

Short communication

LiFePO₄ with enhanced performance synthesized by a novel synthetic route

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Abstract

Pure LiFePO₄ was synthesized by heating an amorphous LiFePO₄. The amorphous LiFePO₄ obtained through lithiation of FePO₄·xH₂O by using oxalic acid as a novel reducing agent at room temperature. FePO₄·xH₂O was prepared through co-precipitation by employing FeSO₄·7H₂O and H₃PO₄ as raw materials. X-ray diffraction (XRD), scanning electron microscopy (SEM) observations showed that LiFePO₄ composites with fine particle sizes between 100 nm and 200 nm, and with homogenous sizes distribution. The electrochemical performance of LiFePO₄ powder synthesized at 500 °C were evaluated using coin cells by galvanostatic charge/discharge. The synthesized LiFePO₄ composites showed a high electrochemical capacity of 166 mAh g⁻¹ at the 0.1 C rate, and possessed a favorable capacity cycling maintenance at the 0.1 C, 0.2 C, 0.5 C and 1 C rate. © 2008 Elsevier B.V. All rights reserved.

Keywords: Lithium ion battery; LiFePO₄; Nanocrystalline; Electrochemical performance

1. Introduction

Lithium iron phosphate (LiFePO₄) is a promising cathode material for lithium rechargeable batteries. This material has many advantages compared with conventional cathode materials such as LiCoO₂, LiNiO₂ and LiMn₂O₄, namely, it is environmentally benign, inexpensive, and thermally stable in the fully charged state [1–3]. In addition, LiFePO₄ has a large theoretical capacity of 170 mAh g⁻¹, good cycle stability, and a flat discharge potential of 3.4 V versus Li/Li⁺. However, LiFePO₄ suffers from the limitations of poor electronic conductivity and slow lithium ion diffusion, and hence performs unsatisfactorily at lower temperature and/or higher current densities [4,5]. The approach to overcome the insulating nature has been to coat the active particles with conductive carbon, either by its incorporation as a powder initially [6,7], or doped with high valence metal ions. The way to solve the limitation of lithium ion diffusion focus mainly on synthesizing small particles with high purity [8].

The olivine LiFePO₄ can be synthesized by different synthesis techniques including solid-state reaction [9], sol–gel [10],

hydrothermal [11], co-precipitation [12–14], microwave heating [15], etc. Traditional solid-state reactions are adopted by many researchers. However, the lengthy and complex procedures requiring repeated grindings and calcinations usually lead to the formation of larger particles with lower electrochemical performance. Solution methods usually have been developed for preparing LiFePO₄ with small particle sizes. However, many obstacles have been encountered because of the complicated synthesis techniques and the hard-controlled synthesis situation. In this paper, we introduce a novel, low cost and easy-controlled method to synthesize pure LiFePO₄ by using reducing agent to reduce Fe(III) at room temperature, then followed by heat treatment at low temperature without adding reducing agent again.

In this study, high purity LiFePO₄ cathode material was synthesized through two steps: (1) amorphous LiFePO₄ was obtained through lithiation of FePO₄·xH₂O using oxalic acid as a novel reducing agent at room temperature. (2) The amorphous LiFePO₄ calcined at 500 °C in a tube furnace with flowing argon (99.999%) to form nanocrystalline LiFePO₄.

2. Experimental

FePO₄·xH₂O was synthesized through the following procedure: (1) an equimolar solution of FeSO₄·7H₂O (99 wt.%) and

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H₃PO₄ (85 wt.%) was mixed; (2) then concentrated hydrogen peroxide (30 wt.%) solution was added to the solution under vigorous stirring; (3) subsequently a white precipitate formed immediately and the precipitate (FePO₄·xH₂O) was washed several times in de-ionized water and dried in an oven at 80 °C.

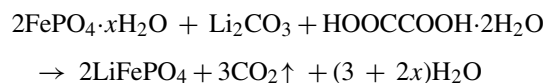
LiFePO₄ was synthesized from Li₂CO₃, FePO₄·xH₂O and HOCCOOH·2H₂O (all chemical 99% purity) taken in stoichiometric quantities. The process steps were: (1) initial mixing by magnetic stirring of all ingredients together as a slurry in 85% of distilled water at room temperature for 2 h, (2) ball milling for 4 h at room temperature, (3) drying in oven at 80 °C for 24 h in the air, and (4) thermal treatment at 500 °C for 12 h in argon atmosphere.

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu Kα_a radiation was employed to identify the crystalline phase of the synthesized materials. The particle size and morphology of the LiFePO₄ powders were measured by scanning electron microscope (JEOL, JSM-5612LV) with an accelerating voltage of 20 kV.

The electrochemical characterizations were performed using CR2025 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10% of carbon black and 10% of polyvinylidene fluoride in *N*-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 120 °C for 12 h in the air. The electrode loading density is about 1.95 mg cm⁻². The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 mol L⁻¹ LiPF₆ in EC, EMC and DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. Electrochemical tests were carried out using an automatic galvanostatic charge–discharge unit, NEWARE battery cyler, between 2.5 V and 4.1 V versus Li/Li⁺ electrode at room temperature.

3. Results and discussion

Raw material FePO₄·xH₂O, Li₂CO₃ and HOCCOOH·2H₂O under ball milling at room temperature reacted as the follows:



The color of the raw material changed from buff to aqua as the reaction went on, which is the proof of the Fe(III) being reduced by HOCCOOH·2H₂O. Fig. 1 shows the XRD pattern of LiFePO₄ prepared by lithiation of FePO₄·xH₂O at room temperature. It can be seen that there is no evidence of diffraction peaks in Fig. 1, indicating the synthesized LiFePO₄ is amorphous. Fig. 2 shows the X-ray diffraction pattern of the amorphous material after heating in argon at 500 °C for 12 h. The XRD pattern shows a series of diffraction peaks, indicating that a transformation from amorphous to a crystalline phase occurred at this temperature. The spectra of LiFePO₄ is almost the same as the spectra of pure ordered orthorhombic olivine structured LiFePO₄ (JCPDS card no. 40-1499). Besides, the diffraction

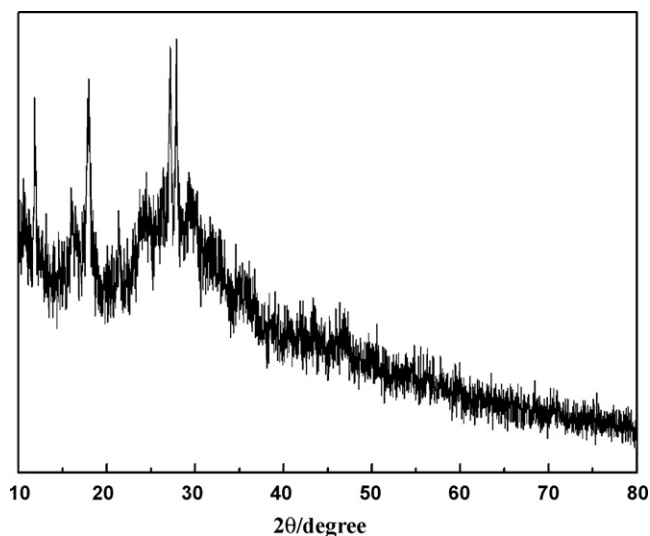


Fig. 1. XRD pattern of LiFePO₄ prepared by lithiation of FePO₄·xH₂O.

peaks are sharp, and the FWHM (full width at half maximum) is narrow. These indicate the synthesized LiFePO₄ is pure, and having higher crystallinity. The crystal lattice parameters calculated by the XRD data are $a = 10.33392 \text{ \AA}$, $b = 6.00914 \text{ \AA}$, $c = 4.69484 \text{ \AA}$, which is almost the same as it reported in the literature [16]. The crystallite size, t , was calculated from the X-ray line width using the Scherrer formula, $t = 0.9\lambda/\beta_{1/2} \cos \theta$, where λ is the X-ray wavelength, $\beta_{1/2}$ is the corrected width of the main diffraction peak (3 1 1) at half height, and θ is the diffraction angle. The line broadening was corrected using LaB6. The t value of the sample synthesized was found to be 53 nm. The SEM morphology of the LiFePO₄ sample is shown in Fig. 3. Fine particles can be observed, and the particle sizes are about 100–200 nm. The particle sizes are larger than that calculated using the Scherrer formula, this is attributes to particles aggregation.

The charge/discharge performance of the crystalline LiFePO₄ was evaluated in the Li/LiFePO₄ cell configuration

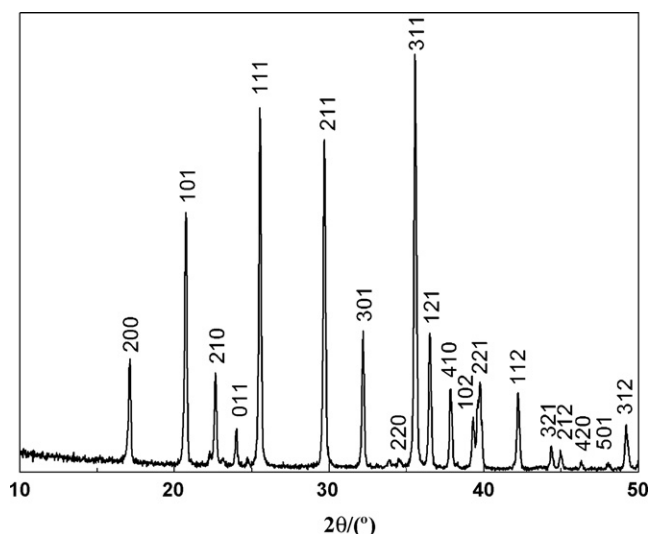


Fig. 2. XRD pattern of nano-crystalline LiFePO₄.

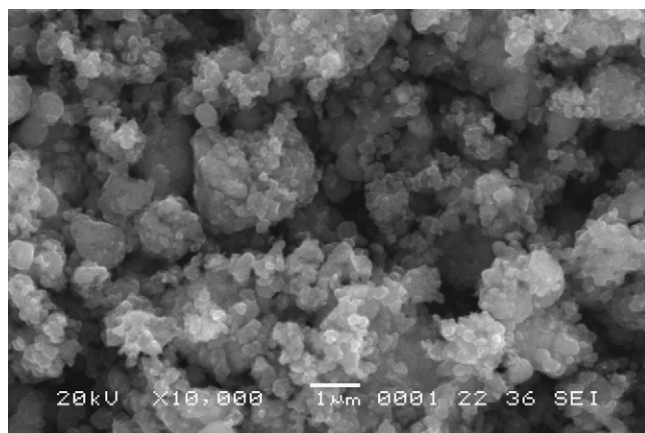


Fig. 3. SEM image of LiFePO₄ prepared at 500 °C, 12 h.

in the voltage of 2.5–4.1 V at room temperature. Fig. 4 shows the charge/discharge profiles of the crystalline LiFePO₄ cathode materials at different rate. As seen in Fig. 4, the initial discharge capacity of LiFePO₄ is about 166 mAh g⁻¹ at 0.1C rate (theoretical value: 170 mAh g⁻¹). By increasing the rate, the utilization of the active material decreased, and 160 mAh g⁻¹, 156 mAh g⁻¹, 154 mAh g⁻¹, 139 mAh g⁻¹, 130 mAh g⁻¹ and 95 mAh g⁻¹ were delivered at 0.2C, 0.5C, 1C, 2C, 5C and 10C rate, respectively. This result appears very good when compared with lithium iron phosphate synthesized by traditional solid-state reaction, in which an increase in the discharge current results in severe capacity decrease [17]. From Fig. 4, it can be seen that the charge/discharge potential plateau is almost around 3.4 V versus Li/Li⁺ at moderate current rates (up to 1C), and the flat has little change, which indicate the polarization is comparatively small. The excellent performances of the compound developed in our work are due to the unique microstructure and the small particle size achieved by the solution-based synthesis, followed by crystallization, compared to the procedures reported in the literature.

The cycle ability of LiFePO₄ at different discharge rates is showed in Fig. 5. The capacity retention was very good.

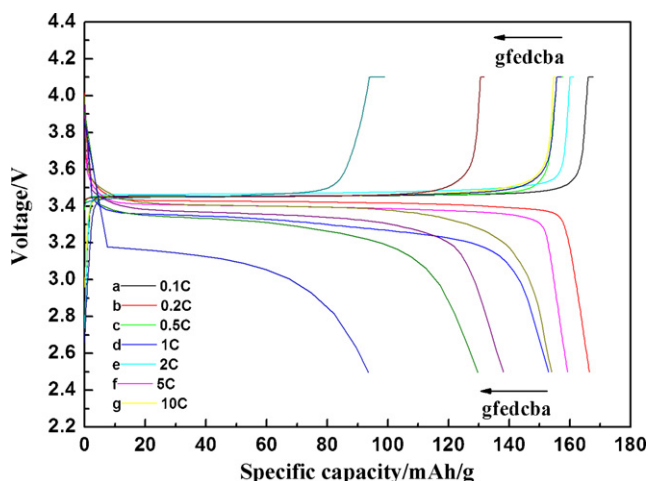


Fig. 4. Charge–discharge curves of LiFePO₄ at different rate.

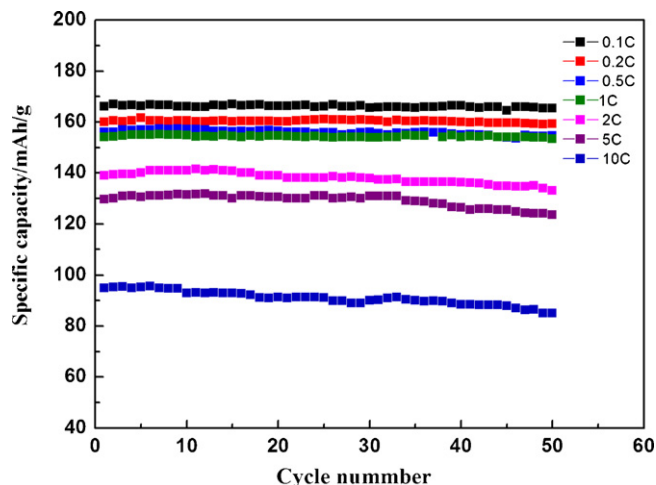


Fig. 5. Electrochemical cycling performance of LiFePO₄.

As seen in Fig. 5, the initial discharge capacity of LiFePO₄ at the rate 0.1C, 0.2C, 0.5C, 1C, 2C, 5C and 10C is about 166 mAh g⁻¹, 160 mAh g⁻¹, 156 mAh g⁻¹, 154 mAh g⁻¹, 139 mAh g⁻¹, 130 mAh g⁻¹ and 95 mAh g⁻¹, and the discharge capacity is about 165 mAh g⁻¹, 159.2 mAh g⁻¹, 154.66 mAh g⁻¹ and 153.4 mAh g⁻¹, 133 mAh g⁻¹, 123 mAh g⁻¹ and 85 mAh g⁻¹ after 50 cycles. The cell retains 99.4%, 99.5%, 99.1%, 99.6%, 95.6%, 94.6% and 89.5% of its initial discharge capacity after 50 cycles at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C and 10C rate, respectively.

4. Conclusions

Pure LiFePO₄ was synthesized by heating an amorphous LiFePO₄ at 500 °C. The amorphous LiFePO₄ obtained through lithiation of FePO₄·xH₂O by using oxalic acid as a novel reducing agent at room temperature. SEM images showed LiFePO₄ with an average particle size between 100 nm and 200 nm. The electrode performance of the pure LiFePO₄ synthesized by this method was shown to be enhanced. An initial discharge capacity of 166 mAh g⁻¹, 160 mAh g⁻¹, 156 mAh g⁻¹ and 154 mAh g⁻¹ were achieved at room temperature with cycle rates of 0.1C (17 mA g⁻¹), 0.2C (34 mA g⁻¹), 0.5C (85 mA g⁻¹) and 1C (170 mA g⁻¹), respectively. The excellent performance of pure LiFePO₄ synthesized by this method makes it feasible as a cathode active material for high-energy density, high-power lithium-ion batteries.

Acknowledgement

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