Synthesis and Electrochemical Properties of Fe-Doped LiMnPO₄ Nanocomposite Prepared by a Hydrothermal Process in a High-Pressure Reactor

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LiMn₁₋ₓFeₓPO₄ powders with varied Fe concentrations (x=0, 0.2, 0.3, 0.4) were prepared in a high-pressure reactor by a hydrothermal process. The effect of the Fe dopant concentration on the crystal structure, morphology, surface area and electrochemical properties were studied. LiMn₁₋₄Fe₂PO₄ with a higher Fe concentration presented better cyclic performance, and the capacity retention of a LiMn₀.₆₆Fe₀.₄₀PO₄ electrode after 20 cycles was 97.2% at 25°C with an initial capacity of 145 mAh/g at a 0.1C rate. LiMn₀.₆₆Fe₀.₄₀PO₄ also delivered discharge capacities of 151 mAh/g and 109.3 mAh/g at rates of 0.05C and 5C, respectively. Because the total charge/discharge capacity of LiMn₁₋₄FeₓPO₄ was enhanced as the Fe concentration increased while the average discharge voltage was reduced, a high specific energy value of 513 Wh/kg was achieved in the LiMn₀.₇₀Fe₀.₃₀PO₄ material.

Keywords: Hydrothermal process; LiMn₁₋₄FeₓPO₄; Lithium-ion battery; Cation doping

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in portable commercial electronic devices such as notebooks and mobile phones. Recently, more research has aimed to develop high-performance LIBs for use in electric vehicles (EVs), hybrid electric vehicles (HEVs) and energy storage systems [1-3]. Developing high-capacity cathode materials for use in commercial LIBs has gained extensive research attention worldwide. The phospho-olivines LiMPO₄ (where M stands for Fe, Mn, Co, Ni) have shown great potential as cathode materials for LIBs due to their high specific
capacity (~170 mAh/g), suitable operating voltage and high stability during lithium extraction/reinsertion [4-8]. Of these LiMPO₄ materials, LiMnPO₄ intrinsically offers a lithium ion intercalation potential of 4.1 V versus Li/Li⁺ favoured by most of liquid electrolytes used currently as well as a remarkable high theoretical specific energy (~684Wh kg⁻¹ = 171 mAh g⁻¹ x 4.0 V) [9-11].

However, low ionic and electronic conductivity of LiMnPO₄ limit its application in high-performance LIBs. In order to improve the electrochemical performance of LiMnPO₄, various solutions have been explored to solve the problems. Enhancing the electronic conductivity among the LiMnPO₄ particles [12], controlling the LiMnPO₄ particle morphology and particle size [13-15] were reported to improve the diffusion of Li⁺ in LiMnPO₄ cathode. Doping LiMnPO₄ with transition metals, such as Fe²⁺, Mg²⁺, Ni²⁺, V²⁺ and Co²⁺, have resulted in enhanced electrochemical performance in LiMnPO₄ materials [16-21]. The doping elements induced changes in the lattice structure and deviations in the Li-O band lengths in doped LiMnPO₄ [22-24]. Among the doping transition metal ions, ferric ion has attracted much attention because of the high storage capacity of Mn-Fe solid solutions [25]. An intermediate Fe doping concentration in LiMnPO₄ may win some efficiency expected properties by substituting some the Mn ions by Fe ions. Such investigations have been performed in the recent past. Using a sol-gel method, M. Mastragostino et al. synthesized carbon-coated LiMn₁₋ₓFeₓPO₄ (x=0.2, 0.3), which delivered a capacity of 125 mAh/g at an environmental temperature of 50°C and 95 mAh/g at 30°C [26]. Hong et al. synthesized a series of nanoporous LiFeₓMn₁₋ₓPO₄ compounds (with x = 0, 0.05, 0.1, 0.15, and 0.2) using a solid-state reaction and they found that the electrochemical performance of LiFeₓMn₁₋ₓPO₄ rises continuously with increasing iron content [27]. Muraliganth et al. reported the solid-solution between LiMnPO₄ and LiFePO₄ by a high energy ball milling procedure with 20% carbon in the final product. The discharge capacity increases significantly from 91 mAh/g in LiMnPO₄ to 142 mAh/g in LiMn₀.₇₅Fe₀.₂₅PO₄, and 155 mAh/g for LiMn₀.₅Fe₀.₅PO₄ at 0.05 C [28]. Hu et al. synthesized LiMnPO₄ via co-substitution with Fe and Mg by a solid-state reaction route. The cation substitution shrunk the crystal lattice because of the smaller ionic radii of Mg²⁺ and Fe²⁺. The Fe-, Mg-doped LiMnPO₄ exhibited improved capacity, cycle performance and rate capability [29]. According to previous publications, LiMnPO₄ doped with minor or more dopant had improved electrochemical properties but was still lacking in high-performance LIBs. In this work, we prepared LiMnPO₄ and LiMn₁₋ₓFeₓPO₄ (x=0.2, 0.3, 0.4) in a high-pressure reactor at 180°C using a hydrothermal process. Compared with synthesized LiMnPO₄, synthesized LiMn₁₋ₓFeₓPO₄ possesses considerably enhanced electrochemical performance. LiMn₀.₇Fe₀.₃PO₄ delivered a specific capacity of 143.7 mAh/g at a 0.05C rate and 105.1 mAh/g at a 5C rate.

2. EXPERIMENTAL

2.1. Synthesis

LiMnPO₄ was synthesized in the following steps. MnCl₂ (0.375 mol), H₃PO₄ (0.375 mol) and ascorbic acid (12.5 g) were mixed and stirred. An aqueous solution containing LiOH (26.5 g) was slowly added into the mixed solution with stirring. The solution was further stirred for 2 hours and was
then transferred into a high-pressure reactor placed in an oven at 180°C for 18 hours. The resulting precipitate was collected by centrifugal filtration and washed several times with deionized water before being dried at 60°C for 24 hours. LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0.2, 0.3, 0.4) was prepared by the same procedure as LiMnPO$_4$. MnCl$_2$ and FeSO$_4$·7H$_2$O totalled 0.375 mol with a varied Fe/Mn ratio. The LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4)/C composite material was synthesized by mixing LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4) with glucose at a mass ratio of 4:1. The mixture was ball-milled for 6 hours, transferred into a tube furnace and sintered at 700°C for 5 hours under an Ar atmosphere.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on Bruker D8 Advance with Cu Kα radiation (λ=1.5418 Å). Nitrogen adsorption–desorption isotherms were obtained on a Micromeritics ASAP 2020M instrument. The specific surface areas were calculated by employing the Brunauer-Emmett-Teller (BET) equation. Morphological details were examined using a JEOL JSM-6700F scanning electron microscope (SEM).

2.3. Electrochemical tests

For the electrochemical test, 80 wt% of active material, 10 wt% of acetylene black (AB) and 10 wt% of polyvinylidene fluoride (PVDF) were first mixed evenly with N-methyl-2-pyrrolidinone (NMP). The obtained blended slurry was then cast onto an aluminium foil current collector. After being dried thoroughly under vacuum at 120°C for 12 hours, the electrode sheet was tailored into disks of Φ8 mm and assembled in CR2032 coin-type cells with lithium metal as the counter electrode in an Ar-filled glove box. The loading mass of the active material in the electrode was 1-2 mg (area of 0.785 cm$^2$). A mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) containing 1 M LiPF$_6$ was used as the electrolyte. A Celgard 2400 microporous membrane served as the separator. Galvanostatic charge-discharge measurements were carried out in a voltage window of 2.5–4.3 V (vs. Li/Li$^+$) using a battery test system (BT2000, Arbin, USA).

3. RESULTS AND DISCUSSION

The synthesized LiMnPO$_4$ and Fe-doped LiMnPO$_4$ samples were tested by X-ray fluorescence. The element ratio in the synthesized samples is consistent with the proportion of elements in the feed material, meaning that we synthesized LiMnPO$_4$ and LiMn$_{0.6}$Fe$_{0.4}$PO$_4$, as well as LiMn$_{0.7}$Fe$_{0.3}$PO$_4$ and LiMn$_{0.6}$Fe$_{0.4}$PO$_4$. The crystal structure of LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4) was characterized by high-resolution powder XRD. Fig. 1a shows the XRD patterns of the samples of LiMn$_{1-x}$Fe$_x$PO$_4$ powders. All the diffraction patterns of LiMn$_{1-x}$Fe$_x$PO$_4$ are similar to the diffraction of LiMnPO$_4$, which is well matched to the orthorhombic LiMnPO$_4$ phase with a Pnma space group (JCPDS card no. 33-0803). Fig. 1b is a detail of the enlarged scale of Fig. 1a illustrating the slight movement of the
featured diffraction peak of LiMn$_{1-x}$Fe$_x$PO$_4$ in comparison with LiMnPO$_4$. The reason for this shift is that the Mn and Fe atoms have different atomic radii, substituting an Mn atom with an Fe atom may change the lattice parameters of LiMnPO$_4$. Therefore, LiMn$_{1-x}$Fe$_x$PO$_4$ with varying amounts of Fe will exhibit different lattice parameters.

![Figure 1. XRD patterns of LiMn$_{1-x}$Fe$_x$PO$_4$.](image)

Table 1 shows the lattice parameters of LiMn$_{1-x}$Fe$_x$PO$_4$ refined from Jade 5.0. LiMn$_{1-x}$Fe$_x$PO$_4$ has smaller lattice constants and a smaller unit cell volume than pure LiMnPO$_4$, and the unit cell volume obviously decreases with the increasing Fe dopant concentration in LiMn$_{1-x}$Fe$_x$PO$_4$. Because the ionic radius of Fe$^{2+}$ is smaller than the ionic radius of Mn$^{2+}$, the partial replacement of Mn$^{2+}$ with Fe$^{2+}$ in LiMnPO$_4$ to form LiMn$_{1-x}$Fe$_x$PO$_4$ decreased the atomic distance and contracted the lattice [30]. Also, the substitution of partial Mn by Fe could restrain the Jahn-Tellar distortion in LiMnPO$_4$ and then reduce the electron hopping energy barrier and the distortion of the Li$^+$ transport channels [31].

### Table 1. Refined lattice parameters of LiMn$_{1-x}$Fe$_x$PO$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$<em>{0.60}$Fe$</em>{0.40}$PO$_4$</td>
<td>10.42935</td>
<td>6.05813</td>
<td>4.74165</td>
<td>299.59</td>
</tr>
<tr>
<td>LiMn$<em>{0.70}$Fe$</em>{0.30}$PO$_4$</td>
<td>10.42983</td>
<td>6.05734</td>
<td>4.74245</td>
<td>299.61</td>
</tr>
<tr>
<td>LiMn$<em>{0.80}$Fe$</em>{0.20}$PO$_4$</td>
<td>10.42982</td>
<td>6.05730</td>
<td>4.74253</td>
<td>299.62</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>10.45139</td>
<td>6.10128</td>
<td>4.73492</td>
<td>301.93</td>
</tr>
</tbody>
</table>
The SEM images of LiMn$_{1-x}$Fe$_x$PO$_4$ are shown in Fig. 2. All the samples exhibit a needle-like morphology. However, LiMnPO$_4$ (Fig. 2a) has a larger particle size than the other LiMn$_{1-x}$Fe$_x$PO$_4$ samples. From Fig. 2b to Fig. 2d, the Fe dopant concentration affected the dispersion of the LiMn$_{1-x}$Fe$_x$PO$_4$ samples, and LiMn$_{0.80}$Fe$_{0.20}$PO$_4$ (Fig. 2b) exhibited favourable dispersion with an unobvious reunion phenomenon.

Figure 2. SEM images of LiMn$_{1-x}$Fe$_x$PO$_4$: a. (x=0), b. (x=0.2), c. (x=0.3), d. (x=0.4).

Figure 3. Specific surface area of LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4).

The specific surface area of LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4) was calculated by employing the BET equation. As shown in Fig. 3, LiMnPO$_4$ has the largest specific surface area (12.42 m$^2$/g), and
Fe-doped LiMnPO₄ has a much smaller specific surface area. As the Fe dopant concentration increased in LiMn₁₋ₓFeₓPO₄, the specific surface area decreased from 12.42 m²/g (LiMn₀.8Fe₀.2PO₄) to 9.74 m²/g (LiMn₀.7Fe₀.3PO₄). LiMn₀.6Fe₀.4PO₄ had the highest Fe dopant concentration but the smallest specific surface area of 9.32 m²/g.

Fig. 4 shows the first charge/discharge profile of the LiMn₁₋ₓFeₓPO₄ (x=0, 0.2, 0.3, 0.4) samples at a 0.1C rate with a cut-off voltage between 2.5 V and 4.4 V. The plateau at approximately 4.1 V corresponding to the Mn²⁺/Mn³⁺ redox couple is less clearly observed in the first discharge curve of pure LiMnPO₄. This plateau disappears due to polarization resistance resulting from the poor electronic conductivity and a slow Li ion migration rate in the LiMnPO₄ material. Then, the LiMnPO₄ material shows an initial discharge capacity of 82 mAh/g at the first 0.1C rate. Two distinct plateaus are present in the LiMn₁₋ₓFeₓPO₄ (x=0.2, 0.3, 0.4) sample, which is consistent with previous reports [24, 26]. The first plateau region at approximately 3.5 V corresponds to the Fe²⁺/Fe³⁺ redox couple, and the second plateau at approximately 4.1 V corresponds to the Mn²⁺/Mn³⁺ redox couple. The lengths of the Fe and Mn plateaus are roughly proportional to the Fe/Mn ratio in the nominal composition of the active material. The Mn plateau exhibited a higher discharge voltage and a lower discharge capacity, whereas the Fe plateau exhibited a lower discharge and higher discharge capacity. As a result, a higher Fe concentration in the LiMn₁₋ₓFeₓPO₄ material results in a lower discharge capacity at a high discharge voltage (~4.1 V) and a higher discharge capacity at a low discharge voltage (~3.5 V). The first discharge capacities of LiMn₀.₈₀Fe₀.₂₀PO₄, LiMn₀.₇₀Fe₀.₃₀PO₄ and LiMn₀.₆₀Fe₀.₄₀PO₄ at a 0.1C rate were 132 mAh/g, 138 mAh/g and 145 mAh/g, respectively. In addition, the integrated areas of the discharge curves correspond to the specific energy of the LiMn₁₋ₓFeₓPO₄ (x=0, 0.2, 0.3, 0.4) materials. The total charge/discharge capacity of LiMn₁₋ₓFeₓPO₄ was enhanced as the Fe concentration increased, but the average discharge voltage was reduced; therefore, LiMn₀.₇₀Fe₀.₃₀PO₄ exhibited the largest specific energy value of 513 Wh/kg.

**Figure 4.** The initial charge/discharge curve of LiMn₁₋ₓFeₓPO₄ (x=0, 0.2, 0.3, 0.4) at a 0.1C rate. Solid symbols represent the discharge curve, and hollow symbols represent the charge curve.
Fig. 5 shows the cyclic performance of LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4). After 20 cycles, the capacity of LiMnPPO$_4$ decreased from 82 mAh/g to 71 mAh/g with an 86.5% capacity retention of the initial capacity, LiMn$_{0.80}$Fe$_{0.20}$PO$_4$ decreased from 132 mAh/g to 123 mAh/g with a 93.2% capacity retention of the initial capacity, LiMn$_{0.70}$Fe$_{0.30}$PO$_4$ decreased from 138 mAh/g to 128 mAh/g with a 92.7% capacity retention of the initial capacity, LiMn$_{0.60}$Fe$_{0.40}$PO$_4$ decreased from 145 mAh/g to 141 mAh/g with a 97.2% capacity retention of the initial capacity. LiMn$_{1-x}$Fe$_x$PO$_4$ with a higher Fe concentration presented better cyclic performance. The improved cycle ability of LiMn$_{1-x}$Fe$_x$PO$_4$ is probably attributed to the suppressed Mn dissolution in the electrode due to the Fe doping. During the Li extraction process, delithiated phases created from the Fe$^{2+}$/Fe$^{3+}$ redox favour the stability of the subsequent Mn$^{2+}$/Mn$^{3+}$ redox couples[32].

![Figure 5](image-url)  
**Figure 5.** Cycle performances of an LIB based on LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0) with varied Fe dopant concentrations (x=0, 0.2, 0.3, 0.4) as the anode at a rate of 0.1C.

Fig. 6 shows the galvanostatic discharge profile of the LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4) electrodes at various current rates in the voltage region of 2.7 and 4.4 V. As plotted in Fig. 6, the specific capacities of all the LiMn$_{1-x}$Fe$_x$PO$_4$ (x=0, 0.2, 0.3, 0.4) materials faded as the discharge current increased. The LiMnPPO$_4$ sample (Fig. 6a) has a discharge plateau-voltage of approximately 4.1 V, corresponding to the Mn$^{2+}$/Mn$^{3+}$ redox couple at a 0.05C rate. However, the discharge plateau-voltage was not stable and disappeared at high C rate, indicating that LiMnPPO$_4$ as a cathode material suffered serious polarization under a high C rate and that the increased polarization resistance resulted in a rapidly decreased voltage and small discharge capacity. The Fe-doped LiMnPPO$_4$ samples (Fig. 6b-d) have two distinct plateaus corresponding to the Fe$^{2+}$/Fe$^{3+}$ redox couple (3.5 V) and Mn$^{2+}$/Mn$^{3+}$ redox couple (4.1 V), and the discharge plateau-voltage decreased with the increased discharge rates. A high
Fe concentration in LiMn$_{1-x}$Fe$_x$PO$_4$ has a positive influence on the stability of the discharge plateau, whereas an increased discharge current has a negative effect on the stability of the discharge plateau. From Fig. 6, the Fe-doped LiMnPO$_4$ sample shows a considerable retention of the capacity at different C rates. The initial discharge capacity of pure LiMnPO$_4$ is 93.9 mAh/g at a 0.05C rate, and the discharge capacities of LiMn$_{0.80}$Fe$_{0.20}$PO$_4$, LiMn$_{0.70}$Fe$_{0.30}$PO$_4$, and LiMn$_{0.60}$Fe$_{0.40}$PO$_4$ are 137.7 mAh/g at 0.05C, 143.7 mAh/g at 0.05C and 151.8 mAh/g at 0.05C, respectively. The existence of the Fe dopant plays a positive role in the high rate performance of LiMn$_{1-x}$Fe$_x$PO$_4$. Even at a 5C rate, the discharge capacity of pure LiMnPO$_4$ is 36.5 mAh/g, whereas the discharge capacities of LiMn$_{0.80}$Fe$_{0.20}$PO$_4$, LiMn$_{0.70}$Fe$_{0.30}$PO$_4$, and LiMn$_{0.60}$Fe$_{0.40}$PO$_4$ are 97.9 mAh/g, 105.1 mAh/g and 109.3 mAh/g, respectively. A higher Fe doping concentration in LiMn$_{1-x}$Fe$_x$PO$_4$ means that more Fe atoms replaced Mn atoms in LiMnPO$_4$ and the substitution of Fe in a LiMnPO$_4$ nanoplate results in a decreased volumetric change between LiMnPO4 and delithiated MnPO4 during charge/discharge process, increased mobility and enhanced electrochemical performance of the LiMn$_{1-x}$Fe$_x$PO$_4$ electrode at high C rates[32,33].

![Figure 6](image_url)

**Figure 6.** Discharge curve of LiMn$_{1-x}$Fe$_x$PO$_4$ with varied Fe concentrations (x=0, 0.2, 0.3, 0.4). The discharge current varied from 0.05C to 5C.

4. CONCLUSIONS

LiMn$_{1-x}$Fe$_x$PO$_4$ powders with varied Fe concentrations (x=0, 0.2, 0.3, 0.4) were successfully prepared in a high-pressure reactor by a hydrothermal process. LiMn$_{1-x}$Fe$_x$PO$_4$ with a higher Fe
concentration presented better cyclic performance, and the capacity retention of the LiMn$_{0.60}$Fe$_{0.40}$PO$_4$ electrode after 20 cycles was 97.2% at 25°C with an initial capacity of 145 mAh/g at a 0.1C rate. Additionally, LiMn$_{0.60}$Fe$_{0.40}$PO$_4$ exhibited the best discharge capacities of 151 mAh/g and 109.3 mAh/g at rates of 0.05C and 5C, respectively. The total charge/discharge capacity of LiMn$_{1-x}$Fe$_x$PO$_4$ was enhanced as the Fe concentration increased, but the average discharge voltage was reduced; thus, LiMn$_{0.70}$Fe$_{0.30}$PO$_4$ exhibited the largest specific energy value of 513 Wh/kg. These improved properties were ascribed to the suppressed Mn dissolution in the electrode due to Fe doping, leading to a lower charge-transfer resistance and a better electronic conductivity. The observed excellent electrochemical performance of LiMn$_{1-x}$Fe$_x$PO$_4$ ($x=0.2, 0.3, 0.4$) should enable the widely acceptable and safe use of this material in long-lived LIBs with high power and high energy density.

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