



## Original Research Paper

## Urea decomposition enhancing the hydrothermal synthesis of lithium iron phosphate powders: Effect of the lithium precursor

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## ABSTRACT

The synthesis of LiFePO<sub>4</sub> (hereafter referred as LFP) using urea as a reducing agent under hydrothermal conditions was investigated. The synthesis was carried out by varying the temperature (150–200 °C), at different times from 6 to 24 h, and using different precursors of Li ions (LiCl, LiNO<sub>3</sub>, LiOH, and Li<sub>2</sub>SO<sub>4</sub>), to determine the effect of these parameters on the crystallization process of the reaction products. These were characterized by XRD, FT-IR, and FE-SEM. The results showed that the differences in the lattice parameters calculated by Rietveld refinement are affected by the synthesis temperature. In addition, the crystallization of single-phase LiFePO<sub>4</sub> powders was achieved by the urea decomposition that occurred at reaction times longer than 12 h and at moderate temperatures (170–180 °C). The crystallization of LFP particles was promoted by a dissolution-precipitation mechanism, but it was not conducted in a single step, because intermediate secondary phases were produced at reaction intervals below 6 h. A crystal growth stage involving the dissolution-crystallization of intermediate secondary phases led to the formation of large particle agglomerates of LiFePO<sub>4</sub> exhibiting a flower-like morphology when the synthesis was carried out using Li<sub>2</sub>SO<sub>4</sub>. When LiCl, LiOH, and LiNO<sub>3</sub> were used, large bulky agglomerates were obtained.

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## 1. Introduction

Over the last few decades, many studies have been conducted in the field of ceramic materials, in particular for specific technological applications. Ceramics with electric properties have particularly attracted the interest of scientists because of their potential application in power sources in different areas such as electronic devices, hybrid-electric vehicles, tablets, cellular phones, laptop computers, etc. [1–3]. In particular, a tremendous research effort has been focused on the development of lithium ion rechargeable batteries. Since its discovery in 1997 [4], lithium iron phosphate (LiFePO<sub>4</sub>, LFP) has attracted the attention of various research groups worldwide, because it has the potential to operate as a cathode material in lithium rechargeable batteries, due to its excellent properties, mainly its excellent thermal stability promoted by covalent bonding of PO<sub>4</sub> tetrahedra with a chemically stable pair of Fe<sup>2+</sup>/Fe<sup>3+</sup> ions, in addition to its low cost and low environmental toxicity [5–8]. Therefore, LFP has a superior performance compared

to other lithium cathode materials such as LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> [9,10]. Although LFP has a high theoretical capacity of ~170 mAh g<sup>-1</sup>, the main barrier in its utilization is associated with the low intrinsic electronic conductivity of the olivine structure. In addition, lithium motion in the orthorhombic crystal structure occurs through one-dimensional channels, with little possibility of crossing between channels [11–13]. These paths are particularly susceptible to blockage by defects and impurities [9,14,15]. In order to solve the low conductivity problem, various approaches have recently been proposed. Some possible solutions include the reduction of the particle size and the use of a homogeneous particle size distribution [9,11–13], coating the particles with carbon [9,11–13,16], tailoring the morphology of the particles by applying different methods of synthesis, and doping the crystal structure with different cations in the Fe-site to increase the intrinsic conductivity [9,11–15].

Soft chemistry synthesis methods have been widely applied to produce single-phase LFP powders, including solid-state reactions [17], co-precipitation [18], the sol-gel route [19], and non-equilibrium processes such as hydrothermal and solvothermal techniques. Soft chemical preparation methods have an indis-

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putable advantage compared to solid-state reactions in achieving better homogeneity and mixing of the starting compounds at the molecular level. In particular, hydrothermal synthesis is an easy and rapid method to prepare fine particles. Some advantages associated with this process are its low-cost, energy saving and easy scalability. In hydrothermal processing, the product is obtained via precipitation of the hydrolyzed ions in saturated solutions [9]. Preliminary studies investigating optimal conditions for synthesizing pure LFP demonstrated that the minimum temperature required to achieve its crystallization is 170 °C; as a consequence, iron disorder is minimized, obtaining non-distorted unit cell lattice parameters. In addition, hydrothermal synthesis produces well-crystallized materials with homogeneous submicron particle sizes [9,20]. In general, the formation of LFP during hydrothermal and solvothermal synthesis involves heterogeneous nucleation enhanced by a dissolution-recrystallization process, while crystallite growth greatly depends on various reaction factors including solvent type, concentration, temperature, reaction time, and the pH of the hydrothermal medium [20]. Furthermore, in hydrothermal fluids, a reducing agent is required to avoid the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>, which is one of the principal disadvantages associated with this route. Hence, various chemical reagents, organic in nature, decompose at hydrothermal conditions, producing a reducing environment, avoiding the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Among this kind of compounds employed are ascorbic acid [21], pyrrole [22], glucose [23] and sucrose [24].

A literature review indicates that no attempts for using urea as a potential reducing agent have yet been conducted to produce LFP particles under hydrothermal conditions. Under these conditions, urea (CH<sub>4</sub>N<sub>2</sub>O) decomposes at a temperature of over 120 °C, producing ammonium hydroxide and carbon dioxide (CO<sub>2</sub>) gas. The partial pressure of the gas inside the autoclave is autogenously increased during the reaction, and the gas is dissolved in the reaction medium. Urea provides CO<sub>3</sub><sup>2-</sup> ions to the hydrothermal reaction medium, which might result in the generation of a reducing atmosphere inside the reactor. The reaction equilibrium of urea occurring under hydrothermal conditions above 120 °C is given by Eq. (1).



The increase of urea concentration in the aqueous medium promotes an increment in the amount of CO<sub>2</sub> gas due to the urea decomposition, which then leads to the saturation of the aqueous phase with carbonate ions and ammonia, allowing autogenous pH control and generating a reducing environment to avoid the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. This study aims to investigate exhaustively the feasibility of applying urea as a potential reducing reagent to obtain LFP particles under hydrothermal conditions. A series of different experiments was carried out to determine the effect of processing parameters, such as temperature, reaction time, Li:Fe:P molar mixing ratio, urea content and Li ion precursor reagent, on the synthesis of LFP. In addition, aspects of the crystalline structure of the single-phase LFP and the reaction pathways are discussed as a function of the investigated parameters.

## 2. Experimental procedure

The main objective of this work was to investigate the effect of hydrothermal processing parameters and the effect of different Li ion reagent precursors, as well as the use of urea as a reducing agent to prevent the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> during the preparation of LiFePO<sub>4</sub> powders. Hydrothermal treatments were carried out with no convection of the fluid media. Particles of lithium iron phosphate (hereafter referred to as LFP) were obtained using chemical reagents of analytical grade (Sigma Aldrich, 99% purity)

of lithium sulfate (Li<sub>2</sub>SO<sub>4</sub> · H<sub>2</sub>O), lithium nitrate (LiNO<sub>3</sub>), lithium hydroxide (LiOH), lithium chloride (LiCl), iron sulfate (FeSO<sub>4</sub> · 7H<sub>2</sub>O), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, >85%) and urea (CH<sub>4</sub>N<sub>2</sub>O). Precursor solutions were prepared at a concentration of 1 M by dissolving each compound in ion-exchanged water, and then pouring it into a Teflon-lined autoclave in stoichiometric Li:Fe:P mixing ratios of 1.5:1:1, 2:1:1 and 3:1:1. These mixing ratios were selected in accordance with those reported elsewhere [1–3,5–7,9]. All the experiments were conducted at a liquid constant volume of 50 ml that corresponds to 70% of the autoclave's inner volume. A specific amount of urea powder was added to control the nominal concentration of urea in the reaction medium; three different concentrations of 5, 10 and 20 mmol of urea were chosen. Urea is a highly soluble compound in both acidic and alkaline media; thus, it completely dissolved into the mother liquor mix after it was added to the latter. The stainless steel vessel was then sealed and heated inside a convection-heating oven to reach the desired temperature. The treatments were conducted at different temperatures ranging from 150 to 200 °C, for various reaction intervals in the range of 3–24 h. After the treatment, the pH of the remaining liquid mixture was measured and the reaction products were collected and washed vigorously four times with hot water (60 °C) to remove any traces of other compounds. The produced powders were dried overnight in an oven at 80 °C.

### 2.1. Characterization

X-ray diffraction powder analyses were conducted to determine the crystalline phases and reaction by-products; as a consequence, an overview of the chemical reaction pathway associated with the present chemical reaction system was proposed. In addition, aspects related to the stability of the LFP phase and the mechanism associated with its synthesis were also determined from these analyses. The diffraction patterns were collected in the 5–80° 2θ range at a constant scanning speed of 20 °/min with a 0.02° step, using monochromatized Cu Kα radiation at 40 kV and 20 mA. These analyses were conducted in a Rigaku Ultima IV diffractometer. In addition, Rietveld refinement of samples containing single-phase LFP reaction product were carried out in order to determine the crystallite size and lattice parameters using the TOPAZ software; the initial atomic spatial distribution values and the space group details used for refinement purposes were taken from the crystalline data of LiFePO<sub>4</sub> reported elsewhere [7,25–28]. The Wickoff positions reported elsewhere [7] are summarized in Table 1, which shows the data used to carry out the Rietveld refinement of the XRD patterns. Table 1 presents information of the sites and positions of the constituents in the crystal structure. The morphological aspects and sizes of the particles produced at short and long reaction intervals were revealed by field-emission scanning electron microscopy (FE-SEM JEOL JSM-7100F). The particle size

**Table 1**  
Atomic coordinates corresponding to the tetragonal LiFePO<sub>4</sub> olivine structure employed to conduct the Rietveld refinements using TOPAS 4.2 software, the spatial positions were reported by Anderson et al. [7].

Atom	Spatial coordinates		
	x	y	z
Li	0	0	0
Fe	0.9716	0.2822	0.25
P	0.4179	0.0954	0.25
O	0.7403	0.0946	0.25
O	0.2056	0.4538	0.25
O	0.2861	0.1615	0.0521

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