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Synthesis of $LiVPO_4F$ with high electrochemical performance by sol-gel route

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Abstract: $LiVPO_4F$ was synthesized by a novel sol-gel method under Ar atmosphere using $V_2O_5{\cdot}nH_2O$, LiF, $NH_4H_2PO_4$, and citric acid as starting materials, and its physicochemical properties were characterized using X-ray diffractometry (XRD), SEM, and electrochemical methods. The XRD patterns show that $LiVPO_4F$ displays a triclinic structure with a space group of $p\bar{1}$. The SEM results indicate that the particle size of $LiVPO_4F$ is about 0.8 μm together with homogenous distribution. The optimal sintering temperature and sintering time are 600 ℃ and 20 h, respectively, in order to obtain pure triclinic $LiVPO_4F$ with good electrochemical performance. $LiVPO_4F$ has the discharge capacity of 134 mA·h/g in the range of 3.0−4.4 V at the first cycle, and the discharge capacity remains 125 mA·h/g after 30 cycles. The sol-gel method is suitable for the preparation of $LiVPO_4F$ cathode materials with good electrochemical performance for lithium ion batteries.
Key words: lithium-ion batteries; $LiVPO_4F$; cathode material; sol-gel method

1 Introduction

Recently, phosphate-based compounds, such as $Li_3V_2(PO_4)_3$[1−3], $LiVPO_4F$[4−10], $LiFePO_4$[11−14] and $LiMnPO_4$[15], have been proposed as a new class of cathode materials for lithium-ion batteries. Lithium vanadium fluorophosphate, $LiVPO_4F$, is a highly promising cathode material and has attracted particular interests. $LiVPO_4F$ is isostructural with the naturally-occurring mineral tavorite, $LiFePO_4{\cdot}OH$ or ambylgonite, $LiAlPO_4F$, crystallizing with a triclinic structure (space group $p\bar{1}$). The reversible Li extraction/insertion reaction for $Li_{1-x}VPO_4F$, based on the $V^{3+/4+}$ redox couple, operates at about 4.2 V versus Li^+/Li. However, the conductivity of lithiated transition metal phosphates is not good. To improve the conductivity of lithiated transition metal phosphates, an effective way is to decrease the particle size by changing synthesis routes. The reduction of particle size may shorten the diffusion path of Li ion, and accordingly enhance the electrochemical performance. In this work, $LiVPO_4F$ was synthesized by a novel sol-gel method using citric acid as both reduction agent and carbon sources. The results showed that the particle size of $LiVPO_4F$ was decreased dramatically, and the electrochemical performance especially the reversibility is improved.

2 Experimental

2.1 Synthesis of $LiVPO_4F$

Firstly, $V_2O_5{\cdot}nH_2O$ hydro-gel was prepared. V_2O_5 was melted in a crucible by heating at 700 ℃ for 2 h in the furnace, and then the molten V_2O_5 was poured into water and a red brown solution was formed in a stainless steel container. Product was obtained by keeping the solution at room temperature for 10 h. Secondly, citric acid of equivalent mole to V_2O_5 and stoichiometric amounts of $NH_4H_2PO_4$ and LiF were added to the above

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$V_2O_5 \cdot nH_2O$ hydro-gels. The mixture was strongly stirred at room temperature for 2 h, and finally dried at 80 ℃ in an oven. The mixture was pressed into pellets and heated at 300 ℃ in a tubular furnace with flowing argon gas for 4 h to decompose and obtain precursor. The precursor was then ground again, pressed into pellets, heated at 600 ℃ and held for 20 h in flowing argon gas to obtain $LiVPO_4F$ sample.

2.2 Physical characterization

The powder X-ray diffractometry (XRD, Rint−2000, Rigaku) measurement using Cu K_α radiation was employed to identify the crystalline phase of the synthesized materials, and recorded at room temperature. The particle size and morphology of the $LiVPO_4F$ powders were observed by scanning electron microscope (JEOL, JSM−5600 LV) with an accelerating voltage of 20 kV. The carbon content of samples was determined by a carbon-sulfur analyser (Mlti EA2000).

2.3 Electrochemical test

The $LiVPO_4F$ electrodes were prepared by mixing with acetylene black, PVDF, and 1-methl-2-pyrrolidone in acetone to ensure homogeneity. The mass ratio of active material, acetylene black and PVDF in the electrodes was 80:10:10 except for special statement. The resulting slurry was pasted on an aluminium foil current collector with a diameter of 12 mm. After being dried in a vacuum oven at 120 ℃ for 24 h, the resulting electrodes with an active material loading of about 8 mg/cm^2 were transferred to an Ar-filled glove box to assemble testing cells. The testing cells comprise $Li_3V_2(PO_4)_3$ cathode, lithium metal anode and Celguard−2300 separator placed between the cathode and anode. The electrolyte was 1 mol/L $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. The cells were charged and discharged over a voltage range of 3.0−4.4 V versus Li^+/Li electrode. The electrochemical impendence spectrum (EIS) measurements were carried out with a CHI 600A electrochemical analyzer. Electrochemical impendence spectrum (EIS) measurements were performed in the frequency range of 10 kHz−10 mHz with an AC voltage of 5 mV. The EIS experiments were performed in the three-electrode system using metallic foils as both counter and reference electrode.

3 Results and discussion

Fig.1 shows the XRD patterns of $LiVPO_4F$ synthesized at different temperatures. $LiVPO_4F$ with triclinic structure appears at sintering temperature of 600 ℃, which suggests that there is sufficient sintering for the samples prepared at 600 ℃. When the sintering temperature is higher than 700 ℃, the diffraction peaks of the samples become sharp. Moreover, the impurity phase $Li_3V_2(PO_4)_3$ can be observed and the diffraction intensities become strong with the increase of the sintering temperature.

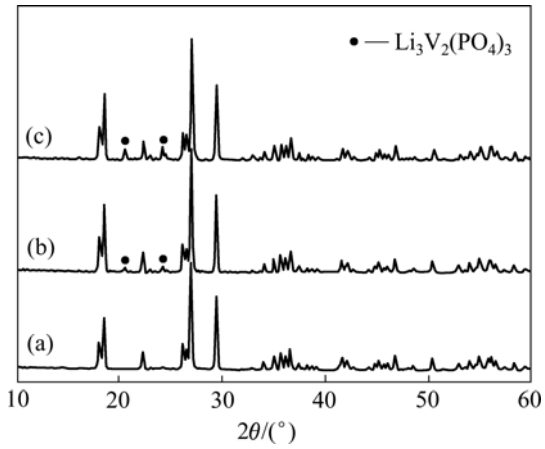

Fig.1 XRD patterns for $LiVPO_4F$ synthesized at different temperatures: (a) 600 ℃; (b) 700 ℃; (c) 800 ℃

The first charge-discharge curves of $LiVPO_4F$ samples prepared at various temperatures with 0.2*C* rate are shown in Fig.2. For these samples, the shape of charge and discharge curves is similar, while the initial charge and discharge capacities of $LiVPO_4F$ depend on sintering temperature. The sample synthesized at 600 ℃ exhibits the highest initial charge and discharge capacities of 140 and 134 mA·h/g, respectively. The columbic efficiency is about 95.71%.

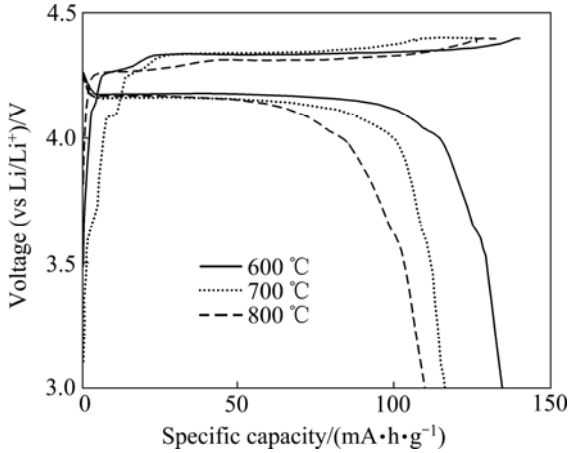

Fig.2 First charge-discharge curves of $LiVPO_4F$ synthesized at different temperatures

In order to explain why the first charge-discharge capacities of the sample depend strongly on sintering temperature, the SEM images are used to identify the morphologies of samples, as shown in Fig.3. When the samples were sintered at 700 ℃ and 800 ℃, the non-

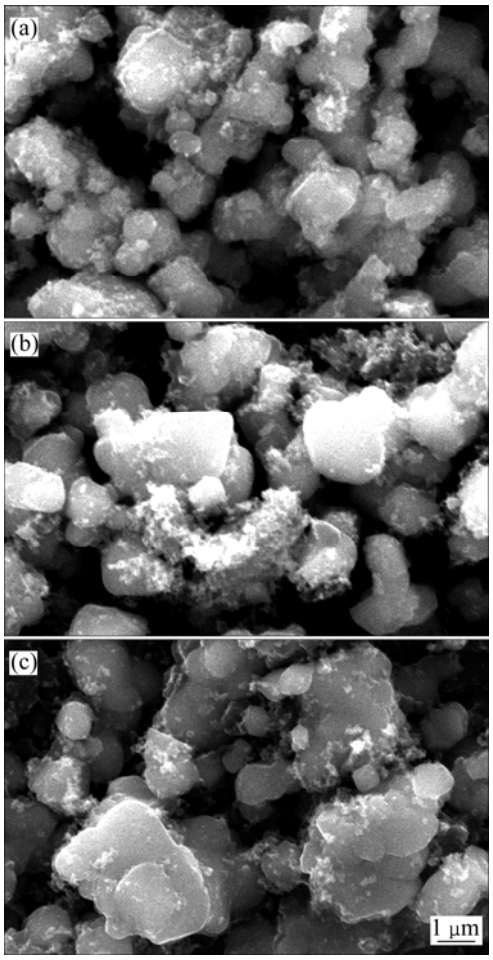

Fig.3 SEM images of $LiVPO_4F$ synthesized at 600 ℃(a), 700 ℃(b), and 800 ℃(c)

uniform particles with a smooth surface appear to be somewhat larger, which are agglomerated due to a higher sintering temperature and an abrupt decrease in capacity is observed.

Based on the above-mentioned results, it is necessary to study further the electrochemical properties of the composite prepared at 600 ℃. The cyclic performance of $LiVPO_4F$ synthesized at 600 ℃ is presented in Fig.4. It can be found that the $LiVPO_4F$ sample exhibits good rate capability with initial discharge capacities of 134 mA·h/g (0.2*C*), 132 mA·h/g (0.5*C*) and 127 mA·h/g (1*C*). At a rate of 0.2*C*, the discharge capacity reaches 125 mA·h/g after 30 cycles, which reaches the previously published result for the $LiVPO_4F$ samples prepared by two-step solid-state reactions[5]. When discharge rate increases to 1*C*, the discharge capacity still approaches to 111 mA·h/g after 30 cycles.

The electrochemical impedance spectra (EIS) of $LiVPO_4F$ electrodes materials were measured at different charging states. The typical Nyquist plots of EIS are presented in Fig.5 for three samples. Similar EIS patterns

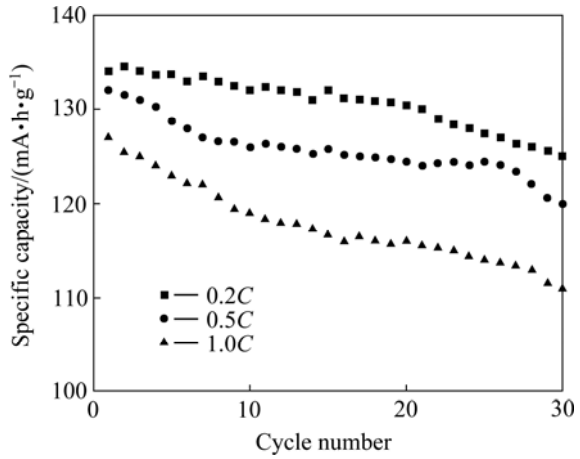

Fig.4 Discharge capacities vs cycle number at various rates between 3.0 and 4.4 V for $LiVPO_4F$ sample synthesized at 600 ℃

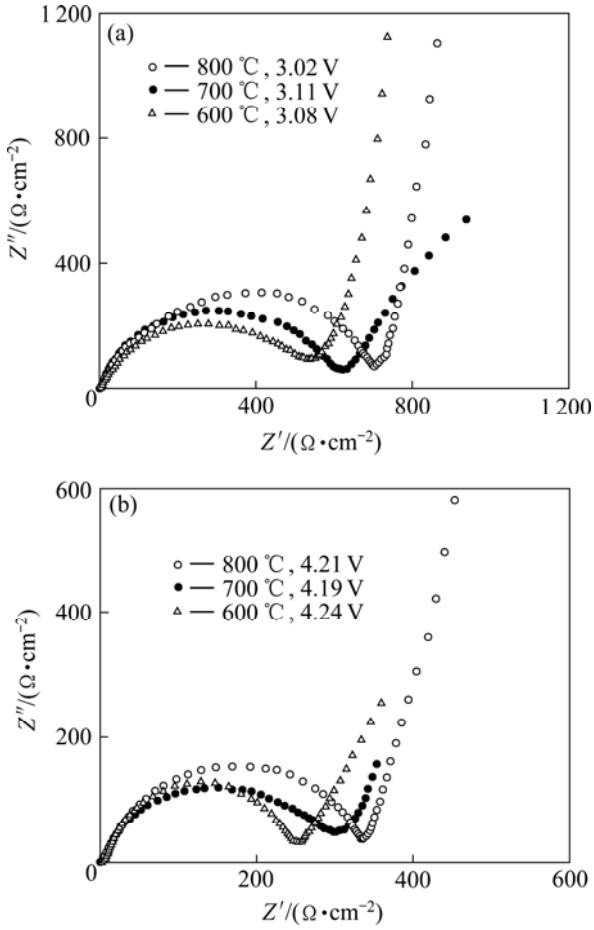

Fig.5 Nyquist plots for EIS of $LiVPO_4F$ synthesized at different temperatures at different charge states

are observed for $LiVPO_4F$ samples. A semicircle is observed to center on the real axis in the higher frequency range. In the lower frequency range, a straight line with an angle of about 45° to the real axis corresponds to the Warburg impedance. The higher

frequency semicircle is related to the charge-transfer resistance (R_{ct}) and the double-layer capacitance. The lower frequency tails are resulted from the diffusion of lithium ions in the bulk active mass. In the case of $LiVPO_4F$ synthesized at 600 ℃, the diameter of the semicircle significantly depends on the potential during the charging, which indicates that the film formation process is dependent on the lithium ion content. On the other hand, the charge transfer resistance, R_{ct}, shows a greater dependence on the lithium insertion and extraction levels. In the highly charged states, the sample is found to give lower R_{ct} values. By comparing the diameter of the semicircle of the above two systems, it can be found that $LiVPO_4F$ synthesized at 600 ℃ shows lower R_{ct} value than $LiVPO_4F$ synthesized at 700 ℃ or 800 ℃, which indicates that the proper synthesized temperature may increase the electronic conductivity and improve the Li^+ kinetic behavior.

4 Conclusions

1) $LiVPO_4F$ sample can be synthesized by a novel sol-gel method under Ar atmosphere when the sintering temperature is higher than 600 ℃. The electrochemical properties of $LiVPO_4F$ samples are seriously influenced by the sintering temperatures. Among the samples synthesized at various temperatures, the sample synthesized at 600 ℃ presents the highest initial capacity of 134 mA·h/g and a capacity of 125 mA·h/g after 30 cycles at 0.2*C*. At the discharge rate of 0.5*C* and 1*C*, the initial discharge capacities are 120 and 111 mA·h/g, respectively.

2) These results indicate that the sol-gel method is suitable for the preparation of $LiVPO_4F$ cathode materials with good electrochemical performance for lithium ion batteries.

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