

## Batch and continuous hydrothermal synthesis of LiFePO<sub>4</sub> micro- and nanoparticles.

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### ABSTRACT

Lithium iron phosphate (LiFePO<sub>4</sub>) is a promising cathode material for lithium ion batteries because it can be synthesized from low cost starting materials, it is relatively non-toxic (compared with LiCoO<sub>2</sub> or LiNiO<sub>2</sub>), and because it is intrinsically stable at potentials greater than 3.45 V [1]. The solid-state synthesis of LiFePO<sub>4</sub> has therefore received much attention. However, this process is costly and very time-consuming since it involves at least four steps [2] and leads to relatively large particles (average size greater than 30 μm) [3].

This work reports new hydrothermal routes for the synthesis of nanoparticles of lithium ion phosphate. The hydrothermal synthesis has been carried out in batch as well as continuous reactors, and at subcritical as well as supercritical (solvent) temperatures. Reaction temperature, pH, residence time, and reactant concentrations were adjusted to investigate their effect on particle characteristics such as size, size distribution, specific surface area, and morphology. The particles were characterized using optical and XRD, XPS, SEM, and TEM methods. In general, submicron and nanoparticles of uniform size and shape could be obtained at both subcritical and supercritical temperatures, and neutral pH. Particles of higher crystallinity, which is expected to be beneficial in battery applications, could be obtained at supercritical temperatures and at higher residence times in the continuous process.

### RESULTS

Lithium iron phosphate was synthesized according to the following reaction:



Batch synthesis was carried out in a Paar reactor (Model 4576) and continuous synthesis in the apparatus shown in Figure 1. It was found that LiFePO<sub>4</sub> could only be obtained at neutral pH. Representative SEM images of the particles obtained in batch experiments are shown in Figure 2. As can be seen in this figure, there is a distinct difference between particles synthesized at subcritical temperatures and at supercritical temperatures. Micron-sized and highly agglomerated particles were produced at subcritical temperatures, with the particle shape becoming more uniform with increasing temperature. By contrast, the particles obtained at supercritical temperatures were an order of magnitude smaller, and not very agglomerated. Also, the particle shape was spherical and very uniform.

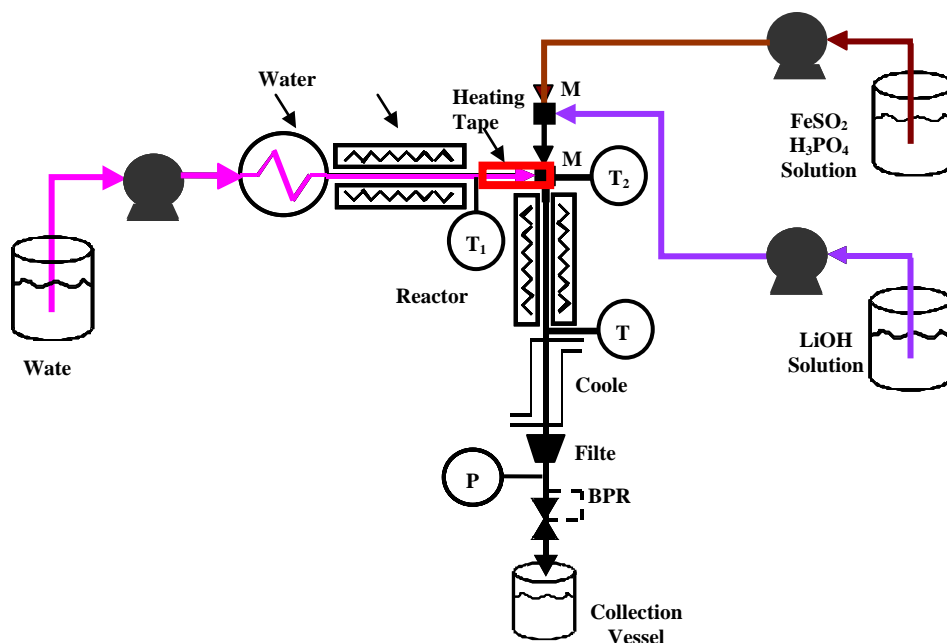


Figure 1. Schematic diagram of the continuous reactor.

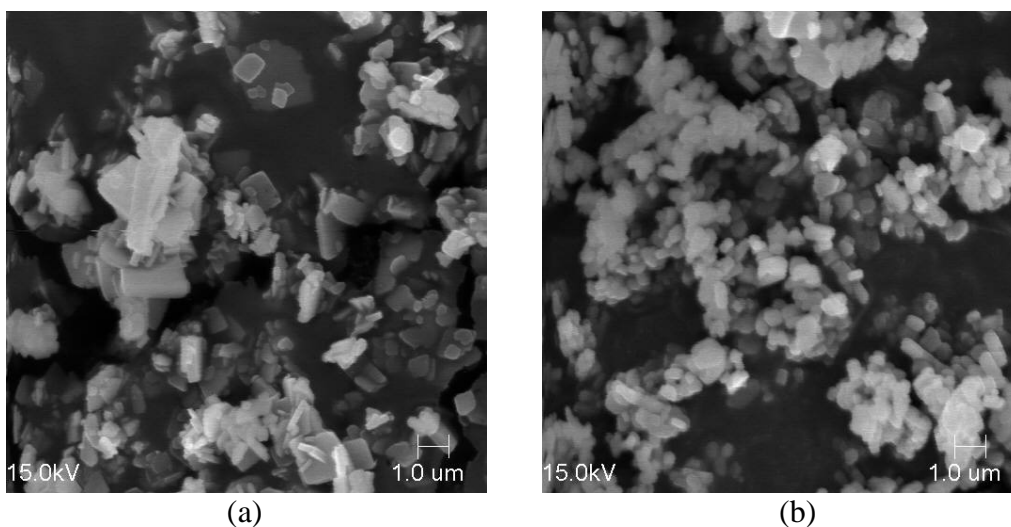


Figure 2. SEM images (x 5,000) of particles obtained at (a) 194 °C after 1hr, (b) at 387 °C after 1 hr.

Primary particle size appears to be determined by competition between the nucleation rate and the growth rate [4] during crystallization. Nucleation rate is a function of temperature, degree of supersaturation, and interfacial tension [5], whereas growth rate is mainly dependent on the diffusivity of the solute [6]. At supercritical temperatures, the degree of supersaturation and diffusivity of the solute are much higher and the interfacial tension is much lower than at subcritical temperatures [7, 8]. These factors lead to high nucleation and growth rates and smaller particles at supercritical conditions.

Particle size is also strongly dependent on residence time, and this can be controlled relatively easily in a continuous (flow) apparatus. Figure 4 shows TEM images of particles obtained in the continuous reactor shown in Figure 1. As is obvious, morphologies of the particles are much different from those synthesized in a batch reactor. It was also possible to get fine particles with average sizes less

than 100 nm. The small size of the particles may be attributed to the short residence time, which was less than one minute in this case. However, particles of different shapes (spherical, needle type) were obtained due to fluctuations in temperature and pressure during the synthesis.

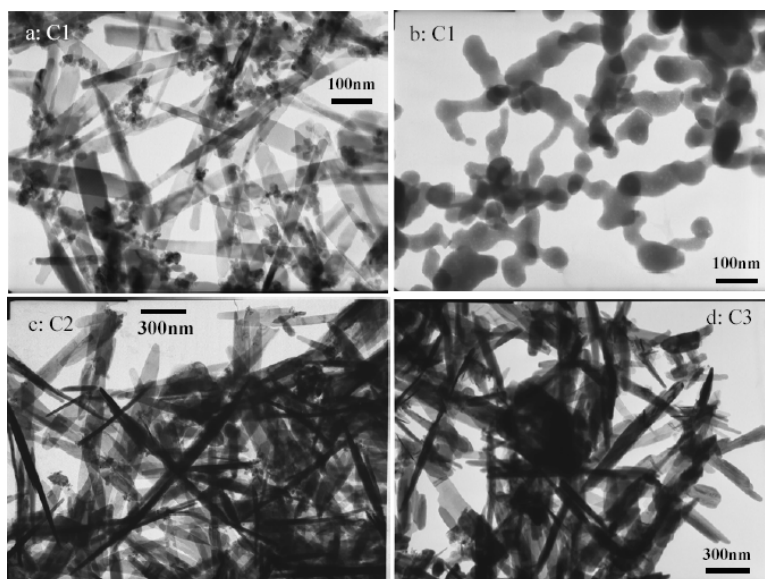


Figure 4. TEM images of the  $\text{LiFePO}_4$  obtained at supercritical state in continuous reactor.

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