



Short communication

## Synthesis of LiFePO<sub>4</sub>/C composite with high-rate performance by starch sol assisted rheological phase method

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### ABSTRACT

LiFePO<sub>4</sub>/C composite was synthesized at 600 °C in an Ar atmosphere by a soluble starch sol assisted rheological phase method using home-made amorphous nano-FePO<sub>4</sub> as the iron source. XRD, SEM and TEM observations show that the LiFePO<sub>4</sub>/C composite has good crystallinity, ultrafine sphere-like particles of 100–200 nm size and *in situ* carbon. The synthesized LiFePO<sub>4</sub> could inherit the morphology of FePO<sub>4</sub> precursor. The electrochemical performance of the LiFePO<sub>4</sub> by galvanostatic cycling studies demonstrates excellent high-rate cycle stability. The Li/LiFePO<sub>4</sub> cell displays a high initial discharge capacity of more than 157 mAh g<sup>-1</sup> at 0.2C and a little discharge capacity decreases from the first to the 80th cycle (>98.3%). Remarkably, even at a high current density of 30C, the cell still presents good cycle retention.

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## 1. Introduction

In the past decade, much attention has been devoted to the Olivine-type LiFePO<sub>4</sub>, which was first reported as a positive electrode for rechargeable lithium-ion batteries in 1997 by John Goodenough and co-workers [1]. LiFePO<sub>4</sub> exhibits various advantages such as low toxicity, lower cost, and high thermal and chemical stability in the fully charged state. Especially, though it shows a slightly lower voltage than the widely used commercial LiCoO<sub>2</sub>, it has a higher theoretical specific capacity (170 mAh g<sup>-1</sup>) and an increased safety. The 3.45 V potential versus Li/Li<sup>+</sup> is very flat and higher than that of previously known iron-based cathode materials [2,3].

However, LiFePO<sub>4</sub> has low specific capacity and poor capacity retention at high rate due to their poor kinetics of lithium intercalation/deintercalation process and low electronic conductivity, which poses a great challenge for power-demanding applications such as hybrid electric vehicles [4–6]. Many attempts such as carbon-coating [7–12], using smaller particle sizes [13–18] have been directed to overcome these drawbacks of LiFePO<sub>4</sub>. The reason is that a small particle size of LiFePO<sub>4</sub> could shorten the diffusion length of Li-ion while the carbon-coating would increase the surface electronic conductivity.

In order to improve the electrochemical performance of the LiFePO<sub>4</sub>/C composite by carbon-coating and controlling the particle size, the rheological phase method was performed for the synthesis of LiFePO<sub>4</sub>/C in this study. We report the synthesis and electrochemical characterization of LiFePO<sub>4</sub> material prepared by a soluble starch sol assisted simple rheological phase method using home-made amorphous nano-FePO<sub>4</sub> as the iron source. Although the soluble starch has been used as carbon source to synthesize the LiFePO<sub>4</sub>/C composite by several research groups [19,20], but the special equipments and complicated synthesis techniques should be involved. The method we presented here does not need any additional treatment to improve the cycle performance, such as ball milling and pre-sintering treatments compared with traditional solid-state reaction synthesis routine and some other complicated synthesis techniques. Furthermore, this method using FePO<sub>4</sub> as starting material is cheap and environmentally benign for the production of LiFePO<sub>4</sub> material, compared with divalent iron starting materials such as FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and (CH<sub>3</sub>COO)<sub>2</sub>Fe, which are expensive and toxic. Meanwhile, the use of starch sol could further develop the synthesis technique and iron out costs.

## 2. Experimental

### 2.1. Synthesis of amorphous nano-FePO<sub>4</sub>

Amorphous nano-FePO<sub>4</sub> was synthesized by spontaneous precipitation from aqueous solutions. An equimolar solution of H<sub>3</sub>PO<sub>4</sub> was added to a solution of FeSO<sub>4</sub>·7H<sub>2</sub>O at ambient temperature

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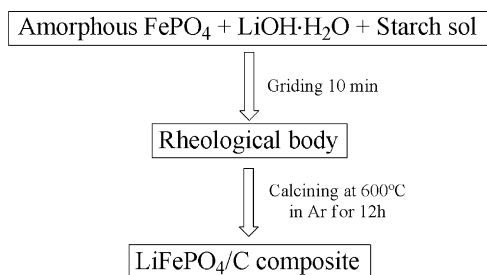


Fig. 1. Flow chart of synthesis of LiFePO<sub>4</sub>/C composite.

under stirring. Typically, the concentration of both solutions is 0.05 mol L<sup>-1</sup>. Then concentrated hydrogen peroxide solution was slowly added to the mixed solution under vigorous stirring (the molar ratio of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> is 1.2:2). A milk-white precipitate started to form immediately and the addition rates of H<sub>2</sub>O<sub>2</sub> were maintained constant in order to keep the pH at 1.0–2.0 by dropwise addition of concentrated ammonium hydroxide solution. The precipitate was filtered by G<sub>4</sub> sand filter funnel and washed several times with distilled water. After dried in oven at 80 °C for 12 h, yellowish-white amorphous FePO<sub>4</sub> was obtained.

## 2.2. Synthesis of LiFePO<sub>4</sub>/C composite

A rheological phase method was employed to synthesize LiFePO<sub>4</sub>/C composite. Stoichiometric amount of amorphous FePO<sub>4</sub>, LiOH·H<sub>2</sub>O and soluble starch (45.0 g starch/1 mol FePO<sub>4</sub>) were used as the starting materials. The soluble starch was mixed with appropriate amount of distilled water. This mixture was then heated under stirring until a homogeneous transparent starch sol was obtained. As shown in the flow chart (Fig. 1), the starch sol was mixed with amorphous FePO<sub>4</sub> and LiOH·H<sub>2</sub>O, and then the mixture was ground for 10 min to get a solid–liquid rheological body, it looks like a kind of mushy slurry. Finally, the rheological body was calcined at 600 °C in a tube furnace for 12 h under argon flow. Cooling to room temperature and grinding the resulting product, the carbon-coated LiFePO<sub>4</sub> composite was obtained. All the reagents used in the experiment were of analytical purity and were purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC) and used without further purification.

## 2.3. Measurements

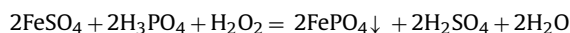
The water content of home-made amorphous FePO<sub>4</sub> was determined by TGA test (Netzsch STA 449C, Germany) in static air at a heating rate of 10 °C min<sup>-1</sup>. The crystalline phase of the synthesized material was analyzed by powder X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) using Cu Kα<sub>1</sub> radiation. The particle morphology and microstructure was observed using a scanning electron microscope (SEM, QUANTA 200, Holland) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010FEF, Japan). The electrochemical characterizations were performed using CR2016 coin-type cell. For cathode fabrication, the as-synthesized LiFePO<sub>4</sub>/C composite was mixed with carbon black and PTFE binder with a weight ratio of 75:20:5. And then, the mixture was pressed onto a 177 mm<sup>2</sup> stainless mesh which was used as the current collector and dried at 120 °C for 6 h in an oven. The test cell consisted of a cathode and a lithium foil anode separated by a Celgard 2300 micro-porous film, and 1 M LiPF<sub>6</sub> (EC:DMC = 1:1) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were galvanostatically charged and discharged between 2.0 and 4.4 V versus Li<sup>+</sup>/Li on a battery cyler (LAND, CT2001A, China). Cyclic voltammetry measurements were

performed using an electrochemical workstation (Shanghai Chenhua, CHI660C, China) at a scan rate of 0.1 mV s<sup>-1</sup> range from 2.0 to 4.4 V versus Li<sup>+</sup>/Li. Unless stated elsewhere, the electrochemical tests were carried out at room temperature (20 °C).

## 3. Results and discussion

### 3.1. Composition of the amorphous FePO<sub>4</sub>

Amorphous FePO<sub>4</sub> was synthesized by spontaneous precipitation method according to the following precipitation reaction:



TGA test was used to determine the water content of synthesized amorphous FePO<sub>4</sub>. The TGA result shows that there is a continuous weight loss (about 21.0%) over the temperature range from ambient temperature to 500 °C. The weight loss corresponds to the elimination of water physically absorbed on the amorphous FePO<sub>4</sub> [21]. From the water loss, it can be calculated that the synthesized FePO<sub>4</sub> has two moles water per mole of compound and should be written as FePO<sub>4</sub>·2H<sub>2</sub>O.

### 3.2. Structure analysis of amorphous FePO<sub>4</sub> and LiFePO<sub>4</sub>/C

XRD patterns of the synthesized FePO<sub>4</sub>·2H<sub>2</sub>O and LiFePO<sub>4</sub>/C composite are shown in Fig. 2. As seen in Fig. 2(a), the synthesized FePO<sub>4</sub>·2H<sub>2</sub>O is completely amorphous. Fig. 2(b) shows that olivine LiFePO<sub>4</sub> with orthorhombic *Pnma* space group is the only major crystalline phase in the sample. This indicates that this soluble starch sol assisted rheological phase method using the Fe(III) raw material can be used to synthesize pure and well-crystallized LiFePO<sub>4</sub>. This LiFePO<sub>4</sub> formation is made possible by the reduction of Fe(III) species by gases such as H<sub>2</sub> or gaseous hydrocarbons evolved during the calcination of the polymer [3], such as the starch used in this work. The crystal lattice parameters calculated by the XRD data are *a* = 10.331 Å, *b* = 6.009 Å, *c* = 4.691 Å, which are very close to the standard date (*a* = 10.330 Å, *b* = 6.010 Å, *c* = 4.693 Å) given by JCPDS 83-2092. There are no obvious carbon diffraction peaks, possibly due to the carbon generated from soluble starch is amorphous carbon and/or its low content. The carbon content in the LiFePO<sub>4</sub>/C composite is about 5.1 wt.% determined by the TGA date using the method reported by Yang et al. [22].

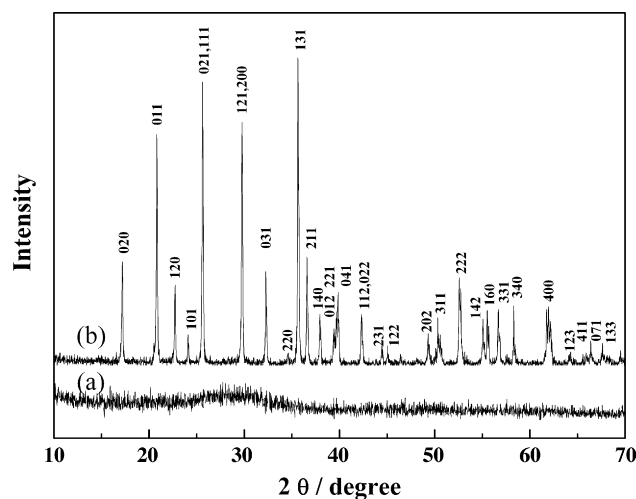


Fig. 2. XRD patterns of (a) amorphous FePO<sub>4</sub> and (b) synthesized LiFePO<sub>4</sub>/C composite.

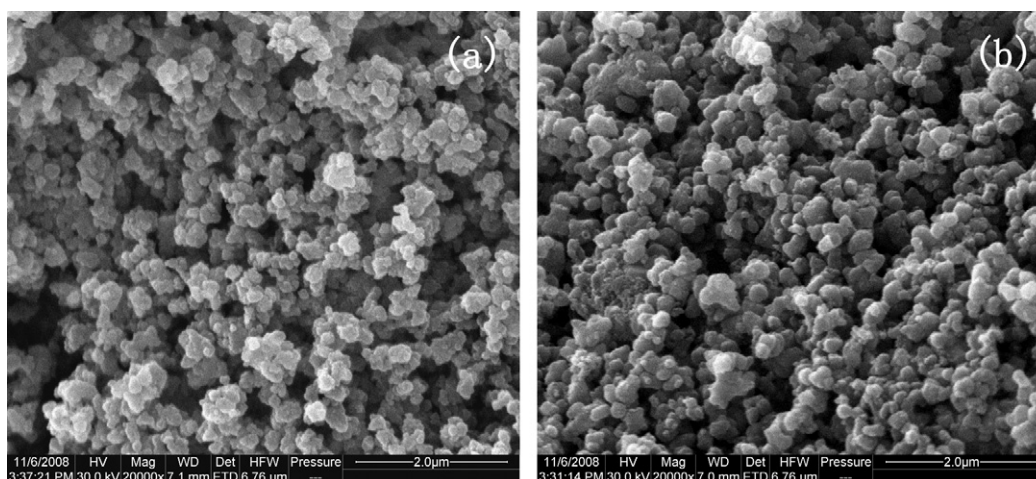


Fig. 3. SEM images of (a) amorphous  $\text{FePO}_4$  and (b) synthesized  $\text{LiFePO}_4/\text{C}$  composite.

### 3.3. Morphology of amorphous $\text{FePO}_4$ and $\text{LiFePO}_4/\text{C}$

Scanning electron micrographs (SEM) of amorphous  $\text{FePO}_4$  and  $\text{LiFePO}_4/\text{C}$  composite are shown in Fig. 3. It can be seen that the particle sizes of the  $\text{FePO}_4$  and  $\text{LiFePO}_4/\text{C}$  are about 100 nm and 100–200 nm, respectively. Furthermore, crystallites of  $\text{LiFePO}_4$  are linked together by a carbon network can be observed. Fig. 3 also shows the particles of the two samples are sphere-like and well-dispersed, although a few agglomeration exist. Namely, the morphology of  $\text{FePO}_4$  can be retained in the formation of  $\text{LiFePO}_4/\text{C}$  composite during the heating process. The formation of homogeneous ultrafine particles of  $\text{LiFePO}_4/\text{C}$  composite might be ascribed to the following three factors: (1) the amorphous nano- $\text{FePO}_4$  precursor as a core for forming  $\text{LiFePO}_4$ , it plays an important role for the formation of  $\text{LiFePO}_4$  ultrafine and sphere-like particles. The morphology and size of  $\text{LiFePO}_4$  particles depends on the morphology and size of  $\text{FePO}_4$  particles. (2) The rheological phase reaction process can leads to homogeneous mixing of the starting materials. In this experiment, an adhesive starch sol containing  $\text{Li}^+$  coated evenly on the surface of amorphous  $\text{FePO}_4$ . The starting materials are mixed at molecular level, during the subsequent heat treatment, reactants with uniform distribution will facilitate the formation of fine particles with uniform size. (3) Decomposition of starch results in a carbonaceous deposit on the surface of the  $\text{LiFePO}_4$  particles. The *in situ* carbon would limit the growth of the particles and impede the agglomeration of the  $\text{LiFePO}_4$  particles.

Fig. 4 shows the TEM image of the synthesized  $\text{LiFePO}_4/\text{carbon}$  composite. As shown in Fig. 4(a), the  $\text{LiFePO}_4$  crystallites have sphere-like shape, loose agglomeration and fine crystallite size ranging from 100 to 200 nm. This is consistent with the SEM observation. The TEM image shown in Fig. 4(b) shows a typical example of individual crystallites of  $\text{LiFePO}_4/\text{C}$  composite. It can be seen that the crystallites are wrapped and connected with carbon formed from the decomposition of starch, thereby increasing the surface electronic conductivity of  $\text{LiFePO}_4$  crystallites and ensuring a good electric connection between the crystallites. The high resolution TEM image of the  $\text{LiFePO}_4$  crystallite shown in Fig. 4(c) reveals the coating of the  $\text{LiFePO}_4$  crystallite by amorphous carbon (thickness of about 1.3–2.5 nm).

### 3.4. Electrochemical characteristics

Because the particle size and *in situ* carbon were suggested to be two key parameters to enhance the electric conductivity of  $\text{LiFePO}_4$  at a high current density due to the short diffusion length of lithium ions and high electronic conductivity of carbon, we expect that the synthesis of good  $\text{LiFePO}_4/\text{C}$  material with a small particle size and *in situ* carbon will benefit the improvement of its electrochemical performance. To validate the truth of this idea, the cell was tested at different rates ranging from 0.2C to 30C.

Fig. 5 shows the voltage versus capacity and the retention of the capacity of a  $\text{Li}/\text{LiFePO}_4$  cell at 0.2C between 2.0 and 4.4 V. The first cycle charge/discharge curves of the  $\text{Li}/\text{LiFePO}_4$  cell was shown

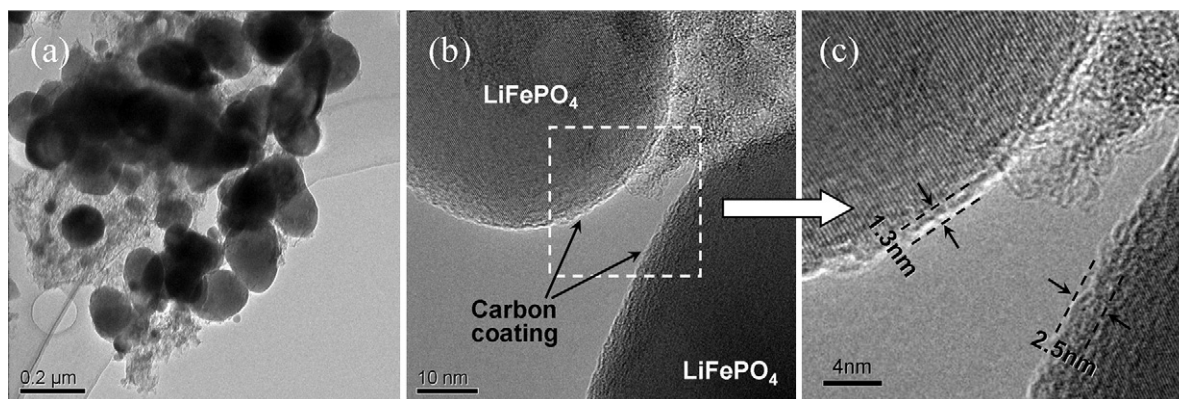


Fig. 4. (a) TEM image of synthesized  $\text{LiFePO}_4/\text{C}$  composite, (b) typical TEM image for individual  $\text{LiFePO}_4/\text{C}$  crystallites and (c) typical HRTEM image for the carbon-coated crystallites.



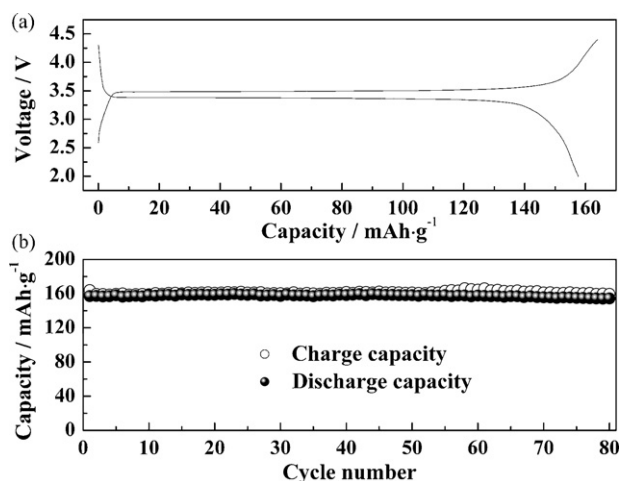


Fig. 5. (a) Initial charge/discharge curves and (b) capacity retention of Li/LiFePO<sub>4</sub> cell at 0.2C.

in Fig. 5(a). The long and flat voltage plateaus at 3.5 and 3.4V for lithium extraction and insertion respectively imply the two-phase redox reaction between FePO<sub>4</sub> and LiFePO<sub>4</sub> [1]. The cell shows a high initial charge capacity of more than 163 mAh g<sup>-1</sup>, however, it presents a slightly reduced discharge capacity of 157.1 mAh g<sup>-1</sup>, the efficiency ( $\eta$ ) of the first cycle is 96.4%. It was considered that the mismatched charge/discharge curve results from the non-optimized test condition, such as the powder morphology and electrolyte condition [17]. Fig. 5(b) shows the cycle performance of the Li/LiFePO<sub>4</sub> cell. The efficiencies  $\eta$  are almost 100% from the 2nd cycle to the 50th cycle. After the 50th cycle, the efficiencies  $\eta$  show a little decrease. A discharge capacity of over 154.4 mAh g<sup>-1</sup> was retained until 80 cycles (>98.3%).

To succeed in preparing a LiFePO<sub>4</sub> material with high discharge capacity and good cycle retention rate, some research groups have performed the rheological phase method using different raw materials [23–25]. LiFePO<sub>4</sub> materials with small particle sizes were synthesized by these research groups. Moreover, these materials exhibited high initial discharge capacities over 160 mAh g<sup>-1</sup> at the low current rate 0.1C. Regrettably, no cycling data was presented at rates over 3C in their reports.

Fig. 6 presents the result of the cycle characterizations of the Li/LiFePO<sub>4</sub> cell at various rates from 1C to 30C. Inset is the typical charge/discharge curves of the Li/LiFePO<sub>4</sub> cell at various rates. The cell delivers a high specific capacity of 151 mAh g<sup>-1</sup> in the initial dis-

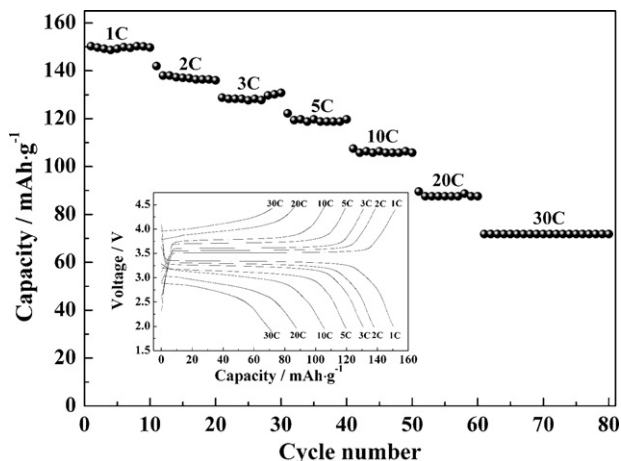


Fig. 6. The high-rate cycling performance and the typical charge/discharge curves of Li/LiFePO<sub>4</sub> cell at various charge/discharge rates (1–30C).

charge at 1C and shows a similar value during the following nine cycles. The discharge capacity decreases while the over-potential increases with the C-rate increasing. At a high current density of 30C, the cell still presents a discharge capacity of 72 mAh g<sup>-1</sup> and exhibits quite good cycle retention. From the results, we conclude that the LiFePO<sub>4</sub>/C composite synthesized by the soluble starch sol assisted rheological phase method in this study presents excellent high-rate performance. It could be attributed to the ultrafine LiFePO<sub>4</sub> particle size and *in situ* carbon coated on the surface of LiFePO<sub>4</sub> particle.

#### 4. Conclusion

LiFePO<sub>4</sub>/C composite was synthesized at 600 °C in an Ar atmosphere by a soluble starch sol assisted rheological phase method using home-made amorphous nano-FePO<sub>4</sub> as the iron source. Its ultrafine sphere-like particles of 100–200 nm size might be ascribed to the morphology of FePO<sub>4</sub> precursor and the starch assisted rheological phase method. The Li/LiFePO<sub>4</sub> cell shows a high initial discharge capacity of more than 157 mAh g<sup>-1</sup> at 0.2C and 151 mAh g<sup>-1</sup> at 1C. Even at a high current density of 30C, the cell still presents good cycle retention. The excellent high-rate performance of the LiFePO<sub>4</sub>/C material resulted from the homogeneous ultrafine sphere-like particles and *in situ* carbon, which increased the electronic conductivity and diffusion of lithium ions in the electrode. Furthermore, the method using FePO<sub>4</sub> and starch sol as starting materials in this work is simple, cheap, environmentally benign and efficient, so it is commercially feasible.

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