Short communication

Novel synthesis of LiVPO$_4$F cathode material by chemical lithiation and postannealing

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ABSTRACT

Here, we report a chemical process for the preparation of nano-carbon coated LiVPO$_4$F cathode material for lithium ion batteries. V$_2$O$_5$ powders are first lithiated in the mixture of LiF, NH$_4$H$_2$PO$_4$ and oxalic acid at room temperature and then form an amorphous Li-V-P-O-F precursor by ball milling, which is subsequently converted to LiVPO$_4$F by a short postannealing. X-ray photoelectron spectroscopy (XPS) results reveal that the V^{5+} in the Li-V-P-O-F precursor is reduced to V^{3+} by oxalic acid at room temperature. X-ray diffraction results show that the LiVPO$_4$F sample is triclinic structure. TEM image indicates the LiVPO$_4$F particles are about 100 nm in diameter and wrapped by nano-carbon webs. The LiVPO$_4$F/C composites synthesized at 500 °C for 2 h deliver a discharge capacity of 143 mAh g^{-1} at 0.5 C in the range of 3.0–4.4 V at the first cycle, and possess a favorable capacity cycling maintenance at the 0.5C, 1C and 3C rates.

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1. Introduction

LiVPO$_4$F is a novel fluorophosphates cathode material reported by Barker et al. [1–4]. It promises to deliver good rate capability, long cycle life, safety, high energy density, and high voltage, in lithium ion batteries, and it is an alternative to the commonly used LiCoO$_2$ [5–7]. Usually, LiVPO$_4$F was synthesized by conventional two-step solid reactions [8,9] and sol–gel method [10]. Solid-state reactions generally need high temperature and long heating time, it is difficult to obtain LiVPO$_4$F with good electrochemical performance. For sol–gel method, the synthesis techniques are complicated, and synthesis situation is hard to control.

In this paper, we report a simple chemical lithiation and postannealing process to synthesize LiVPO$_4$F cathode material. No need of preparation of intermediates (such as VPO$_4$), pre-sintering treatment and high temperature reaction compared with traditional solid-state reaction and some other complicated synthetic routes.

2. Experimental

2.1. Preparation of LiVPO$_4$F

The LiVPO$_4$F compound was synthesized from V$_2$O$_5$, NH$_4$H$_2$PO$_4$, LiF (all chemical 99% purity) taken in stoichiometric amounts, and V$_2$O$_5$:oxalic acid molar ration is 1:4. The process steps were: (1) initial mixing by magnetic stirring of all ingredients together as a slurry in alcohol at room temperature for 1 h, (2) high energy ball milling 2 h (speed: 200 rpm, ball:powder ratio (in g): 5:1, ball milling in argon atmosphere), (3) drying in oven at 80 °C for 6 h in the air, and (4) sintered at 500 °C for 2 h in argon atmosphere.

The chemical reaction may occur as follows:

$$V_2O_5 + 2LiF + 2NH_4H_2PO_4 + 2HOOCCOOH \cdot 2H_2O \rightarrow 2LiVPO_4F$$
$$+ F4CO_2 + 2NH_3 + 9H_2O$$
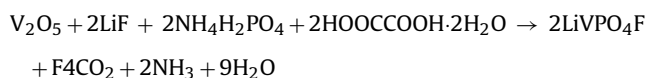
2.2. Sample characterization

The surface element's content of LiVPO$_4$F powders was determined by an X-ray photoelectron spectrometer (XPS, Kratos Model XSAM800) equipped with an Mg Kα achromatic X-ray source (1235.6 eV). Structural and crystalline phase analyses of the products were taken from the powder X-ray diffraction (XRD, Rint-2000, Rigaku) using CuKα radiation. Elemental carbon analysis of sample was performed by C–S analysis equipment (Eltar, Germany). The samples were observed by SEM (JEOL, JSM-5600LV) and a Tecnai G12 transmission electron microscope (TEM).

2.3. Electrochemical tests

The electrochemical characterizations were performed using CR2025 coin-type cell. Typical positive electrode loadings were in the range of 3–3.5 mg cm^{-2}, and an electrode diameter of 14 mm was used. For positive electrode fabrication, the prepared powders were mixed with 10% of carbon black and 10% of polyvinylidene

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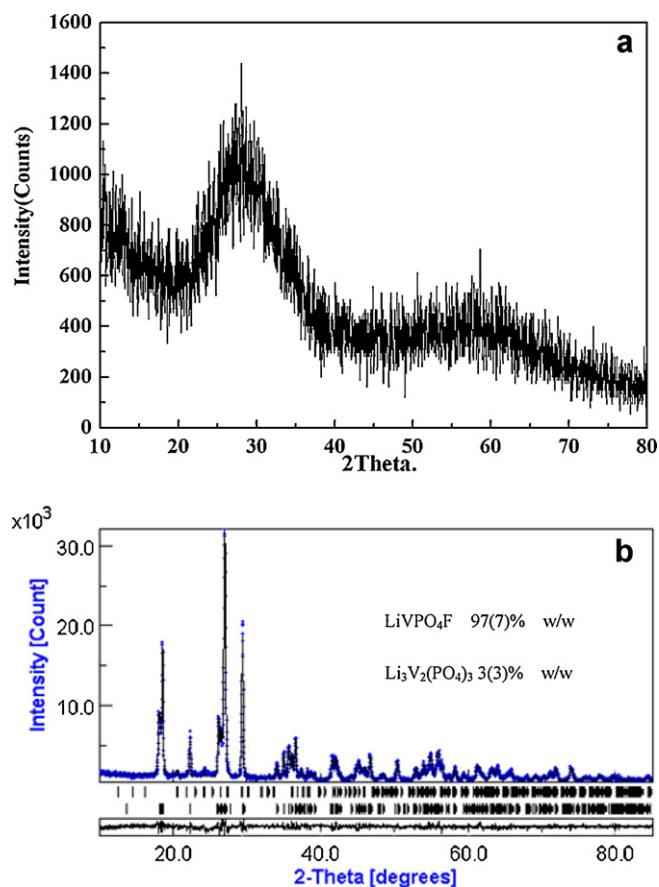E-mail address: jczheng@csu.edu.cn (B. Zhang).

Fig. 2. XPS spectrum of V2P in the amorphous Li-V-P-O-F precursor after ball milling.

Fig. 1. (a) XRD pattern of Li-V-P-O-F precursor after ball milling. (b) Rietveld refinement performed with X-ray diffraction pattern for LiVPO$_4$F synthesized at 500 °C for 2 h.

fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 120 °C for 12 h in vacuum. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 mol L^{-1} LiPF$_6$ in EC, EMC and DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. Electrochemical tests were carried out using an automatic galvanostatic charge–discharge unit, NEWARE battery cycler, between 2.5 V and 4.4 V vs. Li/Li$^+$ electrode at room temperature.

3. Results and discussion

3.1. Li-V-P-O-F precursor

The color of the precursor changed from buff to aqua after ball milling, which is one of the proofs for the V^{5+} being reduced by HOOCCOOH·2H$_2$O. Fig. 1(a) is the XRD pattern of Li-V-P-O-F precursor after ball milling. No evidence of diffraction peaks in the XRD pattern, indicating the Li-V-P-O-F precursor is amorphous.

In order to find out whether the oxalic acid can reduce the V^{5+}, we did XPS test, the results are shown in Fig. 2. It shows the binding energy values of V2p are 517.2 eV and 523.0 eV, which correspond to energy level of V2P$_{2/3}$ and V2P$_{1/2}$, respectively. The results matched well with that observed in V$_2$O$_3$ [11] and LiVPO$_4$F [6]. It was also reported that the binding energy for the V2p in LiVPO$_4$F was 517.2 eV [10]. It indicates that the oxidation state of V in the amorphous precursor is V^{3+}.
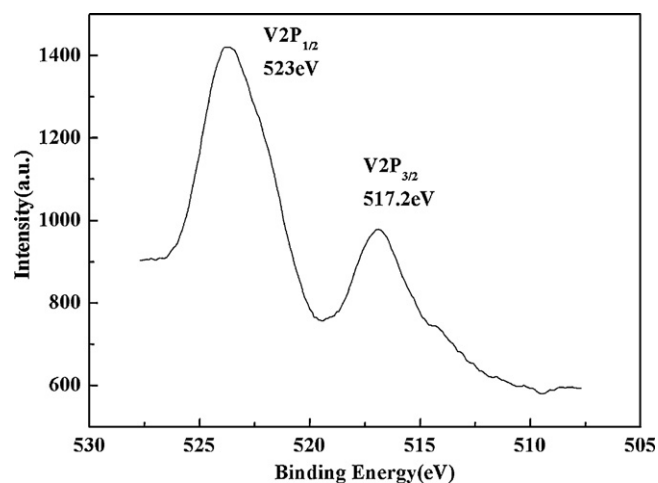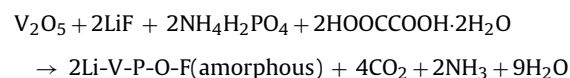
From the above analysis it is quite evident that the chemical reaction occurs as the follows:

$$V_2O_5 + 2LiF + 2NH_4H_2PO_4 + 2HOOCCOOH·2H_2O$$
$$\rightarrow 2Li\text{-}V\text{-}P\text{-}O\text{-}F(amorphous) + 4CO_2 + 2NH_3 + 9H_2O$$

3.2. LiVPO$_4$F

Fig. 1(b) shows the XRD pattern of LiVPO$_4$F synthesized at 500 °C for 2 h, it indicates that all the peaks can be indexed on the basis of the triclinic structure. The calculated lattice parameters are: $a = 0.5163$ nm, $b = 0.5304$ nm, $c = 0.7500$ nm, $\alpha = 66.90°$, $\beta = 66.91°$, $\gamma = 81.52°$ and $V = 0.1740$ nm^3. The results compare well with those reported by Barker et al. [12] ($a = 0.5169$ nm, $b = 0.5306$ nm, $c = 0.7503$ nm, $\alpha = 66.85°$, $\beta = 67.00°$, $\gamma = 81.58°$ and $V = 0.1742$ nm^3) and Reddy et al. [6] ($a = 0.5175$ nm, $b = 0.5304$ nm, $c = 0.7503$ nm, $\alpha = 66.95°$, $\beta = 66.88°$, $\gamma = 81.53°$ and $V = 0.1741$ nm^3). Most of the Bragg peaks agree well in position and relative intensity with those reported by Barker's group [1–4]. The sample consists of two phases: LiVPO$_4$F [97(7)% w/w], and Li$_3$V$_2$(PO$_4$)$_3$ [3(3)% w/w] as determined by Rietveld analysis of X-ray diffraction data (Fig. 1b). Carbon remaining in LiVPO$_4$F composite material was not detected, which indicates that residual carbon is amorphous or the thickness of the residual carbon on the LiVPO$_4$F powders is too thin [13]. The amount of carbon in the LiVPO$_4$F/C composite is about 0.53 wt.% determined by C-S analysis method.

Fig. 3(a) presents the SEM image of the composite showing near-spherical particles with a uniform morphology. The particle size ranges from 100 to 500 nm. The nature of surface coating of carbon, as analyzed by TEM, is shown in Fig. 3(b) and (c). It shows a nano-sized web of amorphous carbon, about 6 nm in thickness, surrounding the LiVPO$_4$F particles. The nano-carbon webs are seen to be highly porous, existing across the entire surface of particles, enveloping and connecting them, thus minimizing inter-particle agglomeration. To the best of our knowledge, the nano-carbon webs coating formed could lead to improved charge transfer kinetics of the material and result in higher reversible capacity, as detailed below.

Fig. 4(a) shows the discharge profiles of LiVPO$_4$F at different rates at room temperature. The cell was recharged at 0.1C rate to assure identical initial conditions for all the discharges. The cell delivered a specific capacity of 143 mAh g^{-1} with a plateau at 4.2 V vs. Li/Li$^+$ at a current density of 78 mA g^{-1} (0.5C). As the discharge current density increased, the plateau voltage, and
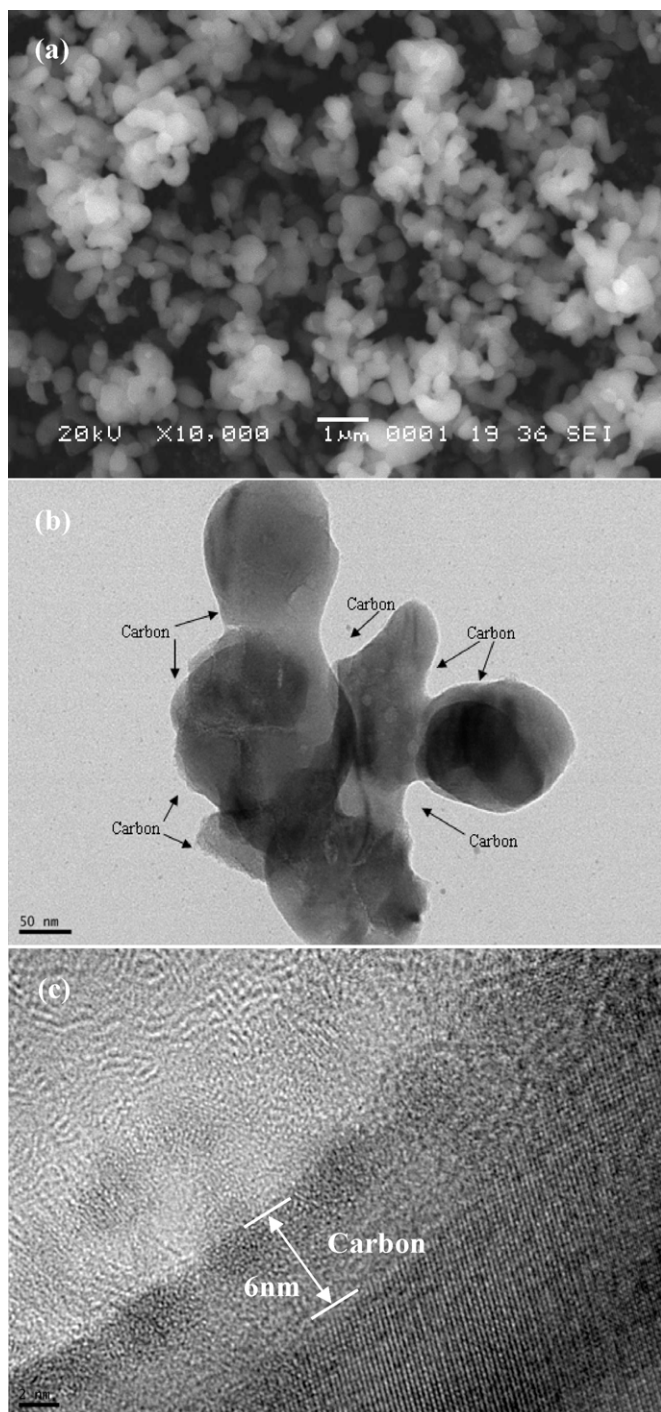
Fig. 3. (a) SEM image of LiVPO₄F; (b) and (c) TEM image of LiVPO₄F.

Fig. 4. (a) Discharge profiles of LiVPO₄F at different rates at room temperature. (b) Cyclic performance of LiVPO₄F at different discharge rates at room temperature.

after 50 cycles. The results are very good when compared with the LiVPO₄F prepared by other synthetic routes [8–10].

Cyclic voltammogram (CV) of LiVPO₄F cathode, with Li-metals as the counter and reference electrode, in the potential range 3.0–4.8 V at room temperature and a scan rate of $0.05\,mV\,s^{-1}$, is shown in Fig. 5. It shows a typical CV of LiVPO₄F cathode. The 0.10 V separation between the anodic and cathodic peaks is representative of its good kinetics, especially considering that the electrochemical

specific discharge capacity decreased. At a higher discharge rate 3C ($468\,mA\,g^{-1}$), the cell was able to deliver a capacity of $110\,mAh\,g^{-1}$ with a plateau at 4.1 V vs. Li/Li⁺. This result is better than Zhou [9], Li [10] and Zhang [14] previously reported. Besides, two small discharge voltage plateaus at around 3.6 and 4.1 V were observed in Fig. 4(a) other than the typical 4.2 V discharge plateau expected for LiVPO₄F. These plateaus are caused by the small amount of Li₃V₂(PO₄)₃ phase in the composite, as it shown in the XRD pattern. It is the same as Zhou [9] previously reported.

The cycling performance of the LiVPO₄F cathode material is shown in Fig. 4(b). It can be seen that the composite has excellent cycle performance. No obvious capacity fading was observed
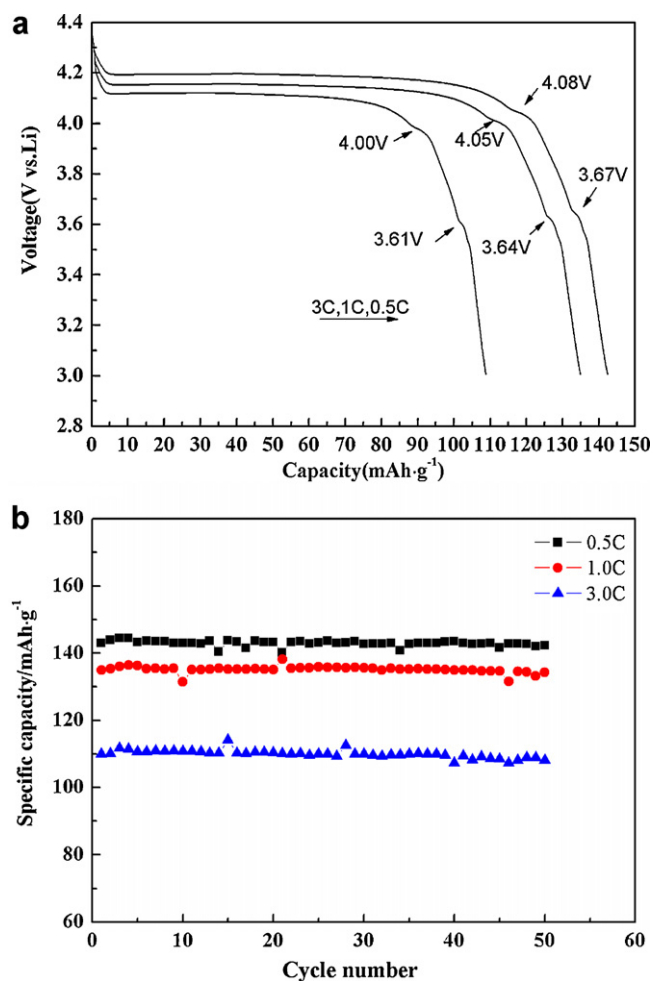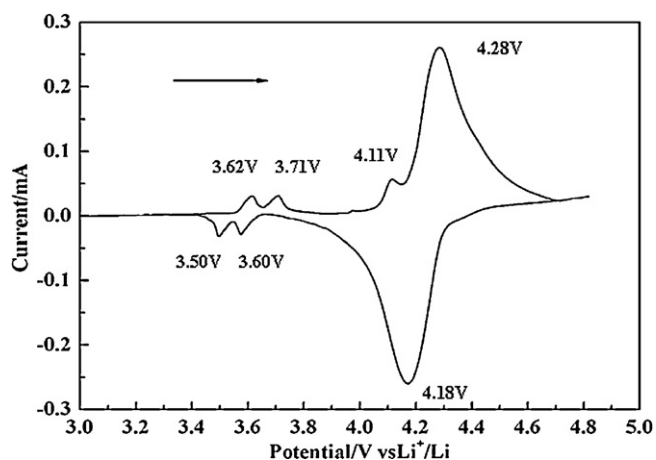

Fig. 5. Cyclic voltammogram recorded for LiVPO₄F at a scan rate of $0.05\,mV\,s^{-1}$.

process involves diffusion of lithium ions in a solid phase and electron jumping across a poorly conducting compound. Oxidation peak around 3.62 V, 3.71 V and 4.11 V can be ascribed to the oxidation of $Li_3V_2(PO_4)_3$. The results are in accordance with the discharge profiles.

4. Conclusions

$LiVPO_4F/C$ nano-composite cathode material with good electrochemical performance was synthesized by chemical lithiation and postannealing. The V^{5+} in Li-V-P-O-F precursor was reduced to V^{3+} by oxalic acid at room temperature. The obtained $LiVPO_4F$ powders were about 100 nm in size on average and wrapped by nano-carbon webs. It delivered specific capacity of 143, 135 and 110 mAh g^{-1} at 0.5, 1.0, and 3.0C rates, respectively, in the range of 3.0–4.4 V at the first cycle, and possessed a favorable capacity cycling maintenance after 50 cycles. The good electrochemical performance attributes to the nano-size and nano-carbon webs coating of $LiVPO_4F$ particles synthesized by this new synthetic route.

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