

# Biosynthesis and electrochemical characteristics of LiFePO<sub>4</sub>/C by microwave processing

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**Abstract** The yeast cells are adopted as a template and cementation agent to prepare LiFePO<sub>4</sub>/C with high surface area by co-precipitation and microwave processing. The electrochemical properties of the resultant products are investigated. The synthesized LiFePO<sub>4</sub>/C is characterized by means of X-ray diffraction, transmission electron microscopy (TEM), Brunauer–Emmett–Teller method, and battery test instrument. The LiFePO<sub>4</sub>/C particles with average size of 35–100 nm coated by porous carbon are observed by TEM. The LiFePO<sub>4</sub>/C, with the specific surface area of 98.3 m<sup>2</sup>/g, exhibits initial discharge specific capacity of 147 mAh/g and good cycle ability. The yeast cells as a template are used to synthesize the precursor LiFePO<sub>4</sub>/cells compounds. In microwave heating process, the use of yeast cells as reducing matter and cementation agent results in the enhancement of the electrochemical properties.

**Keywords** Composite materials · Chemical synthesis · Microstructure · Electrochemical properties

## Introduction

Lithium iron phosphate has recently become the object of great interest in the field of positive electrode materials for lithium batteries due to its particular advantages, such as low cost, nontoxicity, environmental friendliness, and high safety [1]. The specific capacity of LiFePO<sub>4</sub> positive electrode approaches 170 mAh/g for thousands of cycles at C/5 discharge rate, and the reversible capacity loss at higher discharge rates is small [2]. However, the main drawbacks in the choice of this material are related to low electronic conductivity (10<sup>-9</sup> S/cm) and slow diffusion rate of lithium ions across the two-phase boundary, which may result in losses in capacity during high-rate discharge [3]. Recent researches have suggested that this limitation of conductivity can be overcome by adding a conductive material when synthesizing the LiFePO<sub>4</sub> powders [4, 5]. To increase the electronic conductivity, various chemical routes are employed to produce carbon coating on the surface of LiFePO<sub>4</sub> particles [6, 7]. An order of magnitude increase in the electronic conductivity can be reached by the addition of carbon [8].

Using microbe cells as carbon source to prepare LiFePO<sub>4</sub>/C has not been reported. A few preparative approaches have been reported for the preparation of mesoporous material using microbe cells as template [9]. Previous studies have shown that inorganic minerals can be precipitated on or within microbial cells by infiltrating the template in soluble metal salts aqueous solution [10].

Several processing methods have been reported to prepare LiFePO<sub>4</sub> with varied morphology and fine particle sizes, such as microwave processing [11], hydrothermal synthesis [12], and carbothermal reduction method [13, 14]. The microwave irradiation has been shown to provide a novel, rapid, and economical method of preparing many

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important materials [15, 16]. Carbon is known to exhibit extremely high heating rates when subjected to microwave irradiation at the wavelength used in commercial ovens. In the meantime, microwave processing is used to avoid destroying the mesoporous structure of the  $\text{LiFePO}_4/\text{C}$  samples when heated at high temperature.

This paper introduces the research on the preparation, modification, and electrochemical characteristics of  $\text{LiFePO}_4/\text{C}$  cathode material for the lithium ion batteries. Yeast cells as a template are used to synthesize the  $\text{LiFePO}_4$  material with mesoporous structure. In microwave heating processing, the yeast cells as microwave absorbent and cementation agent enhance the electronic properties of  $\text{LiFePO}_4$  electrode materials.

## Experimental

The  $\text{LiFePO}_4/\text{C}$  samples were prepared by co-precipitation and microwave processing following the procedure. Quantitative instant dry yeast cells (0, 0.3, 0.6, 0.9, and 1.2 g) were cultivated in 60 ml glucose aqueous solution for 30 min at 36 °C, then stirred for 5 min with blowing nitrogen gas into the solution. One mole  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$  were dissolved in 40 ml distilled water. The  $\text{Fe}^{2+}$  and  $\text{Li}^+$  solution was dropped into the microbe culture solution with vigorous stirring and blowing nitrogen gas into the solution. The resulting solution was continuously stirred at room temperature for 2 h under nitrogen gas atmosphere; then, 50 ml 0.2 M  $\text{Na}_2\text{HPO}_4$  aqueous solution was slowly added to the aqueous suspension of Fe–Li microbes under a constant stirring condition. After stirring for 0.5 h under nitrogen gas atmosphere, a green color deposit was obtained. The resultant composite was recovered by centrifugation, followed by washing with distilled water and ethanol. The deposit was dried in vacuum oven at 80 °C. After drying, the resulting powders were calcined at 350 °C for 3 h. The resultant mixture was pressed into a disk-shaped pellet at a pressure of about 8 MPa. The pellets were put inside the melting pot filled with activated carbon, and the pot was placed inside the household microwave oven (650 W). After a few minutes of microwave irradiation, the  $\text{LiFePO}_4/\text{C}$  composites containing different amounts of carbon (0%, 2.8%, 7.4%, 12.1%, and 17.2%) were obtained.

The identification of the crystal phases of the obtained products was carried out by the X-ray diffraction (XRD) technique, using a PANalytical X'Pert PRO X-ray diffractometer with  $\text{Cu K}\alpha$  ( $\lambda=0.15418$  nm) incident radiation. The microstructural and morphological features of the obtained products were investigated with a JEM-100X electron microscope (JEOL, Japan) operated at 100 kV. The Brunauer–Emmett–Teller surface areas of the powders were

calculated from nitrogen adsorption isotherms with a Micromeritics apparatus (ST-08A, China, Beijing Huapu Analytic Instrument). The electrical conductivities of the  $\text{LiFePO}_4/\text{C}$  composites with various carbon amounts were determined by the ZL10 LCR instrument (Shanghai Instrument Research Institute, China).

For electrochemical measurements, the  $\text{LiFePO}_4/\text{C}/\text{polyvinylidene difluoride}$  mixture with weight ratio of 80:15:5 was used as the cathode. The electrolyte was a mixture of 1 M  $\text{LiPF}_6$ -ethylene carbonate/dimethyl carbonate (1:1, v/v). The cells were assembled in an argon-filled glove box. The electrochemical experiment was performed on a battery test instrument (BTS54, Xinwei, China) at a voltage range of 2.6–4.1 V at 0.1 C at room temperature.

## Results and discussion

It is generally believed that Fig. 1 shows typical XRD pattern of  $\text{LiFePO}_4$  obtained by microwave processing (firing at 650 W for 6 min) identified by JCPDS file (40-1499). The  $\text{Fe}_2\text{P}$  phase does not appear because of the thermal decomposition of the organic matter (yeast cells) at 350 °C for 3 h [17]. The elements composition of yeast cells mainly includes C, O, H, N, P, and microelements (Ca, K, Mg, Na, and S). After calcining at 350 °C for 3 h, some elements (O, H, N, P, and S) transform into gas, and residua are mostly carbon and some microelements (Ca, K, Mg, and Na). Through analyzing the XRD result, the impurities in the residua do not alter the crystallization of  $\text{LiFePO}_4$ . The main reason is that the impurity amount is too small. Meanwhile, we can infer that the size of the  $\text{LiFePO}_4$  crystallite estimated from the Scherrer law is about 25.2 nm.

The morphological features of the  $\text{LiFePO}_4/\text{C}$  powders have been investigated by transmission electron microscopy (TEM) as shown in Fig. 2. The surface of the  $\text{LiFePO}_4$  particles is coated with a carbon layer, while parts of carbon connect the  $\text{LiFePO}_4$  particles. The average size of the

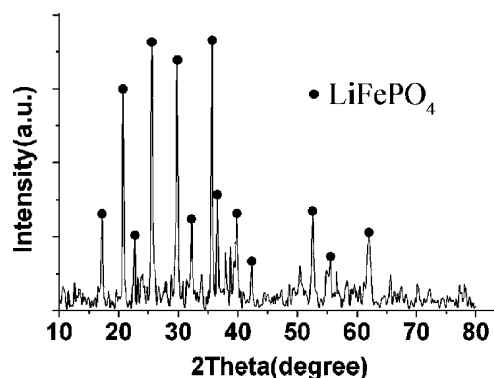
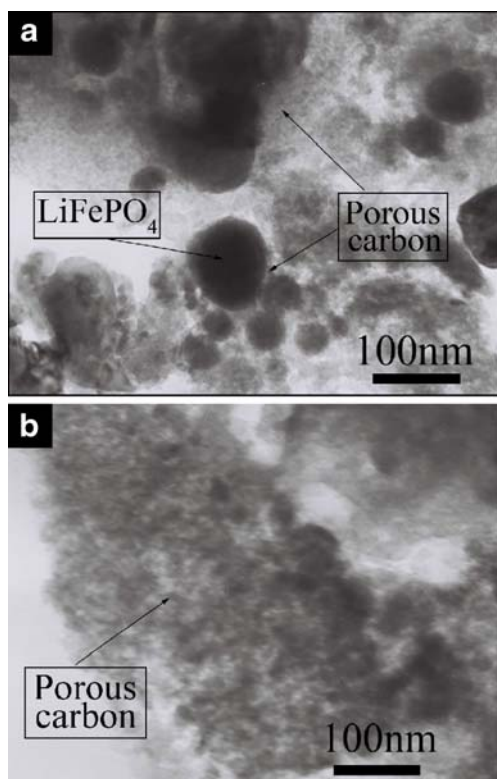


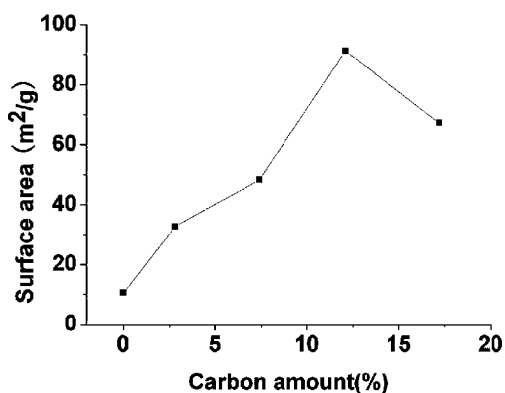
Fig. 1 XRD pattern of  $\text{LiFePO}_4$  synthesized by microwave processing



**Fig. 2** a, b TEM images of LiFePO<sub>4</sub>/C after 6-min microwave heating

LiFePO<sub>4</sub> particles with uniform spheric morphology is 35–100 nm, which is shown in Fig. 2a. The amorphous carbon is highly porous (Fig. 2b), which results in an irregular coating of the crystallites and high surface areas of LiFePO<sub>4</sub>/C powders. Such a carbon network leads to electronic interparticle connection and the enhancement of the electrochemical properties.

Figure 3 shows the specific surface areas of the samples with various carbon amounts. The specific areas of the samples rapidly increase with increasing of the carbon amount. The sample containing 12.1% carbon exhibits the



**Fig. 3** Specific surface areas of samples with various carbon amounts

**Table 1** Electrical conductivities of LiFePO<sub>4</sub>/C with various carbon amounts

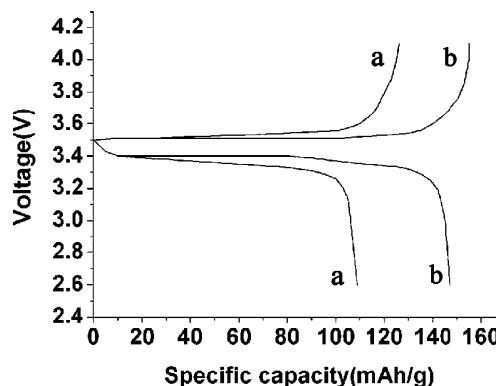
	Carbon amounts (%)				
	0	2.8	7.4	12.1	17.2
Electrical conductivity (S/cm)	$7.8 \times 10^{-9}$	$6.9 \times 10^{-5}$	$8.3 \times 10^{-4}$	$3.6 \times 10^{-2}$	$7.1 \times 10^{-2}$

highest specific surface area of 98.3 m<sup>2</sup>/g. The specific surface area of mesoporous LiFePO<sub>4</sub>/C is observably higher than that of the LiFePO<sub>4</sub>/C obtained by ordinary cementation process [18]. The high specific surface area is mainly attributed to the porous network structure of amorphous carbon. With continuous increase in carbon amount, the specific surface area decreases due to the accumulation of the excessive carbon and the disappearance of porous structure.

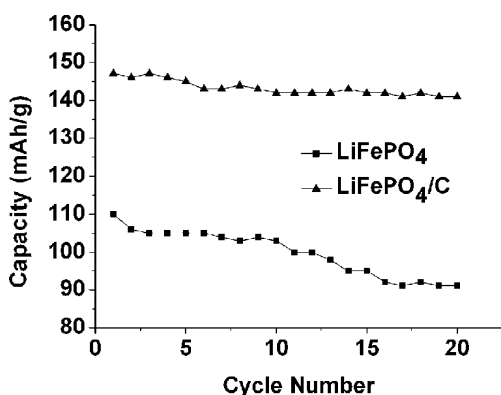
The electrical conductivities of LiFePO<sub>4</sub>/C composites with various carbon amounts are shown in Table 1. The carbon obtained by heating yeast cells plays an important role in the enhancement of electrical conductivity. With the increase of carbon amounts, the electrical conductivities of LiFePO<sub>4</sub>/C composites increase obviously from  $7.8 \times 10^{-9}$  to  $7.1 \times 10^{-2}$  S/cm. When the carbon amounts to more than 12.1%, the LiFePO<sub>4</sub>/C composites have steadily high electrical conductivity ( $10^{-2}$  S/cm).

The first charge and discharge curves of the samples between 2.6 and 4.1 V at 0.1 C are shown in Fig. 4. The initial discharge capacity of the LiFePO<sub>4</sub>/C containing 12.1% carbon is 147 mAh/g, whereas the pure LiFePO<sub>4</sub> powder is 110 mAh/g. As described in the previous section, the LiFePO<sub>4</sub>/C containing 12.1% carbon powder shows phase purity, small particle size, large surface area, and high electrical conductivity. As a result, the LiFePO<sub>4</sub>/C sample shows the better discharge capacity.

The cycle performances of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C powders at a current density of 0.1 C are shown in Fig. 5.



**Fig. 4** The initial charge/discharge curves of the LiFePO<sub>4</sub> (a) and LiFePO<sub>4</sub>/C containing 12.1% carbon (b)



**Fig. 5** Cycling performances of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C at 0.1 C

The discharge capacities of the LiFePO<sub>4</sub> powders drop from 110 to 91 mAh/g by the 20th cycle. The carbon-free LiFePO<sub>4</sub> powders show poor electrochemical activity, primarily due to their poor electrical conductivity. As for the LiFePO<sub>4</sub>/C containing 12.1% carbon powders, the discharge capacity is 147 mAh/g at the first cycle and 141 mAh/g after 20 cycles. The capacity retention rates over 20 cycles at 0.1 C are close to 97%, which indicate the good cycling stability of the sample.

The possible mechanism of synthesis and increase in the discharge capacity of LiFePO<sub>4</sub>/C are depicted in Fig. 6. In the synthetic process, yeast cells as a template provide nucleation sites for LiFePO<sub>4</sub> (Fig. 6a). Microbial cells have greater surface area and abundant surface charges within a broad range of pH and ionic strength [19, 20]. Therefore, yeast cells can adsorb massive Fe<sup>2+</sup> and Li<sup>+</sup> ions on the surface and in yeast cells. When Na<sub>2</sub>HPO<sub>4</sub> aqueous solution was added to the aqueous suspension of Fe–Li cells, the amorphous LiFePO<sub>4</sub> nanoparticles were synthesized on the surface and in yeast cells (Fig. 6b). The yeast cells can provide a multitude of nucleation centers and immobilize the LiFePO<sub>4</sub> nanoparticles by reacting between metallic ions and organic macromolecules to establish highly dispersed nanoparticle systems. After heat treatment, the LiFePO<sub>4</sub>/C composites with network structure were obtained (Fig. 6c). During the heat treatment process, yeast cells were carbonized and the porous carbon network structure formed. The LiFePO<sub>4</sub>/C composites with porous network structure can suck up electrolyte to shorten

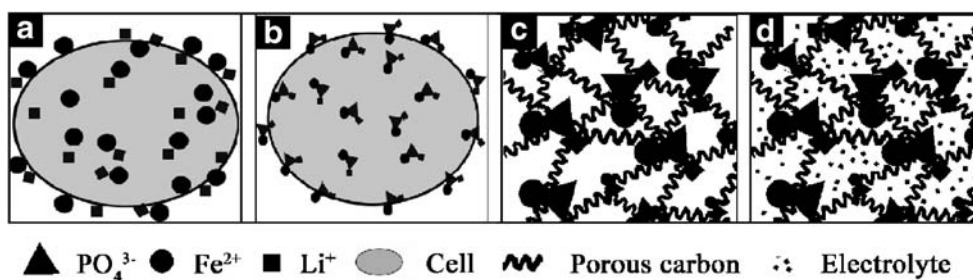
enormously the diffusive distance of lithium ions (Fig. 6d). The good electrochemical properties are attributed to perfect porous network structure that provides multidimension channels for diffusion of lithium ions. Meanwhile, the porous network structure of carbon layer has large specific surface area, which could provide large active sites for lithium ions' intercalation/deintercalation into/from LiFePO<sub>4</sub> nanoparticles. Therefore, the porous network structure of carbon layer plays a significantly important role in improving the electrochemical properties of LiFePO<sub>4</sub>.

## Conclusions

The addition of carbon has the advantage of much better electronic conductivity and high capacity. At present, it is necessary to optimize carbon source and prepare LiFePO<sub>4</sub>/C composite with excellent electrochemical properties. Using various carbon sources, which include carbon black [21], sugar [22, 23], malonic acid [24], and phenolic resin [25], the preparations of LiFePO<sub>4</sub>/C cathode materials have been reported in many publications. In comparison with the previous research results, the novel technique in this study has many merits. (1) The synthesis mechanism is completely different from that of the previous researches. In all previous researches, most carbon-doped methods are physical mixing. In this study, yeast cells connect metal ions by chemical binding [26, 27], and LiFePO<sub>4</sub> nanoparticles are synthesized on the surface and in yeast cells. After heat treatment, the in situ composite carbon is supposed to obviously improve the electrochemical properties of LiFePO<sub>4</sub>/C electrode materials. (2) The technique presented in this paper is a more economical and simpler way of preparing mesoporous LiFePO<sub>4</sub>/C materials. The synthesis conditions are simple. Using different amounts of yeast cells, the mesoporous LiFePO<sub>4</sub>/C with different specific surface area can be easily synthesized.

In this study, yeast cells are adopted as a template and cementation agent to prepare mesoporous LiFePO<sub>4</sub>/C by co-precipitation and microwave heating. The uniform spheric LiFePO<sub>4</sub> nanoparticles coated by porous carbon are observed by TEM. The LiFePO<sub>4</sub>/C powders containing

**Fig. 6 a–d** The possible mechanism of synthesis and increase in the discharge capacity of LiFePO<sub>4</sub>/C



12.1% carbon have the highest specific surface area of 98.3 m<sup>2</sup>/g, and the electrode material has the initial discharge capacity of 147 mAh/g and good cycling stability (more than 141 mAh/g at the 20th cycle). The electrochemical properties of the LiFePO<sub>4</sub>/C obviously increase mainly due to in situ composite carbon, large surface area, and the porous network structure of carbon layer. Meanwhile, the microwave heating process avoids destroying the mesoporous structure of LiFePO<sub>4</sub>/C. Therefore, using yeast cells as a template and cementation agent to biosynthesize mesoporous LiFePO<sub>4</sub>/C by co-precipitation and microwave processing is a potential method.

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