

CONTINUOUS HYDROTHERMAL SYNTHESIS OF IRON PHOSPHATE HYDROXIDE IN SUPERCRITICAL WATER

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In this work iron phosphate hydroxide nanoparticle was continuously synthesized in the environment of sub- and supercritical water. The investigated temperature ranged from 250 ~ 400 °C at 30 MPa above its critical pressure. Although literatures reported that LiFePO₄ could be obtained by batch and continuous hydrothermal synthesis, this work demonstrated that different flowing pattern of the reactor produced Fe₄(PO₄)₃(OH)₃. The flowing pattern of the reactor would change the nucleation mechanism of the precipitation. In the first flowing pattern, the mixed aqueous solutions of FeSO₄ and H₃PO₄ were pumped into the reactor, after LiOH aqueous solution was pressurized and heated to fill up the reactor. With this procedure, LiOH would primary precipitate in the reactor because LiOH did not dissolve in the supercritical water. Due to the lack of lithium ions, the FeSO₄ and H₃PO₄ aqueous solution will precipitate as Fe₄(PO₄)₃(OH)₃. In a second flowing pattern, the mixing of FeSO₄, H₃PO₄ and LiOH at room temperature primarily precipitated Fe₄(PO₄)₃(OH)₃ and the following heated up by supercritical water did not allow lithium ions merged into the matrix. This work demonstrates two flowing patterns that could not product LiFePO₄ via supercritical water synthesis.

1. INTRODUCTION

Metal oxide prepared by hydrothermal synthesis is a well known process. In the past decade, researchers from Tohoku University promoted the continuous hydrothermal crystallization into the supercritical state. Many oxides were produced in the supercritical state [1-4]. Lee et. al. showed the feasibility to produce LiFePO₄ by batch and continuous hydrothermal synthesis [5]. In Lee's work, the cold aqueous solution of LiOH and aqueous solution of FeSO₄ and H₃PO₄ were pumped and mixed in a tee before heated up by supercritical water. However, the mixing of the two aqueous solutions will result precipitation. It was therefore assumed that the cold mixing will form the precursor and the following heated up by the supercritical water will induce phase transformation of the precursor to form the LiFePO₄. In this work, we tried to change the feeding pattern to see the difference of the obtained particles in a continuous flow system.

In a batch reactor, the aqueous solution of reactants is loaded into an auto clave and the pressure increases after heating up the reactor. This is an isochoric process. The reaction initiates as the activation energy of the reaction is overcome. Therefore, it is difficult to investigate the nucleation and crystal growth of the precipitation of produced particles, because the initiated temperature is not available for this isochoric hydrothermal process and the state of the reacting environment is unclear. For safety reason, particles produced by a batch reactor were mostly formed in saturated liquid or in the state of compressed gas. In a continuous hydrothermal process, the reaction is conducted at constant pressure. The reaction also initiates at the temperature roughly as that in the batch reactor. It is normally observed that the precipitated particles plugged the flow system at the inlet of the reactor. This result implies that the reaction takes place at the temperature whereat lower the setting temperature of the reactor. Researchers from Tohoku University attempted to solve this problem using a cooling jacket for the stream of precursor's solution right before the reactor to prevent plugging, however, a

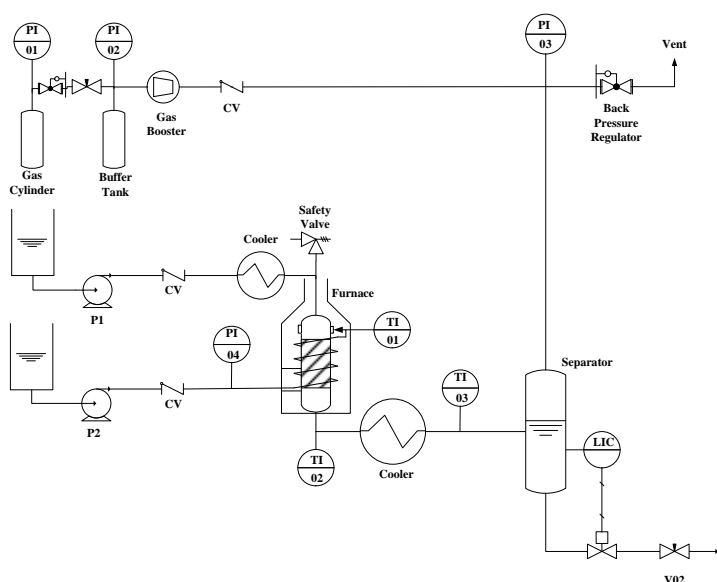
temperature gradient still existed. Consequently, it would gradually plug the flow system as long as the flow rate is low.

To control the pressure of the flow system was also difficult, if on-line filters were installed in the downstream to collect the produced particles. In this work, we designed a gas-liquid separator in the downstream, which could cool the hot stream and also play as a buffer to regulate the system's pressure. The liquid level of the separator was maintained with the aid of a view-through window, and the cooled liquid was therefore periodically discharged and collected from the separator.

2. EXPERIMENTS AND MATERIALS

The flow system used in this study was illustrated in Figure 1. The pressure of the system was controlled by nitrogen gas through a back pressure regulator. The nitrogen from gas cylinder was first regulated to 40 ~ 50 bar, and pressurized by a gas booster. The water was pumped through P2 into a coiled tube to preheat to the designed temperature. After preheated, the water flowed into the reactor. Both the coiled tube and the reactor were installed inside an electric furnace. The temperature of the furnace was controlled by a temperature controller. The water discharged from the reactor was cooled and flowed into a separator where the liquid level was maintained through a view through window. In this study, there were two different methods to feed the reactant. In the first method, water was replaced by aqueous LiOH solution after the set temperature and pressure were reached. The FeSO_4 and H_3PO_4 solution was pumped into the system by pump P1. A cooler was installed right before flowing into the reactor to prevent plugging. The particles would be obtained in the downstream of the separator. The obtained particles were centrifuged and washed for several times. After dried, the particles were analysis by SEM and XRD. In the second method, additional pump was installed to pump the aqueous solution of LiOH individually, which was not shown in Figure 1. The aqueous LiOH solution was mixed with the FeSO_4 and H_3PO_4 solution in a tee installed before the cooler. The sampling and analysis was same as that of the first method.

In order to try to form a carbon layer on the obtained particles, glucose was also dissolved into water before pumping into the system. It was expected that glucose can be adsorbed onto the surface of the growing particles, and decomposes to form carbon on the surface [6].



T1: water	T2: recycling	T3: buffer tank	T4: aqueous solution
P1: pump	CW: cooling water	V1~V5: hand valve	V6: metering valve
BPR: back pressure regulator		PRV: pressure reducing valve	

Figure 1 Illustration of the hydrothermal flow system

3. RESULTS AND DISCUSSION

As the first method was used, the obtained particles were found as $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$ in the temperature range of 250 to 400 °C. If glucose was added, the XRD showed little different pattern from those without glucose. Figure 2 illustrated the XRD pattern for particles obtained at 300 °C. With adding of glucose the obtained $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$ showed better crystalline than that without glucose. It was presumed that glucose can induce the formation of $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$. To alter the reaction temperature did not change the structure significantly due to the XRD pattern as shown in Figure 3. A typical SEM for the obtained particles was also shown in Figure 4. No significant difference in size and shape was observed in this study.

If the LiOH solution was mixed with FeSO_4 and H_3PO_4 solution at room temperature, milky white precipitate was observed. It is, therefore, presumed that the same precipitated solids will also be produced, if the mixing happened at 30 MPa. In the second flowing pattern, the obtained particles were dark yellow green. However, XRD showed similar crystal was obtained. No evidence of the existence of lithium ions was found.

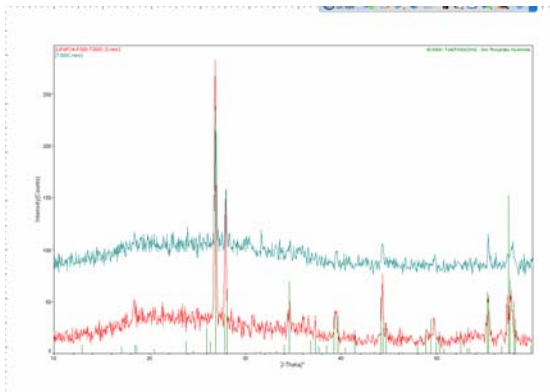


Figure 2 The effect of glucose on the XRD pattern.

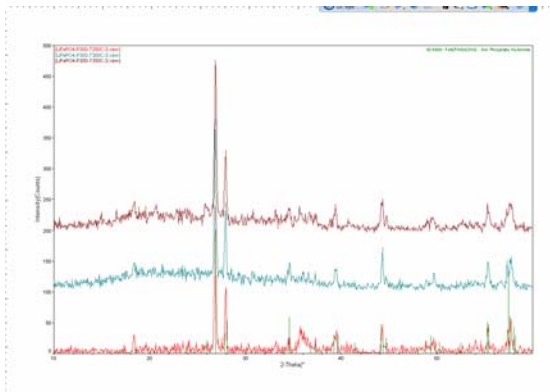


Figure 3 The effect of temperature on the XRD pattern.

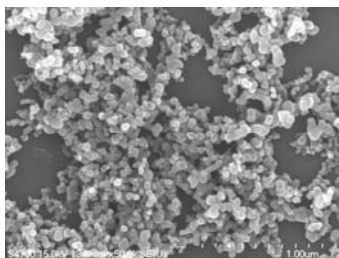


Figure 4 The SEM of the obtained particles

4. CONCLUSIONS

In this work, two procedures were tried to produce LiFePO₄ by supercritical water synthesis. However, no evidence of lithium ions was found in the obtained particles. Adding glucose into the supercritical water did not modify the surface of the obtained particles.

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