



A facile precursor-separated method to synthesize nano-crystalline LiFePO₄/C cathode materials



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ABSTRACT

A facile precursor-separated hydrothermal synthesis (PSHS) method was developed to synthesize LiFePO₄ nano-crystallines at low temperature where the iron sulfate solution precursor was packed in polymer film to divide it from Phosphoric acid and Lithium hydroxide before reaction. X-ray diffraction (XRD), transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) were adopted to characterize the morphology and crystal structure of the products. The electrochemical properties and conductivity of the products were also investigated. This method avoided the probably generated Fe³⁺ at the precursors mixing process. The particle size was reduced to nanoscale without any additives. The as-prepared product showed excellent electrochemical properties especially rate capability. The reaction mechanism of this method was also studied.

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1. Introduction

Since first reported by Padhi et al. in 1997 [1,2], olivine-type lithium iron phosphate (LiFePO₄) has been widely investigated as a storage cathode material for rechargeable lithium batteries owing to the nontoxic, inexpensive, environmentally benign and high thermal stability [3]. These properties are critical for large capacity systems such as plug-in hybrid electric vehicles [4]. LiFePO₄ has a moderate redox potential of 3.4 V versus Li/Li⁺ located in the electrochemical stability window of common electrolytes and the theoretical specific capacity of 170 mA h g⁻¹ [5–7]. The main limitations have been extremely the poor electronic conductivity around at 10⁻⁹ S cm⁻¹ and low Li-ion diffusion rate around at 10⁻¹¹ S cm⁻¹, until now believed to be intrinsic to this compound [8]. Approaches to overcome these limitations were mainly performed on two aspects: coating particles with carbon or other electronic conductors to improve the electronic conductivity [3,9–15]; reducing particle size or doping it with metal super-valents to overcome the low ionic conductivity [16–19]. Miran Gaberscek has shown by general theoretical model that the electrode resistance depends on the mean particle size rather than the effects

of carbon coating because the ionic conductivity is much smaller than the electronic conductivity [20].

Recently, the nano-crystallization process of LiFePO₄ cathode materials has been further improved. Although many studies have focused on the solid-state synthesis of LiFePO₄ particles, this method is costly and time-consuming. In order to obtain size-controlled nano-particles of LiFePO₄ materials in a cheaper and environmental way, solution methods were proposed. Among them, hydrothermal synthesis is an easy method for control of phase purity, grain size and morphology [4,17,21]. The hydrothermal synthesis to reduce particle size focused on the use of surfactant and other organics [21], but all these strategies increased the cost and reduced the stability and repeatability of the product. Continuous supercritical hydrothermal synthesis (SHS) method [22–26] was employed to synthesis nano-scaled LiFePO₄ particles, but the high supercritical temperature and complicated equipment will limit the large scale application of this method. New facile method to synthesize LiFePO₄ with small particle size and good electrochemical properties at low temperatures is necessary.

Herein, we report on a new facile strategy to prepare LiFePO₄ cathode materials by packing one of the precursor FeSO₄ solution in polymer film. The precursors were not mixed until the temperature reached a certain value. The edges of the polymer film started to melt and the FeSO₄ solution was released at the impact of pressure. Such a precursor-separated hydrothermal (PSHS) method allowed the preparation of well crystallized nano-grains and avoided the oxidation of Fe²⁺ to Fe³⁺ at the precursor mixing procedure.

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The particle size was reduced to nano-scale (about 50–200 nm). Based on half-cell testing, it shows a capacity of 148 mA h g^{-1} at 0.1 C rate and 86 mA h g^{-1} at the 10 C rate with good discharge platform and cycling performance. The method could be important not only for further optimization of LiFePO_4 cathodes, but also for the synthesis of other materials.

2. Experimental section

2.1. Preparation

The LiFePO_4 samples in nano-scale were prepared by a precursor-separated hydrothermal method (PSHS) with stoichiometric $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 , and LiOH . In a typical procedure, 48 mmol of $\text{LiOH} \cdot \text{H}_2\text{O}$ was dissolved in 20 ml of 0.8 mol L^{-1} H_3PO_4 solution. 16 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 20 ml of 0.1 mol L^{-1} sucrose solution. Then the FeSO_4 solution was packed in polymer bag (blown film formed by Low-Density Polyethylene (LDPE) and Linear low density polyethylene (LLDPE) was used). The $\text{H}_3\text{PO}_4/\text{LiOH}$ solution and the polymer bag with FeSO_4 solution were placed into a 50 ml Teflon lined stainless steel autoclave simultaneously and maintained at 180°C for 15 h. After the autoclave cooled to room temperature, the products were separated centrifugally and washed with distilled water and alcohol several times to remove the impurity ions. After that, the slurry was dried at 80°C in oven for 12 h to obtain LiFePO_4 powders. For the well crystalline and carbon-coated LiFePO_4 , the activated powders with 10 wt.% sucrose were heat treated at 600°C in Ar atmosphere in a tube furnace for 5 h. The sample obtained in this new method (PSHS) was named as S1.

The traditional hydrothermal synthesis method (HS) was introduced for comparison with the PSHS method. All the processes were same except that the FeSO_4 solution was added to $\text{H}_3\text{PO}_4/\text{LiOH}$ solution directly without packing it in polymer bag. The obtained sample was named as S2.

In order to investigate the possible effect of the bag polymer on the morphology and electrochemical performance of the synthesized LiFePO_4/C , an additional experiment using the traditional hydrothermal method adding an empty polymer bag to the solution was carried out. The obtained sample was named as S3.

2.2. Characterization

The phase purity and crystalline structure of the samples were determined by X-ray diffraction (XRD) using a Philips diffractometer with $\text{Cu K}\alpha$ radiation. The morphology of the particles was studied by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron Microscopy (TEM, JEM-2100).

To calculate the carbon contents of the three samples, the obtained LiFePO_4/C powders were added with 0.1 mol/L HCl solution to dissolve LiFePO_4 . LiFePO_4 was totally removed after 30 min ultrasonication and the rest carbon suspension was centrifuged and washed. After drying in 50°C overnight, the residue carbon powder was weighted and the carbon contents were calculated.

The conductivity of the products was measured by the Hall Effect Measurement System (HMS-3000) at room temperature. Four-point conductivity measurements were made by the van der Pauw method on pressed wafer samples of $\sim 8 \text{ mm}$ diameter and $\sim 500 \mu\text{m}$ thickness. The samples were placed on the customized mould with four gold electrodes.

Electrode preparation and electrochemical performance test: the electrochemical performances of LiFePO_4/C samples were investigated using a CR2025 coin-type cell assembled in a glove box under argon atmosphere. The cell consisted of a cathode, elec-

trolyte, a lithium metal anode, and a separator. Cathodes were manufactured by the mixture of the prepared LiFePO_4/C powders (80 wt%), carbon black (10 wt%), and polyvinylidene fluoride (PVDF 10 wt%). The mixture was dispersed in N-methyl-2-pyrrolidone (NMP) and the formed slurry was spread on Al foil homogeneously and dried in an oven at 120°C for 12 h under vacuum. The electrolyte was 1 M LiPF_6 solution in 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).

The galvanostatic charge and discharge experiment was performed at range of 2.5–4.2 V at room temperature using the electrochemical test instrument (CT2001A, Wuhan Land Electronic Co. Ltd., China).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the LiFePO_4/C products obtained by PSHS method (S1) and HS method (S2 and S3) were indicated in Fig. 1. The peaks of S1 can mainly be assigned to LiFePO_4 with orthorhombic olivine-type structure (JCPDF 81-1173). A small peak of Li_3PO_4 at 33.928° can be detected as shown in the illustration of Fig. 1. This may attribute to that some FeSO_4 in the solution adhered on the polymer bag and cannot be all released and reacted with Li_3PO_4 completely. All reflections of the S2 and S3 can be well indexed to the pure LiFePO_4 . The diffraction peaks of all samples are strong, indicating that the nano-particles are well crystalline. The XRD spectra of S1 yields higher peaks of stronger intensity than S2 and S3 as shown in the illustration of Fig. 1, indicating that the new method causes higher crystallization degree. After the Rietveld-refinement analysis performed using Jade software, the unit cell parameters of S1 were $a = 10.329$, $b = 6.000$, and $c = 4.690 \text{ \AA}$. The S2 has the slightly larger of $a = 10.331$, $b = 6.007$, and $c = 4.695 \text{ \AA}$. The parameters of S3 were $a = 10.333$, $b = 6.007$, and $c = 4.699 \text{ \AA}$. The average crystalline size of sample S1, S2 and S3 were 55 nm, 80 nm and 76 nm respectively estimated from the Scherrer formula [27]. The PSHS method obtained sample has the smallest particle size.

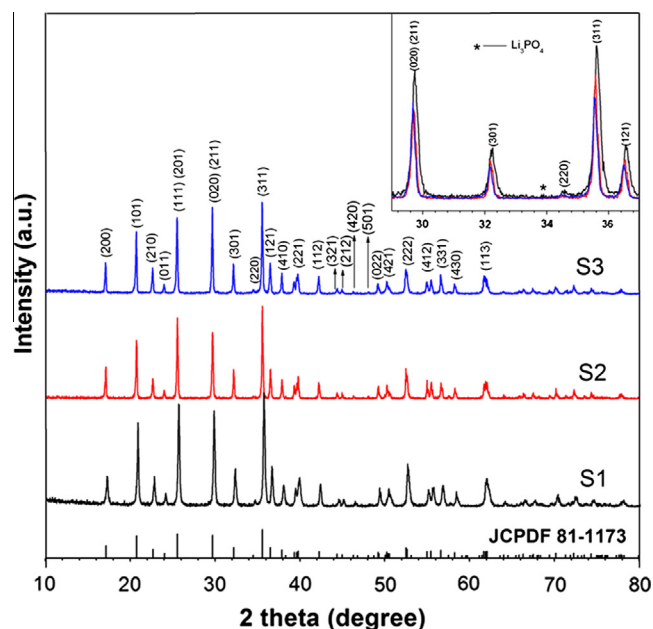


Fig. 1. XRD patterns of LiFePO_4/C obtained by the PSHS method (S1) and HS method (S2 and S3).

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