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Synthesis of $LiMnPO_4$/C composite material for lithium ion batteries by sol−gel method

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Abstract: The $LiMnPO_4$/C composite material was synthesized via a sol−gel method based on the citric acid. The X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical performance tests were adopted to characterize the properties of $LiMnPO_4$/C. The XRD studies show that the pure olivine phase $LiMnPO_4$ can be obtained at a low temperature of 500 °C. The SEM analyses illustrate that the citric acid used as the chelating reagent and carbon source can restrain the particle size of $LiMnPO_4$/C well. The $LiMnPO_4$/C sample synthesized at 500 °C for 10 h performs the highest initial discharge capacity of 122.6 mA·h/g, retaining 112.4 mA·h/g over 30 cycles at 0.05*C* rate. The citric acid based sol−gel method is favor to obtain the high electrochemical performance of $LiMnPO_4$/C.

Key words: lithium-ion battery; cathode material; sol−gel method; $LiMnPO_4$/C; electrochemical performance

1 Introduction

Polyanion compounds $LiMPO_4$ (M=Mn, Fe, Co and Ni) are considered the promising cathode materials for lithium ion batteries. $LiMPO_4$ (M=Mn, Fe, Co and Ni) cathode materials have more advantages than traditional materials, such as low cost and toxicity [1−3]. The high electrochemical and thermal stabilities of $LiMPO_4$ are attributed to their phosphate structure [4,5]. In these compounds, $LiFePO_4$ has received a wide application. Recently, much attention has been paid to $LiMnPO_4$, because of its high voltage platform of 4.1 V. Compared with $LiFePO_4$, the theoretical energy density of $LiMnPO_4$ is about 1.2 times larger than that of the former [6]. However, $LiMnPO_4$ presents a poor electrochemical performance, which is attributed to difficulty in lithium ion diffusion and low electronic conductivity [7,8]. To these disadvantages of $LiMnPO_4$, one effective approach is to control the particle size. Generally, the appropriate particle size can make lithium ion diffusion easy [9]. However, the carbon coating [10−12] and metal ion doping [13−15] were also used to enhance the properties of $LiMnPO_4$. On the other hand, the electrochemical performance of $LiMnPO_4$ can also be improved by the optimized synthesis route. Taking a example of sol−gel method [16], the precursor is dispersed into the molecular level in the solution and the gel can be obtained during stirring process. Meanwhile, chelating agent is adopted to form the gel in this system. Finally, the sintering temperature is lower compared with traditional solid state route, and the particle size is minimized.

In this work, olivine $LiMnPO_4$/C was synthesized via a sol−gel method based on the citric acid. The citric acid was used as chelating agent and carbon source in this route. As a chelating agent, the citric acid can help precursor to disperse into the molecular level in the solution. During the sintering process, the decomposition of citric acid could minimize the particle size of $LiMnPO_4$/C. The effects of sol−gel route on $LiMnPO_4$/C were measured by TG, XRD, SEM and electrochemical performance test. The optimal synthesis conditions of $LiMnPO_4$/C by sol−gel method could be defined from these results.

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2 Experimental

The $LiMnPO_4/C$ composite material was synthesized via a sol−gel method based on citric acid. The stiochiometric amounts of $Mn(CH_3COO)_2\cdot4H_2O$, $CH_3COOLi\cdot2H_2O$, H_3PO_4 and citric acid were dissolved together in distilled water. The PEG400 was added into the aqueous solution. The pH of solution was controlled at 10 by $NH_3\cdot H_2O$. With stirring at 60 °C, the gel was obtained. After drying at 60 °C for 48 h, the precursor powder was sintered at 400−600 °C for 5−15 h under argon atmosphere.

Powder X-ray diffraction (XRD, X'Pert Pro) using Cu K_α radiation over the 2θ range of 10°−80° with a step size of 0.02° was employed to identify the crystalline phase of the synthesized materials. The particle morphologies of the powders were observed using scanning electron microscope (SEM, JSM−6380LV). The electrochemical characterization was performed using CR2025 coin-type cell. For positive electrode fabrication, the prepared active material $LiMnPO_4$ was mixed with 10% carbon 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, and the electrode was dried at 120 °C for 4 h in vacuum. The cathode were punched into circular discs with a diameter of 1.2 cm. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 mol/L $LiPF_6$ in EC+EMC+DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 2.75−4.50 V versus Li/Li^+ electrode on a battery tester (BTS−5V3A) at 0.05*C* rate. The cyclic voltammogram (CV) was investigated by electro-chemical workstation (CHI660A). The CV was tested at a scanning rate of 0.1 mV/s in the voltage range of 2.5−4.5 V.

3 Results and discussion

3.1 TG−DTA curves of precursor

TG−DTA curves for the gel precursor operated at a temperature of 25−1000 °C are shown in Fig. 1. As shown in DTA curve, an endothermic peak is observed at 160 °C, due to the process about thermal decomposition of ammonium salt and organic matter. About 10% of mass loss is observed during the temperature sweep to 160 °C. It can be seen that the mass loss is about 10% in the second mass loss temperature range of 160−200 °C. In the temperature range, citric acid begins the decarboxylation reaction, which is an exothermic reaction. As temperature increases to 300 °C, citric acid begins to burn and release heat. Therefore, a little exothermic peak can be observed at about 300 °C in DTA curve. Meanwhile, about 20% of mass loss is yielded during this combustion process. When temperature increases to about 400 °C, $LiMnPO_4/C$ is primarily formed and about 50% mass retains in the final product. So, $LiMnPO_4/C$ begins to form at 400 °C. It can be known that the synthesis temperature of $LiMnPO_4/C$ is significantly reduced by sol−gel method.

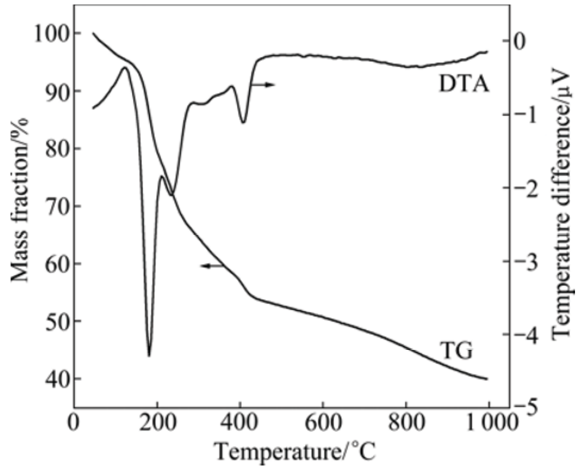

Fig. 1 TG−DTA curves of precursor

3.2 XRD patterns of synthesized $LiMnPO_4/C$ samples

X-ray diffraction (XRD) was adopted to investigate the effects of different sintering temperatures and time on crystal structure of $LiMnPO_4/C$. Figure 2 shows the XRD patterns of $LiMnPO_4/C$ samples calcined at different temperatures. The single olivine phase in $LiMnPO_4$ can be observed in three XRD patterns, and no impurity peak

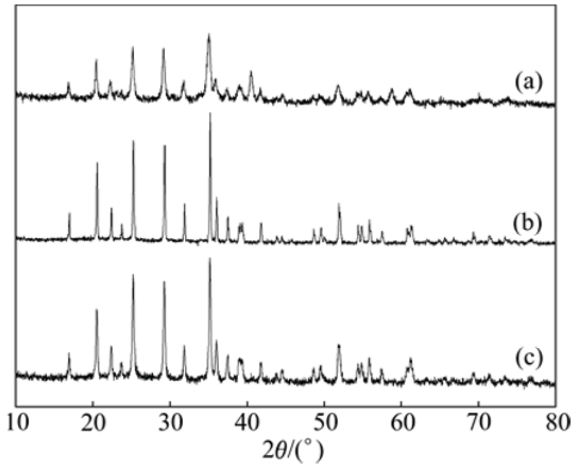

Fig. 2 XRD patterns of $LiMnPO_4/C$ samples calcined at different temperatures for 10 h: (a) 400 °C; (b) 500 °C; (c) 600 °C