Effects of Ni and Mn doping on physicochemical and electrochemical performances of LiFePO_4/C

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Abstract: The $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$), $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y=0.00, 0.01, 0.02, 0.03, 0.04$) and $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{FePO}_4$ composites have been successfully synthesized by a simple solid-state method. The structure, morphology and electrochemical property of the as-prepared materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge/discharge tests. The XRD patterns indicate that doping with Ni^{2+} or Mn^{2+} do not affect the structure of olivine LiFePO_4 . The results of electrochemical performance measurements reveal that the $\text{LiNi}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ shows the best electrochemical performance among all of the single Ni-doped samples. Meanwhile, comparing with other single Mn-doped materials, the $\text{LiMn}_{0.03}\text{Fe}_{0.97}\text{PO}_4/\text{C}$ show the highest initial discharge capacity and excellent cyclic stability. In order to further improve the electrochemical performance of LiFePO_4/C , $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ composite with Ni and Mn co-doping was also synthesized by the same route. Relative to other samples, the

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LiNi_{0.02}Mn_{0.03}Fe_{0.95}PO₄/C delivers higher initial discharge capacity of 164.3 mAh g⁻¹ at a rate of 0.1 C. Moreover, it also exhibits excellent cyclic stability with capacity retention of 98.7% cycled at 1 C after 100 cycles. CV shows that the Ni and Mn dual-doping reduce the electrode polarization, which may be the important factors for improving the electrochemical properties of the cathode materials.

Keywords: Lithium-ion batteries; Cathode material; LiFePO₄/C; Ni and Mn doping; Electrochemical performances

1. Introduction

Rechargeable lithium-ion batteries are the most promising candidates for applications in electric vehicles (EVs), hybrid electric vehicles (HEVs), and power tools in terms of energy densities and power densities [1-3]. Since 1991 when introduced by Sony, rechargeable lithium-ion batteries have relied on lithium transition metal oxides as the main sources of cathode active material. Several lithium transition metal oxides, such as layered LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, spinel LiMn₂O₄, and olivine LiFePO₄, have been commercially used in lithium ion batteries. Among them, olivine LiFePO₄ has attracted considerable attention as perspective intercalation cathode material for lithium-ion batteries due to its inherent merits such as long cyclability, high safety, low toxicity, and potential low cost [4-6]. However, olivine LiFePO₄ has an intrinsically poor electrical and ionic conductivity, seriously affecting its electrochemical performance and limiting its large-scale application [7-9].

Current effective strategies to enhance the electrochemical performance of LiFePO₄

include carbon coating on particle surfaces, LiFePO_4 particle size minimization, customizing particle morphologies and metal doping. The carbon coating process has been massively used in industry because the conductive carbon layer increases the electron migration rate during the charge/discharge processes [10,11]. Besides, the reduction of LiFePO_4 particle size results in the shortening of the Li^+ diffusion path [12,13]. According to the high anisotropy of olivine LiFePO_4 , customizing particle morphologies is of evidently high importance for material properties and electrochemical performances. Therefore, constructing LiFePO_4 material with crystal growth orientations along specific plane and thicknesses becomes very ideal to achieve high rate capabilities of the LiFePO_4 material [14-17]. To specially mention, metal doping is considered to be an effective method to enhance the intrinsic electrical and ionic conductivity of the LiFePO_4 material [18-20]. For example, Zhang reported that the conductivity of LiFePO_4 could be enhanced by doping with Nd on the Fe site, and the Nd-doped sample showed an improved discharge capacity of 115 mAh g^{-1} at 2 C [21]. Recently, Wand reported a mesoporous carbon-coated LiFePO_4 nanocrystals further co-modified with graphene and Mg^{2+} doping [18]. The Mg^{2+} doping improved the intrinsically electronic and ionic transfer properties of LiFePO_4 crystals.

In this work, single Ni-doped $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$) and Mn-doped $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y=0.00, 0.01, 0.02, 0.03, 0.04$) composites were prepared by a simple solid-state method. The influence of Ni and Mn doping on the structure, morphology and electrochemical properties of the material was studied in detail. In addition, a Ni and Mn co-doped $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ cathode material

was also synthesized via the same method for comparison.

2. Experimental

2.1 Synthesis of $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ and $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ composites

5 All the chemicals are analytical grade and used without further purification. The $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x = 0.00, 0.01, 0.03$ and 0.04) composites were prepared as follows. The stoichiometric amounts of Li_2CO_3 (A.R.), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (A.R.) and sugar (the amount of carbon was about 11.5 wt% of LiFePO_4) were mixed in ethanol and ball-milled for 6 h. Then, the mixed
10 slurry was dried at $80\text{ }^\circ\text{C}$ in the oven. After drying, the mixture was calcined in Ar/H_2 (95:5 v%) atmosphere at $350\text{ }^\circ\text{C}$ for 8 h. The resulted powder was ball-milled again for 3 h, and then calcined $700\text{ }^\circ\text{C}$ for 15 h under Ar/H_2 (95:5 v%) atmosphere to form the final product. The synthesis of $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x = 0.00, 0.01, 0.03$ and 0.04) composites was similar with $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ materials.

15 2.2 Synthesis of $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ composites

The $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ composite was also synthesized via similar solid-state method. The appropriate Li_2CO_3 (A.R.), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (A.R.), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (A.R.) and sugar were mixed in ethanol and ball-milled for 6 h, and the subsequent process was the same as
20 that of $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ materials.

2.3 Materials characterization

The phase identification of the samples were performed with a diffractometer

(D/Max-3C, Rigaku, Japan) using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator at 36 kV, 20 mA. The scanning rate was 8° min^{-1} and the scanning range of diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 70^\circ$. The weight percentage of carbon in the samples was determined by a C, H, N Analyser model 1106 Carlo Erba
5 Strumentazione. The morphology of the samples was observed using a scanning electron microscopy (SEM) (JSM-6100LV, JEOL, Japan).

2.4 Electrochemical test

The electrochemical tests of samples were carried out using 2025 coin-type cells assembled in an argon-filled glove box. In all cells, the cathode was consisted of a
10 mixture of active material (80 wt%), acetylene black (5 wt%), graphite (5 wt%) and polyvinylidene fluoride (PVDF) as binder agent (10 wt%); lithium was served as counter and reference electrodes; a Celgard 2400 was used as separator, and the electrolyte was 1 M LiPF₆ solution in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, v/v). The cells were charged and discharged at different current densities
15 (1 C=170 mA g⁻¹) using a Neware battery test system (Shenzhen, China) in the voltage range of 2.3~4.2V at room temperature. Cyclic voltammetry (CV) measurements were performed with an IM6ex electrochemical workstation (Zahner-Elektrick, German).

20 3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the LiNi_xFe_{1-x}PO₄/C (x=0.00, 0.01, 0.02, 0.03, 0.04) cathode materials. The diffraction peaks of the samples were

quite narrow, which indicated a high crystallinity of the materials. As apparently illustrated from the XRD patterns, the Ni-doped materials had typical orthorhombic LiFePO_4 structure with a space group of $Pnmb$. The corresponding lattice parameters are listed in Table 1. As seen from the table, the cell volume was decreased slightly after incorporation of Ni, which probably attributed to the little smaller radius of Ni^{2+} (0.69 Å) than that of Fe^{2+} (0.74 Å). The change of the lattice parameters also indicated that Ni has been introduced into the lattice of LiFePO_4 rather than formed impurities.

Fig.1. XRD patterns of the $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ cathode materials
(a) $x=0$, (b) $x=0.01$, (c) $x=0.02$, (d) $x=0.03$, (e) $x=0.04$

Table 1. Lattice parameters of the $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ cathode materials

x	a (Å)	b (Å)	c (Å)	$V(\text{Å}^3)$
0	10.328	5.996	4.685	290.127
0.01	10.325	5.996	4.686	290.104
0.02	10.324	5.997	4.685	290.063
0.03	10.325	5.997	4.682	289.905
0.04	10.326	5.994	4.683	289.850

The surface morphologies of the samples were examined by SEM. As shown in Fig. 2, the particle size of the samples is decreased and then increased with the increasing content of Ni. Especially, the $\text{LiNi}_{0.02}\text{Fe}_{0.08}\text{PO}_4/\text{C}$ has the least particle size and well uniform size distribution. SEM images reveal that the Ni doping could affect particle

size of the materials. It is generally known that reducing the particle size can shorten the diffusion distance of Li^+ as well as increase the electrochemical activation area, which is beneficial to improve the electrochemical properties of the cathode material [18].

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Fig. 2. SEM images the $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ cathode materials
(a) $x=0$, (b) $x=0.01$, (c) $x=0.02$, (d) $x=0.03$, (e) $x=0.04$

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To explore the advantages of the Ni doping for cathode active material, coin cell tests were performed using the as-prepared $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x=0.00, 0.01, 0.02, 0.03,$

0.04) as the cathode and Li metal as a counter electrode. Fig. 3 shows the discharge capacity at a rate of 0.1 C (1 C corresponds to 170 mA g⁻¹ current density) between 2.3 V and 4.2 V and cycle performance at 1 C. The corresponding data are summarized in Table 2. From the initial discharge curves (Fig. 3A), all the samples had a typical ~3.4 V voltage platform, which was corresponding to reduction reaction based on the couple of Fe²⁺/Fe³⁺ during lithium-ion insertion process. In addition, the LiNi_{0.02}Fe_{0.98}PO₄/C sample displayed a highest capacity of 162.2 mAh g⁻¹ among all of the samples. As shown in the Fig. 3B and Table 2, the LiNi_{0.02}Fe_{0.98}PO₄/C also exhibits the excellent cycling performance at a rate of 1 C, which delivered an initial discharge capacity of 141.0 mAh g⁻¹ with capacity retention of 98.4% after 50 cycles. Based on the above results, it can be concluded that the Ni doping can effectively improve the electrochemical properties of LiFePO₄/C, especially LiNi_{0.02}Fe_{0.98}PO₄/C.

Fig. 3. (A) Initial discharge curves and (B) cycle performance of the LiNi_xFe_{1-x}PO₄/C cathode materials
(a) x=0, (b) x=0.01, (c) x=0.02, (d) x=0.03, (e) x=0.04

Table 2. The discharge capacity and cycle performance of the LiNi_xFe_{1-x}PO₄/C cathode materials

Samples	1 st discharge capacity (mAh g ⁻¹)	1 st discharge capacity (mAh g ⁻¹)	50 th discharge capacity (mAh g ⁻¹)

	0.1 C	1 C	1C
x=0	153.4	125.2	117.7 (94.0%)
x=0.01	158.3	139.0	136.4 (98.1%)
x=0.02	162.2	141.0	138.7 (98.4%)
x=0.03	155.2	137.1	134.6 (98.2%)
x=0.04	155.3	133.6	130.1 (97.4%)

The LiFePO₄/C with various content of Mn²⁺-doping was also investigated, and the physical and electrochemical properties were also discussed in detail as follow. Fig. 4 shows the XRD pattern of the LiMn_yFe_{1-y}PO₄/C materials. The diffraction peaks of all the samples can be unambiguously indexed and assigned to the typical orthorhombic LiFePO₄ structure. Meanwhile, the cell volume was decreased with increasing of Mn doping due to the litter smaller radius of Mn²⁺(0.60 Å) than that of Fe²⁺(r=0.74 Å), as shown in Table 3. As revealed by the SEM images in Fig. 5, the LiMn_yFe_{1-y}PO₄/C particles had corn kernels-like shape with some of agglomerate phenomena. With the increasing of Mn doping, the particle size of the samples decreased and then increased, and the LiMn_{0.02}Fe_{0.98}PO₄/C and LiMn_{0.03}Fe_{0.97}PO₄/C samples had lower particle size and less agglomerate phenomena. The electrochemical properties of the LiMn_yFe_{1-y}PO₄/C composite were tested using the 2025 coin-type cell. Fig. 6 shows the initial discharge capacity and cycle performance of the as-prepared samples. As being seen from Fig. 6, the LiMn_{0.03}Fe_{0.97}PO₄/C electrodes delivered a highest discharge capacity of 162.4 mAh g⁻¹ at 0.1 C (Fig. 6A), and showed superior cyclic stability with 98.3% of its initial capacity after 50 cycles at 1 C (Fig. 6B).

Fig.4. XRD patterns of the $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode materials
(a) $y=0$, (b) $y=0.01$, (c) $y=0.02$, (d) $y=0.03$, (e) $y=0.04$

Table 3. Lattice parameters of the $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode materials

y	a (Å)	b (Å)	c (Å)	V (Å ³)
0	10.328	5.996	4.685	290.127
0.01	10.328	5.992	4.686	289.995
0.02	10.327	5.994	4.685	290.002
0.03	10.327	5.995	4.686	290.112
0.04	10.326	5.994	4.684	289.912

Fig. 5. SEM images the $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode materials
(a) $y=0$, (b) $y=0.01$, (c) $y=0.02$, (d) $y=0.03$, (e) $y=0.04$

Fig. 6. (A) Initial discharge curves and (B) cycle performance of the $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode materials
(a) $a=0$, (b) $b=0.01$, (c) $c=0.02$, (d) $d=0.03$, (e) $e=0.04$

We found in the above research that the $\text{LiNi}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ and $\text{LiNi}_{0.03}\text{Fe}_{0.97}\text{PO}_4/\text{C}$ cathode materials showed the best electrochemical properties comparing with the other single Ni-doped and Mn doped LiFePO_4/C materials, respectively. How about the Ni and Mn co-doped samples? Next, we discussed the physical and electrochemical performance of the Ni and Mn co-doped $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ composites. Fig. 7A shows the XRD patterns of the pristine LiFePO_4/C and $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ cathode materials. The XRD pattern of the $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ was consistent with the pristine LiFePO_4/C , but the cell

volume was decreased when co-doped with the Ni and Mn (Table 4). In order to investigate the surface morphology of $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$, TEM was been introduced. As shown in Fig. 7B, the whole surface of $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4$ particles has been covered by a light shade carbon coating layer represented by the grayish regions in the TEMs.

Fig. 7. (A) XRD patterns of synthesized samples and (B) TEM image of $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$

Table 4. Lattice parameters of the LiFePO_4/C and $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ cathode materials

Samples	a (Å)	b (Å)	c (Å)	V(Å ³)
LiFePO_4/C	10.328	5.996	4.685	290.127
$\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$	10.315	5.981	4.671	288.173

The electrochemical properties of $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ and LiFePO_4/C are illustrated in Fig. 8. As shown in Fig. 8A, the Ni and Mn co-doped $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ displayed an initial discharge capacity of 165.2 mAh g⁻¹ at 0.1 C, which was higher than that of the pristine LiFePO_4/C (153.2 mAh g⁻¹), even the single Ni-doped $\text{LiNi}_{0.02}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ (162.2 mAh g⁻¹) and Mn-doped $\text{LiMn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ (162.4 mAh g⁻¹). In addition, the $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ cathode material revealed excellent cyclic stability with capacity retention of 98.4% at 1 C after 100 cycles, while only 94.0% for the pristine sample, 96.0% for the $\text{LiNi}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ and 93.6% for the $\text{LiMn}_{0.03}\text{Fe}_{0.97}\text{PO}_4/\text{C}$ (Fig. 8B).

Fig. 8. (A) Initial discharge curves and (B) cycle performance of the as-prepared cathode materials

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are

the complementary and well-suited technique to evaluate the electrochemical

5 performance of the electrode material [22]. Fig. 9A compares the cyclic

voltammograms of the pristine LiFePO₄/C and LiNi₀.₀₂Mn₀.₀₃Fe₀.₉₅PO₄/C electrodes

obtained at a scan rate of 0.1 mV s⁻¹ at room temperature. From Fig. 9A, a more

symmetric curve with smaller interval between the cathodic and anodic peak current

was obtained by Ni²⁺ and Mn²⁺ co-substitution. This denoted decreasing of

10 polarization with Ni²⁺ and Mn²⁺ co-substitution, which illustrated an enhancement of

electrochemical performances. As shown in Fig.9B, the impedance spectra are

composed of a semicircle in the high frequency region and a straight line in the low

frequency region. The semicircle in the middle frequency range represents the

charge-transfer resistance (R_{ct}). The inclined line in the low frequency indicates the

15 Warburg Impedance (W_s) [23]. The parameters of the samples are recorded in Table 5.

The resistance of the LiNi₀.₀₂Mn₀.₀₃Fe₀.₉₅PO₄/C electrode was much smaller than that

of the pristine LiFePO₄/C. The great decrease of impedance is considered to be the

effect of the co-doped with Ni²⁺ and Mn²⁺, which results in the improvement of the

electronic conductivity of the material. Therefore, it can be conclude that co-doping metal ion is an effective way to improve the electrochemical properties of LiFePO₄/C.

In addition, the lithium-ion diffusion coefficient (D_{Li}) could be calculated using the following equation [23]:

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$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma_w^2} \dots\dots\dots(1)$$

Herein, R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of lithium-ion, and σ_w is the Warburg factor which is associated with Z' .

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$$Z' = R_s + R_{ct} + \sigma_w \omega^{-1/2} \dots\dots\dots(2)$$

Herein, R_s is the electrolyte resistance, R_{ct} is the charge transfer resistance and ω is the angular frequency in the low frequency region.

Fig. 9C shows the relationship plot between Z_{re} and reciprocal square root of the angular frequency ($\omega^{-1/2}$) at low-frequency region. Based on the Eqs. (1) and (2), the

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calculated lithium-ion diffusion coefficients of LiNi_{0.02}Mn_{0.03}Fe_{0.05}PO₄/C and LiFePO₄/C are 7.50×10^{-14} and 1.38×10^{-14} cm² s⁻¹, respectively. It is obvious that the

R_{ct} for the LiNi_{0.02}Mn_{0.03}Fe_{0.05}PO₄/C decreases drastically and lithium-ion diffusion coefficient for the sample increases slightly. Therefore the electrochemical performance of LiNi_{0.02}Mn_{0.03}Fe_{0.05}PO₄/C is enhanced.

Fig. 9. (A) CV curve, (B) EIS spectra and (C) The relationship plot between Z' and $\omega^{-1/2}$ at low-frequency region of the synthesized samples

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Table 5. Electrode kinetic parameters obtained from EIS of as-synthesized samples

Sample	R_s (Ω)	R_{ct} (Ω)	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)
$\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$	2.546	95.02	7.50×10^{-14}
LiFePO_4/C	3.007	218.3	1.38×10^{-14}

4. Conclusions

Ni and Mn doped LiFePO_4/C composites have been synthesized via simple solid-state method. The XRD results indicate that the Ni or Mn doping do not affect the structure of olivine LiFePO_4 . The particles of all of the samples are in micron size, which are affected by the doping content of metal ions. From the results of electrochemical performance tests, the single Ni doped $\text{LiNi}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ sample

and single Mn doped $\text{LiMn}_{0.03}\text{Fe}_{0.97}\text{PO}_4/\text{C}$ sample show the best electrochemical performance among all of the $\text{LiNi}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$) and $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y=0.00, 0.01, 0.02, 0.03, 0.04$) samples, respectively. However, comparing with the pristine LiFePO_4/C , $\text{LiNi}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ and $\text{LiMn}_{0.03}\text{Fe}_{0.97}\text{PO}_4/\text{C}$,
5 the Ni and Mn co-doped $\text{LiNi}_{0.02}\text{Mn}_{0.03}\text{Fe}_{0.95}\text{PO}_4/\text{C}$ sample delivers higher initial discharge capacity of 164.3 mAh g^{-1} at a rate of 0.1 C between 2.3 and 4.2V . In addition, it also exhibits better cyclic stability with capacity retention of 98.7% cycled at 1 C after 100 cycles. CV tests show that the Ni and Mn dual-doping reduce the electrode polarization and electrochemical impedance, which may be the main reason
10 for the improvement of electrochemical properties. The results show that the appropriate cation metals doping can effectively enhance the electrochemical performance of LiFePO_4/C cathode material.

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