

A novel sol–gel method to synthesize nanocrystalline LiVPO_4F and its electrochemical Li intercalation performances

Yuzhan Li, Zhen Zhou*, X.P. Gao, Jie Yan

Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China

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Abstract

Lithium vanadium fluorophosphate, LiVPO_4F , a cathode material for lithium ion batteries, was synthesized by a sol–gel method followed by low temperature calcinations. $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel, $\text{NH}_4\text{H}_2\text{PO}_4$, LiF and carbon were used as starting materials to prepare a precursor, and LiVPO_4F was finally obtained by sintering the precursor at 550°C for 2 h. X-ray diffraction results show that the LiVPO_4F sample is triclinic structure. TEM image indicates that the LiVPO_4F particles are about 70 nm in diameter embedded in carbon network. The LiVPO_4F system showed the discharge capacity of about 130 mAh g^{-1} in the range of 3.0–4.6 V at the first cycle, and the discharge capacity remained about 124 mAh g^{-1} after 30 cycles. The sol–gel method is suitable for the preparation of LiVPO_4F cathode materials with good electrochemical Li intercalation performances.

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Keywords: Lithium-ion batteries; Cathode material; Sol–gel method; LiVPO_4F

1. Introduction

Lithium-ion secondary batteries have been playing an important role as supplies for cellular phones, portable computer, camcorder, etc. The ever-growing demand for lithium ion batteries with higher quality and lower cost has spawned many explorations for novel superior lithium insertion materials both in cathodes and anodes [1–4]. Among the cathode candidates, LiCoO_2 , spinel LiMn_2O_4 , and their substituting derivative compounds [5–10] are currently used in lithium-ion batteries, but alternative cathode materials have been pursued to replace the oxidative unstable lithium transition metal oxides. Recently, novel compounds based on transition metal polyanions [11–32] have been proposed as a new class of cathode materials for lithium ion batteries. Considerable studies have been performed to the lithium conducting phosphates such as LiFePO_4 [11–13], LiMnPO_4 [14–17], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [18–26], etc. Phosphate-based Li ion batteries may have better performances and safety characteristics than metal oxide batteries because phosphate-based cathode materials possess a structural advantage that limits the likelihood of oxygen liberation and combustion.

Another framework material based on the phosphate polyanion, LiVPO_4F , was proposed by Barker et al [27–31]. LiVPO_4F is isostructural with the naturally-occurring mineral tavorite, $\text{LiFePO}_4 \cdot \text{OH}$ [27] or ambylgonite, LiAlPO_4F [33], crystallizing with a triclinic structure (space group $P\bar{1}$). The reversible Li extraction/insertion reaction for $\text{Li}_{1-x}\text{VPO}_4\text{F}$, based on the $\text{V}^{3+/4+}$ redox couple, operates at about 4.2 V versus Li. Usually LiVPO_4F was synthesized by conventional two-step solid reactions. Solid-state reactions generally need high heating temperature and long heating time. It is very difficult to obtain LiVPO_4F sample with high purity, which is crucial to its electrochemical performances, especially the cyclic stability [32]. In this investigation, the LiVPO_4F sample was synthesized by a sol–gel method followed by low-temperature calcinations, and its electrochemical Li intercalation performances were evaluated.

2. Experimental

$\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel was firstly prepared as follows; 10% (v/v) H_2O_2 solution was slowly added to V_2O_5 , while vigorously stirred at room temperature until a clear orange solution formed. Stoichiometric $\text{NH}_4\text{H}_2\text{PO}_4$, LiF , and 50 wt.% excess high-surface-area carbon were added to the above $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gels and strongly stirred for 6 h at room temperature, and finally dried at 80°C in an oven. The mixture was pressed into

* Corresponding author. Tel.: +86 22 23498941; fax: +86 22 23498941.
E-mail address: zhouzhen@nankai.edu.cn (Z. Zhou).

pellets and heated at 300 °C in a tubular furnace with flowing argon gas for 4 h. After slowly cooling to room temperature, the pellets were ground for 20 min, pressed into pellets again, and then heated to 550 °C and held at this temperature for 2 h. It is apparent that the subsequent thermal treatments used in this investigation were performed at quite low temperatures. In conventional solid-state carbonthermal reactions, the precursors are usually heated to 600–800 °C and held for 8–16 h [30].

The crystallinity and structure of the samples were monitored by a D/Max III X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The oxidation state of V in LiVPO $_4$ F was determined by X-ray photoelectron spectra (XPS) using PHI5300 spectrometer with monochromatic Mg K α radiation ($h\nu = 1253.6 \text{ eV}$). The surface morphology of the samples was observed using the Hitachi S-3500N scanning electron microscopy (SEM). The nanoscale microstructure was examined using the JEM 1010 transmission electron microscope (TEM). Before observation, the samples were dispersed in anhydrous ethanol, and the suspension solution was dropped onto a standard copper TEM grid.

Teflon-type testing cells were assembled for electrochemical measurements of LiVPO $_4$ F materials. A 85 wt.% active material was firstly mixed with 10 wt.% carbon black and 5 wt.% colloidal PTFE binder. The mixture was pressed into a circular pellet electrode whose diameter was 8 mm. The pellets were then dried at 100 °C for 24 h. The cells were assembled in an argon-filled dry glove-box with the LiVPO $_4$ F as positive electrode and Li metal as negative electrode. The electrolyte was 1 mol l $^{-1}$ LiPF $_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volumetric ratio of 1:1.

Galvanostatic charge/discharge and cyclic voltammetry (CV) tests were conducted using a computer-controlled Land battery tester and CHI 600A electrochemical analyzer, respectively. The cells were galvanostatically charged and discharged in the voltage range of 3.0–4.6 V. CV tests were also performed at a scan rate of 0.05 mV s $^{-1}$.

3. Results and discussion

Structural analysis of the LiVPO $_4$ F cathode materials was carefully performed by XRD. The XRD profile of the sample is shown in Fig. 1. The diffraction patterns were refined based on a triclinic structure using space group $P\bar{1}$, and the following crystallographic parameters are generated; $a = 0.5170 \text{ nm}$, $b = 0.5311 \text{ nm}$, $c = 0.7257 \text{ nm}$, $\alpha = 72.512^\circ$, $\beta = 107.964^\circ$, $\gamma = 81.396^\circ$, and cell volume = 0.17452 nm 3 , similar to the previous reports [27,32]. Excess carbon left in LiVPO $_4$ F material was not detected by XRD, the same as the previous report [34]. The size of LiVPO $_4$ F crystallites was estimated in the range of 50–80 nm using Scherrer's relation $t = 0.9\lambda / (B \cos \theta)$, where λ is the X-ray wavelength, θ is the Bragg angle and B is the angular full-width-half maximum of the chosen (hkl) reflection in radian. The crystallite size is much smaller than those prepared through conventional solid-state reaction [27,32].

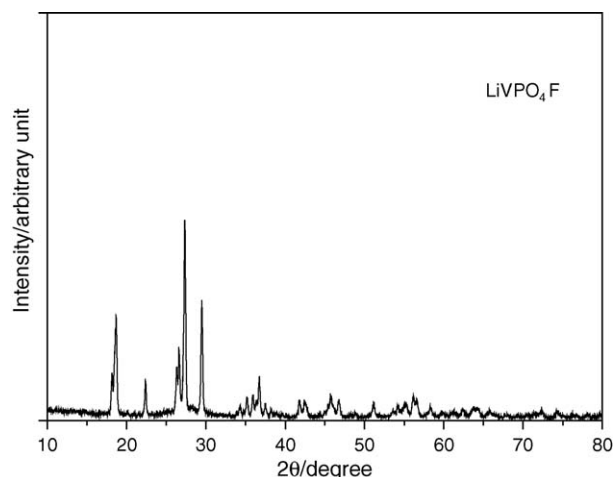


Fig. 1. XRD profile for the LiVPO $_4$ F cathode materials synthesized by calcining a precursor at 550 °C for 2 h.

Fig. 2 shows the V XPS core level for the LiVPO $_4$ F sample. The V $2p$ XPS spectrum shows the characteristic satellite peak with the binding energy (BE) at 517.21 eV, matching well with that observed in V $_2$ O $_3$ (517.34 eV) [35].

The morphology of the LiVPO $_4$ F sample was examined by SEM, and is shown in Fig. 3. In the micrograph, the small particles show good crystallinity and uniformity. TEM investigation was also conducted to examine the LiVPO $_4$ F particles. In the TEM image in Fig. 4, the dark region is LiVPO $_4$ F, and the light grey region is carbon, indicating that the LiVPO $_4$ F particles are embedded in the network of carbon. The carbon network structure can provide good electrical contact between the LiVPO $_4$ F particles. The average size of the particles in Fig. 4 is about 100 nm, but the dark regions indicative of LiVPO $_4$ F particles are averaged to be about 70 nm, in agreement with the XRD results.

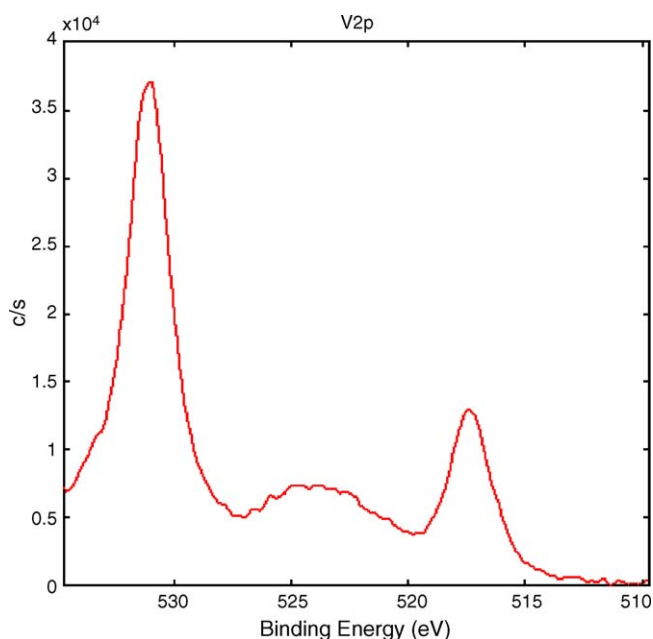


Fig. 2. XPS spectrum of V $2p$ in the LiVPO $_4$ F sample.

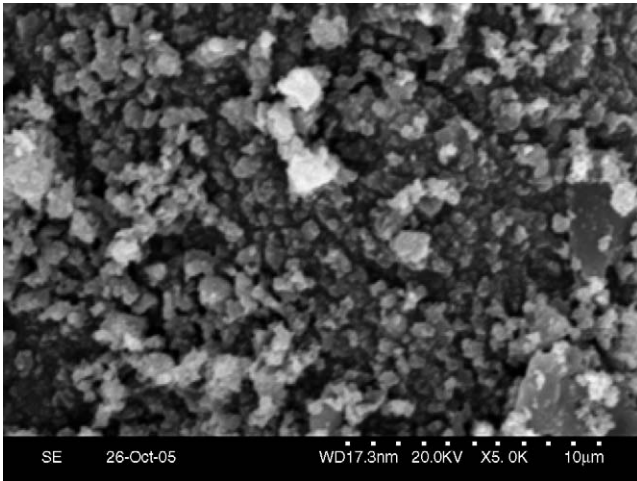


Fig. 3. SEM of LiVPO_4F synthesized at 550°C for 2 h in argon.

Fig. 5 shows the first charge/discharge curves of the LiVPO_4F electrode. It exhibits a charge plateau around 4.1 V and discharge plateau around 4.0 V, which is identified as the single phase transition process between LiVPO_4F and VPO_4F phase. There were two closely-spaced voltage plateaus during the charging process of LiVPO_4F in the previous electrochemical voltage spectroscopy (EVS) results [27], and the voltage profile could be subdivided into two compositional regions corresponding to the approximate stoichiometries, $x=0\text{--}0.30$ and $0.30\text{--}0.88$ in $\text{Li}_{1-x}\text{VPO}_4\text{F}$. However, the charge process was characterized by a single sloping profile in the present LiVPO_4F sample prepared by sol–gel method, which is quite different from the results of the samples prepared through conventional solid-state reaction [27,32]. This difference may be due to the microstructures of the samples originating from different routes, but further investigations are needed to clarify it completely. In the first charge/discharge cycle, the LiVPO_4F sample exhibits a charge capacity about 139.1 mAh g^{-1} , and a discharge capacity about 130.6 mAh g^{-1} at the current density

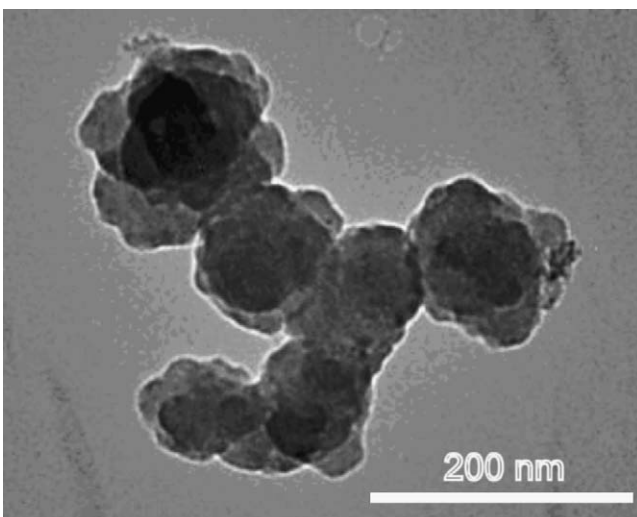


Fig. 4. TEM of LiVPO_4F synthesized at 550°C for 2 h in argon.

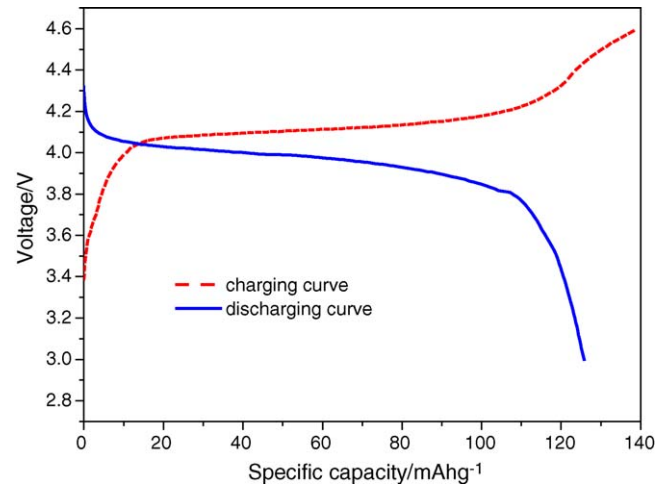


Fig. 5. The first charge/discharge profiles of LiVPO_4F at 30 mA g^{-1} in the voltage range of 3.0–4.6 V at room temperature.

of 30 mA g^{-1} , indicating a high coulombic efficiency of about 93.9%.

The cyclic performances of the LiVPO_4F samples were evaluated in the voltage range of 3.0–4.6 V at room temperature in the cell configuration $\text{Li/LiVPO}_4\text{F}$, and the results are shown in Fig. 6. As shown in Figs. 5 and 6, the initial discharge capacity of LiVPO_4F material is about 130.6 mAh g^{-1} , and after 30 cycles, the discharge capacity is 124.0 mAh g^{-1} , indicating a lower capacity loss rate of about 5.1% for the LiVPO_4F material prepared by sol–gel method. The above results are very close to those of the LiVPO_4F samples, which were prepared through conventional high-temperature solid-state reactions, reported by Barker et al. [30] and our group [32].

CV curves were recorded for the LiVPO_4F sample using Li metal as counter and reference electrodes in stimulant cell configuration, and are shown in Fig. 7. The CV curves indicate the potential range in which the lithium deintercalation/intercalation occurs and the phase transitions (if there is

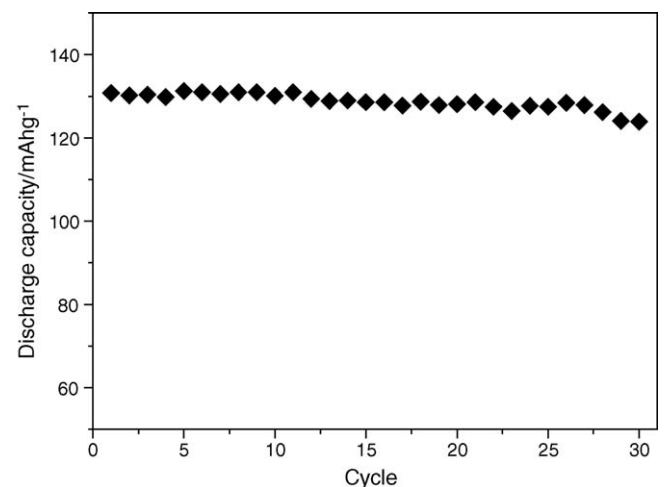


Fig. 6. Cyclic performance of the LiVPO_4F sample at room temperature at 30 mA g^{-1} in the voltage range of 3.0–4.6 V.

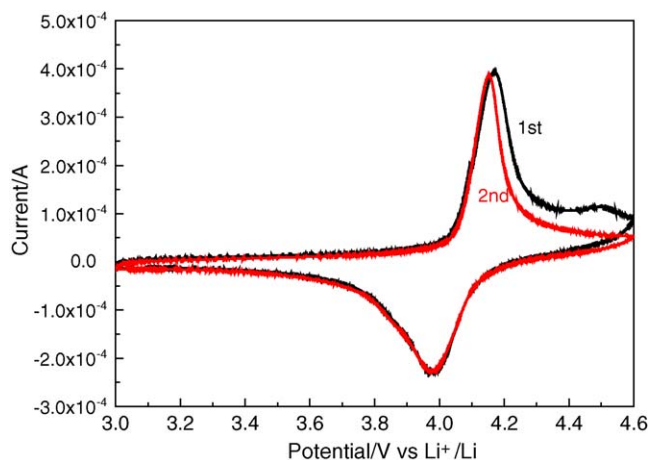


Fig. 7. Cyclic voltamograms recorded for LiVPO₄F at a scan rate of 0.05 mV s⁻¹ in the potential range of 3.0–4.6 V vs. Li⁺/Li.

any) occur during this process. For the first cycle, the deintercalation and intercalation processes occurred at 4.170 and 3.995 V, respectively, and for the second cycle, the deintercalation and intercalation processes occurred at 4.140 and 3.995 V, respectively, in agreement with the results of the above galvanostatic charge/discharge curves. Two deintercalation peaks were not detected as in the samples prepared through solid-state reactions [32].

The LiVPO₄F material has ever been successfully synthesized using a range of preparative strategies such as solid-state, hydrothermal, ion exchange methods, all using VPO₄ that was prepared through a carbothermal reaction as an intermediate phase. In the initial results, LiVPO₄F offered some encouraging performances, but the cyclic stability was rather disappointing [28]. Recently it has been found that the electrochemical performance of LiVPO₄F can be improved due to the underlying sample purity [31]. Accordingly, the purity control is very crucial to obtain high-quality LiVPO₄F cathode materials. In this investigation, the sol–gel method was proposed to synthesize the LiVPO₄F material. The obtained materials showed good electrochemical Li intercalation performances. Moreover, the sol–gel method has some advantages such as lower calcination temperature and shorter heating time; especially nanocrystalline particles with narrow distribution range can be obtained through this method.

4. Conclusion

LiVPO₄F cathode materials were successfully synthesized through a sol–gel method followed by low temperature calcination. X-ray diffraction results show a pure single phase with triclinic structure. The LiVPO₄F particles were about 70 nm in diameter covered with carbon network. The LiVPO₄F cathode materials exhibit a charge plateau around 4.1 V with the charge capacity of 139.1 mAh g⁻¹, and discharge plateau around 4.0 V with the discharge capacity about 130.6 mAh g⁻¹ at the current density of 30 mA g⁻¹. The discharge capacity was held to be 124.0 mAh g⁻¹ after 30 cycles. The above performances approach those of the LiVPO₄F samples prepared through con-

ventional high-temperature solid-state reactions. The sol–gel method proposed in this investigation is hopeful in the LiVPO₄F synthesis, and may promote the application of this cathode material to commercial Li ion batteries.

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