



Solvothermal synthesis of nano $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$: Reaction mechanism and electrochemical properties



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HIGHLIGHTS

- Feeding sequences is important in synthesis of LMFP through solvothermal.
- (010) face orientated LiMFP presents high electrochemical performance.
- A synthesis reaction mechanism of feeding sequence is proposed.
- The synthesized $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ presents the discharge capacity of 150 mAh g^{-1} .

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ABSTRACT

Solvothermal approach is used to synthesize $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ (LMFP) nanomaterial for Li-ion batteries (LIBs). Experimental parameters such as feeding sequences, reaction time and reaction temperature are discussed and the obtained LMFP are characterized by XRD, SEM and TEM. To understand the formation of LMFP, a reaction mechanism is proposed. The proposed mechanism indicates that the suitable concentration of M_{Li} ($\text{M} = \text{Fe}, \text{Mn}$) antisite defect can improve the electrochemical performance of the material. The charge–discharge data of obtained LMFP shows that the $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ material synthesized at 180°C for 4 h and then sintering with sucrose at 650°C for 5 h under argon protection has the highest discharge capacity, which is 149.2 mAh g^{-1} at 0.1C rate.

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1. Introduction

Polyoxyanion cathode materials have been widely studied over the past 15 years [1–7], and the electrochemical properties of LiFePO_4 have improved significantly. Due to its high theoretical specific capacity, low cost, good electrochemical performance and chemical stability [8], LiFePO_4 has become a promising anode material.

For the reason of the theoretical energy density of LiMnPO_4 is 697 Wh kg^{-1} , much higher than 578 Wh kg^{-1} of LiFePO_4 [9], LiMnPO_4 become more and more popular recently [10,11]. However, its low electronic conductivity ($<10^{-10} \text{ S cm}^{-1}$) becomes one of the major obstructs of LiMnPO_4 , which even lower than the LiFePO_4 ($1.8 \times 10^{-9} \text{ S cm}^{-1}$) [12,13]. Thereby, in order to make it as a promising candidate for future anode materials, one should focus on improving its conductive ability of both ions and electrons.

Approaches such as nanominiaturization, carbon-coating and doping are used to improve the conductive of LiMnPO_4 . Nanominiaturization has the advantage of shortening the lithium ion migration distance. Other than solid-state reaction [14], more synthesis methods, such as sol–gel method [15], hydrothermal [16] and solvothermal methods [16,17] have been applied to nanominiaturize LiMnPO_4 . Carbon-coating and cations (Fe, Co, Mg, Ti, Zr,

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V, Fe, Gd and Zn) doping of LiMnPO_4 can improve its electrochemical performance [18]. It is reported that the carbon-coated $\text{LiMn}_{0.71}\text{Fe}_{0.29}\text{PO}_4$ can provide better electronic conductivity and has better electrochemical performance [19].

In this study, we report facile solvothermal processes that use two different feeding sequences to synthesis $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$. Reaction time and temperature are discussed as well. To investigate the reaction mechanism, we select the optimal solution feeding sequences (M + P + L) under the solvothermal condition of 180 °C for 12 h, and the reaction is monitored by apparent pH value and ICP analysis. To characterize the phase and morphology, the XRD, SEM and TEM are employed. The significant shift of infrared absorption can be used to detect the antisite defects. Finally, the synthesis condition is optimized to be at 180 °C with 4 h.

2. Experimental

2.1. Synthesis

All chemicals (AR grade) are purchased from Xilong Chemical Co., Ltd. The syntheses of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ by two different feeding sequences are prepared as follows: the first feeding sequence is $\text{S1} = \text{L} + \text{P} + \text{M}$, by which the ethylene glycol solution of transition metal salts ($\text{MnCl}_2 \cdot \text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is slowly dripped into the ethylene glycol, $\text{LiOH} \cdot \text{H}_2\text{O}$ and H_3PO_4 mixture solution; The other feeding sequence is $\text{S2} = \text{M} + \text{P} + \text{L}$, by which the ethylene glycol solution of $\text{LiOH} \cdot \text{H}_2\text{O}$ is slowly dripped into the ethylene glycol solution with mixture of H_3PO_4 and transition metal salts. The molar ratio of $\text{M}^{2+}:\text{PO}_4^{3-}:\text{Li}^+$ is set at 1:1:2.7, and the concentration of transition metal ions is 0.2 mol L^{-1} . The mixture is stirred for 10 min, and then poured into a 50 mL Teflon vessel, the Teflon vessel then sealed in a stainless-steel autoclave. Then it is put into a furnace, and then heated at 100 °C–180 °C for different reaction time from 1 h to 24 h, and the temperatures in the autoclave are measured. After the solvothermal reaction finish, the autoclave is taken out from the furnace and then cooled down at room temperature. Apparent pH is recorded through the method of diluting supernatant 10 times with distilled water. Samples are also centrifuged, and then dried at 80 °C for 12 h. Finally, carbon coated $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ is obtained by sintering of the mixture of the solvothermal product with 5 wt% carbon by sucrose at 650 °C for 5 h under argon atmosphere.

Previous reports on the solvothermal synthesis always regarded the heating temperature as reactor temperature [20–30]. However, we find that there is a significant difference between the heater temperature and the reactor temperature. Therefore, we calibrate the temperature. The details are in [Supplementary data](#).

2.2. Characterization

The samples are characterized by powder XRD (Bruker D8 Advance X-ray diffractometer in a Bragg–Brentano configuration), SEM (JSM-5600LV, JEOL, Japan), FTIR (PerkinElmer) and TEM (FEI, Tecnai G² 20). The pH is measured by microprocessor pH meter (pHS-25, Shanghai).

2.3. Electrochemical measurements

The electrochemical measurements are carried out by using a 2032-type coin cell. The electrolyte is 1 M LiPF_6 dissolved in volume ratio of 1:1:1 with ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate. The electrode is prepared in mass ratio of 8:1:1 with cathode composite/acetylene black/poly (vinylidene fluoride). Galvanostatic charging–discharging tests are carried out on Land

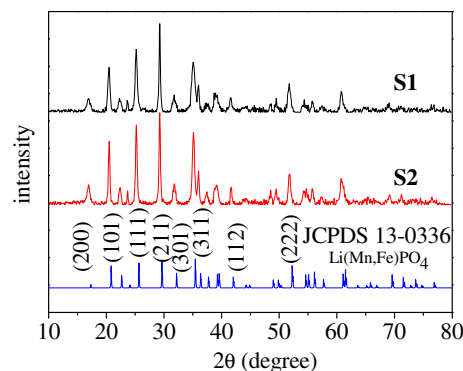


Fig. 1. X-ray diffraction (XRD) patterns of $\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$.

CT2001A cycler (Wuhan Kingnuo Electronic Co.) in a voltage range 2.5–4.5 V.

3. Results and discussion

3.1. Sample characterization

The influence of feeding sequences for LiFePO_4 synthesis has already illustrated in our previous report [31]. In this study, the synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ by two feeding sequences ($\text{S1} = \text{L} + \text{P} + \text{M}$, $\text{S2} = \text{M} + \text{P} + \text{L}$) is investigated by solvothermal process at 180 °C for 12 h. In order to study the crystal structure of the product, powder X-ray diffraction (XRD) test is carried out. As shown in Fig. 1, all of the XRD patterns can be indexed as the orthorhombic $\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$ (space group Pnmb, JCPDS Card No: 13-0336). However, as shown in Table 1, the composition of the product shows difference in Li proportion.

To confirm the horizontal face of two LMFP samples with different feeding sequences, high-resolution transmission electron microscopy (HRTEM) is applied for analysis. Figs. 2 and 3 are SEM and TEM images of samples S1 and S2.

Fig. 3 shows that the morphology of $\text{S1} = \text{L} + \text{P} + \text{M}$ is nanoplate and the (100) face which is perpendicular to (010) face is the exposed surface, nevertheless, the morphology of $\text{S2} = \text{M} + \text{P} + \text{L}$ is nanorod and the exposed surface is (010) face which is perpendicular to (100) face and (001) face. The result obtained shows that the product of S2 feeding sequence expose a large (010) face and the [010] direction is the thinnest direction of the particle.

The differences of morphology and crystal orientation are result of the effect of precursor and nuclei. The precursor of S2 is $\text{M}_3(\text{PO}_4)_2$ ($\text{M} = \text{Mn}, \text{Fe}$) and the precursor of S1 is Li_3PO_4 . From our result we deduce that the constitution of precursor would influence synthetic process and will discuss that in detail in our further work.

Electrochemical performance tests are carried out for the $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ samples of S1 and S2. Fig. 4 is the charge/discharge data of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ of two feeding sequence. The data shows that the sample S2 delivers a capacity of 130.6 mAh g^{-1} at the current density of 0.1C, which is much higher than 81.2 mAh g^{-1} of S1. From the data, we find out that the S2 has a better performance in both polarization and discharge capability. $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ particles in [010] direction present the most facile pathway for lithium

Table 1
Cell parameters of different feeding sequences S1 and S2.

Feeding sequences	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
S1 = L + P + M	10.4219	6.0806	4.7519	301.14
S2 = M + P + L	10.4194	6.0827	4.7469	300.85

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