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# Synthesis and performance of LiVPO<sub>4</sub>F/C-based cathode material for lithium ion battery

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**Abstract:** LiVPO<sub>4</sub>F/C-based material was prepared by heating a precursor, which was obtained through ball milling with slurry of  $H_2C_2O_4$ ·2 $H_2O$ ,  $NH_4H_2PO_4$ ,  $NH_4VO_3$  and LiF. In this process,  $H_2C_2O_4$ ·2 $H_2O$  was used as a reducing agent as well as carbon source. The properties of the precursor and the prepared sample were characterized by TG-DTA, XRD, SEM, TEM and C–S analysis. XRD analysis shows that the precursor is amorphous and the prepared LiVPO<sub>4</sub>F sample coexists with Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, as well as a small amount of V<sub>2</sub>O<sub>3</sub>. Homogeneous powders with an average particle size of 2 µm are observed by TEM. HRTEM image shows that the crystal particles are coated by amorphous carbon uniformly, with a coating layer of about 2 nm. The synthesized material shows the specific discharge capacities of 151.3 and 102.5 mA·h/g at 0.1C and 10C respectively, in the voltage range of 3.0–4.4 V, and it keeps 90.4% of initial discharge capacity at 10C after 50 cycles.  $V^{3+}/V^{4+}$  redox peaks corresponding to both LiVPO<sub>4</sub>F and Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are seen clearly in the CV curve.

Key words: lithium ion battery; LiVPO<sub>4</sub>F; ball milling; cathode material; carbon coating

#### **1** Introduction

Framework materials based on the phosphate polyanion, such as LiFePO<sub>4</sub>, LiMnPO<sub>4</sub> and Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, have been firmly believed to be potential electro-active materials for lithium-ion battery applications [1-7]. Fluorophosphate, represented by the general formula RMPO<sub>4</sub>F, where R represents lithium or sodium and M represents a 3d transition metal, was reported as electroactive material by BARKER et al [8,9]. LiVPO<sub>4</sub>F, namely lithium vanadium fluorophosphate, owing to its good electrochemical performance, high voltage platform, high energy density and excellent thermal stability, is considered to a novel 4 V cathode material to substitute LiCoO<sub>2</sub> commonly used in the first-generation lithium-ion batteries [10,11]. It is isostructural with the naturally occurring minerals tavorite LiFePO4·OH, or amblygonite LiAlPO4F, crystallizing with a triclinic structure (space group  $P\overline{1}$ ) [12–14]. The reversible Li<sup>+</sup> extraction/insertion reaction for Li1-rVPO4F based on the  $V^{3+/4+}$  redox couple operates at about 4.2 V versus Li, which is 0.2 or 0.7 V higher than that exhibited by LiCoO<sub>2</sub> or LiFePO<sub>4</sub>, respectively [11,15]. Usually, LiVPO<sub>4</sub>F is synthesized by conventional two-step carbon thermal reaction (CTR), which generally operates at high temperatures for a long time. BARKER et al [8] first introduced the two-step CTR method for preparing LiVPO<sub>4</sub>F/C successfully, and did much to improve its electrochemical properties by two-step CTR method [10,16,17]. Unfortunately, though the utilization of lithium ion is increased, the poor rate performance still hinders its further development as the next commercial high-potential cathode material. One-step CTR method is also employed to prepare LiVPO<sub>4</sub>F/C. ZHONG et al [18] employed humic acid as reduction agent as well as carbon source, and prepared porous LiVPO<sub>4</sub>F/C particles by one-step method successfully. A sol-gel method was also employed to synthesize LiVPO<sub>4</sub>F. LI et al [19] reported a novel sol-gel method to prepare  $LiVPO_4F/C$ , using  $H_2O_2$  as coordinating agent to prepare  $V_2O_5 \cdot nH_2O$ precursor, which has an important significance. ZHONG et al [15] and QIAO et al [20] employed citric acid to prepare Li-V-PO<sub>4</sub>-F gel and then sintered it at high temperatures to obtain crystal LiVPO<sub>4</sub>F [15,20]. But it may not be an effective way for large scale production.

In this work, a simple method is presented to synthesize carbon coated LiVPO<sub>4</sub>F, namely chemical

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reduction assisted with mechanical activation followed by short-time calcinations. The V(+5) is reduced to V(+3) by oxalic acid at room temperature and it is not necessary to prepare VPO<sub>4</sub> intermediate at high temperatures compared with traditional CTR method. The short-time calcination can save a large amount of energy. The carbon is decomposed from gas-phase reaction and can be deposited on the surface of the crystal particle uniformly. The electrochemical performance of prepared samples is evaluated.

#### 2 Experimental

The LiVPO<sub>4</sub>F sample was prepared as following steps. Firstly, stoichiometric NH<sub>4</sub>VO<sub>3</sub> (AR, 99%), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (AR, 98.5%), LiF (AR, 99.5%), 50% excess oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, AR, 98.5%) were added to a sealing can, and ball milled in the alcohol media at a revolving speed of 250 r/min for 4 h. The ball mill type was ND6-2L with rated power of 0.75 kW. The oxalic acid dihydrate here was introduced as reducing agent as well as carbon source. Secondly, the obtained slurry was dried in a drying oven at 80 °C for 6 h. Finally, the dried powders were sintered at 350 °C for 5 h, and then at 750 °C for 90 min under argon atmosphere.

The TG–DTA analysis was tested by SDTQ600 with a step time of 10 °C/min under argon atmosphere. The powder X-ray diffraction (XRD, Rint–2000, Rigaku) using Cu K<sub>a</sub> radiation was employed to identify the crystalline phase of the synthesized material. The mass fractions of the crystal phases were evaluated by multiphase refinement with Maud Program. The morphology of the LiVPO<sub>4</sub>F powders was observed on a scanning electron microscope (SEM, JEOL, JSM–5612LV) with an accelerating voltage of 20 kV, and on a transmission electron microscope (TEM, Tecnai G12). Carbon content was tested by a C–S analyzer (Eltar, Germany).

The electrochemical characterizations were conducted with CR2025 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10% acetylene black and 10% polyvinylidene fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurry was pasted onto an aluminum current collector, followed by drying at 120 °C for 12 h in the air. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, using 1 mol/L LiPF<sub>6</sub> 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 chargedischarge unit, NEWARE battery circler, between 3.0 V and 4.4 V versus Li/Li<sup>+</sup> at room temperature. A constant current-constant voltage condition was employed for charge process and a galvanostatic condition was conducted for discharge process. The cyclic voltammetry measurement at a scan rate of 0.05 mV/s between 3.0 V and 4.4 V was carried out with a CHI660D electrochemical analyzer.

### **3 Results and discussion**

In the process of ball milling for raw materials NH<sub>4</sub>VO<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, LiF and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O at room temperature, the pentavalent vanadium is reduced to trivalent vanadium by H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and the color of the material changes from creamy white to green. Figure 1(a) shows the XRD pattern of LiVPO<sub>4</sub>F precursor prepared by ball milling at room temperature. It can be seen that there is no obvious evidence of diffraction peaks in Fig. 1(a), which indicates that the precursor is nearly amorphous. The TG-DTA curves of the precursor are shown in Fig. 1(b). It is clear that three endothermic peaks and mass loss stages appear at 75-135 °C, 250-390 °C and 450-700 °C, which represent the loss of absorbed water, decomposition of oxalic acid as well as ammonium dihydrogen phosphate, formation accompanied crystallization of LiVPO<sub>4</sub>F, respectively. Two distinct changes are observed at 450 and 630 °C. The change at 450 °C may correspond to



Fig. 1 XRD pattern (a) and TG–DTA curves (b) of  $LiVPO_4F$  precursor

further decomposition of intermediate product  $H_3PO_4$ and  $H_4P_2O_7$  to  $(HPO_3)_x$  and  $H_2O(g)$ , and the mass loss at 630 °C may result from formation of crystal LiVPO<sub>4</sub>F, in which the volatilization of  $H_2O(g)$  may induce HF sublimation. According to the above analysis, two-step calcination schedule should be introduced to ensure sufficient decomposition and contact among the reactants, and finally materials with good electrochemical performance can be obtained.

Figure 2 shows the XRD pattern of the prepared material after heat treatment under argon atmosphere. The XRD pattern shows a series of diffraction peaks, indicating that a transformation of the precursor from amorphous to a crystalline phase occurs during the calcination process. A multiphase refinement method was employed to analyze the XRD based on the models of LiFePO<sub>4</sub>(OH,F) (ICSD #20808), Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (ICSD #98362) and  $V_2O_3$  (ICSD #1473). The result shows that the mass fractions of LiVPO<sub>4</sub>F, Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and V<sub>2</sub>O<sub>3</sub> are 79.2%, 17.6%, 3.2%, respectively. Generally, the fitting inequality level factors  $R_w$  value should be less than 15%. Herein, the value of  $R_{\rm w}$  is 8.86%, indicating the refined results are credible. The existence of  $Li_3V_2(PO_4)_3$  in the prepared material may be on account of reactions between fluorochemicals and  $H_2O(g)$  at high temperatures, causing formation of HF. The volatilization of HF results in decrease of fluorine and vanadium contents in solid phase, causing the formation of Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.



Fig. 2 XRD pattern of prepared material after heat treatment

Figure 3(a) shows the SEM image of  $LiVPO_4F$ sample. In the micrograph, particles with the average size of about 2 µm show good crystallinity and uniformity and the grains are even compared with those synthesized by sol–gel method [19]. The morphology and surface state of the prepared LiVPO<sub>4</sub>F particles were observed by TEM and HRTEM, as shown in Figs. 3(b) and (c). From the result, it can be seen that a carbon layer of about 2 nm adheres on the surface of the prepared particles. The fast Fourier transform (FFT) (inset in Fig. 3(c)) shows the lattice planes according to (110) and (010) planes of LiVPO<sub>4</sub>F crystal. C–S analysis shows that the carbon content is about 3.7%. The carbon derives from the decomposition of excessive oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), and is helpful to electronic conductivity during electrode process. It is worth taking a moment to flag the fact that H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is decomposed to C and CO<sub>2</sub> at low temperature indirectly, which can be described as the following chemical equation:

$$H_2C_2O_4 = CO(g) + CO_2(g) + H_2O(g)$$
 (1)

$$2CO(g) = C(s) + CO_2(g) \tag{2}$$

When the temperature is lower than 400 °C, CO gas is unstable and decomposes to C(s) and  $CO_2$  gas. But the stability of CO increases with elevating the temperature. So, it is necessary to keep a period of time at lower temperatures to ensure production of carbon.



**Fig. 3** SEM (a), TEM (b) and HRTEM (c) images of prepared sample after heat treatment

Figure 4(a) shows the discharge profiles of the LiVPO<sub>4</sub>F/C cathode at different rates. In the discharge curves, there is a long plateau at about 4.2 V, which corresponds to  $\text{Li}^+$  insertion in  $\text{Li}_{1-x}\text{VPO}_4\text{F}$  ( $0 \le x \le 1$ ). A short plateau at about 4.0 V following the long one indexes with the reduction of  $V^{4+}$  to  $V^{3+}$  in  $Li_{3-x}V_2(PO_4)_3$  $(1 \le x \le 2)$ . Two short continuous plateaus at 3.7–3.5 V are in accordance with Li<sup>+</sup> further insertion into  $Li_{3-x}V_2(PO_4)_3$  ( $0 \le x \le 1$ ). From Fig. 4(a), it can be seen that the initial discharge capacity of LiVPO<sub>4</sub>F sample is about 151.3 mAh/g at 0.1C (1C equals to 150 mA/g). Judged from the plateaus of the discharge curve, the capacity is about 120 mA·h/g delivered by LiVPO<sub>4</sub>F and 30 mA·h/g displayed by Li<sub>3</sub>V<sub>2</sub>(PO4)<sub>3</sub>, which is consistent with the XRD analysis of prepared sample, as shown in Fig. 2. And the utilization of the active material decreases by the increase of rate, performing 150.9, 147.6, 122.8, and 102.5 mA·h/g, at 0.5C, 2C, 5C and 10 C, respectively. The above results appear excellent compared with those synthesized through traditional two-step CTR method [8,12] and sol-gel method [15]. The prepared material possesses a relatively good cycle performance at a high discharge rate and the capacity retention keeps 90.4% after 50 cycles at 10C, as shown in Fig. 4(b).

The relatively high capacity and good cycle performance of the material may be attributed to



**Fig. 4** Initial discharge curves (a) and cycle performance (b) at various rates

structural stability of LiVPO<sub>4</sub>F [14]. Due to the strong electro-negativity of fluorine, the addition of fluorine atoms makes the PO<sub>4</sub> tetrahedron and VO<sub>4</sub>F<sub>2</sub> octahedron more stable, thus offering more pourable passageways for Li<sup>+</sup> insertion/extraction. It is also attributed to the micro-size particles and carbon coating. The small particles have a large contact area between the electrode material and electrolyte solution in an electrochemical cell. As is well known, the coated carbon is a favorable conductive agent, and it can obviously improve the electronic conductivity in the electrochemical process. In addition, Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> impurity may affect the electrochemical performance of the prepared materials [21,22].

For further investigating the effects of  $Li_3V_2(PO4)_3$ on the electrochemical performance of the prepared electrode, a cyclic voltammogram (CV) test was conducted at the scan rate of 0.05 mV/s between 3.0 and 4.4 V. From the CV curves in Fig. 5,  $V^{3+}/V^{4+}$  redox peaks for both  $Li_{3-x}V_2(PO_4)_3$  and  $Li_{1-x}VPO_4F$  are observed clearly in their curves, which are consistent with the initial charge–discharge test. This indicates that two independent electro-active materials,  $LiVPO_4F$  and  $Li_3V_2(PO_4)_3$ , coexist in the prepared sample. The peaks for  $Li_{1-x}VPO_4F$  are sharper than those for  $Li_{3-x}V_2(PO_4)_3$ , indicating that  $LiVPO_4F$  is the main capacity contributor.



Fig. 5 CV curve of prepared sample at scan rate of 0.05 mV/s

#### **4** Conclusions

1) Carbon coated  $LiVPO_4F$ , coexisting with  $Li_3V_2(PO4)_3$  and  $V_2O_3$ , is prepared by chemical reduction assisted with mechanical activation followed by short-time calcination. The oxalic acid is used as reducing agent as well as carbon source, and the pentavalent vanadium is reduced to trivalent vanadium by oxalic acid.

2) The synthesized crystal particles are adhered by an amorphous carbon layer. The high electronic conductive carbon film is deposited from CO at low temperatures, which is decomposed from the excess oxalic acid.

3) Both LiVPO<sub>4</sub>F and Li<sub>3</sub>V<sub>2</sub>(PO4)<sub>3</sub> act as

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electro-active materials and contribute to the capacity.

4) The prepared sample possesses good electrochemical performance, which is attributed to the stable structure of  $LiVPO_4F$ , micro-size particles and coated carbon layer.

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## 锂离子电池用 LiVPO<sub>4</sub>F/C 基正极材料的制备和性能

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**摘 要:**将H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O,NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>,NH<sub>4</sub>VO<sub>3</sub>和 LiF 通过球磨反应、烧结,合成了 LiVPO<sub>4</sub>F/C 基正极材料。在 这个过程中,草酸起还原剂和碳源的作用,利用热重、 X 射线衍射、 扫描电镜、透射电镜和碳-硫分析等手段 对合成的前驱体和材料进行检测和分析。XRD 分析表明,球磨反应后所得到的前驱体为无定形态,而烧结后的材 料中除了 LiVPO<sub>4</sub>F 的衍射峰外,还存在 Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>和 V<sub>2</sub>O<sub>3</sub>衍射峰。材料颗粒均匀,尺寸约 2 μm。透射电镜分 析表明,合成的材料颗粒表面包裹着一层约 2 nm 厚的无定形碳。在截止电压 3.0~4.4 V 时,合成的材料在 0.1C 和 10C 倍率下的放电比容量分别为 151.3 和 102.5 mA·h/g。在 10C 倍率下循环 50 次后容量保持率为 90.4%。在 LiVPO<sub>4</sub>F 和 Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 的循环伏安曲线中可以明显看到 V<sup>3+</sup>/V<sup>4+</sup>的氧化还原峰。

关键词: 锂离子电池; LiVPO<sub>4</sub>F; 球磨; 正极材料; 碳包覆