Novel Synthesis of Plate-like LiFePO₄ by Hydrothermal Method

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Abstract: *Lithium iron phosphate (LiFePO₄) was prepared by hydrothermal synthesis method using FeSO₄·7H₂O and LiH₂PO₄ as resource of Li and Fe. The ratio of Li: Fe was maintained 1:1. The results suggested that pH value played a crucial role in the synthesis of LiFePO₄, especially for the generation of impurities. We found that adding citric acid to the precursor was an effective way for chelating ferrous ions, thereby preventing the undesirable iron compounds during hydrothermal treatment. The particle morphology and the crystal orientation of the prepared LiFePO₄ particles were investigated by the XRD and SEM results. The X-ray diffraction pattern of the samples indicated that single-phase LiFePO₄ were successfully synthesized by hydrothermal method with a stoichiometric 1:1 ratio of Li :Fe.*

1. INTRODUCTION

In recent years, lithium-ion battery material in the field of new energy application has received considerable attention [1–4]. LiFePO₄, with an olivine structure, is considered to be a promising positive electrode due to its high theoretical capacity, low cost, environment benignity, cycling stability and high safety, all of which has naturally led to a fast development in the application of plug-in hybrid vehicles [5-9]. Meanwhile, LiFePO₄ is one of the anode materials in various applications such as electric power; the battery needs better performance of low temperature and the ratio of the corresponding requirement of the lithium iron phosphate material nano-particles [10-12]. Nonetheless, LiFePO₄ has some intrinsic shortcomings, including poor electronic conductivity and limited lithium ion diffusion coefficiency, which result in less impressive performance at high rates. Many efforts have been made to overcome these limitations, several researchers reported that reducing the particle size and carbon-coating on the LiFePO₄ particles were effective in improving its electrochemical reactivity.

The crystal orientation of LiFePO₄ particles is also an important characteristic, which is strongly related to electrode kinetics.

The most common methods to synthesize LiFePO₄ are solid-state reaction, coprecipitation, hydrothermal, solvothermal, sol–gel and microwave reaction, during which hydrothermal is one of the most effective method, which is widely applied and systemically studied. In order to increase the utilization of LiFePO₄ for charge and discharge, smaller particles should be prepared under suitable conditions. Many efforts have been made to overcome these limitations. However, the former reaction methods for synthesizing LiFePO₄ reported are unproductive because they need 3mol LiOH as Li source [13].

In this paper, we developed a novel routine based on hydrothermal method for synthesizing LiFePO₄. We use FeSO₄·7H₂O and LiH₂PO₄ as raw materials, and the molar ratio of Li: Fe in the precursor was controlled to be 1:1. The addition of citric acid to the precursor was effective in preventing the undesirable iron compounds during hydrothermal treatment. Compared with the other methods, the advantage of our method is that we used only 1mol Li source to produce LiFePO₄ powders instead of the use of costly LiOH in threefold excess.
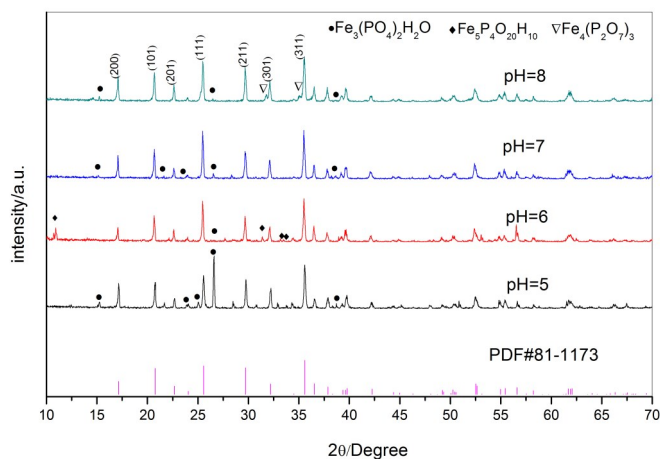
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Figure 1. XRD patterns of the prepared products synthesized at various pH values.

2. EXPERIMENTAL

LiFePO$_4$ was synthesized via an optimum hydrothermal method. The raw materials, FeSO$_4$·7H$_2$O (99%) were dispersed in 30 ml deionized water by stirring for a period of time in a 100 ml Teflon liner. Then the LiH$_2$PO$_4$ (99.6%) were added into the solution under vigorous stirring. Here, it should be emphasized that the ratio of Fe to Li resource was maintained at 1:1 in our experiments. To evaluate the influence of pH value on crystal structures and crystal morphologies, the pH values, were modified by adding a chemical agent of ammonia into the mixtures mentioned above, and were ranged from 5 to 8. Then the solution was poured into a beaker placed into a sealed Teflon lined steel autoclave and heated at 180 °C for 6 hours. After cooling to room temperature naturally, the products were collected and washed several times using deionized water and air-dried at 80 °C for hours.

According to the impurity content at pH 7 was of the lowest, to obtain a single phase and reduce the impurity content, citric acid were transferred into the solution for pH value of 7. The molar ratio of citric acid and FeSO$_4$·7H$_2$O was controlled to be 1:9.

The X-ray diffraction (XRD) data was measured on an X-ray diffractometer (Model D/Max2500 PC, Rigaku Co., Japan) with CuK$_\alpha$ irradiation using a tube voltage and current of 40 kV and 150 mA. The diffraction data were collected in the range between 10° and 70°, with an acquisition step of 0.02°.

The crystal morphologies of the powder were characterized on scanning electron microscopy (SEM; Model JSM-840, JEOL Co., Japan).

3. RESULTS AND DISCUSSION

Fig. 1 shows powder XRD patterns of samples prepared from the precursors with different pH values of the reaction solution. It should be pointed out that the primary crystalline phases were LiFePO$_4$ (space group: Pnma) for all the products. Whereas, the impurity crystalline phases were different. As can be seen from Fig. 1, Fe$_3$(PO$_4$)$_2$H$_2$O and Fe$_5$P$_4$O$_{20}$H$_{10}$ were generated as impurities at lower pH values of 5 and 6, and Fe$_4$(P$_2$O$_7$)$_3$ impurity was formed when the pH value was 8. However, when the pH value was adjust-

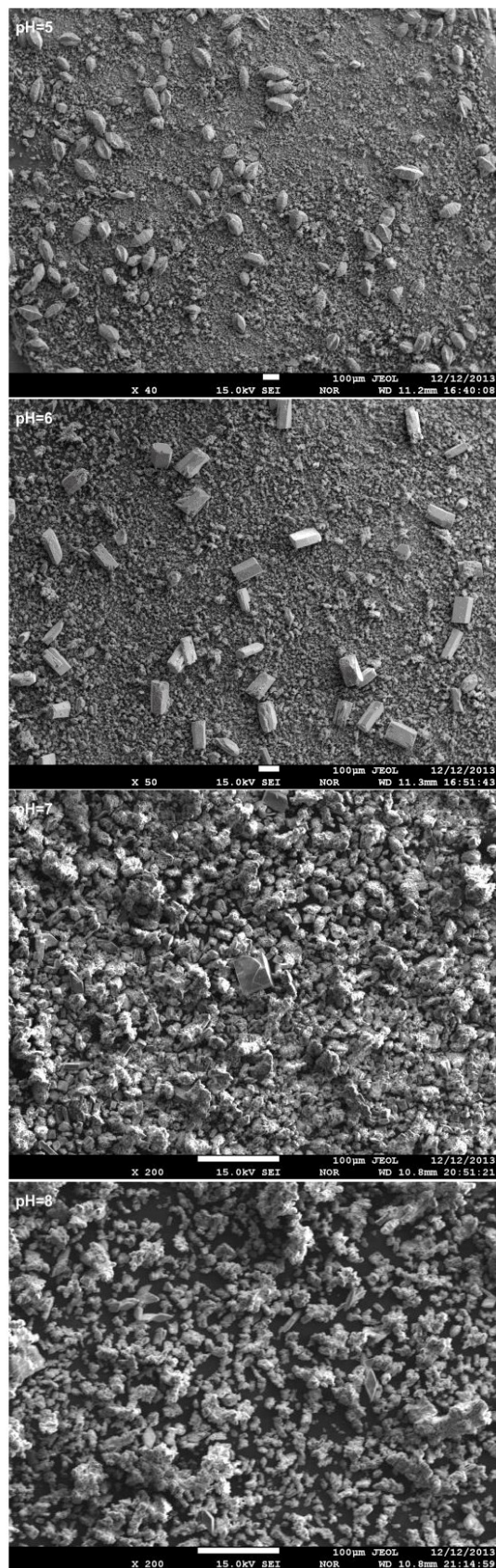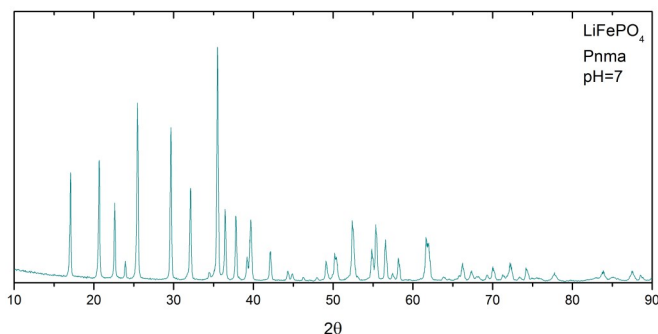Figure 2. SEM image of LiFePO$_4$ obtained at different pH 5, 6, 7 and 8.

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Figure 3. XRD pattern of LiFePO₄ synthesized at pH7 after adding the citric acid.

Figure 4. SEM image of LiFePO₄ obtained at pH 7 after adding the citric acid.

Figure 5. Comparison of the experimental and calculated XRD patterns of LiFePO₄.

ed to 7, the majority of the product was orthorhombic LiFePO₄, with a small amount of impurities. Apparently, the XRD results gave the evidence that the pH values of the solution played crucial roles for the composition of the product. As we known that, the variety of pH values means the concentration of H^+ or OH^- species in the solutions changes, which can naturally affect the solubility of precursor and dissoluble/depositional ratio of configurational ions. With the increase of pH value, some high energy surfaces remain because the deposition rate of configurational ions is higher than the dissolution rate, and finer particles are obtained because of quick nucleation rate. [14] And with a decreased pH value, there would be more H^+ in the starting solution which has higher mobility that may affect the formation activation energy. Therefore, it may be easier to form Li vacancies and also result in Li, Fe inter-site mixing. So orthorhombic LiFePO₄ (space group: Pnma) was obtained from the precursor solution at pH 7.

Fig. 2 displays SEM images of the as-synthesized products at different pH values. It can be seen from the figure that the morphologies of the products varied in terms of the pH values of the solutions. The primary particle size of pH 7 was as large as 1mm.

In order to diminish the formation of impurities such as $Fe_3(PO_4)_2H_2O$, $Fe_5P_4O_2$ $(OH)_{10}$ and $Fe_4(P_2O_7)_3$, we add the citric acid to the precursor to synthesize a single phase of orthorhombic LiFePO₄. Fig. 3 shows the XRD patterns for LiFePO₄ synthesized at pH 7 after adding the citric acid. It can be seen from Fig.3 that the samples are single phase of LiFePO₄ which can be indexed to the orthorhombic olivine type structure (PDF#81-1173). The strong and narrow peaks suggest that the LiFePO₄ has high crystallinity. No impurities such as $Fe_3(PO_4)_2H_2O$, $Fe_5P_4O_2$ $(OH)_{10}$ and $Fe_4(P_2O_7)_3$, were tested. In comparison with Fig. 1, another important feature of the XRD pattern of LiFePO₄ is that the intensity of the main peak of LiFePO₄ in Fig. 3 is stronger than Fig. 1, suggesting that the existence of citric acid affected the crystalline process of the generation of LiFePO₄. We believe that the crystalline of LiFePO₄ is herein the location of Li^+, Fe^{2+} and PO_4^{3-} onto their crystalline positions. With the citric acid in the system, it will be incorporated with Fe^{2+}. The release of Fe^{2+} controlled the reaction process during the forming LiFePO₄.

Fig. 4 displays SEM images of the as-synthesized LiFePO₄ at pH 7 after adding the citric acid. It is noteworthy that very tiny plate-like crystals were obtained, the resulting microstructure of the sample was homogeneous, the length and width respectively of the
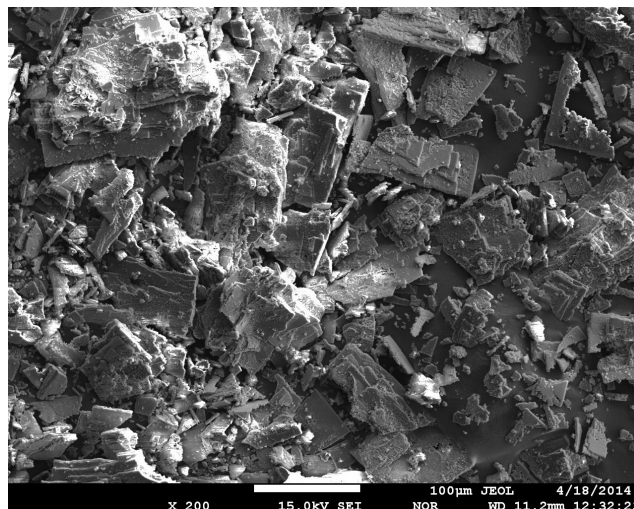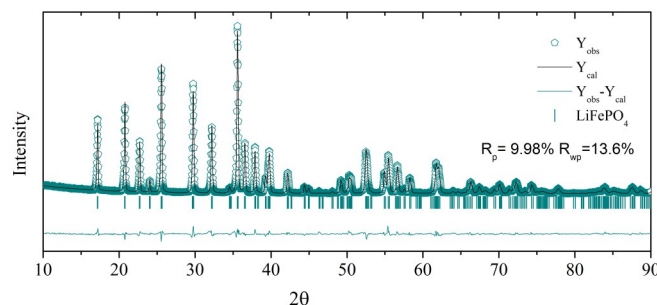
sheet structure of 100μm.

Fig. 5 is the X-ray diffraction patterns of the samples LiFePO₄ were refined. The XRD pattern of LiFePO₄ together with its refinement is shown in Fig.5. The pattern could be indexed using Rietveld refinement with unit cell parameters of a=10.336(35)Å, b=6.004(48)Å and c=4.701(90)Å.

4. CONCLUSIONS

A single orthorhombic LiFePO₄ was successfully synthesized by hydrothermal routine with the stoichiometric Li/Fe of 1:1 from the precursor solution of pH 7. The addition of citric acid to the precursor was effective in chelating ferrous ions, control the release rate during the hydrothermal reaction, thereby preventing the undesirable iron compounds during hydrothermal treatment.

5. ACKNOWLEDGEMENTS

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