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# Hydrothermal synthesis of spindle-shape and craggy-faced $LiFePO_4$/C composite materials for high power Li-ion battery

Weiyan Yu [a,b], Lili Wu [a,b,*], Jinbo Zhao [c], Yanpeng Zhang [a,b], Gaozeng Li [a,b]

[a] Key Laboratory for Liquid-Solid Structural Evolution and Process of Materials (Ministry of Education), Shandong University, Jinan 250061, China
[b] School of Materials Science and Engineering, Shandong University, Jinan 250061, China
[c] School of Materials Science and Engineering, Shandong Polytechnic University, Jinan 250353, China

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ABSTRACT

The large surface area and excellent conductivity are two important factors for $LiFePO_4$ to achieve high power capability in Li-ion batteries. This paper presents a hydrothermal method to obtain large surface, spindle-shape and carbon-coated $LiFePO_4$ particles. Pyrogallic acid was added to serve as reducing agent, surface growth directing template and carbon source to synthesize craggy-faced $LiFePO_4$/C composite materials. It helps to control the morphology and implement carbon coating on the particles. The $LiFePO_4$/C particle synthesized with 8 wt.% pyrogallic acid demonstrates excellent electrochemical performance, cyclic ability and rate capability.



## 1. Introduction

Among the Li-ion battery cathode materials, the olivine $LiFePO_4$ has attracted great attention owing to its potential application as a cathode material. It possesses high theoretical capacity, environmental benignity, particularly high thermal stability, outstanding high-rate capacity, excellent cycle performance and cheap cost [1–6]. It is occupying the rapid demand in the market for Electric Vehicles (EVs) and Plug-in Hybrid Electric Vehicles (PHEVs) [2]. However, the poor electronic conductivity and slow lithium ion diffusion block the lithium ion battery for high-end consumers' need [6,7]. Numerous attempts have been made to improve its intrinsic drawback by carbon coating and ion doping in crystal [8–12]. The $LiFePO_4$ nanoparticles can be embedded in a nanoporous carbon matrix [13] or be Carbon-Nanotube-Decorated [14] to get superior high-rate performance for lithium-ion batteries.

It is also suggested that lithium ion diffusion kinetics is the direct aspect related to superior high-power electrochemical properties and the ability of lithium ion to travel across the interface between $LiFePO_4$ and electrolyte phase is crucial for ultra-fast diffusion [15]. Creating large surface area in electrode materials could be conducive to the high-rate capability by shortening the lithium ion diffusion path and increasing the interfacial contact between active particles and the surrounding electrolyte [16–19].

Recently, a few synthetic methods have been used to prepare large-surface $LiFePO_4$. Zhao et al. [6] have synthesized $LiFePO_4$ nanospheres in tridimensional porous carbon framework. This $LiFePO_4$/C composite possesses the considerably enhanced electronic conductivity of about $10^{-2}$ S cm$^{-1}$ and amazing high surface area of 200.5 m$^2$ g$^{-1}$, and the lithium ion diffusion gets up to $\sim 10^{-15}$–$10^{-14}$ cm$^2$ s$^{-1}$. Sun et al. [20] demonstrated a novel solvothermal synthesis of large scale $LiFePO_4$ microspheres consisting of nanoparticles with an open three-dimensional porous microstructure. These $LiFePO_4$ microspheres show excellent rate capability and cycle stability.

In this report, we first demonstrate by adding pyrogallic acid to synthesize craggy-faced and spindle-shape $LiFePO_4$ via hydrothermal method. Due to the adsorption of the assistant agent molecules onto the particle surface during the particle growth [21], a proper assistant agent in hydrothermal systems can tune the particle size and morphology. In this procedure, pyrogallic acid was used as template agent, reducing agent as well as carbon source. It is attractive in hydrothermal reaction as a synthetic medium. Effects of the template agent on the morphology and microstructures of $LiFePO_4$ are studied.

* Corresponding author at: Key Laboratory for Liquid-Solid Structural Evolution and Process of Materials (Ministry of Education), Shandong University, Jinan 250061, China. Tel.: +86 531 88392724.
*E-mail address:* wulili02002@yahoo.cn (L. Wu).

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## 2. Experimental

### 2.1. Synthesis

The powder of $LiFePO_4$ was synthesized using $LiOH{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $H_3PO_4$ and pyrogallic acid. The starting precursor solution was prepared in 3:1:1 molar ratio using the source materials. First, $Fe^{2+}$ salt (0.6 mol/L) and $H_3PO_4$ water solution were prepared and mixed together. Pyrogallic acid was added to avoid the oxidation of $Fe^{2+}$ to $Fe^{3+}$. Then $LiOH{\cdot}H_2O$ was added to this solution and stirred the precursor for five minutes. Ammonia was used to regulate pH at 8.2. This mixture was then quickly transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 6 h. After cooling to the room temperature, the precipitate was centrifuged and washed with deionized water, then dried at 80 °C for 6 h. Later, these products were heat treated at 600 °C for 4 h in Ar gas atmosphere to convert the residual pyrogallic acid to conductive carbon coating to improve the conductivity and restrain the growth of the products.

The samples obtained in this manner are hereafter abbreviated as LFP1 (sample obtained with the ratio pyrogallic acid/$LiFePO_4$ = 4:96 by wt. during synthesis), LFP2 (pyrogallic acid/$LiFePO_4$ = 8:92 by wt.), LFP3 (pyrogallic acid/$LiFePO_4$ = 16:84 by wt.).

### 2.2. Characterization

The crystallographic structure and purity of $LiFePO_4$/C composite were examined by X-ray diffraction (XRD) with a Philips diffractometer using Cu Kα radiation. The diffraction data were collected in the $2\theta$-range between 15° and 80°, with a step of 0.02°. The microstructure was observed using the field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and the high-resolution transmission electron microscopy (HRTEM, JEM-2100) at 200 keV.

The electrochemical performances of $LiFePO_4$ as cathode-active materials were carried out by using a coin-type cell. The $LiFePO_4$/C composite was mixed and ground with carbon black and poly vinylidene fluoride fluoride (PVDF) in the weight ratio of 75:15:10, dissolved in N-methylpyrrolidone (NMP) solvent to form homogeneous slurry. The prepared slurry was spread on Al foil. The coated electrodes were dried in vacuum at 120 °C for 12 h to remove NMP and moisture. The mass loading of these three electrodes were around 1.5 mg/cm$^2$. The electrolyte consists of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, volume). And the negative electrode was a lithium metal foil. The cells were galvanostatically charged and discharged between 2.5 V and 4.2 V versus $Li/Li^+$ under different current densities at room temperature (25 °C) on the electrochemical test instrument (CT2001A, Wuhan Land Electronic Co. Ltd., China). We include the carbon weight of composites to obtain the capacity values.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 shows the XRD patterns of the samples synthesized with the presence of pyrogallic acid. The results show that the well-resolved diffraction peaks of the three samples correspond to $LiFePO_4$ indexed in space group Pnma [JCPDS Card No. 83-2092] and the purity degree is high. No detectable reflections corresponding to carbon could be found in Fig. 1 due to its amorphous structure. The diffraction peaks of the products are intensive and narrow. It illustrates that the highly crystalline nature of $LiFePO_4$ was achieved.

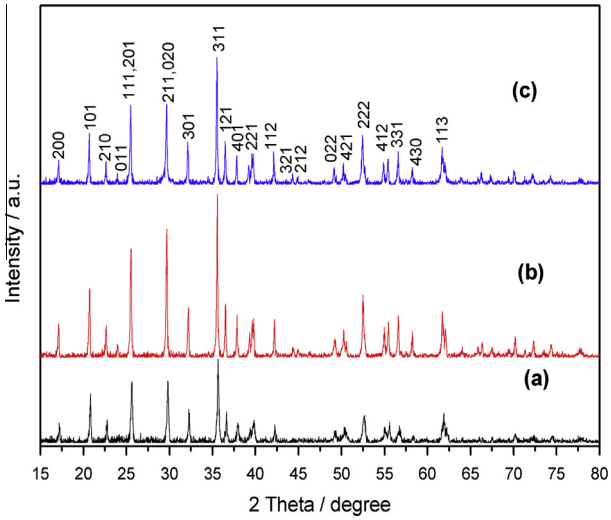


**Fig. 1.** XRD patterns of (a) LFP1 (prepared with 4 wt.% pyrogallic acid), (b) LFP2 (prepared with 8 wt.% pyrogallic acid), and (c) LFP3 (prepared with 16 wt.% pyrogallic acid).

### 3.2. Morphology studies

Morphologies of the $LiFePO_4$ particles were examined by field emission scanning electron microscopy (FE-SEM). Fig. 2a and b show the SEM images of LFP1 (prepared with 4°wt.% pyrogallic acid). The particles have a spindle shape with size distribution ranging between 1 and 2 μm and a mid-diameter about 600 nm (Fig. 2a). The particles have good dispersancy with little aggregation. This is mainly because that the hydroxyl of the pyrogallic acid is easy to form hydrogen bond with the oxygen atoms. When the nuclei formed, pyrogallic acid could easily adhere to the surface of the nuclei at the O-terminate by the hydrogen-bonding interaction. During the crystal growth process, pyrogallic acid influences the ordering manner of the crystal growth, leading to the change in crystal shape. It suggests that the pyrogallic plays the role of surface growth directing agent during the nucleation and growth stage of the process. Furthermore, pyrogallic acid owns stereo-hindrance effect, which restrains the growth of the crystal nuclei and prevents the aggregation of the particles [22]. In Fig. 2b, it can be found that the particle surface is full of ravines. The rough face could create a large surface area in active cathode materials, enhancing the interfacial contact between active particles and the surrounding electrolyte. It is conducive to the high-power capability by reducing the transport resistance of electron and lithium ion during intercalation/de-intercalation process. Pyrogallic acid plays a crucial role in controlling the morphology of $LiFePO_4$. While adding 8 wt.% pyrogallic acid (LFP2), the particle size and shape does not change apparently as shown in Fig. 2c. But the surface of the particles becomes more rugged as seen in Fig. 2d. Fig. 2e indicates that compared to the LFP2, the particle diameter expanded after 16 wt.% pyrogallic acid added (LFP3). As seen in Fig. 2f, the surface of the particles is etched with deep ridges. It is rougher than LFP1 and LFP2.

The HRTEM image of LFP2 is presented in Fig. 3. From the image, it could be seen that a uniform carbon coating layer is formed on the surface of the $LiFePO_4$ particles with a thickness about 3.4 nm. Such carbon layer could raise the electronic conductivity of $LiFePO_4$/C composite by connecting and wrapping the $LiFePO_4$ particles during the intercalation/de-intercalation process [23]. Then, the pyrogallic acid plays three different roles: (i) it serves as a reducing agent to avoid the oxidation of $Fe^{2+}$ to $Fe^{3+}$ under the hydrothermal condition. (ii) It controls the crystal