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# Electrochemical performances of $LiFePO_4$/C composites prepared by molten salt method

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**Abstract:** $LiFePO_4$/C composites were synthesized by a molten salt (MS) method using the mixture of LiCl, LiOH and NaCl. The prepared $LiFePO_4$/C composites are characterized by X-ray diffractometry (XRD), field emission scanning electron microscopy (FESEM) and charge−discharge test. XRD patterns indicate that $LiFePO_4$ prepared in the temperature range of 550−700 ℃ crystallizes well in an olivine-type structure. Through FESEM images, the sphere-like and homogeneous particles of 0.2 μm can be observed. The charge−discharge test shows that the materials prepared at 600 ℃ for 12 h have good electrochemical performance. At the rates of 0.2*C* (34 mA/g) and 0.5*C*, the discharge capacities are 144.6 and 122.3 mA·h/g, respectively, together with good cycle performances.

**Key words:** lithium iron phosphate; molten salt method; cathode material; Li-ion batteries

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## 1 Introduction

Olivine-type $LiFePO_4$ has been one of the most promising candidates as cathode intercalation material for lithium-based secondary batteries since it was reported by PADHI et al[1]. Compared with conventional cathode materials, such as $LiCoO_2$ and $LiNiO_2$, it shows many advantages, such as nontoxicity, low cost, excellent structural stability and high theoretical capacity (170 mA·h/g). So, it is suitable to be used as the cathode material for the large-size lithium battery in the electric and hybrid electric vehicles (EV & HEV). However, its poor rate capability at high rates during the charge−discharge process due to the low intrinsic electronic conductivity and poor lithium ion diffusion becomes an obstacle to be applied extensively[2−3]. To overcome this limitation, a lot of efforts have been paid. Carbon coating is one of the efficient methods which can improve the surface electronic conductivity of active particles[4]. Super valence metal ion doping on Li-site or Fe-site is another way to enhance the intrinsic electronic conductivity or the lithium ion diffusion[5]. According to the model of ANDERSSON and THOMAS[6], producing small particles is also an available technique that can amend the electrochemical performance. Small particles can be synthesized by a variety of material processing methods, such as sol-gel method, hydrothermal method and liquid-state co-precipitation method[7−9]. Recently, the molten salt method (MS) has been widely employed to manufacture nano-materials, including cathode materials for lithium-based secondary batteries[10−12]. The small particles can be obtained at relatively low temperatures due to the high ion diffusion rates between reaction components in the molten media[13]. Olivine-type $LiFePO_4$/C has prepared by MS in this work, and its electrochemical performances are studied.

## 2 Experimental

### 2.1 Preparation of $LiFePO_4$/C

$LiFePO_4$/C was synthesized by the molten salt method from stoichiometric amounts of LiCl, $LiOH\cdot H_2O$, $FePO_4\cdot 2H_2O$ and NaCl in a molar ratio of 0.63:0.37:1:4. A certain amount of $C_6H_{12}O_6\cdot H_2O$ as carbon source was

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added. The precursors were mixed in a ball-milling machine at 500 r/min for 4 h with anhydrous ethanol as the dispersion medium. Then, the milled mixture was dried at 60 ℃ and calcined at a set temperature between 550 ℃ and 700 ℃ for 12 h. Finally, the products were washed completely with de-ionized water and anhydrous ethanol, filtered and dried in vacuum.

### 2.2 Characterization

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out on a simultaneous thermal analysis apparatus (NETZSCH STA409PC, Germany) to determine the sintering temperature. The milled mixtures were heated from room temperature to 750 ℃ at a heating rate of 5 ℃/min under nitrogen flow.

The phase purity and structure were characterized by X-ray diffractometry (XRD, D/max−2000 Rigaku, Japan) with Cu K$_\alpha$ radiation ($\lambda$=1.540 56 Å) operating at 40 kV and 40 mA. The scan range was $10^\circ < 2\theta < 90^\circ$, and a step of 0.01° was used.

The morphology was observed with field emission scanning electron microscopy (FESEM, Sirion, Holland). Transmission electron microscopy (TEM, Tecnai G 20 ST) observation was conducted in order to reveal the location of amorphous carbon, and the combined electron diffraction spectroscopy (EDS) investigation was performed for analyzing the spatial distribution of carbon element in the samples.

The content of carbon was investigated on the high-frequency infrared carbon-sulfur analyzer apparatus (CS−600, Leco Corporation). The corresponding carbon contents were 6.01%, 6.06%, 6.04% and 6.03% in the samples prepared at 550, 600, 650 and 700 ℃, respectively. The contents of Fe and P were determined by chemical analysis (YS/T53P.6−2006, Ammonium phosphate precipitation−acid-base titration), and the contents of other elements, such as Li, Na and K, were detected by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Advantage 1000).

### 2.3 Charge−discharge test

The positive electrode consisted of 80% as-prepared composites, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) as a binder, and metal Al was used as collector. Celgard 2400 was used as separator which was soaked in 1.0 mol/L $LiPF_6$/EC+DMC (EC:DMC=1:1 in volume ratio) electrolyte. Lithium metal foil was used as the counter electrode during electrochemical measurements. All cells were assembled in an argon-filled glove box. The charge−discharge tests were carried out by using a Land−BTL10 automatic battery test system. If not specified, the charge−discharge test was completed at 2.5−3.9 V and the density of current was 0.1*C* (17 mA/g).

Cyclic voltammetry was carried out on a CHI660B electrochemical working station (Chenhua, Shanghai, China) between 2.0 and 4.5 V at a scanning rate of 0.1 mV/s.

## 3 Results and discussion

### 3.1 TG-DSC analysis

Fig.1 shows the TG-DSC curves of the precursors used to prepare $LiFePO_4$/C. Mass loss takes place from room temperature to 500 ℃. The mass loss in the range of 20−500 ℃ is 22.29%, which is attributed to the degradation of $C_6H_{12}O_6\cdot H_2O$, $FePO_4\cdot 2H_2O$ and $LiOH\cdot H_2O$ and the reaction between $FePO_4$ and LiOH. There are two obvious endothermic peaks and a clear exothermic peak on DSC curve. The values of the peak position are 125.5 ℃, 170 ℃ and 424.5 ℃. The two endothermic peak positions correspond to the mass loss on TG curve. The clear exothermic peak at 424.5 ℃ may be attributed to $LiFePO_4$ transforming from amorphous form to crystalline[14−15]. Therefore, it is reasonable to set the sintering temperature between 500 and 750 ℃. Since the ion diffusion rates of the components in molten salts are much higher than those in the solid-state reaction, it probably takes less time to carry out the reaction. So, the heating time is also shortened to 12 h compared with the traditional solid state method, in which the precursor is usually sintered for more than 24 h[16].

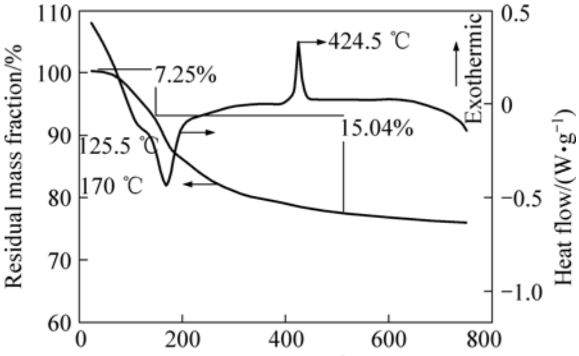

**Fig.1** TG-DSC curves of reaction precursors

### 3.2 XRD analysis

Fig.2 shows the X-ray diffraction (XRD) patterns of the $LiFePO_4$/C prepared at different temperatures. All samples are mainly identified as an olivine-type $LiFePO_4$ with space group of *Pnmb* (JCPDS card No. 83-2092) and minor $NaFePO_4$ (JCPDS card No. 29-1216) phase is also detected in the $LiFePO_4$/C composites. Carbon phase is not found, and it maybe exists in amorphous form.

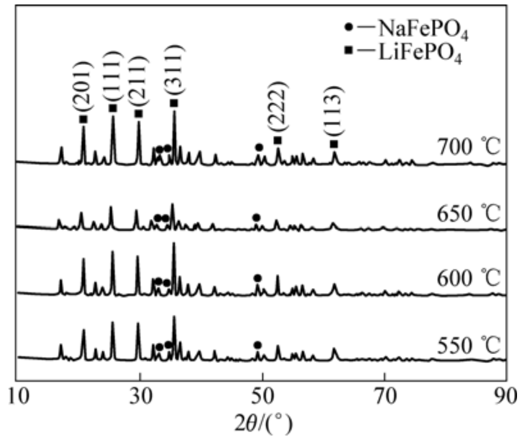

**Fig.2** XRD patterns of $LiFePO_4$/C composites

### 3.3 Electrochemical performance of $LiFePO_4$/C composites

Fig.3 shows the charge and discharge curves of $LiFePO_4$/C prepared at different temperatures for 12 h, all of which exhibit good electrochemical performances. The first discharge capacities of $LiFePO_4$/C prepared at 550, 600, 650 and 700 ℃ are 114.7, 136.3, 150.8 and 108.6 mA·h/g, respectively. The $LiFePO_4$/C composites prepared at 600 ℃ manifest the highest average discharge voltage and good shape among all the prepared samples. The average discharge voltages of $LiFePO_4$/C prepared at 550, 600, 650 and 700 ℃, are around 3.28, 3.36, 3.34 and 3.29 V, respectively. It may be attributed to the fact that the $LiFePO_4$/C powder prepared at 600 ℃ has better crystallinity than the samples prepared at lower temperatures, and smaller particle size than that prepared at 700 ℃[17]. So, an appropriate temperature must be carefully selected to prevent the undesirable particle growth and the presence of a noncrystalline phase.

Fig.4 shows the cycle performance of the $LiFePO_4$/C composites prepared at 600 ℃ and 650 ℃ at the rates of 0.1*C*, 0.2*C* and 0.5*C* at room temperature. The $LiFePO_4$/C composites prepared at 600 ℃ and 650 ℃ show comparable specific discharge capacities of 136.3 and 150.8 mA·h/g at 0.1*C*, 144.6 and 135.4 mA·h/g at 0.2*C*, and 122.3 and 111.8 mA·h/g at 0.5*C*, respectively. The $LiFePO_4$/C composites prepared at 600 ℃ exhibit good electrochemical performances at 0.5*C*, while obvious capacity loss is observed for other samples. The reason could be the higher content of $Na^+$ in the sample prepared at 650 ℃. According to XRD and ICP-AES analyses, $NaFePO_4$ phase are detected and the contents of $Na^+$ are 0.18% and 0.56% in the two samples prepared in 600 ℃ and 650 ℃, respectively. The presence of $Na^+$ in the $LiFePO_4$ crystal lattice could be harmful to the transmission of $Li^+$. The mechanism is still to be explored in the following work.

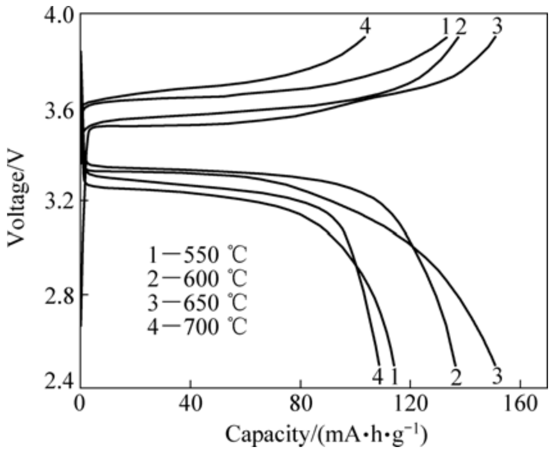

**Fig.3** Charge−discharge curves of $LiFePO_4$/C composites

Fig.5 shows the cyclic voltammetry curves of the $LiFePO_4$/C composites prepared at 600 ℃. The oxidation and reduction peaks appear at around 3.694 and 3.106 V, respectively, with the potential interval of 0.588 V. The peak of profiles are rather symmetric and spiculate, indicating a good cycle reversibility.

### 3.4 Morphology observation

Fig.6 shows the FESEM images of the $LiFePO_4$/C

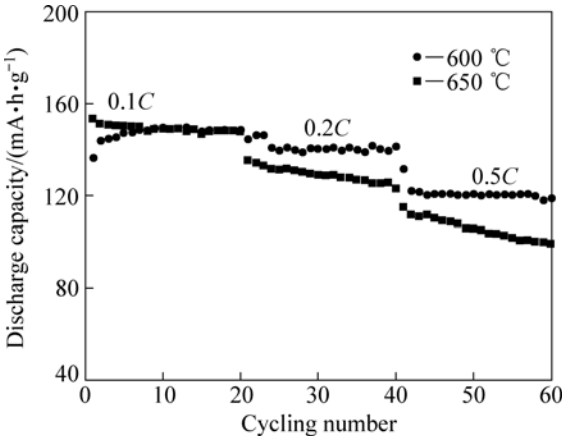

**Fig.4** Cycle performances of $LiFePO_4$/C composites

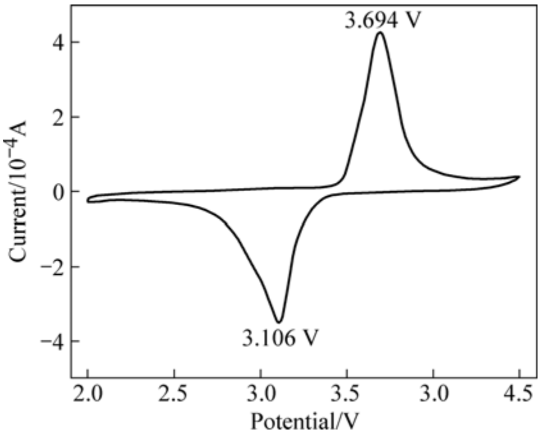

**Fig.5** Cyclic voltammograms of $LiFePO_4$/C composites (Scan rate 0.1 mV/s)

composites prepared at different temperatures in LiOH-LiCl-NaCl molten system. It is very obvious that the $LiFePO_4$ particles gradually grow up from 0.2 to 1.5 μm when the calcination temperature increases from 550 to 700 ℃. Those amorphous carbons, which are flaky in most cases, continuously distribute among homogeneous $LiFePO_4$ particles. In these cases of 550, 650 and 700 ℃, smoothly-edged polyhedral $LiFePO_4$ particles are observed, while they do not exist in the sample prepared in 600 ℃. Even so, in all these cases most particles are in spherical shape. With respect to the charge−discharge properties (Fig.4), it seems that the spherical shape of $LiFePO_4$ contributes to the better cycling behavior. The particles of $LiFePO_4$/C prepared by conventional solid-state reaction present the irregular geometry shape and aggregate seriously[18], the size of which is larger than that of samples prepared by MS method. It is also indicated that the presence of LiOH-LiCl-NaCl contributes to hindering the aggregation of $LiFePO_4$ particles. In the temperature range of 550−700 ℃, the growth behavior of $LiFePO_4$ particles in the LiOH-LiCl-NaCl may be similar with that in aqueous solution. Spherical shape morphology may result from the higher ion diffusion rate, rapid heat exchange and strong tensile force from the molten salt.

Fig.7 shows the TEM image and EDS analysis results of the $LiFePO_4$/C composites prepared at 600 ℃ in LiOH-LiCl-NaCl molten system. In Fig.7, the EDS analysis corresponds to the chemical composition of locations 1 and 2. It can be obviously observed that some amorphous carbons coat on the surface of the $LiFePO_4$ particles, and other dissociative carbons interconnect to form network, which contributes to the enhanced electric conductivity.

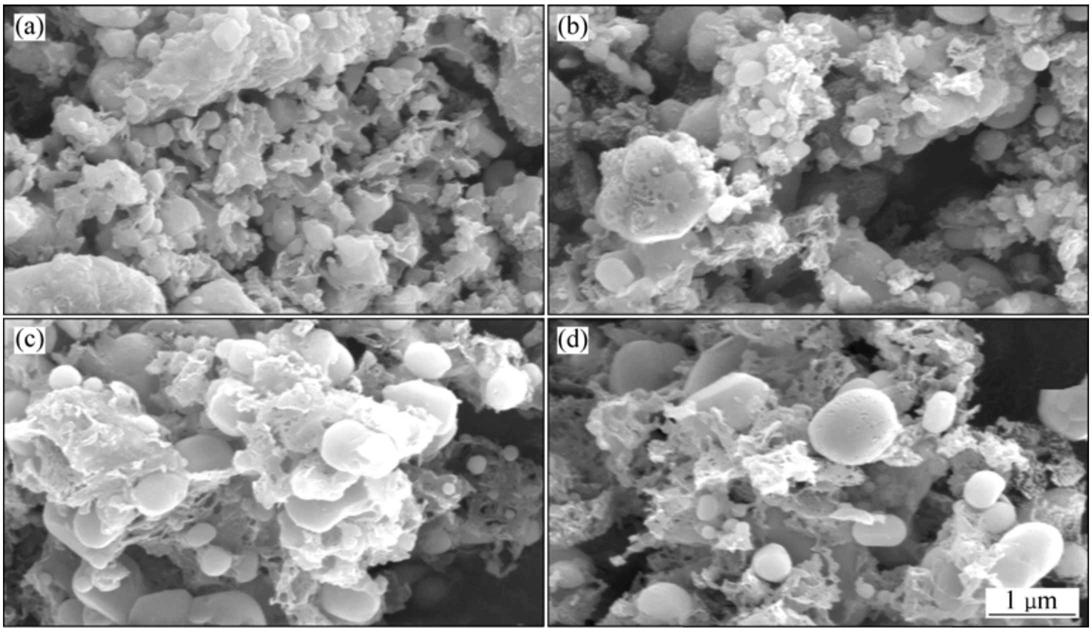

**Fig.6** FESEM images of $LiFePO_4$/C composites prepared at different temperatures in LiOH-LiCl-NaCl molten systems: (a) 550 ℃; (b) 600 ℃; (c) 650 ℃; (d) 700 ℃

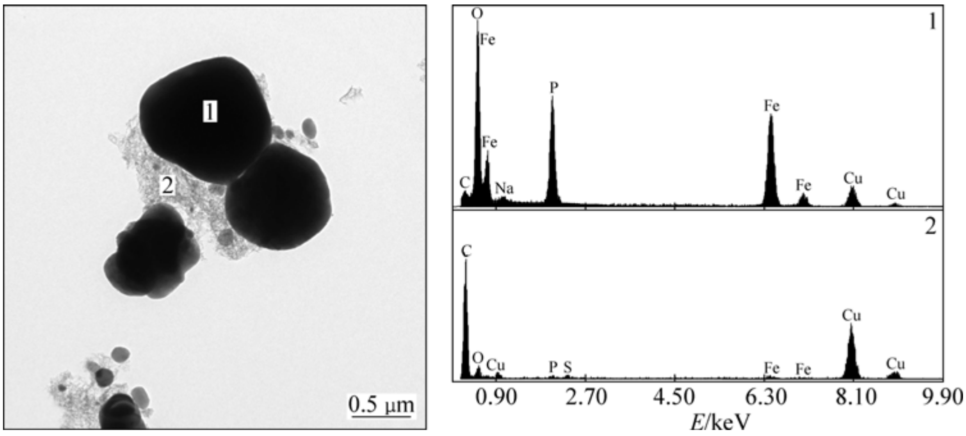

**Fig.7** TEM image and EDS spectra of $LiFePO_4$/C composites prepared at 600 ℃

## 4 Conclusions

1) Well-crystallized lithium iron phosphate has been successfully synthesized by molten salt method. The temperature of $LiFePO_4$ transforming from amorphous form to crystalline in LiOH-LiCl-NaCl molten system is 424.5 ℃. Compared with the solid-state reaction, $LiFePO_4$ synthesized by molten salt method requires lower temperature and shorter synthesized time.

2) Sphere-like and homogeneous particles of 0.2 μm can be observed through FESEM and TEM images.

3) $LiFePO_4$ synthesized at 600 ℃ for 12 h exhibits good electrochemical performance. At the rate of 0.2*C* (34 mA/g) and 0.5*C*, the discharge capacities are 144.6 and 122.3 mA·h/g, respectively, together with good cycle performances.

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