



Continuous synthesis of lithium iron phosphate nanoparticles in supercritical water: Effect of process parameters



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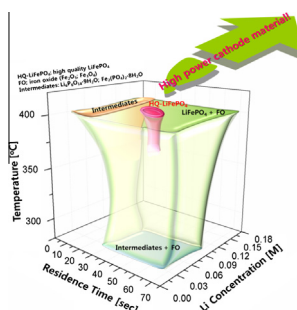
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HIGHLIGHTS

- Effect of process parameters on formation of LiFePO₄.
- Particle formation and reaction mechanism at different conditions presented.
- LiFePO₄ formed at high temperature, low concentration, and low flow rate condition.
- Limits of process parameters to form LiFePO₄ presented.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the effect of various process parameters during continuous synthesis in supercritical water on the physicochemical and electrochemical properties of lithium iron phosphate (LiFePO₄) for use in large-scale lithium 2nd battery applications. The process parameters include reaction temperature (300–400 °C), precursor solution concentration (0.01–0.18 M), precursor solution flow rate (1.5–3.0 g/min), water flow rate (9.0–36.0 g/min), and residence time (9–72 s). Under subcritical water conditions, mixed Fe₃(PO₄)₂·8H₂O, Fe₂O₃, and Fe₃O₄ particles formed; in contrast, under supercritical fluid conditions, well-crystallized LiFePO₄ particles with some Fe³⁺ impurities (i.e., Fe₂O₃ and Fe₃O₄) were obtained. In supercritical water, an increase in the precursor concentration leads to an increase in the Fe³⁺ impurity content. At a high water flow rate, a significant decrease in crystallinity and the formation of Fe₃(PO₄)₂·8H₂O and Li₆P₆O₁₈·9H₂O phases rather than LiFePO₄ were observed. Highly crystalline LiFePO₄ with good discharge capacity was obtained with high temperature, low precursor concentration, and low flow rate conditions. Depending on the synthetic conditions, bare LiFePO₄ particles exhibit discharge capacities of 55–85 mA h/g at 0.1 C-rate after 30 cycles. After carbon coating, a marginal capacity decay from 141 to 135 mA h/g was observed during the 30 charge–discharge cycles.

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1. Introduction

Recently, large-scale lithium-ion battery (LIB) applications such as plug-in hybrid electric vehicles, electric vehicles, and backup power systems are of great interest due to the current issues of global warming and fossil fuel depletion [1,2]. For such applications, it is highly desirable for the LIBs to be inexpensive and have high energy and power densities, a high level of safety, and excellent cyclability. Lithium cobalt oxide (LiCoO_2) with a layered structure, which is a widely used cathode-active material for small-scale portable electronic devices, is unsuitable for large-scale LIB applications due to its instability at high temperatures, lack of safety under harsh conditions, toxicity, and high cost [3]. Lithium manganese oxide (LiMn_2O_4) with a spinel structure has been extensively studied as an inexpensive and safe cathode-active material. However, one of the major drawbacks of LiMn_2O_4 is its instability during charge and discharge due to the dissolution of Mn ions from LiMn_2O_4 [4]. Lithium iron phosphate (LiFePO_4) with an olivine structure is considered to be a promising cathode active material due to its high stability at high operating temperatures, high theoretical capacity of 170 mA h/g, good energy density (~ 250 W h/kg), and low cost [5,6]. However, the major drawbacks of LiFePO_4 include its low electronic conductivity ($\sim 10^{-10}$ S/cm) and sluggish Li^+ ion diffusivity (10^{-14} – 10^{-17} cm^2/S) [7,8]. Many synthetic strategies, including solid-state [9,10], sol–gel [9,11], hydrothermal [12], solvothermal [13], co-precipitation [14], microwave [15], emulsion drying [16], mechanical milling [17], molten salt [18], and spray pyrolysis [19] methods, have been developed to overcome the drawbacks associated with LiFePO_4 ; however, only a few of them are currently used for the large-scale production of LiFePO_4 [6]. Therefore, considerable efforts are still underway to develop simpler, more reliable, and less expensive techniques to produce high-quality LiFePO_4 at a commercial scale.

Supercritical fluids are a very promising media for the synthesis of high-quality, highly crystalline, nanosize particles [20–26]. Among the various types of supercritical fluids, supercritical water (scH_2O) is unique and has many advantageous features for the synthesis of metal oxide nanoparticles, as follow: (1) the physical properties of scH_2O can be easily controlled by adjusting process parameters such as temperature and pressure. For example, the density of scH_2O can be controlled between liquid-like and gas-like values without a phase transition by varying the temperature and pressure within a narrow range [21]. In addition, the dielectric constant of scH_2O can be controlled in a wide range from 11.6 to 1.8 with varying temperature from 377 to 502 °C at 30 MPa [27]; these values are much lower than that at ambient conditions (~ 80). (2) Most charged inorganic species that are soluble in water at ambient conditions are insoluble in scH_2O due to the non-polar characteristics of scH_2O . This can lead to extreme supersaturation during the nucleation stage [28], which results in the simple production of nanosized particles. (3) The diffusivity of molecules in scH_2O is approximately fifteen times higher than that under normal conditions [29], which is beneficial for diffusion-limited crystal growth. In addition, the high diffusivity and supersaturation ratio can lead to an extremely high production rate: The typical residence time to produce metal oxide nanoparticles is less than one minute [20]. (5) scH_2O is non-toxic and environmentally friendly.

These beneficial properties of supercritical water have been utilized to synthesis various types of cathode- and anode-active materials, including LiCoO_2 [30,31], LiMn_2O_4 [32], $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [33], LiMnPO_4 [34], LiFePO_4 [35–39], and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [40,41], in either a batch or continuous mode. In 2010, the first commercial plant for the production of LiFePO_4 using continuous supercritical hydrothermal synthesis was constructed in Korea

[42]. This plant can continuously produce LiFePO_4 at a capacity of 1000 tons per year. Despite this commercialization, the precise effects of various process parameters on the physicochemical and electrochemical properties of LiFePO_4 have not yet been fully elucidated and are generally absent from literature. The continuous synthesis of LiFePO_4 in sub- and supercritical water has been investigated at different temperatures, water flow rates, and concentrations within relatively small ranges and without reaction mechanisms [36,37]. Furthermore, the charge–discharge capacity of LiFePO_4 was either not reported [36] or was reported within limited charge–discharge capacity values of 70–75 mA h/g without efforts to improve its capacity via, e.g., carbon coating [37].

This work investigates the effects of various process parameters on the physicochemical and electrochemical properties of LiFePO_4 during continuous scH_2O -based synthesis. The manipulated parameters include reaction temperature (300–400 °C), precursor solution concentration (0.01–0.18 M), precursor solution flow rate (1.5–3.0 g/min), water flow rate (9–36 g/min), and residence time (9–72 s). We varied these parameters in wide ranges to fully comprehend the formation mechanism of LiFePO_4 in scH_2O and its resultant properties; this not only enabled optimization of these parameters but also revealed their functional limits. The size, size distribution, surface area, morphology, and phase structure of the particles synthesized in sub- and supercritical water using different process parameters are discussed in detail. The charge–discharge capacities of bare LiFePO_4 and carbon-coated LiFePO_4 (C-LiFePO_4) synthesized under different conditions are also discussed.

2. Experimental

2.1. Materials

Lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, purity of ≥ 98 wt%), iron sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, purity of ≥ 99 wt%), phosphoric acid (H_3PO_4 , purity of ≥ 98 wt%), and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$, purity of ≥ 99 wt%) were supplied by Sigma–Aldrich (St. Louis, MO, USA). Nitrogen (purity of 99.9%) and argon with 5% hydrogen (purity of $\geq 99.999\%$) were purchased from Shinyang Sanso Co. (Seoul, Korea). Distilled and deionized (DDI) water was prepared using a Milli-Q Ultrapure water purification system with a 0.22 μm filter (Billerica, MA, USA). Poly(vinylidene difluoride) (PVDF; Kureha Chem. Co., Tokyo, Japan), acetylene black (DENKA Co., Ltd., Tokyo, Japan), and *N*-methyl-2-pyrrolidinone (NMP; purity of ≥ 98 wt%, Alfa-Aesar, MA, USA) were used as received.

2.2. Apparatus and procedures

A continuous high-pressure, high-temperature apparatus has been used for the synthesis of metal or metal oxide nanoparticles in supercritical water or supercritical alcohols [38,39,43–45]. The schematic of the apparatus is shown in Fig. S1. Details on the apparatus and experimental procedure have been described previously [38,39,44]. Herein, two reactors with volumes of 47 and 114 cm^3 , respectively, were used to examine the effect of the residence time. The geometry of the mixing tee affects the size, morphology, and crystallinity of the particles and prevents plugging [46,47]. In the current study, the scH_2O flow and room-temperature precursor solution flow met at a 50° angle in the mixing tee [38]. The LiOH and $\text{FeSO}_4/\text{H}_3\text{PO}_4$ solutions, pumped from different reservoirs, met at MP1 prior to heating and the mixed $\text{LiOH}/\text{FeSO}_4/\text{H}_3\text{PO}_4$ solution was introduced to MP2 where the solution met the supercritical water flow (see Fig. S1). The Reynolds number downstream

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