



## Review article

# A review: Conventional and supercritical hydro/solvothermal synthesis of ultrafine particles as cathode in lithium battery



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## ABSTRACT

Olivine  $\text{LiMPO}_4$  ( $M = \text{Mn, Fe, Co and Ni}$ , LMP) materials are considered to be the most promising cathode candidates for high energy storage devices. In this work, the feasibility of the thermodynamics of powder formation is discussed for explaining such a reaction mechanism, as well as the recent progress of conventional and supercritical hydro/solvothermal syntheses, are summarized. The association among synthesis conditions, structure, morphology and electrochemical properties, especially for rate capability and tap density under hydro/solvothermal condition, are highlighted. Notably, this work primarily concentrates on the processes in which additives participate in the hydrothermal synthesis of LMP and considers less the subsequent treatments of synthesized LMP with extra additives. In other words, the modifications during the synthesis process with additives are the primary topic. Recently, supercritical hydro/solvothermal synthesis has been demonstrated to be a promising approach for generating high-crystalline micro-nanoparticles with short reaction times (less than 2 min) and high crystallization rates affected by the specific characteristics in supercritical fluids. Additionally, the smallest powders among the reported LFP nanoparticles (less than 15 nm) had been synthesized via SHS (supercritical hydrothermal synthesis). Inspired by the structure-function relationships that are gained by hydro/solvothermal synthesis, rapid and continuous supercritical hydro/solvothermal synthesis is of interest for the commercial production of high-performance micro/nanocrystals due to its environmental friendliness and easy scale-up.

## 1. Background

With increasing energy crises and environmental pollution, rechargeable lithium ion batteries have received significant attention as one of the most promising energy storage systems for high-performance applications of electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. Among lithium cathode materials, olivine-structured  $\text{LiMPO}_4$  is considered to be a prospective candidate cathode, especially for lithium iron phosphate ( $\text{LiFePO}_4$ , LFP) due to its outstanding inherent merits of environmental benignity, low-cost, thermal stability, superior safety, non-toxicity, and accepted operating voltage platform, since it is reported in 1997 [2].

$\text{LiFePO}_4$ , a semiconductor (0.3 eV band gap), the material of one-dimensional channel diffusion mechanisms, is parallel to the b-axis that is oriented in the [010] direction [3,4], which is different from diffusion in two-dimensional or three-dimensional mechanisms [5,6]. Hence LFP has two major intrinsic drawbacks: poor electronic conductivity and low lithium ion diffusion, which hinders its application in high-power systems. To improve its electrochemical properties, many strategies have been adopted to overcome its shortcomings. These include

reducing the particle size, conducting carbon coating [7–10], and using a doping cation [11–14]. The reduced particle size can decrease the lithium ion and electronic diffusion path, enhance transport kinetics and alleviate polarization. The coated conducting carbon can improve conductivity and inhibit particle growth and agglomeration. The doping can facilitate electron and lithium diffusion, but the doping mechanisms are controversial [15].

Carbon coating and small particles have been proven to be effective in enhancing electrochemical properties. However disordered packing of nanocrystal or excess carbon decrease the tap density and affect volumetric energy density. Furthermore, nanomaterials are easily to agglomerate due to high surface energy. These challenges are also reported by excellent reviews as future developments [16,17]. Therefore, a balance among tap density, nanostructure and carbon coating should be deeply considered [18]. The quality of carbon coating and effective nanostructure arrangement appear to be potential to solve the issues. However, if nanomaterials assemble themselves to form ordered and dense micromaterials, the tap density would be increased [19,20]. Hence, micro-nanostructured LMP is relatively attractive, containing the merits both nanomaterials and micromaterials. In addition, the

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sphere  $\text{LiMnPO}_4$  micro-nanostructure is easy to pack closely and tightly to obtain a high tap density [21]. Therefore, controlling morphology and assembly is crucial to gain a high-performance LMP with high power and energy density.

Although  $\text{LiMPO}_4$  is generally synthesized commercially with a solid-state method due to its simplicity and high-crystalline products, the method is time-consuming, energy-consuming and has multiple steps. Meanwhile, particles that are synthesized by solid state reactions are always large with a broad size distribution and poor reproducibility. Hydrothermal synthesis is a more feasible procedure to produce ultra-fine particles than the conventional route of solid-state chemistry because of its narrow particle size distribution and higher crystallization and phase purity. Furthermore, hydrothermal synthesis is also advantageous in its tuned morphology with tailored orientation at the atomic level among various approaches (solid state reaction [22–25], sol-gel [26], carbothermal reduction [27,28], co-precipitation [29,30], microwave heating [10,31]). Rapid and continuous supercritical hydrothermal synthesis (SHS) has potential to be applied for commercial production of high-crystalline nanoparticles with a narrow particle distribution, which is being used to generate various nanoparticles due to its unique properties (rapid reaction rate, high supersaturation, high diffusion rate [33]), such as with such as  $\text{AlOOH}/\text{Al}_2\text{O}_3$  [34],  $\text{CuO}$  [35,36],  $\text{NiO}$ ,  $\text{ZrO}_2$  [35],  $\text{CeO}_2$  [37,38]. Recently, electrode materials in lithium ion batteries were produced via SHS [39,40]. This is because organic compounds are soluble and inorganic compounds are insoluble under critical water due to lower dielectric constants [41]. Supercritical hydro/solvothermal synthesis not only shortens reaction time (less than 2 min) but also enhances the crystallization rate that is affected by the specific characteristic in supercritical water [42]. Additionally, the smallest powders among reported LFP nanoparticles (less than 15 nm) have been synthesized via SHS [43]. The Hanwha Chemical Corporation (Republic of Korea) constructed the first industrial plant for SHS in 2010 [44] that uses  $\text{LiFePO}_4$  with a capacity of 1000 t annually. However, the detailed effects of  $\text{LiMPO}_4/\text{C}$  composites under supercritical conditions have not yet been determined. Additionally, the performances of LFP synthesized by SHS are not yet satisfactory, hence much work is needed to modify the bare LMP.

Compared to SHS, supercritical solvothermal synthesis (SSS) has the extra merits to produce high-performance cathodes: (i) SSS allows for moderate conditions and reductive atmosphere, whereas SHS provides an oxidative atmosphere [45,46]. (ii) SSS can avoid line and filter clogging that results from unreacted and precipitated surface modification agents during the continuous synthesis [47,48]. (iii) SSS can enhance dispersion, especially for higher-concentration and in situ controlled specific crystal orientation and morphology [49,50]. Similar to SHS, SSS also has unique properties and easy commercial-scale production capacity through a rapid and continuous process.

The aim of the paper is first to clarify the mechanism of conventional and supercritical hydro/solvothermal synthesis from the perspective of thermodynamics nucleation analysis. Next, a modification principle of conventional hydro/solvothermal synthesis is presented in detail to create LMP with a high rate-capacity and tap density. For the hydrothermal synthesis, additives are typically used to tailor morphology and size due to altered solubility that affects nucleation and growth from the thermodynamic perspective. Notably, the additives for in situ hydrothermal synthesis of LMP are mainly concentrated, less considering the condition that additives are used post-processing to modify synthesized LMP. Finally, recent progresses in the rapid supercritical hydro/solvothermal synthesis of high-crystalline LMP are summarized. Inspired by the features of modification in hydro/solvothermal synthesis, supercritical hydro/solvothermal synthesis should be investigated in terms of its performance optimization.

## 2. Hydro/solvothermal and supercritical hydro/solvothermal synthesis

### 2.1. Hydro/solvothermal process

#### 2.1.1. Definition

Hydrothermal synthesis, which originated in geology, was first used to describe the formation of rock in the earth's crust under the conditions of high temperature and high pressure, which led to the production of many minerals on the earth's surface that experienced long evolutionary changes.

To be exact, the hydrothermal synthesis method involves the synthesis of inorganic materials through the dissolution-recrystallization process of sparingly soluble or insoluble materials in a special sealed reactor such as an autoclave. This uses an aqueous solution as the reaction system, which creates a relatively high temperature and high pressure reaction environment through heating and pressurizing or autogenous vapor pressure, which belongs to the category of the liquid phase chemical. It is of considerable convenience to regulate the properties of the products by tuning the adjustable variables. Hydrothermal synthesis can prepare ultrafine powders, even nanostructures [51].

#### 2.1.2. Merits

Hydrothermal synthesis is important because

- (1) there are a variety of starting materials and additional substances (e.g., morphology-controlled agents, surfactants, co-solvents);
- (2) it is easy with a simple operation process and mild reaction process, resulting in the lower energy consumption;
- (3) it produces morphology-controlled materials with a small particle size distribution, high crystallization and phase purity;
- (4) it is a molecular reaction in a fluid solution.

As for solvothermal synthesis, the synthesis conditions are almost the same except that an organic solution instead of water is used as the main medium. In addition to the merits of hydrothermal synthesis, solvents also possess additional effects:

- (1) they cling to some lattice planes to inhibit growth and flexibility for controlling morphologies and size;
- (2) they are reducing agents;
- (3) they inhibit aggregation because of their high viscosity;
- (4) they have a chelating ability to trap the cation and increase stability;
- (5) they have a soft template; and
- (6) they decrease anti-site detection [52].

#### 2.1.3. Thermodynamic analysis of crystallization

Hydrothermal synthesis involves the issue of solute precipitation. Generally, it incorporates three processes. First is the formation of a supersaturated solution. Then, a nucleation procedure follows. Next is the growth of the nuclei of crystals. The conversion from fluids to the powder phase is controlled by fluctuations in the supersaturated solution. The Gibbs free energy, the rate of the nucleation and the critical radius are functional to the supersaturation ratio,  $S$  [53,54].

The driving force of the nucleation and growth process is the degree of the supersaturation ( $S$ ) [55], which is defined as follows:

$$S = C/C_S \quad (1)$$

where  $C$  is the solution concentration and  $C_S$  is the saturation concentration.

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