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

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Abstract. The battery grade precursor FePO 4 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 FePO 4·2H 2O under the experimental conditions is amorphous iron phosphate. And the prepared FePO 4 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 FePO 4 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, LiFePO 4 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 oxic acids. In this paper, a clean and green experimental scheme to prepare $\text{FePO}_4$ was studied, to adapt the green production process policy. Ferro-phosphorus was used as raw material to provide $\text{Fe}^{3+}$ and $\text{PO}_4^{3-}$. Nitric acid solution is used to dissolve ferro-phosphorus. Then, deionized $\text{H}_2\text{O}$ 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 $\text{Fe}^{3+}$. 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 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 $\text{Al}_2\text{O}_3$ crucibles under air atmosphere and heated up to 700°C at the heating rate of 10°C/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 400–4000 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 $\text{FePO}_4$ (hexagonal [77-0094], space group P3121 (152), with lattice parameters $a=5.036$ nm, $b=5.036$ nm, and $c=11.255$ nm). These characteristics
Confirm to the crystal of iron phosphate. It suggests that the synthesized samples have perfect crystal construction. 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 FePO₄•2H₂O has the best crystallinity when pH=1.0.

The microstructures of the FePO₄•2H₂O precursors were identified by SEM, as shown in Fig. 2. It can be found that the diameter of the synthesized FePO₄•2H₂O 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 FePO₄•2H₂O prepared at pH=1.0 are shown in Fig. 3. A weight loss of 19.25% was observed in the TG curve of the FePO₄•2H₂O 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, FePO₄•2H₂O 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 FePO₄, as reported in the literature.

![TG-DSC curves of the sample prepared at pH=1.0](image)

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

| 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 FePO₄ 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 FePO₄ was studied in FTIR spectra at the region of 400–4000 cm⁻¹. The infrared characteristic peaks of FePO₄•2H₂O are mainly composed of the absorption peaks of PO₃ groups, bound water and Fe. In addition, the FTIR spectra showed that PO₄ 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 FePO₄ originated from the intramolecular vibrations of PO₄ 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 PO₄³⁻. The absorption peak at 581.75 cm⁻¹ is a strong absorption peak of antisymmetric flexural vibration of PO₂ in PO₄³⁻. The absorption peak at 832.52 cm⁻¹ is the stretching vibration of 2 bridged oxygen ions in the PO₄ 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 FePO₄•2H₂O by using ferro-phosphorus as raw material.

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References
[1] Ai M, Ohdan K. Oxidative dehydrogenation of lactic acid to pyruvic acid over iron phosphate catalyst [J]. Journal of Jingzhou Teachers College, 2000, 150(1):13-20.
[2] Zhou D, Qiu X C, Liang F, et al. Comparison of the effects of FePO₄ and FePO₄•2H₂O as precursors on the electrochemical performances of LiFePO₄/C [J]. Ceramics International, 2017, 43:13254-13263.
[3] Wang Y, Wang J, Yang J, et al. High-Rate LiFePO₄ Electrode Material Synthesized by a Novel Route from FePO₄•4H₂O [J]. Advanced Functional Materials, 2006, 16(16):2135-2140.