



Modified sol–gel synthesis of nanosized $\text{LiVPO}_4\text{F/C}$ cathode material with mechanical blending assist

Zhongqiong Xiong, Guoqing Zhang*, Junqiao Xiong, Xiaoqing Yang, Yunyun Zhang

Faculty of Material and Energy, Guangdong University of Technology, Guangzhou 510006, PR China

ARTICLE INFO

Article history:

Received 12 June 2013

Accepted 20 August 2013

Available online 27 August 2013

Keywords:

Lithium-ion batteries

Cathode material

Lithium vanadium fluorophosphates

Nanocomposite

Sol–gel preparation

ABSTRACT

Nanosized $\text{LiVPO}_4\text{F/C}$ cathode material is synthesized by heating the precursor obtained through a sol–gel method with mechanical blending assist. XRD and SEM results indicate that $\text{LiVPO}_4\text{F/C}$ composite is pure phase, possesses good crystallinity and uniform particle size distribution. The average size of $\text{LiVPO}_4\text{F/C}$ is about 40 nm. In the range of 3.0–4.6 V, the $\text{LiVPO}_4\text{F/C}$ electrode presents excellent cyclic performance. At 0.1 C rate, it delivers initial discharge capacity of about 138.3 mAh g^{-1} and maintains 135.7 mAh g^{-1} after 50 cycles. Even carried out at 55°C , this composite displays discharge capacities of 119.3 mAh g^{-1} at the rate of 0.5 C and 104.1 mAh g^{-1} at the rate of 1 C, and maintains about 115.5 and 97.4 mAh g^{-1} after 30 cycles, respectively.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently, framework materials based on phosphate polyanion building block have been proposed as a new class of cathode materials to substitute LiCoO_2 for lithium-ion batteries. Among those, LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are the first to be identified and characterized [1]. Not long ago, Barker, J. group has described the insertion properties of lithium vanadium fluorophosphates, LiVPO_4F [2]. The high power density and excellent thermal stability allows LiVPO_4F to be employed as cathode materials for lithium-ion batteries [3,4]. In addition, LiVPO_4F also exhibits a discharge voltage plateau of about 4.2 V vs. Li^+/Li , which is higher than the average potential of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (3.9 V), LiFePO_4 (3.5 V) and LiCoO_2 (3.9 V). However, the electric conductivity of LiVPO_4F is much lower than that of LiMn_2O_4 and LiCoO_2 [5], and its lower electric conductivity is unfavorable and still a main task in the research field of LiVPO_4F cathode material.

Carbon coating is an effective method to improve electronic conductivity of the electrode materials [4–6], and can restrict the growth of particles [7], consequently enhancing the electrochemical performance of LiVPO_4F . Usually, $\text{LiVPO}_4\text{F/C}$ is synthesized by solid-state reaction, this method not only operates at high temperature and time-consuming, but also is easy to obtain impurity phase $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ which is induced by sublimation of HF or VF_3 [8]. In this work, pure phase $\text{LiVPO}_4\text{F/C}$ is synthesized by annealing the precursor obtained via a sol–gel method at low temperature for a short time. Compared with the traditional sol–gel method,

this modified method with mechanical blending assist, and the particle size of LiVPO_4F is smaller. The electrochemical performance of the electrode under the condition of high temperature is tested.

2. Experimental

The synthetic procedure was briefly described as follows: V_2O_5 was first dissolved in H_2O_2 solution to form $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, then acetylene black (45 wt% excess) and $\text{NH}_4\text{H}_2\text{PO}_4$ were added to the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and stirred for 4 h for reduction of V^{+5} to V^{+3} at room temperature. After drying in an oven, the above mixture was mixed with LiF by ball milling for 4 h. All the reagents were stoichiometric ratio. The precursor was heated at 300°C for 4 h under nitrogen atmosphere to obtain black powder. Then the black powder was pressed into pellets after grinding, and then the pellets were heated at 550°C for 4 h in a tubular furnace with flowing nitrogen gas.

The crystalline phase of synthesized $\text{LiVPO}_4\text{F/C}$ was detected by an X-ray diffractometer (XRD, D/MAX-Ultima IV, Japan) with $\text{Cu K}\alpha$ radiation in the 2θ range from 10° to 80° . The morphology of composite was observed by scanning electron microscope (SEM, Hitachi S-3400N, Japan) and transmission electron microscope (TEM, JEM-2100, Japan). Elemental carbon content in the composite was determined by C-S analysis equipment (Elstar, Germany), and the specific surface area of $\text{LiVPO}_4\text{F/C}$ was also measured.

Cathode was made from a mixture of $\text{LiVPO}_4\text{F/C}$, acetylene black and polyvinylidene fluoride (PVDF) binder dissolved in NMP in a weight ratio of 8:1:1. And then the mixture was coated onto an Al-foil, dried at 120°C for 24 h under a vacuum. The cells

* Corresponding author. Tel.: +86 13570563896.

E-mail address: 357412936@qq.com (G. Zhang).

(CR2032 coin type) were assembled in an argon-filled glove-box with the Li metal as negative electrode. The electrolyte was 1 mol L^{-1} LiPF_6 in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1:1:1, v/v/v). The cells were measured using galvanostatic charge–discharge instrument (Neware BTS, 5 V 10 mA) over a voltage range of 3.0–4.6 V versus Li/Li^+ electrode at room temperature ($20^\circ\text{C} \pm 3$) and at elevated temperature (55°C), respectively. The cyclic voltammetric (CV) measurement was carried out with a CHI 660C electrochemical analyzer at room temperature ($20^\circ\text{C} \pm 3$), and the scan rate was 0.05 mV s^{-1} .

3. Results and discussion

The XRD pattern of LiVPO_4/C is shown in Fig. 1. All fundamental peaks of LiVPO_4 agree well with those which have been reported [2]. It is isostructural with the triclinic LiFePO_4 (OH) (PDF42-1412) [3]. The diffraction data was refined based on a triclinic structure using space group $P\bar{1}$, and the following are the refined cell parameters for LiVPO_4 , $a=0.5146 \text{ nm}$, $b=0.5304 \text{ nm}$, $c=0.7451 \text{ nm}$, $\alpha=66.998^\circ$, $\beta=67.427^\circ$, $\gamma=81.964^\circ$, and cell volume $=0.17285 \text{ nm}^3$. These compare well with relevant data from other literature sources [9,10]. Without other impurity phase such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is detected. Moreover, the C-S analysis shows the mass fraction of carbon is about 8.98%, but there is no diffraction peak corresponding to carbon, indicating that the carbon is amorphous. The average size of LiVPO_4/C crystallite is estimated 40 nm using Scherrer's relation $d=0.89\lambda/(B\cos\theta)$, where λ is the X-ray wavelength, θ is the Bragg angle and B is the angular full-width-half maximum. This crystallite size is smaller than those prepared through the traditional sol–gel method [11].

Fig. 2(a) shows the SEM image of the prepared composite. The particles are small and relatively uniform. Small and uniform particle size of LiVPO_4/C could exhibit better electrochemical performance. For further investigation of the morphology of LiVPO_4/C , TEM image is shown in Fig. 2(b). It can be seen that the prepared powders are coated with a carbon layer and the amorphous carbon evenly distributes on the particle surface. Carbon is in favor of reducing the particle size to shorten the diffusion path of Li ions [12]. The primary particle size in TEM is about 20–70 nm, similar to the XRD results. The measured specific surface area of LiVPO_4/C is $9.67 \text{ m}^2 \text{ g}^{-1}$, which is typical of well crystalline composite material.

The charge–discharge performance of the composite at 0.1 C (1 C rate equals to 156 mAh g^{-1}) with cut-off potential of 3.0 and 4.6 V at room temperature is depicted in Fig. 3(a). The initial charge and discharge capacities are about 153.6 mAh g^{-1} and 138.3 mAh g^{-1} , indicating a higher coulombic efficiency of about 90%. Only a slight capacity fading during the follow cycling, and

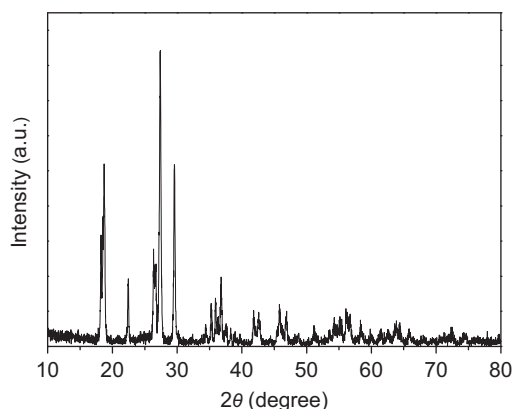


Fig. 1. XRD pattern of the composite LiVPO_4/C .

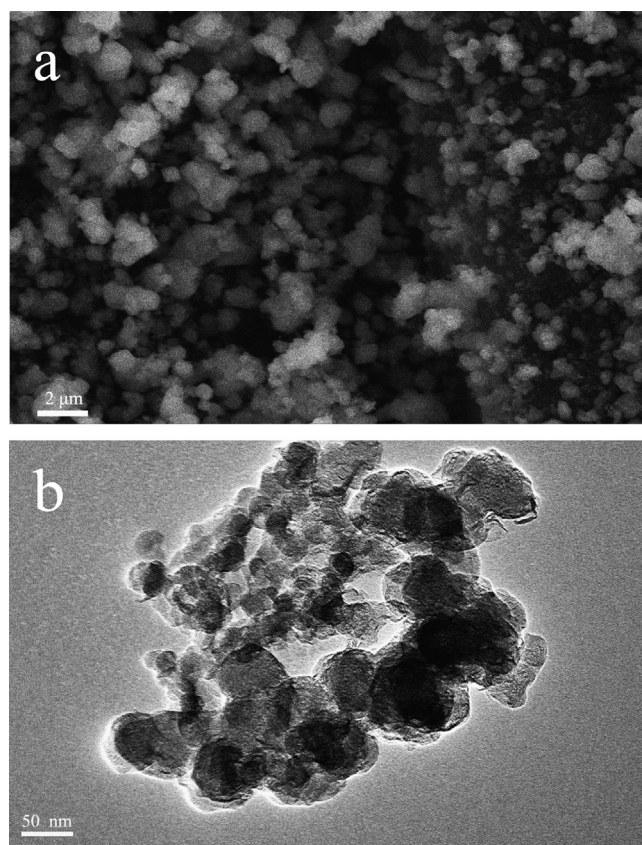


Fig. 2. SEM and TEM images of LiVPO_4/C . (a) SEM and (b) TEM.

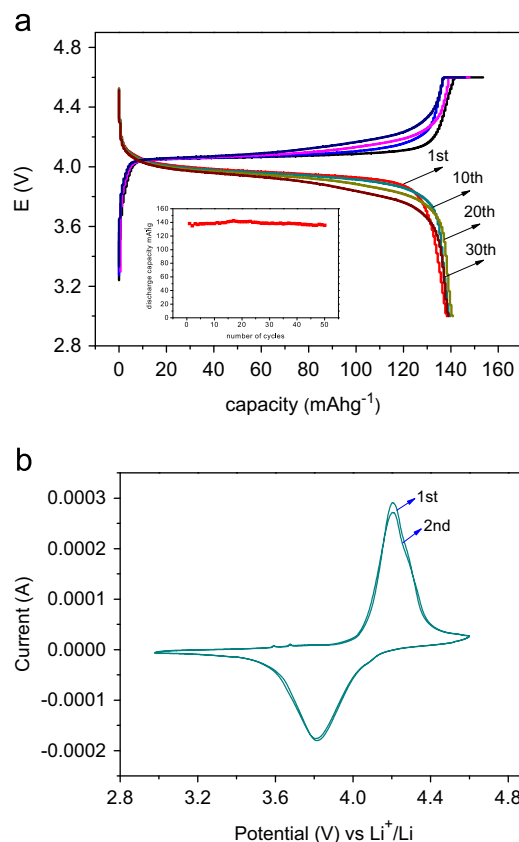


Fig. 3. Electrochemical performance of LiVPO_4/C at room temperature, (a) Cycle performance of LiVPO_4/C at 0.1 C and (b) cyclic voltammograms recorded for LiVPO_4/C .

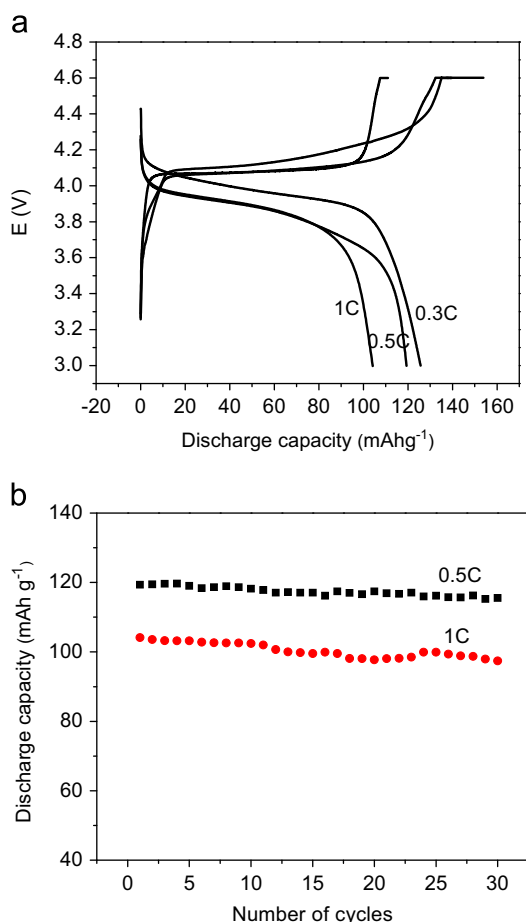


Fig. 4. Electrochemical performance of LiVPO₄F/C at high temperature (55 °C). (a) Charge-discharge curves of LiVPO₄F/C and (b) cycle performance of LiVPO₄F/C.

the specific capacities are 138.3, 140.8, 138.3 mAh g⁻¹ at the 10th, 20th and 30th cycles, respectively. The specific capacity is still kept 135.7 mAh g⁻¹ after 50 cycles (the insert in Fig. 3(a)), higher than that of LiVPO₄F presented in the previous report [11], indicating a lower capacity loss rate of about 1.9% for the LiVPO₄F/C composite material prepared by our introduced method.

Fig. 3(b) shows the cyclic voltammetry (CV) for the prepared sample at a scan rate of 0.05 mV s⁻¹ between 3.0 and 4.6 V at room temperature. There is only one peak in the composite deintercalation process, as well as in the intercalation process. For the first cycle, LiVPO₄F/C shows 4.21 V for oxidation peak correspond to 3.81 V for reduction peak, and for the second cycle, the extraction potential decreases to 4.16 V and the insertion potential increases to 3.86 V. Similar with the previous report [11], and broadly in line with the result of the above charge-discharge curves. The smaller value of potential interval shows the enhancement of electrode reaction reversibility. However, the extraction-insertion potential values are lower than the results of the samples prepared through the solid-state method [13] (4.28 V, 4.18 V). This difference may be due to the samples originating from different routes, and affects the reversible capacity at high current density, further investigations are needed to clarify it completely.

To further elucidate the electrochemical performance of LiVPO₄F/C, the charge-discharge curves and cycle performance in the voltage range of 3.0–4.6 V at various rates tested at 55 °C are

shown in Fig. 4(a) and (b). As shown in Fig. 4(a), the discharge specific capacities are 125.7, 119.3 and 104.1 mAh g⁻¹ at 0.3 C, 0.5 C and 1 C, respectively. After 30 cycles, the reversible capacities retain 115.5 and 97.4 mAh g⁻¹ at the rate of 0.5 C and 1 C, such that it only has 3.2% and 6.4% capacity loss of the initial values, respectively. It should be noted that the discharge capacities operating at 55 °C are higher than the corresponding capacities (here it is not showed) at room temperature, this is maybe due to the reason of high Li diffusion rate at an elevated temperature in cathode materials particles [14]. Nonetheless, we must admit that the capacities of LiVPO₄F/C prepared by our introduced method at high current density do not compare favorably with that of literatures [5,15].

From above results, it may be concluded that the improvement of electrochemical performance of LiVPO₄F was mainly attributed to the decrease of particle size caused by the addition of carbon, which could shorten Li⁺ diffusion length, and provide a highway for electron movement, and finally improve the reversible capacity and cycleability of the electrode.

4. Conclusions

The carbon-coated nano-LiVPO₄F cathode material has been successfully synthesized by a modified sol-gel method with mechanical blending assist route. The composite material exhibits good electrochemical performance when carried out at room and high temperature, which can be attributed to the reduced particle size and the existence of conductive carbon. The composite material LiVPO₄F/C is a considerable promising cathode candidate for commercial lithium ion batteries.

Acknowledgments

This work was financially supported by Science and Technology of Guangzhou City (11A51020737) and 2011 Key Technical Project of Strategic Emerging Industries of Guangdong Province (2011A010802001).

References

- [1] Barker J, Saidi MY, Gover RKB. *Journal of Power Sources* 2007;174:927–31.
- [2] Barker J, Saidi MY, Swayer JL. *Journal of the Electrochemical Society* 2003;150(10):A1394–8.
- [3] Liu JQ, Zhong SK, Wu L. *Transactions of Nonferrous Metals Society of China* 2012;22:s157–61.
- [4] Wang JX, Wang ZX, Li XH, Gao HJ, Xiao W, Huang S, et al. *Journal of Solid State Electrochemistry* 2013;17:1–8.
- [5] Qiao XC, Yang JD, Wang YB. *Journal of Solid State Electrochemistry* 2012;16:1211–7.
- [6] Gong HX, Yu Y, Li T, Mei T, Xing Z, Zhu YC, et al. *Materials Letters* 2012;66:374–6.
- [7] Qiao YQ, Wang XL, Xiang JY, Zhang D, Liu WL, Tu JP. *Electrochimica Acta* 2011;56:2269–75.
- [8] Zhou F, Zhao XM, Dahn JR. *Electrochemistry Communications* 2009;11:589–91.
- [9] Reddy MV, Subba Rao GV, Chowdari BVR. *Journal of Power Sources* 2010;195:5768–74.
- [10] Barker J, Gover RKB, Burns P, Bryan A, Saidi MY, Swayer JL. *Journal of Power Sources* 2005;146:516–20.
- [11] Li YZ, Zhou Z, Gao XP. *Journal of Power Sources* 2006;160:633–7.
- [12] Cheng FQ, Wan W, Tan Z, Huang YY, Zhou HH, Chen JT, et al. *Electrochimica Acta* 2011;56:2999–3005.
- [13] Zheng JC, Zhang B, Yang ZH. *Journal of Power Sources* 2012;202:380–3.
- [14] Takahashi M, Tobishima S, Takei K, Takei Y. *Solid State Ionics* 2002;148:283–9.
- [15] Wang JX, Li XH, Wang ZX, Guo HJ, Zhang YH, Xiong XH, et al. *Electrochimica Acta* 2013;91:75–81.