



# General synthesis and morphology control of $\text{LiMnPO}_4$ nanocrystals via microwave-hydrothermal route

Hongmei Ji<sup>a</sup>, Gang Yang<sup>a,b,\*</sup>, Huan Ni<sup>a</sup>, Soumyajit Roy<sup>a</sup>, João Pinto<sup>b</sup>, Xuefan Jiang<sup>a</sup>

<sup>a</sup> Jiangsu Laboratory of Advanced Functional Material, Department of Chemistry, Changshu Institute of Technology, Changshu 215500, China

<sup>b</sup> I3N, University of Aveiro, 3810-193 Aveiro, Portugal

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## ABSTRACT

Olivine structure  $\text{LiMnPO}_4$  has been considered as one of the very promising electrodes for lithium-ion batteries because of their low cost, low toxicity and high voltage plateau compared with  $\text{LiFePO}_4$ . In order to improve the electrochemical performance a key challenge in the field of lithium-ion battery, is to explore and invent suitable synthetic route to control the size and morphology of  $\text{LiMnPO}_4$ . Here a detailed study exploring the novel route of microwave-hydrothermal (MH) synthesis for successfully obtaining  $\text{LiMnPO}_4$  crystals within few minutes is reported and the reaction process discussed in detail. Variation of the synthetic parameters show that a decrease in reactant concentration could lead to  $\text{LiMnPO}_4$  nanoplatelets orientated in the *ac* plane with a very high electrochemical performance. The effect of the starting precursor (like, Mn) concentration as a means to tailor  $\text{LiMnPO}_4$  electrochemical performance is discussed. The effect of alteration of size, morphology, lattice parameters and crystal structure induced by addition of additives like citric acid ( $\text{H}_3\text{cit}$ ) and sodium dodecyl benzene sulfonate (SDBS) is further described and an example of the first reversible discharge of a product treated with  $\text{H}_3\text{cit}$  obtained by MH route as high as 89.0 mAh/g, is shown. The general investigation demonstrates that there is a relationship among microwave irradiation condition, crystal structure, morphology and electrochemical performance that can be exploited for the design of next generation lithium batteries.

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## 1. Introduction

Microwave-hydrothermal (MH) strategy has made great progress and gained wide acceptance in many types of synthesis reaction since its first use by Koarneni and Katsuki to prepare ceramic powders almost ten years ago [1,2]. Compared with the traditional hydrothermal method, MH method increases the kinetics of crystallization by dramatically reducing the reaction time. Additionally it is environmentally benign and offers the possibility for large scale batch reactions. MH method was used to produce various multi-functional nanomaterials such as zeolites, metal oxides, with intriguing morphologies such as nanospheres, nanowires and nanoporous networks [3–5]. Like the traditional hydrothermal reaction, MH method further offers the possibility to control the product yield and nature by means of careful manipulation of concentration, pH, and reaction time. In recent times, the issue of size and morphology control of suitable cathode materials in the field of lithium battery materials is a difficult challenge [6–8].

In the matter of materials design and synthesis for lithium battery, MH method can be of great help to resolve this problem of the field. The present work is a step in that direction.

Since the phospho-olivine  $\text{LiFePO}_4$  was identified as a promising cathode material, for next generation Lithium batteries, by Padhi et al. [9], strong research efforts have focused on the lithium transition metal phosphates  $\text{LiMPO}_4$  ( $M = \text{Mn, Fe, Co, and Ni}$ ) with ordered olivine structure [6,7,9–13]. Among these compounds,  $\text{LiMnPO}_4$  has the lowest cost, low toxicity as well as excellent chemical stability. Compared with the low gravimetric density and low voltage plateau of  $\text{LiFePO}_4$ ,  $\text{LiMnPO}_4$  has a redox potential of 4.1 V vs  $\text{Li}^+/\text{Li}$ , nearly  $\sim 0.65$  V higher than  $\text{LiFePO}_4$ , which is compatible with the systems presently used in next generation lithium ion batteries. Nevertheless, ab initio calculations indicated that  $\text{LiMnPO}_4$  suffers from lower intrinsic electronic conductivity and may lead to electrochemical inactivity compared to that of  $\text{LiFePO}_4$  [14], which limited the products with high capacity.

In order to make  $\text{LiMnPO}_4$  with high electrochemical activity, many works on carbon coating have been reported, like, ball milling the products with carbon black and applying carbon source as raw material for in situ coating carbon [15–18]. More importantly, decreasing the size or controlling the morphology of the  $\text{LiMnPO}_4$  crystallites are of significant importance to improve the electro-

\* Corresponding author at: Jiangsu Laboratory of Advanced Functional Material, Department of Chemistry, Changshu Institute of Technology, Changshu 215500, China. Tel.: +86 512 52251898; fax: +86 512 52251842.

E-mail addresses: [gangyang@ua.pt](mailto:gangyang@ua.pt), [gyang@cslg.edu.cn](mailto:gyang@cslg.edu.cn) (G. Yang).

**Table 1**  
The list of obtained samples under different reaction conditions.

Name of product	Time (min)	Temperature (°C)	Mn <sup>2+</sup> concentration (mol L <sup>-1</sup> )	Organic additive
2MH120.5	5	120	0.10	Free
2MH150.5	5	150	0.10	Free
2MH180.5	5	180	0.10	Free
1MH180.5	5	180	0.05	Free
8MH180.5	5	180	0.4	Free
2MH180.1	1	180	0.10	Free
2MH180.30	30	180	0.10	Free
2MH180.5.SDBS	5	180	0.10	SDBS
2MH180.5.H <sub>3</sub> cit	5	180	0.10	H <sub>3</sub> cit

chemical performance [18,19]. This is so because, the electrode nanocrystals with small size can offer high powder/electrolyte interface, and an increased mass of active substance, thereby enabling enhanced Li<sup>+</sup> diffusion between the cathode material and the electrolyte. Additionally, the smaller size of the nanocrystals can reduce the path lengths for the lithium ions and electron carriers through the lattice, which further accelerates the electrode kinetic to improve the electrochemical properties of samples. Although nanostructure is a pre-requisite for the Li-ion cathode materials with good application potential, suitable morphology is also important for the olivine structure cathode materials. In this matter, it may be mentioned that the LiMnPO<sub>4</sub> platelets with crystalline domains orientated along the *ac* lattice planes have been considered optimal for good electrochemical performance [19]. The reason is simple. The lattice direction of *b* being the most facile pathway for lithium ion transport, (as shown by Morgan et al.) [20] such orientation of crystalline domains facilitate lithium ion transport in LiMnPO<sub>4</sub> nanoplatelets and hence their electrochemical performance. So now the question emerges: how to control the size and morphology of LiMnPO<sub>4</sub> so as to explore the potential application of LiMnPO<sub>4</sub> as the lithium ion cell cathode material?

The synthesis of controlled size and morphology lithium-compounds is very difficult due to their multi-component and complex structural chemistry. Until now, few general methods have been reported to prepare LiMnPO<sub>4</sub> nanocrystals and to control their size and morphology. As mentioned earlier, MH method has the advantages of easy scale-up and tailor-made production of nanomaterials, but its use in synthesis of cathode materials for lithium ion battery has been limited. For instance, Manthiram group has successfully used MH to synthesize olivine LiMPO<sub>4</sub> (M = Fe, Mn, Co) at 230 °C, but the as-synthesized LiMnPO<sub>4</sub> exhibited inferior electrochemical performance with a low discharge capacity of 20–30 mAh/g [16,21,22]. In our recent work, LiFePO<sub>4</sub> obtained by MH method showed nanoparticle morphology (~20 nm) at 200 °C for 5 min and nanosheet at 200 °C for 20 min [23]. LiMnO<sub>2</sub> synthesized at 160 °C for 30 min presented a discharge capacity as high as 200 mAh/g in the microwave assisted system [24].

This study explores in situ MH synthesis of LiMnPO<sub>4</sub> to understand the mechanism of product growth in the microwave field, and the factors controlling the crystallite morphology. In this paper, we focus and discuss how the reaction time, the precursor concentration and the organic additives influence the morphology and the size of the LiMnPO<sub>4</sub> nanomaterials.

## 2. Experimental

### 2.1. Synthesis

The additive-free LiMnPO<sub>4</sub> samples were prepared from MnSO<sub>4</sub>·H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>, LiOH as starting materials in the stoichiometric ratio 1:1:3 by MH method. Sodium dodecyl benzene sulfonate (simply termed as SDBS) and citric acid (H<sub>3</sub>cit) were used to affect the morphology of the products, in the ratio Mn:P:Li:organic additive as 1:1:3:0.25.

It is important to note that the pure phase of the sample would be depending on the synthesis route. An aqueous solution of H<sub>3</sub>PO<sub>4</sub> and MnSO<sub>4</sub> was first stirred for few minutes. LiOH was then added drop-wise to this mixture and the pH of the mixed system was adjusted to 12–13. The detailed synthetic processes are listed in Table 1. The homogeneous reaction mixtures were sealed in closed high-pressure quartz vessels for microwave irradiation. The rotor containing the closed quartz vessel was then placed on turntable for uniform heating in a MARS5 (CEM Corp., Matthews, NC) microwave reaction system, using a frequency of 2.45 GHz. After the MH process, the reactor was cooled to the room temperature in the MARS5 system naturally. The precipitated products were filtered, washed several times with distilled water and ethanol and finally dried at 120 °C for 10 h. The samples could be synthesized with good reproducibility because the temperature, microwave power, and reaction time could be controlled by computer aided automation. The wattage used in our experiments was 300W, and the power could vary from 0 to 100% dependent on both pressure and temperature to a maximum of 300 psi and 250 °C, respectively.

### 2.2. Characterization

The obtained LiMnPO<sub>4</sub> was characterized by X-ray diffraction (XRD) on a Rigaku D/max-2200/PC diffractometer in the 2θ range from 10 to 70° at a count rate of 1 s per step of 0.02°. XRD patterns were refined by Rietveld methods using the GSAS package with the EXPGUI interface. The morphologies were observed with the JEOL6700 field-emission scanning electron microscope.

### 2.3. Electrochemical measurement

Electrochemical measurements were carried out with coin type cell. The products were ball-milled with acetylene black in the weight ratio of 70:30 to form LiMnPO<sub>4</sub>/C composites. The working electrodes were prepared by mixing the obtained LiMnPO<sub>4</sub>/C, acetylene black, and polytetrafluoroethylene (PTFE) in the weight ratio of 80:15:5. Black slurry finally obtained was dried at 100 °C for 24 h in vacuum. Cells were assembled in an argon filled glove box using a Celgard microporous film as a separator, a solution of 1 mol/L LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 ratio in weight) was added as electrolyte. The charge and discharge cycle was studied in the voltage range of 2.2–4.8 V at a current density of 0.05 C.

## 3. Results and discussion

### 3.1. Reaction mechanism

Fig. 1 shows the different processes of preparation of LiMnPO<sub>4</sub>. Adding the reaction precursor with the sequence of LiOH, H<sub>3</sub>PO<sub>4</sub> and MnSO<sub>4</sub>·H<sub>2</sub>O (noted as P-I as shown in Fig. 1) resulted in the precipitation of an impure LiMnPO<sub>4</sub> solid, which was detectable by X-ray diffraction and the impurity phase is marked in Fig. 2a. In

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