



Short communication

Highly promoted electrochemical performance of 5 V LiCoPO₄ cathode material by addition of vanadium

Fei Wang, Jun Yang*, Yanna NuLi, Jiulin Wang

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China

ARTICLE INFO

Article history:

Received 21 January 2010

Received in revised form 19 April 2010

Accepted 21 April 2010

Available online 28 April 2010

Keywords:

Lithium cobalt phosphate

Vanadium doping

Cathode material

High voltage

Lithium ion battery

ABSTRACT

Li_{1+0.5x}Co_{1-x}V_x(PO₄)_{1+0.5x}/C ($x = 0, 0.05, 0.10$) composites with ordered olivine structure have been synthesized for use as cathode material in lithium ion batteries. The morphology and microstructure are characterized by scanning electron microscope, transmission electron microscopy and X-ray diffraction. The electrochemical test results show that addition of vanadium into LiCoPO₄ remarkably improves its charge and discharge behavior. Li_{1.025}Co_{0.95}V_{0.05}(PO₄)_{1.025}/C electrode gives its initial discharge capacity of 134.8 mAh g⁻¹ at 0.1 C current rate, against 112.2 mAh g⁻¹ for the pristine LiCoPO₄/C, and exhibits much better cyclic stability than the latter. In particular, vanadium doping leads to an enhancement of the discharge voltage plateau for about 70 mV.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Great attention has been paid to the olivine-type LiMPO₄ (M = Fe, Mn, Co, Ni) cathode materials for lithium ion batteries in recent years [1–4]. Owing to its high discharge voltage plateau close to 4.8 V vs. Li/Li⁺ and large theoretical capacity (167 mAh g⁻¹), LiCoPO₄ shows great potential as the attractive 5 V cathode material for high-power electric vehicle application [5]. In addition, a combination of the 5 V cathode with Li₄Ti₅O₁₂ anode may be an option for high-safe lithium ion battery. However, the low electrical conductivity and the decomposition of the conventional electrolytes at such high voltages hinder the LiCoPO₄ material from practical application [6,7]. Recent electrolyte progress, such as making use of ionic liquids, provides the feasibility for 5 V lithium ion batteries.

Some improvements on the rate performance and cyclability of LiCoPO₄ have been achieved by metal ion doping and carbon coating. Han et al. [8] found that Fe doping enhanced Li⁺ diffusivity arisen by the expansion of 1D channel in polyanion structure of LiCoPO₄. Li et al. [9] observed that electrical conductivity of LiCoPO₄ increased three orders of magnitude via coating with uniform carbon film. Covering the LiCoPO₄ cathode with a thin layer of Al₂O₃ could greatly alleviate the capacity fading [10]. Vanadium-doped LiFePO₄/C and the well mixed LiFePO₄–Li₃V₂(PO₄)₃ compounds were investigated and the positive results could be obtained by V-doping at Fe site [11–14]. So far, no vanadium-doped LiCoPO₄ has been reported.

In this paper, Li_{1+0.5x}Co_{1-x}V_x(PO₄)_{1+0.5x}/C ($x = 0, 0.05, 0.10$) composites are prepared and evaluated for 5 V cathode material in lithium ion batteries.

2. Experimental

2.1. Material preparation

The Li_{1+0.5x}Co_{1-x}V_x(PO₄)_{1+0.5x}/C ($x = 0, 0.05, 0.10$) composites were prepared by solid-state reaction using Li₂CO₃, Co(CH₃COO)₂·4H₂O, V₂O₅, NH₄H₂PO₄ and acetylene black. Acetylene black acted as reducing and conducting agent and its amount was about 5 wt% in the final product. For a typical synthesis, 0.103 mol Li₂CO₃, 0.190 mol Co(CH₃COO)₂·4H₂O, 0.205 mol NH₄H₂PO₄, 0.005 mol V₂O₅ and 0.143 mol acetylene black were weighed and put into a zirconia container. The reactants were ball-milled in ethanol media and subsequently dried at 80 °C. The resulting mixture was decomposed at 350 °C for 5 h under argon to expel H₂O and NH₃. The obtained powder was ground, pressed into pellets, and then heated at 750 °C for 16 h in flowing argon to yield Li_{1.025}Co_{0.95}V_{0.05}(PO₄)_{1.025}/C composite. The other composites were also prepared for comparison through the same method.

2.2. Material characterization

X-ray diffraction (XRD) experiments were carried out on a Rigaku D/Max-2200 diffractometer with Cu K α radiation. The morphology and microstructure were observed by JEOL JSM-7401F scanning electron microscope (SEM) and transmission

* Corresponding author. Tel.: +86 21 5474 7667; fax: +86 21 5474 7667.
E-mail address: yangj723@sjtu.edu.cn (J. Yang).

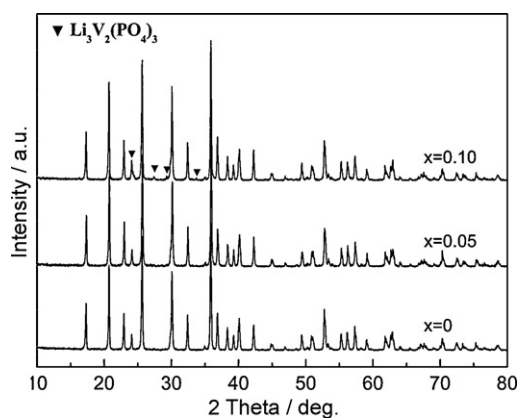


Fig. 1. XRD patterns of $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ composites ($x=0, 0.05, 0.10$).

electron microscopy (TEM, JEOL JEM-2100) equipped with energy-dispersive X-ray spectrometry (EDS, OXFORD INCA). The amount of carbon was measured by PE 2400II elemental analyzer.

2.3. Electrochemical tests

The electrochemical tests were performed with CR2016 coin-type cells. To fabricate the cathodes, 75 wt% active material, 15 wt% carbon black and 10 wt% polyvinylidene difluoride (PVDF) binder in N-methylpyrrolidone (NMP) solution were mixed homogeneously. The resulting slurry was coated on aluminum foil, dried at 120 °C and pressed with 4 MPa. The cells were assembled in an argon-filled box, with lithium metal as anode and 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, volume) as the electrolyte. Galvanostatic charge and discharge was controlled between 3.2 and 5.1 V at 25 °C on a Land CT2001 battery tester. The electrical conductivity was measured by four-point probe method using IM6e electrochemical workstation at room temperature.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ ($x=0, 0.05, 0.10$) composites are shown in Fig. 1. All samples are well crystallized in orthorhombic olivine-type structure with the space group Pmnb (No. 62). With the increase of vanadium content, especially for $\text{Li}_{1.05}\text{Co}_{0.9}\text{V}_{0.1}(\text{PO}_4)_{1.05}/\text{C}$, weak peaks are observed for monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [15]. There is no evidence of diffraction peaks for crystalline carbon and other impurities, indicating the amorphous state of carbon. The lattice parameters of these composites obtained by Rietveld refinement are listed in Table 1. The cell volume of the vanadium-modified phases is slightly smaller than that of LiCoPO_4 . The decrease of unit cell volume suggests that addition of vanadium obviously affects the structure of LiCoPO_4 . Furthermore, vanadium doping results in an increase in the lattice constant c , which will facilitate transfer of Li^+ ions. It has been reported that the diffusion of Li^+ ions along the c -axis has the lowest diffusion energy barriers [16].

Table 1
Lattice parameters of $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ composites.

x	a (Å)	b (Å)	c (Å)	Volume (Å ³)
0	10.1924(5)	5.9168(3)	4.6953(2)	283.1529
0.05	10.1840(5)	5.9144(3)	4.6964(3)	282.8719
0.10	10.1850(4)	5.9150(2)	4.6963(2)	282.9301

3.2. SEM and TEM morphologies

The morphologies of LiCoPO_4/C and $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ composites are shown in Fig. 2a and b, respectively. The particle size of pristine LiCoPO_4/C ranges from 400 nm to 800 nm and exhibits a wide distribution, whereas the $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ displays a more narrow particle distribution (300–500 nm). The TEM image of the $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ composite of Fig. 2c presents a carbon layer coated on a phosphate particle with a thickness from several to near 20 nm, which was formed during the heating process. According to elemental analysis, the amounts of carbon in LiCoPO_4/C , $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ and $\text{Li}_{1.05}\text{Co}_{0.9}\text{V}_{0.1}(\text{PO}_4)_{1.05}/\text{C}$ are 5.05 wt%, 4.96 wt% and 5.29 wt%, respectively. The carbon inside can not only provide the good electrical contact between the $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}$ particles, but also prevent from the formation of large particles during the high-temperature solid-state reaction. TEM image of $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ and its elemental mappings of Co and V, as presented in Fig. 2d–f, indicate that the doped vanadium is uniformly distributed over all the particles and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles have not yet been formed, which is accordance with the XRD result.

3.3. Electrical and electrochemical properties

The powder samples were consolidated into pellets of about 14 mm in diameter and 3.1 mm in thickness with a pressure of 15 MPa. The pellets were coated with Ag paste on both sides for the measurement of the electrical conductivity. The result shows that the electrical conductivity of $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ is $3.58 \times 10^{-3} \text{ Scm}^{-1}$, around 5.3 times of LiCoPO_4/C ($6.80 \times 10^{-4} \text{ Scm}^{-1}$). The changes of lattice parameters for these composites reveal that part of vanadium enters LiCoPO_4 matrix structure. The existence of vanadium can cause some local imperfections and vacancies in the crystal structure, which may be the important reason for the increase of electrical conductivity.

Fig. 3 shows typical charge and discharge profiles (the second cycle) of the $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ ($x=0, 0.05, 0.10$) electrodes at 0.1 C rate in the voltage range of 3.2–5.1 V. The second discharge capacities for LiCoPO_4/C , $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ and $\text{Li}_{1.05}\text{Co}_{0.9}\text{V}_{0.1}(\text{PO}_4)_{1.05}/\text{C}$ are 109.3, 133.9 and 124.2 mAh g^{-1} , respectively. It is very interesting to find that the $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ and $\text{Li}_{1.05}\text{Co}_{0.9}\text{V}_{0.1}(\text{PO}_4)_{1.05}/\text{C}$ composites have higher and more flat discharge voltage plateaus but lower charge plateaus compared with LiCoPO_4/C . Moreover, the discharge capacities of the vanadium-modified composites reach 62 mAh g^{-1} above 4.8 V. In contrast, the voltage plateau of LiCoPO_4/C is below 4.8 V in the whole discharge process. It appears that the enhanced voltage plateaus and smaller hysteresis between charge and discharge are attributed not only to morphology factor, which affects the electrochemical polarization, but also to the material property. On the other hand, a discharge voltage plateau around 4.1 V can be observed for $\text{Li}_{1.05}\text{Co}_{0.9}\text{V}_{0.1}(\text{PO}_4)_{1.05}/\text{C}$ electrode, which is related to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase in the composite. With a further increase in the vanadium content, the 4 V capacity rises but the 5 V capacity declines.

The cyclic performances of the $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ ($x=0, 0.05, 0.10$) electrodes at 0.1 C rate are shown in Fig. 4. The initial capacities of LiCoPO_4/C and $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ are 112.2 and 134.8 mAh g^{-1} , respectively. After 25 cycles, the capacity retention is 85% for $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$, which is much higher than that for LiCoPO_4/C (62%). By all appearances, the vanadium-modified LiCoPO_4/C can not only supply larger capacity,

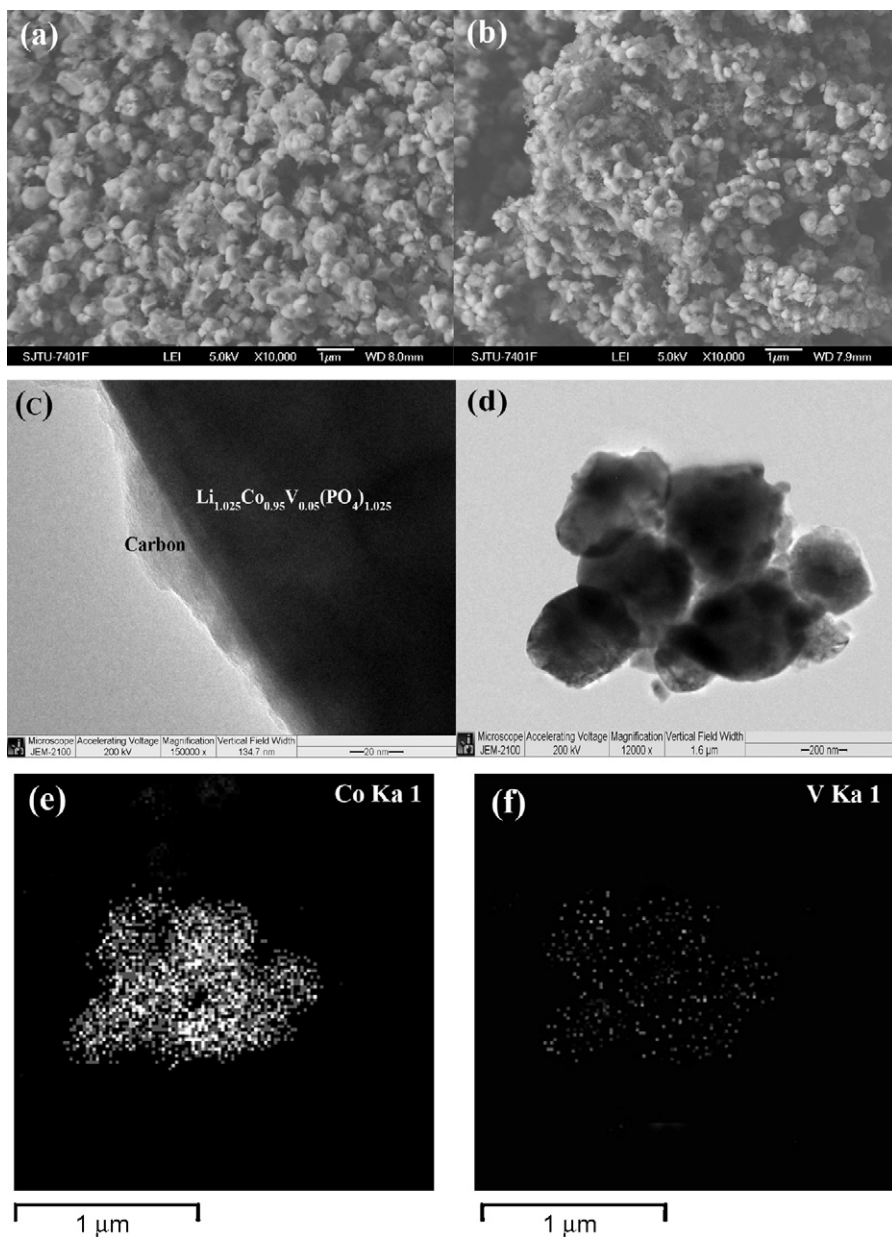


Fig. 2. SEM images of LiCoPO_4/C (a) and $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ (b), and TEM images of $\text{Li}_{1.025}\text{Co}_{0.95}\text{V}_{0.05}(\text{PO}_4)_{1.025}/\text{C}$ (c and d), elemental mappings for Co (e) and V (f).

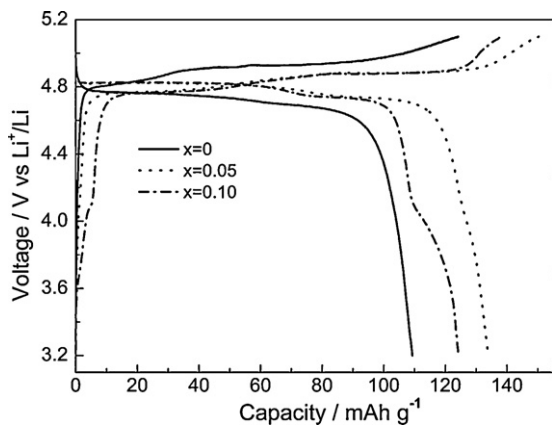


Fig. 3. The second charge/discharge profiles of $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ electrodes at 0.1 C rate.

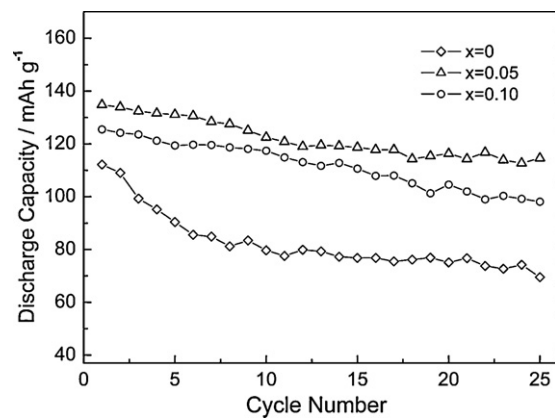


Fig. 4. Cycle performances of $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}/\text{C}$ electrodes at 0.1 C rate.

but also maintain better cycling stability. However, it should be mentioned that the long-term cycling stability of the 5 V cathode is also dependent on the anti-oxidation capability of the electrolyte. A further study should focus on the compatible electrolyte system.

4. Conclusions

Highly crystalline $\text{Li}_{1+0.5x}\text{Co}_{1-x}\text{V}_x(\text{PO}_4)_{1+0.5x}$ ($x=0, 0.05, 0.10$) incorporated with carbon can be successfully synthesized via solid-state reaction. A certain amount of vanadium can dope into LiCoPO_4 crystal structure but more vanadium addition will lead to the formation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The vanadium modification significantly improves the discharge capacity and cyclic stability. Moreover, it can enhance discharge voltage plateaus and suppress the hysteresis between charge and discharge. Therefore, the vanadium-modified LiCoPO_4/C is a promising cathode material for high-voltage lithium ion battery.

Acknowledgement

This work was supported by National 973 Program (No. 2007CB209700).

References

- [1] B. Kang, G. Ceder, *Nature* 458 (2009) 190–193.
- [2] S.K. Martha, B. Markovsky, J. Grinblat, Y. Gofer, O. Haik, E. Zinigrad, D. Aurbach, T. Drezzen, D. Wang, G. Deghenghi, I. Exnar, *J. Electrochem. Soc.* 156 (2009) A541–A552.
- [3] J.M. Lloris, C. Pérez Vicente, J.L. Tirado, *Electrochem. Solid-State Lett.* 5 (2002) A234–A237.
- [4] F. Zhou, M. Cococcioni, K. Kang, G. Ceder, *Electrochem. Commun.* 6 (2004) 1144–1148.
- [5] J.M. Osorio-Guillén, B. Holm, R. Ahuja, B. Johansson, *Solid State Ionics* 167 (2004) 221–227.
- [6] J. Wolfenstine, *J. Power Sources* 158 (2006) 1431–1435.
- [7] J. Wolfenstine, U. Lee, B. Poesse, J.L. Allen, *J. Power Sources* 144 (2005) 226–230.
- [8] D.-W. Han, Y.-M. Kang, R.-Z. Yin, M.-S. Song, H.-S. Kwon, *Electrochem. Commun.* 11 (2009) 137–140.
- [9] H.H. Li, J. Jin, J.P. Wei, Z. Zhou, J. Yan, *Electrochem. Commun.* 11 (2009) 95–98.
- [10] A. Eftekhari, *J. Electrochem. Soc.* 151 (2004) A1456–A1460.
- [11] C.S. Sun, Z. Zhou, Z.G. Xu, D.G. Wang, J.P. Wei, X.K. Bian, J. Yan, *J. Power Sources* 193 (2009) 841–845.
- [12] X.J. Chen, G.S. Cao, X.B. Zhao, J.P. Tu, T.J. Zhu, *J. Alloys Compd.* 463 (2008) 385–389.
- [13] J.-c. Zheng, X.-h. Li, Z.-x. Wang, J.-h. Li, L.-j. Li, L. Wu, H.-j. Guo, *Ionics* 15 (2009) 753–759.
- [14] L. Wang, Z. Li, H. Xu, K. Zhang, *J. Phys. Chem. C* 112 (2008) 308–312.
- [15] X.H. Rui, C. Li, C.H. Chen, *Electrochim. Acta* 54 (2009) 3374–3380.
- [16] M.R. Yang, W.H. Ke, S.H. Wu, *J. Power Sources* 146 (2005) 539–543.