Preparation and characterization of nanoscale flaky iron phosphate from phosphating slag

Xianzhen Song\textsuperscript{1,2}, Ying Cao\textsuperscript{1}, Yi Zhang\textsuperscript{1}, Fangjing Sun\textsuperscript{1}, Xixi Yan\textsuperscript{1}, Xiaoyu Liu\textsuperscript{1} and Lijun Wang\textsuperscript{1,2}

\textsuperscript{1}Faculty of Environmental and Materials Engineering, Shanghai Polytechnic University, Shanghai 201209, P.R. China
\textsuperscript{2}Research Center of Resource Recycling Science and Engineering, Shanghai Polytechnic University, Shanghai 201209, P.R. China
Email: ljwang@sspu.edu.cn

Abstract. Nanoscale flaky FePO$_4$·2H$_2$O was prepared in PTFE lined reactors by hydrothermal recrystallization method. Explored effects of different hydrochloric acid concentrations on purity, particle size, crystal structure and micromorphology. The addition of hydrochloric acid improved the purity of the iron phosphate in the phosphating slag. During the acidity increasing, average particle size decreased, crystal orientation changed twice. At the concentration of hydrochloric acid was 8wt.%, iron phosphate crystal has the best crystallinity, morphology changed into flake with 58.8 nm thickness.

1. Introduction
Phosphating is the most common metal surface treatment method [1], which enhances the adhesion of the paint on the metal surface and improves the corrosion resistance of the metal [2], [3]. Phosphating slag is a precipitate produced during the phosphating process with high biological toxicity, due to it contains heavy metal ions, such as Zn$^{2+}$, Cr$^{2+}$ and Mn$^{2+}$ ions. Therefore, it is necessary to find an effective method to reduce the pollution of waste slag and recycle the waste resources rationally.

Hydrothermal [4-7] is a method for preparing a material by dissolving and recrystallizing with water as a solvent. Hydrothermal can control the crystallinity and crystal size of product, obtain better crystal orientation, which is beneficial for reducing growth defects [4]. It is also easy to generate intermediate states, metastable states and special phases. Some researchers found that hydrothermal in acidic condition has obvious effects on crystal growth [8-10], it changes the solubility of the substance in the solution and the width of the metastable zone, easier to get new structure [7], [9].

The iron is the element with variable valence, different structures of iron phosphate catalysts exhibit superior catalytic properties [8], [11], [12]. At the same time, iron phosphate is also a precursor of LiFePO$_4$/C cathode material [13], [14], lithium iron phosphate nanoplates exhibit low polarization, fine reversible capacity, good cycling performance and high rate capability [15].

In our experiment, the main component of phosphating slag is iron phosphate, which has certain recycling value [16]. Nanoscale flaky iron phosphate was prepared in hydrochloric acid solution by hydrothermal recrystallization method, new iron phosphate crystal orientation has changed, which can be used for catalytic and battery materials. Iron phosphate can obtain better lattice morphology under acidic conditions, which might be possible used for fabricating high-temperature corrosion-resistant coatings.
2. Materials and Methods

2.1. Preparation of Samples
Dilute hydrochloric acid (AR, 36~38 wt.%) with distilled water to concentrations of 4 wt.%, 6 wt.%, 8 wt.%, 10 wt.%, and 15 wt.%. Transfer reactants to PTFE lined reactors after mix phosphating slag (compositions were determined by energy dispersive X-Ray spectroscopy and the results are summarized in table 1.) and diluted hydrochloric acid at the mass ratio of 1:1, reacted at 150°C for 4 hours. Final products were washed with ethanol (GR, 99.8 wt.%) and dried in drying oven at 60°C for 8 hours.

| Elements | Fe  | Zn  | Ca  | Mn  | Cr  |
|----------|-----|-----|-----|-----|-----|
| Mass fraction/(wt.%) | 88.40 | 9.38 | 1.68 | 0.28 | 0.26 |

2.2. Characterization
The content of elements in the sample was detected by energy dispersive X-Ray spectroscopy (EDX, Shimadzu-720, 1 mA, 30 kV). Particle size was analysed by laser particle size analyser (LPS, Mastersizer2000, range: 0.02~2000μm). The as-prepared products were characterized and analysed by the following instruments, Phase analyses were performed using X-ray diffraction (XRD, Bruker-AXS, 10 mA, 10 kV, Cu/Kα X-ray radiation). The microstructure was studied by the scanning electron microscopy (SEM, HITACHI-S4800, 10 mA, 10 kV with energy dispersion spectrometry).

3. Results and Discussions
Figure 1 shows the effect of different hydrochloric acid concentrations on the purity of iron phosphate. As the acid addition increasing, the purity of iron phosphate promoted from 93.18% to 99.92%. It may be that hydrochloric acid reacts with phosphating slag to produce FeCl₃, ZnCl₂, CaCl₂, MnCl₂ and CrCl₃, which are easily dissolved in ethanol. Hydrochloric acid environment and ethanol washing can effectively improve the purity of iron phosphate.

![Figure 1. The purity of iron phosphate under different hydrochloric acid concentrations](image)

For the accuracy of the distribution range of sample size, all samples were ultrasonically dispersed with ethanol to characterize the particle size. The results are shown in Figure 2. The average particle diameter (D50) of the phosphating slag was 18.848μm. At the same time, there was still a small number of large particles (D90) in the sample, particle size is 45.635μm. With acid concentration increasing, the particle size of the sample begins to show a decreasing trend. When D50 was reduced to about 2μm, there were no obvious change in particle size. The smallest D50 is 1.531μm under 15 wt.% HCl.
It shows that the size of iron phosphate can be adjusted by controlling the concentration of hydrochloric acid. Small particle size (D10) was reduced below 0.2μm when the concentration of hydrochloric acid was 15wt.%. It indicated that nanoscale or submicron scale iron phosphate exist in the reaction system.

![Figure 2. Particle size distribution of samples](image)

**Figure 2.** Particle size distribution of samples

Figure 3 is XRD patterns of phosphating slag and products. The main diffraction peaks of all samples correspond to FePO₄·2H₂O (PDF#33-0666), the space group is P2₁/n and belongs to the monoclinic system. With the increase in the concentration of hydrochloric acid, the diffraction peaks corresponding to the (020), (110), (002), (120) and (-112) crystal planes have been enhanced in all samples. Meanwhile, the diffraction (-112) peak (2θ = 32.137°) of FePO₄·2H₂O becomes the strongest peak, instead of the (002) peak (2θ = 20.379°) when the concentration of hydrochloric acid increased from 4wt.% to 6wt.. After the concentration of hydrochloric acid is higher than 8wt.%, the diffraction (020) peak (2θ = 18.084°) is the strongest peak and gradually weakening, the intensity of other peaks remains unchanged. This shows that crystal orientation changes twice. The iron phosphate crystal has the best crystallinity when the concentration of hydrochloric acid is 8wt.%. The concentration of hydrochloric acid exceeds 8wt.% inhibits the growth of crystals along the (020) crystal plane.

![Figure 3. XRD patterns of phosphating slag and products prepared under different hydrochloric acid concentrations](image)

**Figure 3.** XRD patterns of phosphating slag and products prepared under different hydrochloric acid concentrations.
Figure 4 (a) shows the phosphating slag micromorphology, it can be seen that the phosphating slag is a sphere with uneven surface and formed by the agglomeration of a variety of chemically stable phosphates, diameters range from 5 to 20μm. SEM images (Figure 4 (b), (c), (d), (e), (f)) indicated that the iron phosphate on the surface of the spherical phosphating slag is continuously exfoliated until it grows to a flaky shape during the concentration of hydrochloric acid climbing. At 8wt.% hydrochloric acid, the crystal structure is the most complete and the shapes have better homogeneity. At 15wt.% hydrochloric acid, the reaction produces a large number of nanoscale FePO₄·2H₂O particles, this phenomenon illustrates that when the concentration of hydrochloric acid is too high, new crystal nucleus were generated in the reaction system and fast growing to nanoscale iron phosphate. Figure 4 (g) shows the thickness of the flaky FePO₄·2H₂O is about 58.8 nm at the hydrochloric acid concentration is 8wt.%.

4. Summary and Conclusion
In summary, nanoscale flaky FePO₄·2H₂O were prepared in hydrochloric acid environment from phosphating slag by hydrothermal recrystallization method which has uniform thickness and good dispersion. The addition of hydrochloric acid increased the solubility of iron phosphate in solution, wash material with ethanol to remove impurities which can obtain high purity of iron phosphate. By adjusting the addition of hydrochloric acid, the particle size of iron phosphate can be well controlled. Hydrothermal reaction improved crystallinity of iron phosphate crystals and changed crystal structure. Crystal orientation has changed in different acid concentrations. At high acidity, the generation of new nucleation constrained the recrystallization process, this leads to decreasing in the crystallinity of iron phosphate crystals, which provided a new idea for the preparation of iron phosphate nanoparticles from phosphating slag.

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