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Simple and Rapid Synthesis of $LiFePO_4$/C Composite for Lithium Rechargeable Batteries by Microwave-Solvothermal Method Assisted With Short Time Post-Treatment Process

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Abstact A simple and rapid technique to synthesize $LiFePO_4$ by microwave-solvothermal method assisted a short time post-treatment was described. The crystal structure and the charge-discharge performance of the prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and galvanostatic charge-discharge testing. The results indicated that this rapid synthesis technique by microwave-solvothermal method combined short time post-treatment was an effective way to obtain $LiFePO_4$ with a single olivine-type crystal structure and small particle size. The electrochemical research indicated that the resulting $LiFePO_4$/C composite could deliver 141.7mAh·g^{-1} at 0.1C at 25 ℃ and showed good stability retaining 97% after 45 cycles.

Introduction

Since the pioneering work of *Padhi et al*. [1], $LiFePO_4$ has been subjected to extensive study as a positive electrode material for a new generation of Li-ion batteries because of its flat voltage plateau (3.4 V versus Li^+ /Li), moderate theoretical specific capacity (170 $mAhg^{-1}$), high thermal stability, long cycling life, environmental friendliness and abundance of iron (Fe) resources in nature [2, 3]. However, olivine $LiFePO_4$ has suffered from certain disadvantages such as very low intrinsic electronic and ionic conductivities [4, 5], which bring big obstacles to its application in high-rate battery. Many efforts have been devoted to solve these problems and it has been widely proved that carbon coating and small particle size are crucial for $LiFePO_4$ to achieve the desired electrochemical properties [6, 7]. To date, various methods have been proposed to synthesize such an olivine $LiFePO_4$, such as solid-state reaction [8], sol–gel route [9], co-precipitation method [10] and hydrothermal method [11], but almost all the methods require long reaction time and rigid control of the calcinations atmosphere to guarantee Fe^{2+}, which are not economical. As an effective technique, the microwave irradiation method has been proposed for preparing many functional materials [12] including the $LiFePO_4$ phase [13]. Through this way the synthesis can be completed in a very short time, even exposed to the air，thus the preparation process can be greatly simplified. What′s more, a product with small particle can be easily obtained due to the rapid preparation.

In this paper, a simple and rapid synthesis of carbon-coated $LiFePO_4$ by combinating microwave-solvothermal method with the simple heat-treatment was investigated. It was worth noting that thanks to the rapid preparation, small size particle sample with olivine-type crystal structure had been obtained, which demonstrated an improved cell performance.

Experimental

Materials preparation.$LiFePO_4$ sample was prepared by a low-temperature microwave-solvothermal method assisted with a short heat treatment, and the detail procedures were described as following: H_3PO_4 (85.0%, Aladdin) and $FeSO_4 \cdot 7H_2O$ (99.0%, Aladdin) were firstly dissolved in distilled water, and then the above solution was dropwise added to a ethylene glycol

solution of LiOH • H_2O (95.0%, Aladdin) at room temperature to realize a Li: Fe: P molar ratio of 3:1:1 in a quartz vessel. A green mixture appeared in half an hour magnetic stirring, and the reaction was subsequently kept reaction at 160℃ for 10min in the microwave reactor (Biotage, UK) under magnetic stirring. No inert gas was needed in all process. After being cooled slowly to room temperature, the resultant solution was centrifuged, and the obtained grayish precipitate was washed several times with distilled water and finally dried in an oven at 80℃ overnight. Then, the as-prepared precipitate was mixed with a certain amount of sucrose as carbon source for carbon-coating, and the obtained mixture was calcinated at 600℃ for 2 h under pure N_2 to yield $LiFePO_4$/C.

Structural characterization. The sample was characterized by X-ray diffraction (XRD) using X'Pert Pro diffractometer with a step size of 0.02° for Cu Kα radiation (λ = 0.1542 nm). Lattice parameters were obtained using X'Pert HighScore Plus (version 1.0a) software. The sample morphology was characterized by a field emission scanning electron microscopy (FE-SEM) (s-4700, Hitachi, Japan).

Electrochemical measurement. The electrochemical performance of the $LiFePO_4$/C composites as cathode was evaluated using a CR2032 coin-type cell. The test electrode was produced by dispersing active materials (70 wt %), carbon black (20 wt %), and a poly(vinylidenefluoride) binder (10wt %) in N-methylpyrrolidone (NMP) solvent to form a homogeneous slurry. The slurry was then deposited on a current collector consisting of Al foil by blade and then dried at 80℃ for 10 h in a vacuum oven. The coin-type cell was assembled in a glove box filled with pure Ar. The electrolyte used was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1, w/w/w). A Li-foil and a polypropylene micro-porous film (Celgard 2300) were used as the counter electrode and separator, respectively.

Electrochemical capacity measurements were conducted on a Land Battery Test System (CT2001A, Wuhan Land Electronic Co. Ltd., China) with galvanostatic charge and discharge in the voltage range of 2.5–4.2 V at room temperature.

Results and discussion

Structural Analysis and Morphology Characterization. Fig. 1 showed XRD patterns of the samples synthesized by microwave-solvothermal method before and after calcinations. All the diffraction peaks of both samples could be indexed to an orthorhombic structure with a space group of Pnma ((JCPDS card No. 83-2092). The lattice parameters were calculated from the Rietveld refinement on the basis of Pnmb space group and the results were described in Table I. It was obvious that the parameters *a*, *b* and *c* were very well consistent with those of $LiFePO_4$. This clearly indicated that both samples were well crystallized and the carbon-coating process did not destroy the crystal structure of $LiFePO_4$. In addition, no obvious diffraction peaks for crystalline carbon appeared in the diffraction patterns, which indicated that the carbon generated from sucrose was amorphous and its presence had no influence on the olivine structure of $LiFePO_4$.

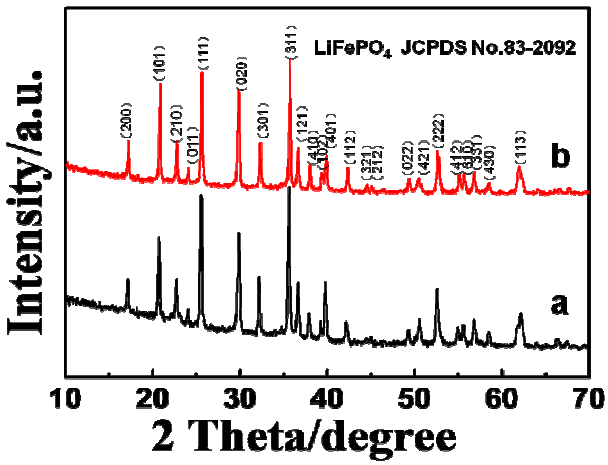

Fig.1 XRD patterns of the *(a)* as-synthesized and *(b)* carbon-coated $LiFePO_4$.

Table I. Lattice parameters of the prepared samples.

Samples	a (Å)	b (Å)	c (Å)	V (Å^3)
$LiFePO_4$	10.334	6.01	4.693	291.47
$LiFePO_4$/C	10.332	6.01	4.692	291.35

The SEM images of the prepared samples were shown in Fig. 2. Many spindle-like grains with a length of 200nm to 500nm and width of 100nm to 300nm could be observed in Fig. 2*a*. This result was similar with the conclusion depicted by *Yourong Wang* [15] and *Fei Teng* [16], which could be explained that ethylene glycol played an important role to control the particles morphology. The small size particle was prepared due to the rapid crystal nucleation process during all process. Also, it can be seen that the morphology of the sample did not change obviously after the calcination (Fig. 2*b*).

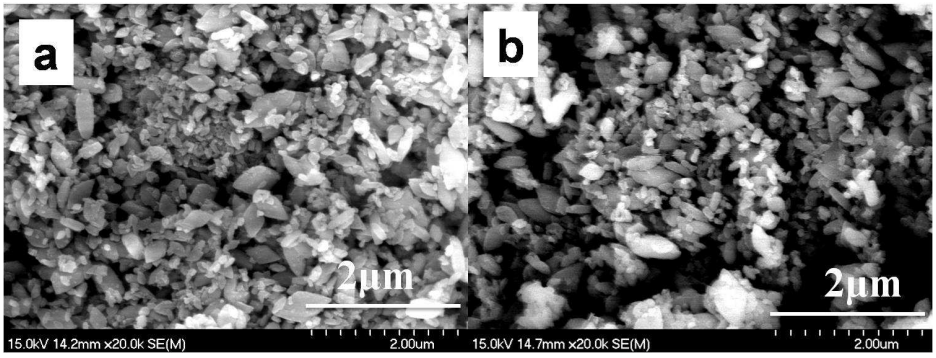

Fig. 2 The SEM images of the as-synthesized *(a)* and carbon-coated *(b)* samples.

Electrochemical Properties

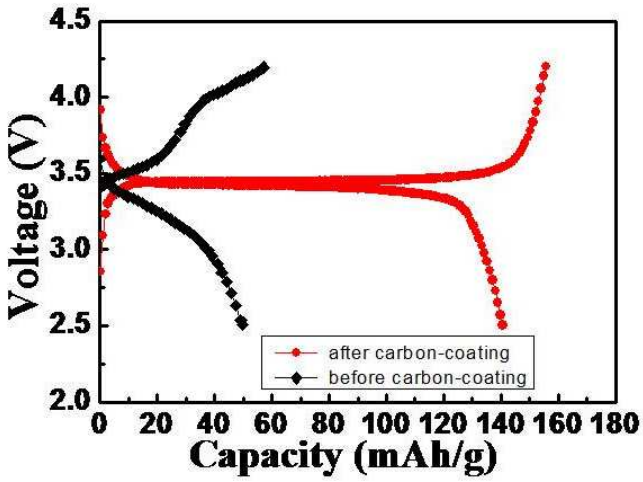

Fig. 3 The first charge–discharge curves of the samples before and after carbon-coating at 0.1C (17 mAg^{-1}).

Fig. 3 showed the first charge and discharge profiles of $LiFePO_4$ and $LiFePO_4$/C electrodes. The first discharge capacity of sample before carbon-coating was about only 49.7 $mAhg^{-1}$. *Dinesh Rangappa* [17] considered this unsatisfactory result may be due to the hydroxyl groups of EG, which was coating on the surface of the $LiFePO_4$ particles during the solvothermal synthesis. These organic groups increased the internal resistance of the cathode materials, leading to a low capacity and large polarization. After calcinations, these organic groups and the sucrose were transformed into carbon to enhance the electronic conductivity. The first charge and discharge capacity were raised up to 155.8 $mAhg^{-1}$ and 141.7 $mAhg^{-1}$ respectively, but a corresponding 14.1 $mAhg^{-1}$ capacity lost in the first charge/discharge process. According to the model proposed by *Anderson*, the irreversible capacity was due to the existence of unreacted $FePO_4$ in the center of large particles [18].

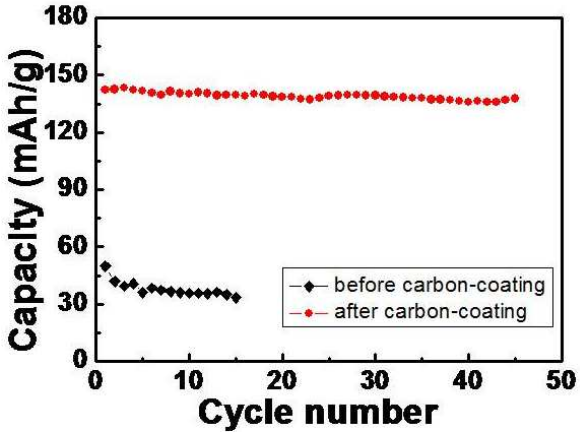

Fig. 4 Cycling performances (herein refers to discharge capacity) of the samples at 0.1C (17 mAg^{-1}).

The cycling performances of the samples at 0.1C were also studied, as shown in Fig. 4. It was found that the sample prepared by our combined method showed a stable cycling performance with less than 2.8% loss of capacity after 45 cycles.

Conclusion

In this work, well-crystallized $LiFePO_4/C$ was successfully prepared by a simple and rapid microwave-solvothermal method at 160℃ in 10min, assisting with a short heat treatment at an ambient temperature in 2h. The rapid preparation limited the crystal growing up and small size particle was obtained. The ambient temperature for calcinations did not destroy the crystal structure and morphology. The small size particle and the carbon-coating promoted the charge-discharge and cycling performances. This combined technique makes it promising as an economical method for $LiFePO_4$ preparation.

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