Fast Preparation of LiFePO₄ Nanoparticles for Lithium Batteries by Microwave-Assisted Hydrothermal Method

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Nanomaterial for lithium batteries can decrease mechanical strain upon lithium intercalation/deintercalation from lattice, and lead to high rate capability. The currently available microwave technology permits the development and implantation of a temperature-controlled microwave-assisted hydrothermal synthesis (TCMH) of nano-sized cathode material for lithium batteries. Unlike in previous reported traditional hydrothermal synthesis of cathode material LiFePO₄, the pure phase of LiFePO₄ can be simply and rapidly synthesized for 5 minutes in water under hydrothermal treatment with microwave irradiation. The homogeneous effects induced by microwave irradiation could create a uniform seeding condition. The colloid precursor Li₃PO₄ plays the key role to be the nucleation center for the new phase while the formation energy for LiFePO₄ would be decreased during the following microwave irradiation. The as-prepared pristine LiFePO₄ without carbon coating are characterized by X-ray diffraction, Raman, scanning and transmission electron microscopy, and tested as the cathode in lithium batteries. The particle sizes of pristine LiFePO₄ are dependent on hydrothermal and microwave-assisted hydrothermal condition and the electrochemical performance are relatively determined.

Keywords: Nanoparticle, Cathode Material, Lithium Iron Phosphate, Microwave-Assisted Hydrothermal Synthesis.

1. INTRODUCTION

LiFePO₄, with high theoretical capacity of 170 mAh·g⁻¹ and a flat discharge potential of 3.4 V versus Li/Li⁺, has become a new commercial cathode material for lithium-ion batteries.¹,² Compared with LiCoO₂, LiFePO₄ has many attractive advantages, such as environmental compatibility, low cost, excellent thermal stability and good cycling performance. The main problem of LiFePO₄ lies in its poor rate capability, because of its low electronic conductivity and slow kinetics of lithium ion diffusion through the LiFePO₄/FePO₄ interphase.³,⁴ To overcome this problem, minimizing the particle size of LiFePO₄ is one of good choices.³,⁵ Nano-sized cathode material can decrease mechanical strain upon lithium intercalation/deintercalation from lattice, and reduce path lengths for lithium-ion/electron transport through the material which can lead to high rate capability.³,⁶–⁷

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A successful cathode material is always dependent on its preparation, which controls the morphology, particle size and cation order, etc. There are many possible approaches to the synthesis of cathode materials, but in the end a commercially viable approach must be used.⁸,¹²,¹³ Traditionally high-temperature solid-state reaction synthesis has been widely used, is a time-consuming, energy consuming method. Soft chemical approaches, such as hydrothermal, solvothermal, and ion exchange show several advantages. Hydrothermal synthesis is a powerful method for the formation of cathode materials.¹¹–¹⁴ Whittingham’s group has been successfully prepared a number of pure phosphates and mixed metal phosphates by using hydrothermal method.¹⁵ The hydrothermal synthesis always required long reaction time in order to obtain highly crystalline phases, however long reaction time leads to the formation of large particles. And for improving the conductivity of LiFePO₄, post heat-treatment processing for carbon coating always needed. For example the pristine
LiFePO$_4$ without carbon coating showed poor electrochemical behavior with a capacity of only 90 mAh/g.\textsuperscript{15} Herein, we investigated the effect of microwave irradiation upon the reactant mixture while in hydrothermal condition and the formation of nanoparticles under the rapid preparation.

The microwave-assisted synthesis method has gradually gained popularity.\textsuperscript{16–18} These processes are understood to be more environmentally friendly, requiring less energy than conventional processes. The recent American Chemical Society monograph on Green Chemistry recommends that microwave energy is found to be more efficient in the selective heating in many processes.\textsuperscript{19} Unlike the traditional heating, the materials are heated on molecular level. Microwave irradiation assures a rapid and homogeneous heating from the outer surface to the interior of the entire sample. The formation of uniform nucleation centers and reaction rates are dramatically enhanced, and the nano-sized sample can be produced in several minutes. In recent years, microwave-assisted hydrothermal method has been widely used in the preparation of metal oxides nanoparticles.\textsuperscript{20–22} and mesoporous catalyst,\textsuperscript{17,23} and shown many advantages from a kinetic perspective as compared to conventional hydrothermal processing of oxides.\textsuperscript{24} Manthiram’s group have been synthesized LiFePO$_4$ nanoparticles by using microwave-solvothermal approach at the temperature of 300 °C. The discharge capacity of the resulting LiFePO$_4$ nanorods is about 130 mAh·g$^{-1}$ (40 nm of nanorods diameter) and 140 mAh·g$^{-1}$ (25 nm of nanorods diameter). Their microwave-solvothermal process employs polyol as a solvent.\textsuperscript{25,26}

In this work, we report on a facile one-pot synthesis of LiFePO$_4$ nanoparticle by taking advantage of microwave irradiation heating and hydrothermal effects simultaneously at a relatively lower controllable temperature. The microwave-solvothermal process employs water as a solvent. The use of microwave heating during hydrothermal treatment dramatically decreases the reaction time required to obtain nanosized LiFePO$_4$ particle. This work takes advantage of the existing capabilities of modern microwave systems to control the temperature and time for the entire synthesis of cathode materials.

2. EXPERIMENTAL DETAILS

2.1. Preparation

Phospho-olivine LiFePO$_4$ was prepared with the starting materials of LiOH·H$_2$O (AR, Shanghai Chemical Reagent Company, SCRC), FeSO$_4$·7H$_2$O (AR, SCRC), H$_3$PO$_4$ (85 wt% solution, SCRC). In a molar ratio for Li:Fe:P = 3:1:1, H$_3$PO$_4$ solution was slowly dropped into LiOH·H$_2$O solution, a white Li$_3$PO$_4$ colloid solution was formed and stirred for 2 hours followed by the rapid addition of FeSO$_4$·7H$_2$O solution. The above mixed solution of 25 mL was vigorously stirred for 2 min, and then put into a glass vessel of 50 mL capacity.

Microwave-assisted hydrothermal treatment was performed using MARS5 (CEM Corp., Matthews, NC) microwave reaction system, which uses a frequency of 2.45 GHz and can operate at a power level of 300, 600, or 1200 W. The wattage used in our experiments was 300 W, and power could be varied from 0 to 100% and was controlled by both pressure as well as temperature to a maximum of 300 psi and 200 °C, respectively. The process was carried out at 200 °C for 5 min, while the reaction system reaches to the set temperature point. During this microwave-hydrothermal process, precipitation took place inside the reactor. The resulting green-gray precipitate was filtered, washed with distilled water for several times, dried at 150 °C in the vacuum oven for 15 hours (termed as MH5). The post heat-treatment was carried out at 400 °C for 4 h and the product was termed as MH5_400C. The heat treatment was carried out in argon atmosphere to avoid the oxidation of Fe$^{2+}$ to Fe$^{3+}$ in order to obtain the relatively higher crystalline phase. For comparison, another batch of Li:Fe:P mixed solution was transferred into a 45 mL capacity Teflon-lined stainless steel autoclave. The autoclave was heated at 200 °C for 10 hours. Precipitates were collected by suction filtration and dried at 150 °C for 15 h in a vacuum oven.

2.2. Characterization

All X-ray studies were done on a Rigaku diffractometer with Cu K$_\alpha$ radiation, and the Rietveld analysis used the GSAS/EXPGUI refinement program. Raman spectra were obtained at room temperature on a JY HR800 spectrometer. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were done with Hitachi X650 microscope (20 kV) and JEOL JEM-200CX (200 kV). A little amount of sample was dispersed in absolute ethanol and ultrasonicated to obtain a homogenous suspension, and then a drop of the suspension was dripped onto a copper grid supported carbon film. After being naturally dried, the carbon film with dispersed sample was observed with TEM.

2.3. Electrochemical Test

To test these materials as cathodes in lithium cells, the as-prepared samples were mixed with carbon black and Teflon powder (Dupont) in the weight ratio 80:15:5. Lithium foil (Aldrich) was used as the anode, and 1 M LiPF$_6$ in EC:DMC = 1:1 (CEM Industries) was used as the electrolyte. Cells were assembled in an argon-filled glove box. Cyclic voltammetry were recorded with a scan rate of 0.2 mV·s$^{-1}$ between 2.6 and 4.1 V on a Solartron system (SI 1287). A lithium foil acted as both the counter electrode and reference electrode. Cycling and charge-discharge performances of the testing cells were carried out.
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Fig. 1. Schematic of the steps involved in the synthesis of LiFePO$_4$ nanoparticle under microwave irradiation.

Fig. 2. XRD pattern for LiFePO$_4$ samples: (a) Hydrothermally formed sample, (b) MH5, (c) MH5_400C.

3. RESULTS AND DISCUSSION

Chemical synthesis by microwave heating is very efficient, since it offers rapid volumetric heating, high reaction rates and selectivity, and is energy saving. In the temperature-controlled microwave-assisted hydrothermal (TCMH) process, the homogeneous effects induced by microwave irradiation could create a uniform seeding condition. Therefore, the production of LiFePO$_4$ crystals with a narrow size distribution is feasible and the reaction can be accelerated. Figure 1 shows a schematic outline of the microwave-assisted hydrothermal crystallization approach to prepare LiFePO$_4$ nanoparticles without the use of any organic reducing agent and argon protection. Since microwave irradiation methods are rapidly approached without suffering thermal gradient effects, this route is ideal for large-scale industrial production of high quality nanomaterials and may also be extended to create other cathode material, especially for materials with metastable structure.

In a typical procedure, H$_3$PO$_4$ solution was dropped into aqueous LiOH solution and a white colloid Li$_3$PO$_4$ was obtained. The following addition of Fe$^{2+}$ solution might be

Fig. 3. Rietveld refinement of microwave-assisted hydrothermally formed LiFePO$_4$ at 200 °C for 5 minutes.
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Fig. 4. Raman spectrum of microwave hydrothermal synthesized LiFePO₄ powder (MH5) at 200 °C for 5 minutes.

absorbed on the surface of Li₃PO₄ colloid. For the rapid formation of olivine LiFePO₄ in 5 minutes, some multiple effects should be induced by microwave irradiation in the reaction. The existence of Li₃PO₄ colloid plays the key role, since no other templates are used in the reaction system (Fig. 1(a)). The colloid precursor Li₃PO₄ might be the nucleation center for the new phase of LiFePO₄ while the formation energy for LiFePO₄ would be decreased during the following microwave irradiation (Fig. 1(a)). By comparison, LiOH and FeSO₄ solution was mixed and a colloid Fe(OH)₂ was formed first. After dropped by H₃PO₄, the colloid was dissolved and a clear precursor solution was obtained. The above clear solution cannot convert to LiFePO₄ phase under microwave irradiation, and a mixture impurity was produced (Fig. 1(b)).

Figure 2 shows the X-ray diffraction patterns of samples synthesized at 200 °C for 5 minutes (MH5), the post heat-treatment of MH5 at 400 °C for 4 hours (MH5_400C), and hydrothermally formed LiFePO₄. High crystallinity and purity of the samples are shown in Figure 2. The only phase observed is LiFePO₄ olivine structure, and all the diffraction peaks can be indexed on the orthorhombic structure with the space group Pnma(62).

In the case of MH5, we performed a Rietveld refinement using the GSAS crystallographic software (as shown in Fig. 3). The cell parameters of MH5 obtained from Rietveld refinement are: a = 10.291(5) Å, b = 5.963(9) Å, c = 4.691(8) Å, which are smaller than the previous results (JCPDS 81-1173, a = 10.332 Å, b = 6.010 Å, c = 4.692 Å) and similar with the results of the other rapid preparation in alcohol solution.¹⁰ The lattice parameter difference would come from the different preparation route. In microwave field, the formation rate of FeO₆ octahedral and PO₄ tetrahedral and the diffusion of Li⁺ ions may be different with that in traditional method.

Figure 4 shows Raman spectrum of LiFePO₄ formed at 200 °C for 5 min by TCMH method. Raman spectroscopy is sensitive to studying the surface of materials compared with XRD. The peaks observed in Figure 4 agree very well to the assignments reported in the literature.²⁹ The PO₄⁻ symmetric stretching band at 953 cm⁻¹ becomes the dominant band in LiFePO₄, and the PO₃⁻ antisymmetric stretching region is a weak band at 1068 cm⁻¹. Many of the bands between 650 and 400 cm⁻¹ belonging to ν₁ and ν₃ in LiFePO₄ appear to be weak and poorly resolved. Below 400 cm⁻¹, bands belonging to the external modes of LiFePO₄ are observed. It further considered that LiFePO₄ pure solid-phase can be formed in 5 minutes, and no Fe²⁺ was oxidized to Fe³⁺ during microwave-hydrothermal process.

The morphology of cathode material LiFePO₄ is of great importance to its electrochemical performance, ultrafine and homogenous spherical sample is preferred.⁸,¹⁰ The SEM images of LiFePO₄ sample (MH5) are depicted in Figure 5. The general appearance of the sample is mostly homogeneous, and the small globular grains are incompactly aggregated in the range of 1–3 μm are distinguishable (as shown in Fig. 5(b)). It might be due to the fact that a large amount of nucleation are rapid formed on the initial reaction upon microwave irradiation with penetrated property and accelerated ion diffusion. These
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Microcrystals cannot grow bigger in the following short reaction time (5 minutes).

Figure 6(a) shows the transmission electron microscopy image (TEM) of LiFePO₄ samples synthesized by hydrothermal and microwave-assisted hydrothermal methods respectively. The hydrothermally formed LiFePO₄ shows relatively large particles (about 250 nm). However, the rapid formation of LiFePO₄ in 5 min by using the microwave-assisted hydrothermal method, the average particle size of MH5 is about 30 nm. The formation of MH5 further confirmed that the rapid microwave-hydrothermal synthesis can form homogeneous nanoparticles. For obtaining the high crystalline LiFePO₄ sample, MH5 has post heat-treatment on 400 °C for 4 hours (MH5_400C), and the globular particles size are increased to 80 nm.

Figure 7 shows the cyclic voltammetry of the synthesized LiFePO₄ material, MH5 and MH5_400C. There is only one peak pair that corresponds to the charge/discharge reaction of the Fe³⁺/Fe²⁺ redox couple, and evidencing the absence of electroactive iron impurities. The cathode MH5 exhibited sharp oxidation (3.53 V) and reduction (3.38 V) peaks, consistent with a two-phase reaction at about 3.4 V versus Li/Li⁺. The well defined peaks and the symmetrical form of the CV plot confirm the outstanding reversibility of the lithium extraction/insertion reactions in this rapid synthesized sample (MH5) by microwave-assisted hydrothermal method.

The separation between the anodic and cathodic peaks of electrode is representative of its kinetics, especially considering that the electrochemical process involves diffusion of lithium ions in a solid phase and electron jumping across a poorly conducting compound. The anodic and cathodic peaks separation 0.33 V of MH5_400C is more than 0.15 V of MH5. It might be due to the fact that the homogenous nanoparticles of MH5 are grown big and aggregated at 400 °C for 4 hours. The body resistance of MH5_400C is increased, and the Li⁺ diffusion between the thickened interphase of LiFePO₄/FePO₄ will be decreased. These kinetics changes also reflect in their capacity.

The initial charge and discharge profiles and cyclability of the LiFePO₄ samples are showed in Figure 8. The cells were cycled between 2.5 V and 4.3 V at room temperature. The hydrothermally formed LiFePO₄ without carbon coating and with relatively large particles shows poor electrochemical behavior, with a capacity of 100 mAh/g. By comparison, the maximum discharge capacity value of MH5 is 136 mAh·g⁻¹, which is nearly 80% of the theoretical capacity (170 mAh·g⁻¹). It is the fact that no carbon coating was used in MH5, the intrinsic lower conductivity decrease its capacity. MH5_400 present a relative lower discharge capacity (125 mAh·g⁻¹) than MH5. The relatively bigger particle size of MH5_400 results in the lower Li⁺ diffusion and the bigger resistance through the thick interphase of LiFePO₄/FePO₄.

Fig. 6. TEM images of (a) MH5, (b) MH5_400 and (c) Hydrothermally formed sample.
Fig. 7. CVs of Li/1 M LiPF₆, EC/DMC/LiFePO₄ cells containing samples (a) MH5, (b) MH5_400C. Scan rate 0.2 mV·s⁻¹.

Fig. 8. (a) Initial charge and discharge curves at 1/10 C rate, and (b) Capacity versus cycle number of LiFePO₄ samples at room temperature. Li counter electrode, LiPF₆ EC:DEC (1:1) electrolyte.

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4. CONCLUSIONS

Pristine LiFePO₄ was rapidly synthesized from LiOH, FeSO₄, and NH₄H₂PO₄ by microwave-assisted hydrothermal process at 200 °C for 5 minutes in one pot. The homogeneous effects induced by microwave irradiation could create a uniform seeding condition. It was important that the colloid precursor Li₃PO₄ plays the key role to be the nucleation center for the new phase while the formation energy for LiFePO₄ would be decreased during the following microwave irradiation. By comparison, the clear precursor solution cannot convert to any LiFePO₄ phase under microwave irradiation. XRD tests indicated that the rapidly as-prepared sample has good crystallinity with olivine structure. The homogeneous effects induced by microwave irradiation with penetrated property and accelerated ion diffusion create a large amount of nucleation rapidly on the initial reaction. The as-prepared cathode material MH5 shows globular grains of sizes smaller than 30 nm. The charge and discharge capacities of microwave-assisted hydrothermally synthesized LiFePO₄ (MH5) were 136 mAh·g⁻¹. The post heat-treatment at 400 °C in argon atmosphere was effective to increase the particle size of MH5. The charge and discharge capacities of the annealed LiFePO₄ were decreased to 125 mAh·g⁻¹ due to the increase interphase of LiFePO₄/FePO₄ particles.

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References and Notes


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