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# Synthesis and Electrochemical Properties of Fe-Doped LiMnPO<sub>4</sub> Nanocomposite Prepared by a Hydrothermal Process in a High-Pressure Reactor

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LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> powders with varied Fe concentrations (x=0, 0.2, 0.3, 0.4) were prepared in a highpressure reactor by a hydrothermal process. The effect of the Fe dopant concentration on the crystal structure, morphology, surface area and electrochemical properties were studied. LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> with a higher Fe concentration presented better cyclic performance, and the capacity retention of a LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> electrode after 20 cycles was 97.2% at 25°C with an initial capacity of 145 mAh/g at a 0.1C rate. LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> 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 LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> 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 LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub> material.

**Keywords:** Hydrothermal process; LiMn<sub>1</sub>-<sub>x</sub>Fe<sub>x</sub>PO<sub>4</sub>; 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 highperformance 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 LiMPO<sub>4</sub> (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 LiMPO<sub>4</sub> materials, LiMnPO<sub>4</sub> intrinsically offers a lithium ion intercalation potential of 4.1 V *versus* Li/Li<sup>+</sup> favoured by most of liquid electrolytes used currently as well as a remarkable high theoretical specific energy (~684Wh kg<sup>-1</sup>=171mAhg<sup>-1</sup>×4.0V) [9-11].

However, low ionic and electronic conductivity of LiMnPO<sub>4</sub> limit its application in highperformance LIBs. In order to improve the electrochemical performance of LiMnPO<sub>4</sub>, various solutions have been explored to solve the problems. Enhancing the electronic conductivity among the LiMnPO<sub>4</sub> particles [12], controlling the LiMnPO<sub>4</sub> particle morphology and particle size[13-15] were reported to improve the diffusion of Li<sup>+</sup> in LiMnPO<sub>4</sub> cathode. Doping LiMnPO<sub>4</sub> with transition metals, such as  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $V^{2+}$  and  $Co^{2+}$ , have resulted in enhanced electrochemical performance in LiMnPO<sub>4</sub> materials[16-21]. The doping elements induced changes in the lattice structure and deviations in the Li-O band lengths in doped LiMnPO<sub>4</sub> [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 LiMnPO<sub>4</sub> 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 carboncoated LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (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  $LiFe_xMn_{1-x}PO_4$  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  $\text{LiFe}_x \text{Mn}_{1-x} PO_4$  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 LiMn<sub>0.75</sub>Fe<sub>0.25</sub>PO4, and 155 mAh/g for LiMn<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> at 0.05 C [28]. Hu et al. synthesized LiMnPO<sub>4</sub> 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  $Mg^{2+}$  and  $Fe^{2+}$ . The Fe-, Mg-doped LiMnPO<sub>4</sub> exhibited improved capacity, cycle performance and rate capability [29]. According to previous publications, LiMnPO<sub>4</sub> doped with minor or more dopant had improved electrochemical properties but was still lacking in high-performance LIBs. In this work, we prepared LiMnPO<sub>4</sub> and LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0.2, 0.3, 0.4) in a high-pressure reactor at 180°C using a hydrothermal process. Compared with synthesized LiMnPO<sub>4</sub>, synthesized LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> possesses considerably enhanced electrochemical performance. LiMn<sub>0.7</sub>Fe<sub>0.3</sub>PO<sub>4</sub> 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

LiMnPO<sub>4</sub> was synthesized in the following steps.  $MnCl_2$  (0.375 mol),  $H_3PO_4$  (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°Cfor 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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0.2, 0.3, 0.4) was prepared by the same procedure as LiMnPO<sub>4</sub>. MnCl<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O totalled 0.375 mol with a varied Fe/Mn ratio. The LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0, 0.2, 0.3, 0.4)/C composite material was synthesized by mixing LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (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 K $\alpha$  radiation ( $\lambda$ =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  $\Phi$ 8 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<sup>2</sup>). A mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) containing 1 M LiPF<sub>6</sub> 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<sup>+</sup>) using a battery test system (BT2000, Arbin, USA).

#### **3. RESULTS AND DISCUSSION**

The synthesized LiMnPO<sub>4</sub> and Fe-doped LiMnPO<sub>4</sub> 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<sub>4</sub> and LiMn<sub>0.8</sub>Fe<sub>0.2</sub>PO<sub>4</sub>, as well as LiMn<sub>0.7</sub>Fe<sub>0.3</sub>PO<sub>4</sub> and LiMn<sub>0.6</sub>Fe<sub>0.4</sub>PO<sub>4</sub>. The crystal structure of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> are similar to the diffraction of LiMnPO<sub>4</sub>, which is well matched to the orthorhombic LiMnPO<sub>4</sub> 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  $LiMn_{1-x}Fe_xPO_4$  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,  $LiMn_{1-x}Fe_xPO_4$  with varying amounts of Fe will exhibit different lattice parameters.



Figure 1. XRD patterns of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub>.

Table 1 shows the lattice parameters of  $LiMn_{1-x}Fe_xPO_4$  refined from Jade 5.0.  $LiMn_{1-x}Fe_xPO_4$  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  $LiMn_{1-x}Fe_xPO_4$ . 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  $LiMn_{1-x}Fe_xPO_4$  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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub>

Sample	a (Å)	b (Å)	c (Å)	V (Å <sup>3</sup> )
LiMn <sub>0.60</sub> Fe <sub>0.40</sub> PO <sub>4</sub>	10.42935	6.05813	4.74165	299.59
LiMn <sub>0.70</sub> Fe <sub>0.30</sub> PO <sub>4</sub>	10.42983	6.05734	4.74245	299.61
$LiMn_{0.80}Fe_{0.20}PO_4$	10.42982	6.05730	4.74253	299.62
LiMnPO <sub>4</sub>	10.45139	6.10128	4.73492	301.93

The SEM images of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> are shown in Fig. 2. All the samples exhibit a needle-like morphology. However, LiMnPO<sub>4</sub> (Fig. 2a) has a larger particle size than the other LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> samples. From Fig. 2b to Fig. 2d, the Fe dopant concentration affected the dispersion of the LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> samples, and LiMn<sub>0.80</sub>Fe<sub>0.20</sub>PO<sub>4</sub> (Fig. 2b) exhibited favourable dispersion with an unobvious reunion phenomenon.



Figure 2. SEM images of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub>: a. (x=0), b. (x=0.2), c. (x=0.3), d. (x=0.4).



**Figure 3**. Specific surface area of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0, 0.2, 0.3, 0.4).

The specific surface area of  $LiMn_{1-x}Fe_xPO_4$  (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<sup>2</sup>/g), and

Fe-doped LiMnPO<sub>4</sub> has a much smaller specific surface area. As the Fe dopant concentration increased in LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub>, the specific surface area decreased from 12.42 m<sup>2</sup>/g (LiMn<sub>0.8</sub>Fe<sub>0.2</sub>PO<sub>4</sub>) to 9.74 m<sup>2</sup>/g (LiMn<sub>0.7</sub>Fe<sub>0.3</sub>PO<sub>4</sub>). LiMn<sub>0.6</sub>Fe<sub>0.4</sub>PO<sub>4</sub> had the highest Fe dopant concentration but the smallest specific surface area of 9.32 m<sup>2</sup>/g.

Fig. 4 shows the first charge/discharge profile of the  $LiMn_{1-x}Fe_xPO_4$  (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  $Mn^{2+}/Mn^{3+}$  redox couple is less clearly observed in the first discharge curve of pure LiMnPO<sub>4</sub>. This plateau disappears due to polarization resistance resulting from the poor electronic conductivity and a slow Li ion migration rate in the LiMnPO<sub>4</sub> material. Then, the LiMnPO<sub>4</sub> material shows an initial discharge capacity of 82 mAh/g at the first 0.1C rate. Two distinct plateaus are present in the  $LiMn_{1-x}Fe_xPO_4$  (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  $Fe^{2+}/Fe^{3+}$  redox couple. and the second plateau at approximately 4.1 V corresponds to the  $Mn^{2+}/Mn^{3+}$  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  $LiMn_{1-x}Fe_xPO_4$  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 LiMn<sub>0.80</sub>Fe<sub>0.20</sub>PO<sub>4</sub>, LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub> and LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> at a 0.1C rate were 132 mAh/g, 138 mAh/g and145 mAh/g, respectively. In addition, the integrated areas of the discharge curves correspond to the specific energy of the LiMn<sub>1</sub>.  $_{x}Fe_{x}PO_{4}$  (x=0, 0.2, 0.3, 0.4) materials. The total charge/discharge capacity of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> was enhanced as the Fe concentration increased, but the average discharge voltage was reduced; therefore, LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub> exhibited the largest specific energy value of 513 Wh/kg.



**Figure 4.** The initial charge/discharge curve of  $LiMn_{1-x}Fe_xPO_4$  (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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0, 0.2, 0.3, 0.4). After 20 cycles, the capacity of LiMnPO<sub>4</sub> decreased from 82 mAh/g to 71 mAh/g with an 86.5% capacity retention of the initial capacity, LiMn<sub>0.80</sub>Fe<sub>0.20</sub>PO<sub>4</sub> decreased from 132 mAh/g to 123 mAh/g with a 93.2% capacity retention of the initial capacity, LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub> decreased from 138 mAh/g to 128 mAh/g to 128 mAh/g with a 92.7% capacity retention of the initial capacity, LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> decreased from 145 mAh/g to 141 mAh/g with a 97.2% capacity retention of the initial capacity. LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> with a higher Fe concentration presented better cyclic performance. The improved cycle ability of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> 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<sup>2+</sup>/Fe<sup>3+</sup> redox favour the stability of the subsequent Mn<sup>2+</sup>/Mn<sup>3+</sup> redox couples[32].



Figure 5. Cycle performances of an LIB based on  $LiMn_{1-x}Fe_xPO_4$  (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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (x=0, 0.2, 0.3, 0.4) materials faded as the discharge current increased. The LiMnPO<sub>4</sub> sample (Fig. 6a) has a discharge plateau-voltage of approximately 4.1 V, corresponding to the Mn<sup>2+</sup>/Mn<sup>3+</sup> redox couple at a 0.05C rate. However, the discharge plateau-voltage was not stable and disappeared at high C rate, indicating that LiMnPO<sub>4</sub> 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 LiMnPO<sub>4</sub> samples (Fig. 6b-d) have two distinct plateaus corresponding to the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple (3.5 V) and Mn<sup>2+</sup>/Mn<sup>3+</sup> redox couple (4.1 V), and the discharge plateau-voltage decreased with the increased discharge rates. A high

Fe concentration in LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> 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<sub>4</sub> sample shows a considerable retention of the capacity at different C rates. The initial discharge capacity of pure LiMnPO<sub>4</sub> is 93.9 mAh/g at a 0.05C rate, and the discharge capacities of LiMn<sub>0.80</sub>Fe<sub>0.20</sub>PO<sub>4</sub>, LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub>, and LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> 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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub>. Even at a 5C rate, the discharge capacity of pure LiMnPO<sub>4</sub> is 36.5 mAh/g, whereas the discharge capacities of LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub>, and LiMn<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> are 97.9 mAh/g, 105.1 mAh/g and 109.3 mAh/g, respectively. A higher Fe doping concentration in LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> means that more Fe atoms replaced Mn atoms in LiMnPO<sub>4</sub> and the substitution of Fe in a LiMnPO<sub>4</sub> during charge/discharge process, increased mobility and enhanced electrochemical performance of the LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> electrode at high C rates[32,33].



**Figure 6.** Discharge curve of LiMn<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> 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<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> 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<sub>0.60</sub>Fe<sub>0.40</sub>PO<sub>4</sub> 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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> was enhanced as the Fe concentration increased, but the average discharge voltage was reduced; thus, LiMn<sub>0.70</sub>Fe<sub>0.30</sub>PO<sub>4</sub> 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<sub>1-x</sub>Fe<sub>x</sub>PO<sub>4</sub> (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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