



Short communication

Enhanced electrochemical properties of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ composites synthesized from $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites

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HIGHLIGHTS

- Pre-synthesized $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites are used to synthesize $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$.
- Well-ordered $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0.85, 0.75, 0.65$) nanostructures form.
- $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ composites have enhanced electrochemical properties.
- $\text{LiFe}_{0.25}\text{Mn}_{0.75}\text{PO}_4$ sample exhibits the best electrochemical performances.

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ABSTRACT

The high discharge potential of LiMnPO_4 , 4.1 V vs. Li/Li^+ , and its theoretical capacity of 170 mAh g^{-1} make it a promising candidate as a cathode material in lithium-ion batteries. But extremely low electronics conductivity, slow lithium diffusion kinetics, and the Jahn-Teller effect of Mn^{3+} limit the electrochemical performances of LiMnPO_4 . In this work, the pre-synthesized and defined $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites are used as one of the raw materials to synthesize $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x = 0.85, 0.75, 0.65$) composites via solid-state reactions. The synthesized $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples show well-crystallized structures and have enhanced electrochemical properties. There exist two plateaus around 3.5 and 4.1 V on both of their charge and discharge curves. Among the samples, the $\text{Fe}_{0.25}\text{Mn}_{0.75}\text{PO}_4$ one exhibits the longest high-voltage charge/discharge plateau at 4.10 V/4.05 V, and has an average discharge voltage of $\sim 3.78 \text{ V}$ vs. Li/Li^+ and a discharge capacity of $\sim 130 \text{ mAh g}^{-1}$ at 0.05 C rate. For the $\text{Fe}_{0.25}\text{Mn}_{0.75}\text{PO}_4$ sample, the noticeable improvement of its electrochemical performances is mainly attributed to iron substitution, the appropriate Mn/Fe ratio, and the well-ordered crystal structure forming by using $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites as one of the raw materials.

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1. Introduction

Olivine structural lithium transition-metal phosphates LiMPO_4 ($M = \text{Fe, Mn, Co, and Ni}$) were found to be ones of the most promising candidates as the cathode materials for large-scale lithium-ion batteries due to their large theoretical capacities and excellent thermal stability [1–4]. Among them, LiFePO_4 has the inherent characteristics of low-cost and environmental friendliness, so it has been extensively studied and its electrochemical properties have been greatly improved by cation substitution/doping and surface modification with conductive materials coating to enhance its low conductivity [5–11].

LiMnPO_4 is of particular interest to battery industry because of its higher theoretical energy density than LiFePO_4 . It has higher discharge potential (4.1 V vs. Li/Li^+) than LiFePO_4 (3.4 V vs. Li/Li^+), and its theoretical capacity of 170 mAh g^{-1} is almost the same as LiFePO_4 . However, the even lower electronic conductivity and slow lithium diffusion limit LiMnPO_4 electrochemical performances [2,3]. Another unavoidable problem is the electrochemical stability of LiMnPO_4 is badly affected by the Jahn-Teller effect of Mn^{3+} . During cycling, the shrinkage of about 8.9% occurs during LiMnPO_4 delithiated to form MnPO_4 , but only 6.8% during LiFePO_4 delithiated to form FePO_4 . Additionally, the cell volume of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ increases with increasing Mn^{2+} content x , while the volume is almost constant in $\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4$ at different Mn^{3+} content x [12–15]. Therefore, appropriate iron substitution is beneficial to keeping stable volume of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ during the lithium extraction/insertion.

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Inspired by the success of LiFePO_4 , researchers have tried similar methods to improve the electrochemical properties of LiMnPO_4 [16–21]. It has been reported that an improvement in kinetics was realized as partial Mn ions were substituted by Fe to form $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, such as $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ [13,20]. The Fe substitution in Mn-sites probably has two main benefits: one is enhancing the transport properties of materials; the other is decreasing the Jahn–Teller effect of Mn^{3+} .

Some researchers synthesized monoclinic phase $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanoparticles at first, and then lithiated them to form LiFePO_4/C composites, which show improved high-rate charge/discharge capability and long-term cyclability [21,22]. Wang et al. synthesized LiFePO_4/C composite using a core–shell structural precursor $\text{FePO}_4/\text{polyaniline}$, and suggested that the LiFePO_4/C nanoparticles form by an *in situ* polymerization restriction mechanism [23]. Additionally, LiMnPO_4 has ever been synthesized from a $\text{MnPO}_4 \cdot 2\text{H}_2\text{O}$ precursor. It was reported that the $\text{MnPO}_4 \cdot 2\text{H}_2\text{O}$ nanoparticles facily react with lithium source and form LiMnPO_4 via solid-state reactions at 550°C [24,25], and the synthesized LiMnPO_4 shows improved electrochemical properties.

In this work, iron substitution is utilized to improve the electrochemical properties of LiMnPO_4 . To synthesize a well-ordered $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ crystal structure, the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites are pre-synthesized and defined, and then are used as one of the raw materials to form a precursor by ball milling with Li-, Mn-, PO_4^- , and carbon-containing chemicals. The precursors finally form $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x = 0.85, 0.75, 0.65$) composites via solid-state reactions at 550°C . The synthesized $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ nanoparticles exhibit well-ordered crystal structures, and show obvious enhanced electrochemical properties.

2. Experimental

$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ were pre-synthesized by a spontaneous precipitation method. Equimolar aqueous solution of H_3PO_4 and FeCl_2 with a concentration of 0.1 M was added into a continuous stirred beaker in water bath at 60°C . After 10 min, excess H_2O_2 solution (30 wt.%), the molar ratio of $\text{H}_2\text{O}_2/\text{FeCl}_2 = 1.1/2$, was fed into the beaker. The pH value of the mixed solution was controlled between 4.0 and 5.0 by adding ammonia. At the initial stage of the reaction, there appeared precipitate in the beaker. After stirring 15 min, the precipitate was filtered and washed with de-ionized water until its pH value became neutral. The obtained precipitate was dried at 120°C for 12 h.

$\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ ($x = 0.85, 0.75, 0.65$) composites were synthesized by solid-state reactions after a two-stage ball milling process. Stoichiometric amounts of the above synthesized $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, Li_2CO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and sucrose (25 wt.% of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$) were dissolved in de-ionized water. This solution was wet ball-milled for 10 h at room temperature and dried in a vacuum oven at 80°C for 12 h. The dried precursor was heated at 300°C for 5 h under argon atmosphere for its main decomposition. Then the decomposed precursor was ball-milled for 10 h at room temperature. Finally the precursor was calcined at 550°C for 10 h in an Ar atmosphere until the expected $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ composites formed. As a contrast, LiMnPO_4/C (i.e., $x = 1.0$) composite was also synthesized using the same synthesis condition only without $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in the precursor.

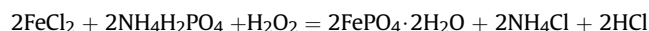
To study the thermal stability of the precursor and optimize the synthesis condition, thermogravimetric and differential scanning calorimetry (TG-DSC) analyses were performed using a simultaneous thermal analyzer (STA 409 PC/PG, NETZSCH). About 10 mg sample was heated from room temperature to appropriate temperatures in N_2 at a heating rate of $10^\circ\text{C min}^{-1}$.

The crystalline structures of the samples were analyzed by a powder X-ray diffractometer (XRD, D/max 2500 V/PC, Rigaku) using $\text{Cu K}\alpha$ radiation. Lattice parameters were calculated from the refined XRD patterns. The crystallite size was obtained from XRD results and calculated by Scherrer formula, $d = k \cdot \lambda / (\beta \cdot \cos\theta)$, where d (nm) is the mean crystallite size, k ($= 0.89$) is the shape factor of particles, λ ($= 0.154056$ nm) is the X-ray wavelength, β (radian) is the half-width of the main diffraction peak, and θ (radian) is the Bragg angle of main diffraction peak. Morphology and microstructure of the samples were investigated using a scanning electron microscope (SEM, XL30, Philips) and a field-emission high-resolution transmission electron microscope (HRTEM, Tecnai G² F20, FEI) with an energy-dispersive X-ray spectroscopy (EDX). An infrared carbon and sulfur analyzer (CS-901B, Haotianhui) was used to analyze the carbon content of the samples.

The electrochemical measurements were performed using 2032 coin-type cells with lithium metal as the anode. For cathode fabrication, at first a mixture was made by well mixing the synthesized $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ composite, conductive carbon black (Super P), and N-methyl-2-pyrrolidinone (NMP) in a weight ratio of 80/10/10. Then the mixture was spread onto aluminum foil and formed a uniform thin layer with a thickness of $150\ \mu\text{m}$. It was dried at 80°C in a vacuum oven for 12 h to remove NMP. The coated aluminum foil was dried at 120°C overnight under vacuum and punched into 13 mm diameter disks, which served as the cathode. 1 M LiPF_6 in ethylene carbonate and dimethyl carbonate (50/50 in volume) was used as the electrolyte. All cells were assembled in an Ar-filled glove box. The coin cells were placed on a battery testing system (CT2001A, LAND) with current density at 0.05 C ($1\ \text{C} = 170\ \text{mA g}^{-1}$) in a voltage window between 2.5 and 4.5 V vs. Li/Li^+ at room temperature.

3. Results and discussion

At first, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ nanocrystallites were synthesized according to the reaction



The precipitation was washed, dried, and used as one of the raw materials to synthesize $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4/\text{C}$ composites.

Fig. 1 shows the XRD pattern of the dried precipitation. The pattern matches well with the monoclinic iron phosphate hydrate,

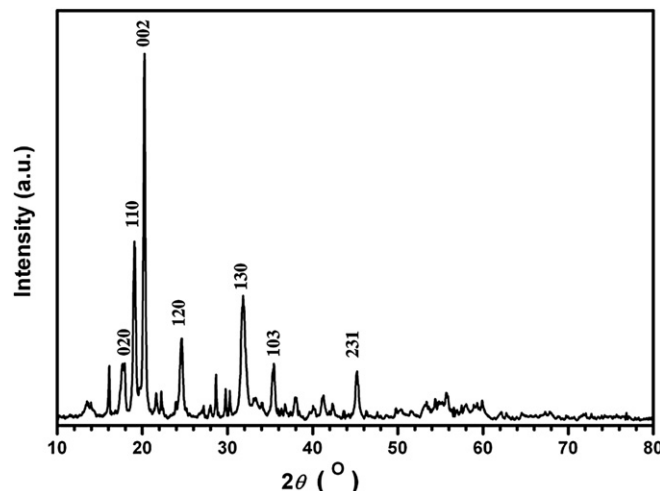


Fig. 1. XRD pattern of the synthesized $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ sample.

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