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To cite this article: Yi Ma *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **252** 022032

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Preparation of Nanoscale Iron (III) Phosphate by Using Ferro-Phosphorus as Raw Material

Yi Ma ^a, Wenzhe Shen ^b, Yaochun Yao ^{*}

Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

^{*}Corresponding author e-mail: Yaochun9796@163.com, ^a1872903434@qq.com, ^b497793959@qq.com

Abstract. The battery grade precursor FePO₄ was synthesized by precipitation method. Ferro-phosphorus was used as the iron source and the phosphorus source. The prepared nanoscale iron(III) phosphate were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), galvanostatic thermogravimetric and differential scanning calorimetry (TG-DSC), and fourier transform infrared (FTIR) spectra test. Also, the influence of different pH values on the performance of iron phosphate crystals was studied. The experimental results show that the prepared FePO₄·2H₂O under the experimental conditions is amorphous iron phosphate. And the prepared FePO₄ had high crystallinity, uniform particle dispersion, and good morphology. No impurity elements are produced in the preparation process, the purity of product is high, and the process route is energy saving and environmental protection. The iron and phosphorus content test shows that the iron content of the sample was 36.84%, the phosphorus content was 20.99%, and the molar ratio of iron to phosphorus was 0.973, which meets the requirement of battery grade FePO₄ precursor.

1. Introduction

Iron phosphate was initially used as catalyst in the steel and glass industries [1]. As a result of excellent catalytic properties, ion exchange ability and electrochemical properties, ionic phosphate has attracted widespread concern in the fields of catalysis and electrode materials for lithium batteries [2]. Due to the low cost, long cycle life, environmental friendliness and thermal stability, LiFePO₄ becomes one of the most promising cathode materials for the lithium ion batteries which was applied to energy storage field [3]. Ferro-phosphorus (FeP) is a by-product of chemical production. It has some characteristics such as wide source, high output and low price. Long-term stacking of a large amount of ferro-phosphorus will cause environmental pollution. Ferro-phosphorus mainly contains phosphorus and iron. It can be used to prepare different grades of iron phosphate by supplementing the phosphorus source to adjust phosphorus ratio to iron. At the same time, the ferro-phosphorus also contains a small amount of metals such as manganese and titanium, which can be effectively doped into the battery-grade iron phosphate. These elements are beneficial to improve the electrochemical performance of the prepared battery-grade lithium iron phosphate.

The synthesis methods of iron phosphate can be divided into two categories according to the valence of iron. Trivalent iron salt solution and phosphoric acid solution are used as the starting



materials. Iron phosphate is obtained by adjusting pH with ammonia solution. On the other hand, divalent iron salt solution reacts with hydrogen peroxide to form dihydrogen iron phosphate. After adjusting the pH of the above solution to 2 by sodium hydroxide or aqueous ammonia solution to form iron phosphate.

The composition of the ferro-phosphorus is in the form of a combined state, and the molecules are strongly bonded by a strong chemical bond, so that the properties of the ferro-phosphorus are stable. Therefore, ferro-phosphorus can only react with oxalic acids. In this paper, a clean and green experimental scheme to prepare FePO_4 was studied, to adapt the green production process policy. Ferro-phosphorus was used as raw material to provide Fe^{3+} and PO_4^{3-} . Nitric acid solution is used to dissolve ferro-phosphorus. Then, deionized H_2O was used to regulate the pH of the solution system. Finally, the influence of different pH values on the properties of iron phosphate materials was discussed.

2. Experimental

The $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ were synthesized by precipitation method. Ferro-phosphorus was used as raw material to prepare iron phosphate. Firstly, the ferro-phosphorus was dissolved in the mixture of nitric acid and sulfuric acid for 4 h. The controlled dissolution temperature is 90°C in the water bath pot. After filtration, pale yellow liquid was filtered. Then heat up the filtrate to 60°C and control the stirring speed at 350 rad/min in the thermostat water bath. Appropriate amount of phosphoric acid solution was added to facilitate the participation of Fe^{3+} . The solution pH was controlled by dropping deionized water. White precipitates are produced when the pH of the solution is 1.0. Aging precipitation at 100°C for 4h. The white precipitate was washed with deionized water, filtered off, and dried at 80°C for 45min. cooling to room temperature, and the amorphous iron phosphate was obtained.

Powder X-ray diffraction (XRD, MiniFlex 600, Rigaku) with $\text{Cu K}\alpha$ radiation was used to determine the crystalline phase of the synthesized material. The particle morphology were observed by using a scanning electron microscopy (SEM, QUANTA 200, and Holland). The thermal behavior of the precursor was done by using thermogravimetric and differential scanning calorimetry (TG-DSC) with Netzsch STA 449F3 thermal analyser. The samples were placed in Al_2O_3 crucibles under air atmosphere and heated up to 700°C at the heating rate of $10^\circ\text{C}/\text{min}$. The contents of iron and phosphorus in the samples were obtained by the method of oxidation and reduction of potassium dichromate. Fourier transform infrared (FTIR) spectra was used to analysis the molecular structure of samples. Fourier transform infrared (FTIR) spectra were collected in the range of $400\text{--}4000\text{cm}^{-1}$.

3. Results and discussion

The XRD pattern of the iron phosphates is shown in Fig. 1a. It can be found that the prepared $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ samples have completely amorphous character under different pH values according to XRD standard card. The XRD pattern of the iron phosphates calcined at 550°C for 4h is shown in Fig.1b. the pattern matches well with monoclinic FePO_4 (hexagonal [77-0094], space group P3121 (152), with lattice parameters $a=5.036\text{ nm}$, $b=5.036\text{ nm}$, and $c=11.255\text{ nm}$). These characteristics

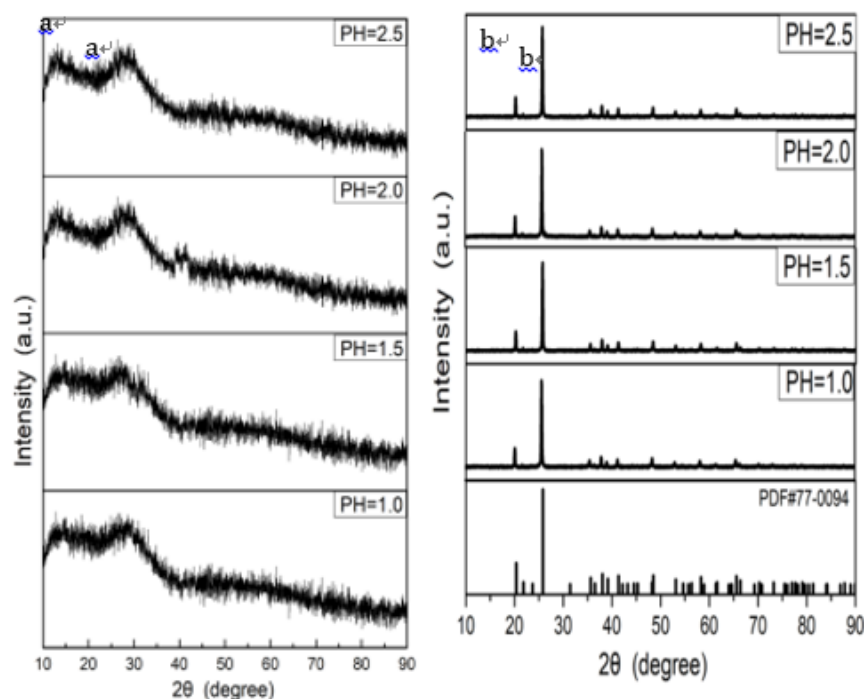


Figure. 1 XRD patterns of samples prepared at different conditions: (a) dried at 80°C, (b) calcined at 550°C

Confirm to the crystal of iron phosphate. It suggests that the synthesized samples have perfect crystal constructure. The peak intensity of (020) is much higher than the other peaks, the peak intensity of sample at pH=1.0 is highest, which suggests that the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ has the best crystallinity when pH=1.0.

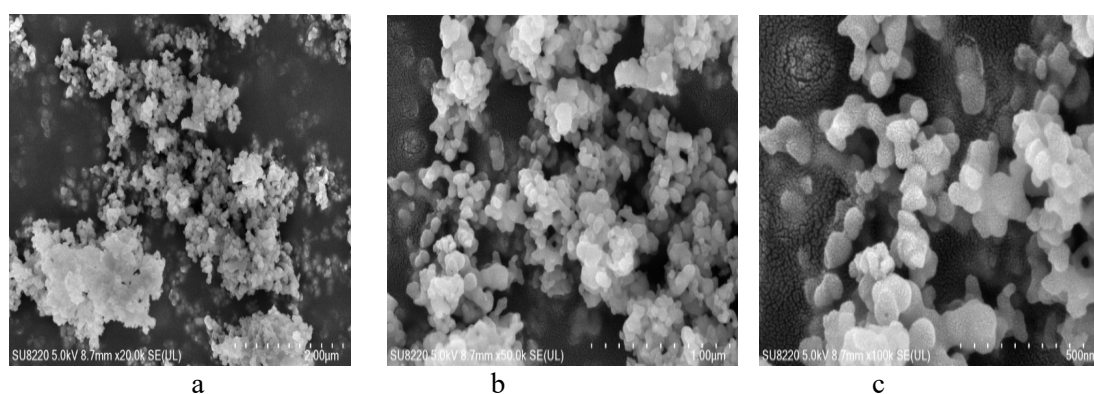


Figure. 2 The SEM images of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ prepared pH=1.0: (a) 20.0k, (b) 50.0k and (c)

The microstructures of the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursors were identified by SEM, as shown in Fig. 2. It can be found that the diameter of the synthesized $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is in the range of 100nm to 200nm. It can be seen clearly that its shape is uniform, and there is no obvious agglomeration phenomenon.

The TG-DSC curves of the amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ prepared at pH=1.0 are shown in Fig. 3. A weight loss of 19.25% was observed in the TG curve of the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ sample, it is related to the elimination of water in the temperature range of 100–500°C. However, the main weight loss (15.57%) occurred in the range of 100–250°C. An exothermic peak and a small loss occurred in the temperature range of 250–450°C is ascribed to the loss of crystalline water. Since most of the mass loss is observed

just below 450°C, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ was previously heated to 450°C lost only 3.68% weight. From the TG curve, the total decrease of the mass is 19.25%, there are two water molecules in one iron phosphate molecule. After the sample lost two crystal waters, an exothermic peak was observed at 680°C. It can be ascribed to a transition from amorphous to crystalline form of FePO_4 , as reported in the literature.

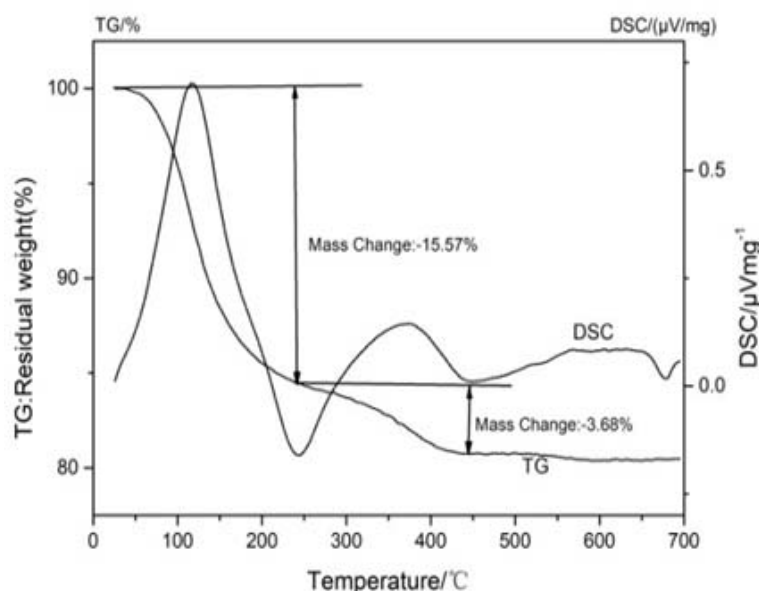


Figure. 3 TG-DSC curves of the sample prepared at pH=1.0

Table. 1 Component inspection and industry standard of FePO_4 .

Detection project	Detection result	Industry standard
W(Fe)/%	36.84	≥ 36.0
W(P)/%	20.99	≥ 20.0
n(Fe):n(P)	0.973	0.96-1.02
W(Ca)/%	2.9×10^{-5}	≤ 0.005
W(Mg)/%	0	≤ 0.005
W(Na)/%	1.8×10^{-4}	≤ 0.01
W(K)/%	4.8×10^{-5}	≤ 0.01
W(Cu)/%	3.8×10^{-4}	≤ 0.005

The iron content in the precursor was determined by potassium dichromate titration. Table 1 is the composition and industry standard for FePO_4 synthesized at pH=1.0. The iron content in the sample was 36.84%. The mass fraction of phosphorus is 16.5%. The molar ratio of iron and phosphorus is 0.973. These major data are conforming to the industry standard, and the impurity content also accords with the industry standard. The crystalline water number was calculated to 2.0, which is in agreement with the estimation in the TG-DSC curves. There is a high level of agreement between the experimental data and the reported data in literature.

Fig. 4 is an infrared spectrogram of sample synthesized at pH=1.0. The structure of the amorphous FePO_4 was studied in FTIR spectra at the region of 400–4000 cm^{-1} . The infrared characteristic peaks of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ are mainly composed of the absorption peaks of PO_3 groups, bound water and Fe. In addition, the FTIR spectra showed that PO_4 tetrahedral units are retained even in amorphous samples. The absorption peak of 1636.61 cm^{-1} and the absorption peak of 3428.34 cm^{-1} indicate the bending and stretching vibrations of water molecules respectively. The internal vibrations of FePO_4 originated from the intramolecular vibrations of PO_4 tetrahedron are universally known to be located in the range

of 400–1220 cm^{-1} . The observed absorption peak in the position of 1063.06 cm^{-1} and 990 cm^{-1} has been assigned to the symmetric stretching and asymmetric stretching vibration modes of P-O in PO_4^{3-} . The absorption peak at 581.75 cm^{-1} is a strong absorption peak of antisymmetric flexural vibration of PO_2 in PO_4^{3-} . The absorption peak at 832.52 cm^{-1} is the stretching vibration of 2 bridged oxygen ions in the PO_4 group. The absorption peak of the Fe-O group is asymmetric stretching vibration at 581.75 cm^{-1} .

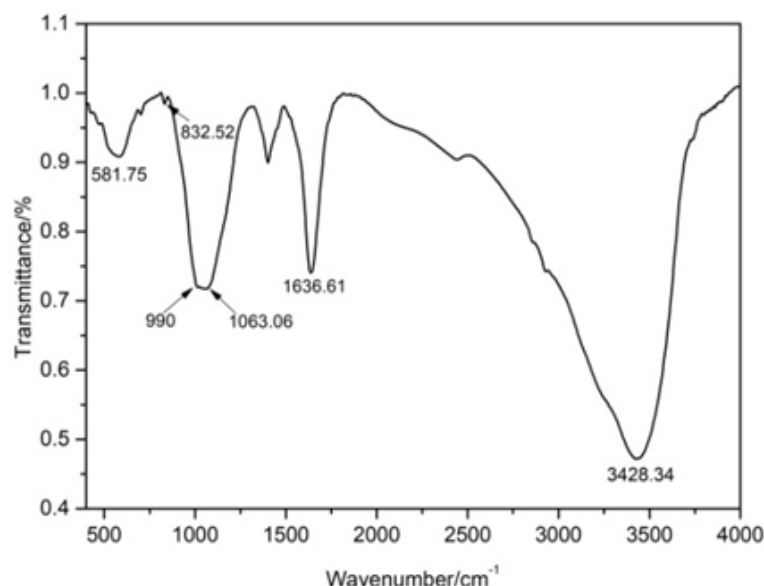


Figure. 4 FTIR spectar of sample prepared at pH=1.0

4. Conclusion

In this paper, ferro-phosphorus was used as raw material to prepare nanometer iron (III) phosphate, and the chemical composition and crystal morphology were also analyzed. The results show that the quality of the obtained iron phosphate can satisfy the demand of the production of cathode material of lithium iron phosphate when the pH of the solution is 1.0. The adopted production process meets the requirements of green production and is environmentally friendly. It provides an effective method for the production of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ by using ferro-phosphorus as raw material.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 51364021).

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