacture of LiFePO$_4$ cathode material. The solid-state reaction route is the most effective method to expand to large-scale industrialization at present.

As is known to all, the electronic conductivity of LiFePO$_4$ is much higher than ionic. And the discharge capacity of LiFePO$_4$-based electrodes drops approximately linearly with average particle size, regardless of the presence/absence of a native carbon coating [21]. However, only controlled particle size is complicated for mass production. Based on the idea that electrochemical reaction in the cathode is composed of connections of intra- and inter-particle conduction and using a simple synthesis method, we have recently proposed the combination of carbon-coating surface modification by thermal decomposition of sucrose and the particle substitution of V ion which enhances the bulk conductivity. It was found that the initial capacity, the capacity fading with cycling and the polarization were significantly improved with the combined modification. In this work, we have reported, through a carbothermal reduction method with mechanical activation, V ions were doped to pursue a

Table 1
V ion contents of precursors determined from ICP.

Samples	b	c	d	e
Target values (at.%)	1	2	3	4
Practice values (at.%)	0.95	1.96	2.96	3.97

kind of sufficient and homogenous doping way. The structure, the electrochemical properties and effects of a substitution of Fe with V have been studied carefully.

2. Experimental

V-doped LiFePO$_4$ samples were prepared by a carbothermal reduction route from the starting material like Li$_2$CO$_3$, Fe$_2$O$_3$, NH$_4$H$_2$PO$_4$, V$_2$O$_5$ and 10 wt% sucrose (all chemicals of 99.5% purity) and final product was expected to contain ca. 2 wt%. The stoichiometric amounts of them (Li, Fe, P) and V$_2$O$_5$ (V ion to Fe ratio value from 0 to 4 at.%) were mixed together by a planet mixer (QM-BP) for 15 h. Liquid medium of ethyl alcohol was employed. After milling, the mixtures were dried in oven at 60 °C for 12 h in the air. Then they were transferred to a temperature-controlled tube furnace equipped with flowing argon and heated at 350 °C for 2 h, and then heated at 700 °C for 12 h. The products were removed from the furnace after cooling, named as a, b, c, d, and e according to the dopant content of V ion 0, 1, 2, 3, 4 at.%.

The structures of the as-prepared materials were characterized by XRD (D8-Advance, Bruker) using Cu-Kα radiation in the range of 15–60° with a scanning rate of 2° min^{-1}. The content of V ion was investigated by inductively coupled plasma (ICP, IRIS intrepid XSP, Thermo Electron Corporation). The morphologies and microstructure of powder particles were observed by SEM (LEO-1430VP) and TEM (H-600, Hitachi Limited).

The cathodes were prepared by mixed with 85 wt% active material, 10 wt% of acetylene black as a conducting material, and 5 wt% of polyvinylidene difluoride as a binder in N-methyl-2-pyrrolidinone solvent to form homogeneous slurry. Then the slurry was coated onto an aluminum foil and cut into 10 mm diameter and then dried by a vacuum oven at 120 °C for 12 h. Finally, coin-type cells 2025 were assembled in a glove box, using lithium foil as the counter electrode, celgard 2400 as the separator, and LiPF$_6$ (1 M) mixed with 1:1:1 (v/v/v) ratio of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC). The electrochemical properties of the cells were characterized using cyclic voltammetry at scan rates of 0.05–1.0 mV s^{-1} (CHI660) and galvanostatic charge and discharge studies over a voltage rang of 2.3–4.3 V (BTS-5 V/1 mA).

3. Results and discussion

The ICP results of different precursor are shown in Table 1, it is clear that V contents of samples 0.95, 1.96, 2.96, 3.97 at.%, respectively, are highly close to target values, 1, 2, 3 and 4 at.%, which demonstrates our method could hold the content of dopant with more accurate.

Fig. 1 shows the X-ray diffraction patterns of V-doped LiFePO$_4$ samples. All peaks can be indexed as an olivine phase with an
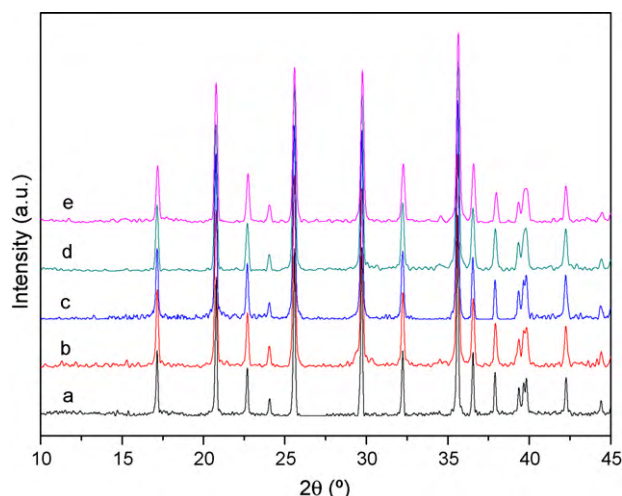

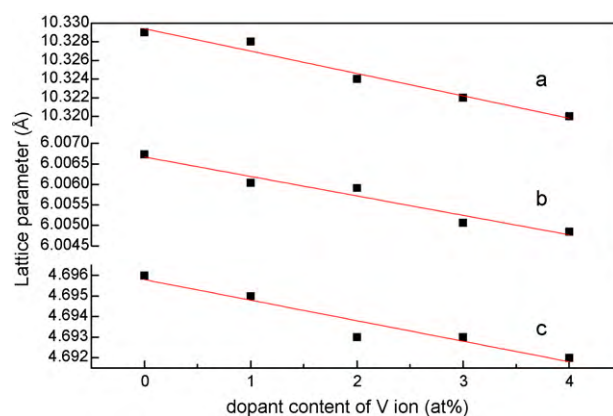**Fig. 1.** X-ray diffraction patterns of various V ion content on samples.

Fig. 2. Variation of lattice parameters with the substitution degree.

ordered orthorhombic structure belonging to the phase group *Pnma*. The absence of any other signals indicates there are no unwanted impurity phases, such as V^{5+} related compounds because of the low doping concentration. There is no evidence of diffraction peaks for carbon, indicating the carbon is amorphous. In this work, Fe^{3+} in the precursor was reduced to Fe^{2+} with the help of strong reductive agent, which was generated by sucrose decomposition and stuck particles of the reactant together. The variation of the refined lattice parameters with the V ion substitution degree is shown in Fig. 2. The lattice parameters decreased almost linearly with the amount of V ion substitution. It is found that the lattice parameters have diminished obviously, that is, the value of a, b and c are both decreased on increasing V ion contents. The possible reason is that V^{5+} permeated into the lattice of LiFePO$_4$/C and substituted Li$^+$ or Fe^{2+} as substitution ions when V$_2$O$_5$ was dropped into furnace and diffused permeated on the surface of the precursor. The ionic radius of V^{5+} is 0.059 nm and smaller than 0.076 nm of Li$^+$ or 0.078 nm of Fe^{2+}. The volume contraction of doped materials should be attributed to the increased vacancies, which would like to benefit the diffusion of Li$^+$ by shortening the pervasion routes.

Fig. 3 shows the influence of various V ion contents on the SEM images of samples. As shown, the particle morphologies of samples are near-spherical, more than one hundred nanometer size and various agglomeration degrees different from every picture. That is to say, the morphology of LiFePO$_4$ can be easily controlled during the calcinations and V ions in the solid solution inhibit particles to conglomerate, which is conductive to shorten the lithium diffusion distance. The morphology of LiFePO$_4$ is of great importance to its electrochemical performance and homogenous spherical LiFePO$_4$ is preferred. Based on our result, such LiFePO$_4$ was easily obtained by employing our preparation method by ball milling time, revs and ball/powder weight ratio. It is obvious that particles of sample d, prepared with 3 at.% V, obtained the optimum distribution.

It is reported that the electronic conductivity is much higher than ionic, which means electrons move ahead of the lithium ions [21]. Besides, it is that there is interplay between electrons and ions, in order to maintain electro neutrality of the crystal lattice, the accelerated electrons are slowed down and the lithium ions will become faster by an internal electric field [22]. Moreover, the shorter lithium ions diffusion distances as discussed above, will benefit lithium insertion and de-insertion. Therefore, both the conductivities of electrons and lithium ions would like to increase more or less, and a better electrochemical performance and cycle ability at various C rates of samples should be expected. The TEM micrograph of V-doped sample d is shown in Fig. 4. The crystal of LiFePO$_4$ appears dark, and the carbon coating appears gray in the TEM picture. The thickness of carbon coating is about 10 nm and it appears as an envelope surrounding the whole crystal.
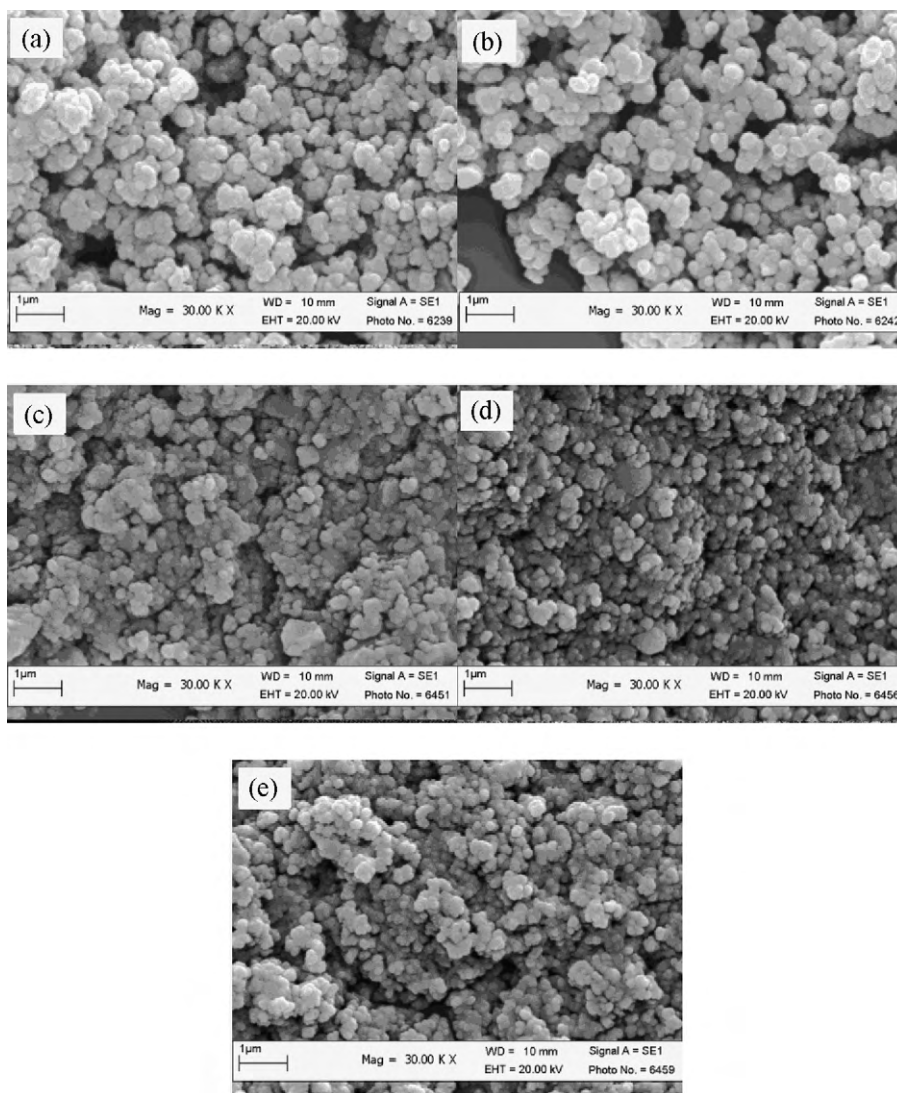
Fig. 3. the SEM images of samples with various V ion contents.

Fig. 5 shows the first charge–discharge capacity plateaus vs. the working voltage at 1 C. The batteries were measured at room temperature, about 20 °C. Extremely flat voltage plateaus at ca. 3.4 V for charging and ca. 3.3 V for discharging are observed. The specific discharge capacities of samples (a, b, c, d and e) are 120.9, 133.4, 138.2, 140.9 and 130.2 mAh g^{-1}, respectively. Under the assumption that only Fe^{2+}/Fe^{3+} redox contributes to the electrochemical reaction, the calculated values should be almost invariable. It was clear that the utilization of Fe^{2+}/Fe^{3+} redox reaction was improved by the doping. It was also seen that the V ion doping reduced the polarization that was defined as the separation between charging and discharging plateaus. These results indicated that kinetic limitations on the electrochemical redox reaction were relaxed with the V ion doping. Besides, the high performance of sample d is partially attributed to its uniform morphology with small particles having a thin and efficient carbon coating as shown in Fig. 4.

The cyclic voltammograms of various V ion content are shown in Fig. 6, where the sweeping rate was fixed at 0.05 mV s^{-1}. Both oxidation and reduction current peaks were observed around 3.5 V and the current peak shape implied that the electrochemical lithiation/delithiation of the samples proceeded with two-phase reaction. The peak value increased with the doped degree up to the 0.03, took a maximum and then decreased with further increase in

the doping. On the V ion doping, the oxidation peak position first shifted higher then lower, and the reduction peak potential was the same as oxidation. The peak potential separation corresponded to the polarization degree, which varied with the doped degree.

In order to reckon the Li$^+$ diffusion coefficient in V ion doped samples, the cyclic voltammetry was carried out at 20 °C, where the sweeping rate was changed, and typical results are shown in Fig. 7, which is sample b. As the sweeping rate was raised, the oxidation peak shifted higher and the reduction peak shifted lower. Fig. 8 shows the relationship between the peak current and the sweeping rate and it was shown that the peak current was proportional to the square root of the sweeping rate. This suggested that the CV result was related to Li$^+$ diffusion within the active material. We can use these data to reckon the effective diffusion coefficient D_{Li} of samples. The variation of the effective diffusion coefficient of the oxidation and reduction reactions was shown in Fig. 9. The obtained values of the D_{Li} were on the order of 10^{-13} cm^2 s^{-1}, and in the same order as the reported values [23–24]. It was found that the D_{Li} on the oxidation reaction was slightly larger than that value on the reduction process, irrespective to the V ion doped degree. From this, it was clarified that the discharging reaction in the olivine compound was slower than the charging reaction. Next, it was found that D_{Li} in both charge and discharge reactions was increased with V ion
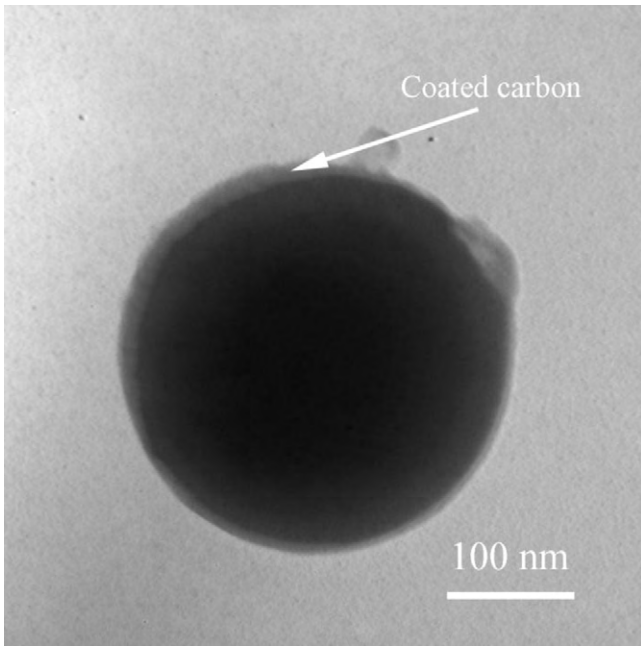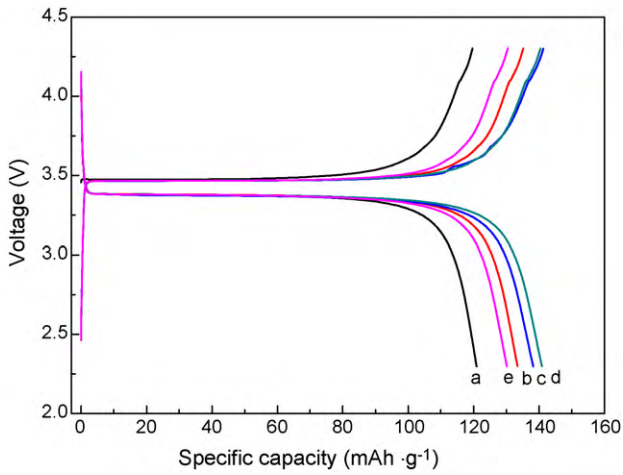
Fig. 4. the TEM micrograph of sample d.

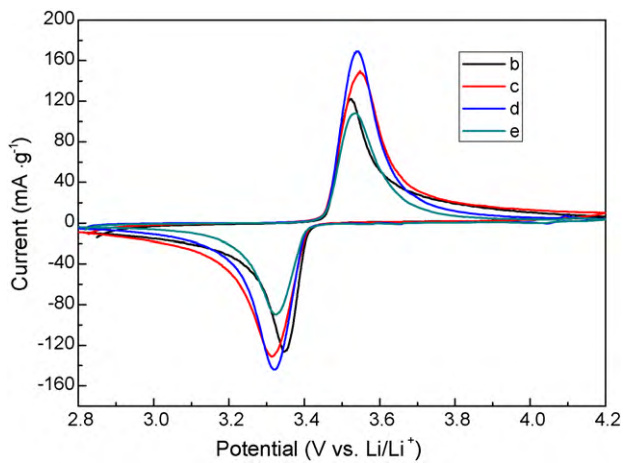**Fig. 5.** The first charge–discharge curves of samples at 1 C.

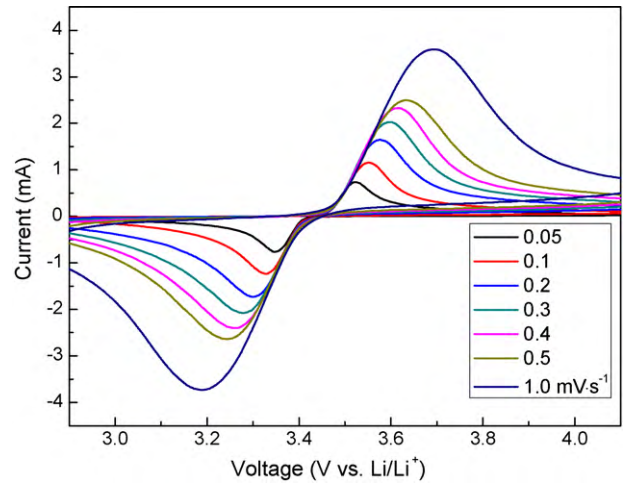**Fig. 6.** CVs of various V ion content with a constant sweeping rate of 0.05 mV s^{-1}.

Fig. 7. CVs of sample b with various sweeping rate from 0.05 to 1.0 mV s^{-1}.
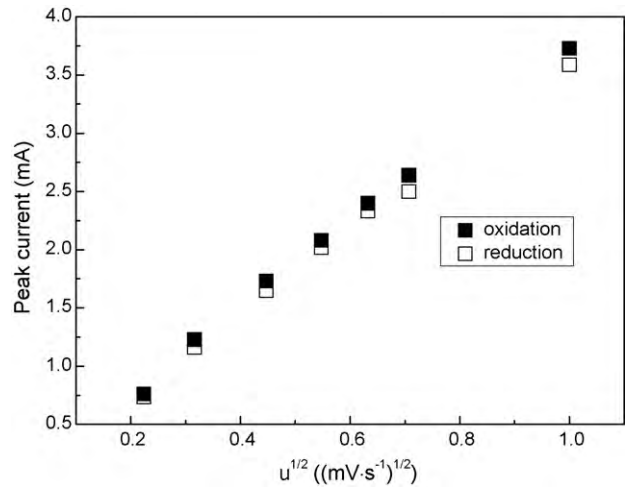

Fig. 8. Plot of peak current to the square root of the sweeping rate.

doped, besides it took a maximum around $x = 3$ at.%. Therefore, the V ion doping may improve the ionic conduction in olivine compound on both delithiation and lithiation processes. It was also possible to explain the experimental facts about the electrochemical performance improvement of the V ion doped from the viewpoint of the ionic conduction, which was shown in Fig. 5.
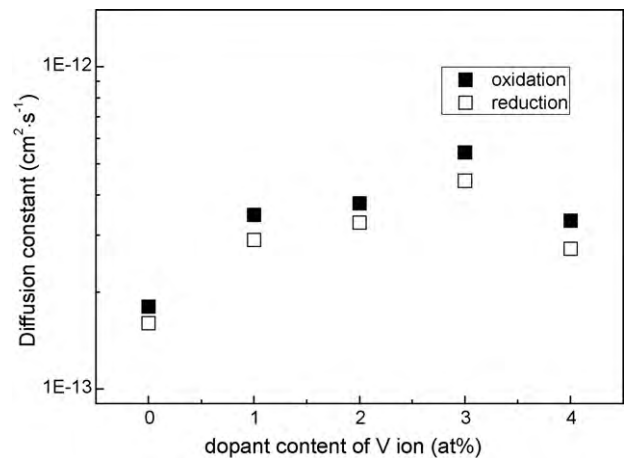

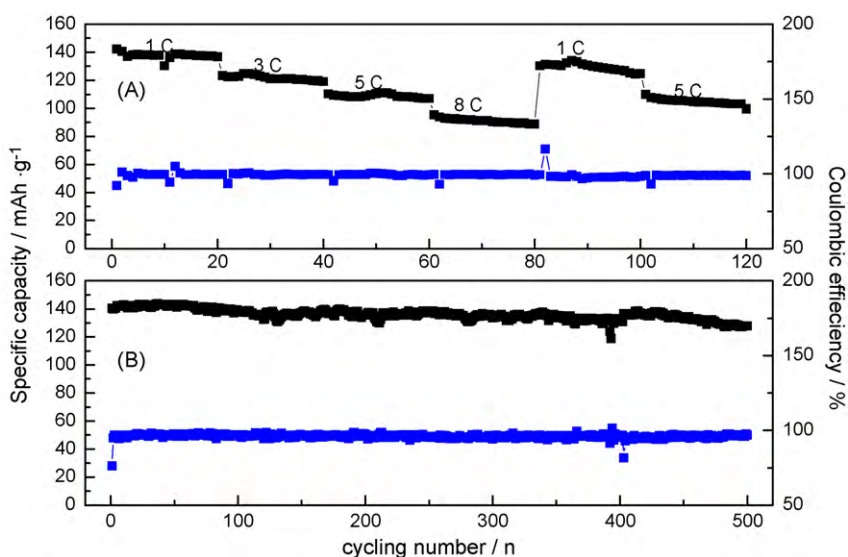**Fig. 9.** Diffusion constant vs. doped degree of samples.

Fig. 10. Cycling performance of V-doped sample d with 3 at.%.

From the above discussion, we show the cycling performance of sample d in Fig. 10. As shown in Fig. 10A, the material shows good cycle reversible capability with little capacity fading at each current density. Though the discharge capacities decreased regularly with the increase of the current density, it can be fully regained once the current density return to 1 or 5 C rates, which exhibits that the LiFePO$_4$/C material has good electrochemical reversibility and structural stability. Good cycling performance is the remarkable advantage of the LiFePO$_4$/C. Fig. 10B shows the long cycle performance of sample d at 1 C rate. The initial capacity was 140 mAh g^{-1}, and increased up to 143 mAh g^{-1} at the following 50 cycles. The reversibility after 250 cycles was retained at more than 98% and there was no noticeable fading for more than 450 cycles. The coulombic efficiency is close to 100%, which indicates that the sample has good electric conductivity. The long cycle performance of this material could be attributed to the well-distributed particle and improved conductivity through carbon coated and V ion doped, as mentioned above.

4. Conclusion

In this study, phase pure V ion doped LiFePO$_4$/C ($x = 1, 2, 3, 4$ at.%) compounds were synthesized by a carbothermal reduction method. ICP and XRD analyses indicate that V ions were sufficiently doped in LiFePO$_4$ and did not alter its crystal structure. It is noted that V ion doping had some influence on the electrochemical performance of the olivine cathode: both the increase of the initial capacity and the suppression of the cycle fading at high rate. It was found from the cyclic voltammetry that the contribution is related to the modification of the ionic conduction with the doped. The effective diffusion coefficient exhibited larger values in the charging reaction than those in the discharging process, and the V ion doping affected the ionic diffusion during both the delithiation and lithiation processes. The diffusion coefficient was maximized around the doped degree of $x = 3$ at.%. From these results, the V ion doping had no direct contribution to the electrochemical reaction but enhanced both electronic and ionic conductivities. Therefore, the doping may release somehow the kinetic limitation in the olivine LiFePO$_4$ structure.

The 3 at.% V ion doped LiFePO$_4$ demonstrates the good cycling performance. Though the discharge capacities decreased regularly with increasing the current density, it can be fully regained once the current density return to 1 or 5 C rates. The initial capacity was 140 mAh g^{-1}, and increased up to 143 mAh g^{-1} at the following 50 cycles. The prepared composite exhibits an excellent cycling performance, with more than 91% discharge capacity retention over 500 cycles.

References

[1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[2] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1609.
[3] M. Thackeray, Nat. Mater. 1 (2002) 81.
[4] M. Higuchi, K. Katayama, Y. Azuma, M. Yukawa, M. Suhara, J. Power Sources 119 (2003) 258.
[5] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
[6] H. Huang, S.C. Yin, L.F. Nazar, Electrochem. Solid State 4 (2001) A170.
[7] N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97–8 (2001) 503.
[8] A.Y. Shenouda, H.K. Liu, J. Alloys Compd. 477 (2009) 498.
[9] J.K. Kim, G. Cheruvally, J.H. Ahn, H.J. Ahn, J. Phys. Chem. Solids 69 (2008) 1257.
[10] X.F. Guo, H. Zhan, Y.H. Zhou, Solid State Ionics 180 (2009) 386.
[11] L.N. Wang, X.C. Zhan, Z.G. Zhang, K.L. Zhang, J. Alloys Compd. 456 (2008) 461.
[12] S.Y. Chung, J.T. Bloking, Y.M. Chiang, Nat. Mater. 1 (2002) 123.
[13] Y.Q. Hu, M.M. Doeff, R. Kostecki, R. Finones, J. Electrochem. Soc. 151 (2004) A1279.
[14] H. Liu, J.Y. Xie, K. Wang, J. Alloys Compd. 459 (2008) 521.
[15] K.S. Park, J.T. Son, H.T. Chung, S.J. Kim, C.H. Lee, H.G. Kim, Electrochem. Commun. 5 (2003) 839.
[16] B.Q. Zhu, X.H. Li, Z.X. Wang, H.J. Guo, Mater. Chem. Phys. 98 (2006) 373.
[17] A. Vadivel Murugan, T. Muraliganth, A. Manthiram, Electrochem. Commun. 10 (2008) 903.
[18] G. Meligrana, C. Gerbaldi, A. Tuel, S. Bodoardo, N. Penazzi, J. Power Sources 160 (2006) 516.
[19] S.F. Yang, P.Y. Zavalij, M.S. Whittingham, Electrochem. Commun. 3 (2001) 505.
[20] B. Zhao, Y. Jiang, H.J. Zhang, H.H. Tao, M.Y. Zhong, Z. Jiao, J. Power Sources 189 (2009) 462.
[21] M. Gaberscek, R. Dominko, J. Jamnik, Electrochem. Commun. 9 (2007) 2778.
[22] J.M. Tarascon, C. Delacourt, A.S. Prakash, M. Morcrette, M.S. Hegde, C. Wurm, C. Masquelier, Dalton Trans. (2004) 2988.
[23] P.P. Prosini, M. Lisi, D. Zane, M. Pasquali, Solid State Ionics 148 (2002) 45.
[24] D.Y.W. Yu, K. Donoue, T. Inoue, M. Fujimoto, S. Fujitani, J. Electrochem. Soc. 153 (2006) A835.