

Synthesis and characterization of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ as a cathode material for lithium-ion battery

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Abstract The olivine-typed cathode materials of LiFePO_4 were prepared via solid-state reaction under argon atmosphere and co-doped by manganese and fluorine to improve their electrochemical performances. The crystal structure, morphology, and electrochemical properties of the prepared samples were investigated using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectrum, X-ray photoelectron spectroscopy, cyclic voltammetry, and charge–discharge cycle measurements. The result showed that the electrochemical performance of LiFePO_4 had been improved dramatically by Mn–F co-doping. The initial discharge capacity of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ samples reached 140.2 mAh/g at 1C rate and only had a small amount of fading in 50 cycles.

Keywords LiFePO_4 · Cathode · Lithium ion battery · Dope

Introduction

LiCoO_2 is the most widely used cathode material in commercial lithium-ion battery due to its superior electrochemical performance. However, LiCoO_2 is expensive, unsafe, and somewhat toxic. As a result, a lot of research has been undertaken in search for more economical and environmental-friendly cathode materials. Among these newly investigated materials, LiFePO_4 , developed by Goodenough and coworkers in 1997 [1], is one of the most

promising candidates. Its advantages include low cost, environmental friendly, good cycle stability, and a relatively high theoretical capacity (170 mAh/g). However, LiFePO_4 still cannot replace LiCoO_2 as the dominant cathode material due to its low electric and ion conductivities, which limit the high-rate performance of LiFePO_4 . Several methods have been proposed to improve the electrochemical diffusion kinetics of LiFePO_4 .

To improve the conductivity of LiFePO_4 , one can add carbon or dope with heteroatom. Carbon coating at the surface of LiFePO_4 particles by sintering carbon sources and other starting raw materials demonstrated excellent electrochemical performance [2–7]. However, a high amount of carbon addition could decrease the volumetric energy density of the materials. On the other hand, element doping has been considered as an established method of improving electronic conductivity of cathode material. Many elements have been used to dope LiFePO_4 as $\text{Li}_x\text{M}_{1-x}\text{FePO}_4$, and the mechanism has been extensively studied. Mg, Mn, Co, and Ni have been used to dope LiFePO_4 as $\text{LiFe}_x\text{M}_{1-x}\text{O}_4$ [8–12]. What is more, doping LiFePO_4 with anion such as F^- has been carried out and reported satisfactory result in enhancing its electrochemical performance [13]. Co-doping as a novel doping method has been proved to be successful in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [14, 15]. In this paper, the co-doped of Mn–F into LiFePO_4 has been synthesized via solid-state method, and the effects of the co-dope on the crystal structure and electrochemical properties of LiFePO_4 have been studied in detail.

Experiment

LiFePO_4/C was synthesized by using $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ as the raw materials in the

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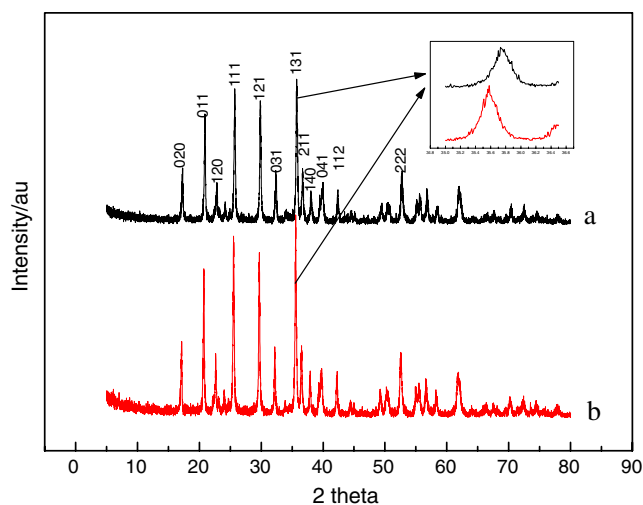


Fig. 1 XRD patterns of LiFePO₄/C (a) and LiFe_{0.99}Mn_{0.01}(PO₄)_{2.99/3}F_{0.01}/C (b)

molar ratio based on the formula of LiFePO₄. The starting materials, with 10% (of the raw materials in mass) amount of sucrose, were mixed and ground using pestle and mortar. After that, the materials were decomposed at 350°C for 5 h in a flow of Ar atmosphere. The decomposed precursor was then pressed into pellets and sintered at 600°C under the same atmosphere for 12 h. Following the similar procedure, LiFe_{0.99}Mn_{0.01}(PO₄)_{2.99/3}F_{0.01}/C was prepared by using Mn(CH₃COO)₂·4H₂O and LiF as doping agents, with all agents of analytical reagent degree.

The X-ray diffraction (XRD) pattern was obtained by employing D/Max-2500 with Cu K α radiation at room temperature. The surface morphology of the materials was observed by scanning electron microscopy (SEM; JSM 6400, JEOL, Japan). The composite positive electrodes were prepared by pressing a mixture of the active materials, conductive material (acetylene black), and binder (PTFE) in a weight ratio of 85/10/5. The average mass of composite loading to electrode is 3 mg. The electrolyte was 1 M LiPF₆ in a 6/3/1 (volume ratio) mixture of ethylene carbonate, propylene carbonate, and dimethyl carbonate. The cells were assembled in an argon-filled dry box. Charge–discharge tests were performed between 2.0 and 4.2 V. The conductivity of the samples was tested as follows: press the materials into pellets, measure their thickness and radius, coat with a thin film of electrically conductive silver epoxy to reduce the contact resistance between materials and molds, using two metal plates to clap the pellet and two

metal wires linked to them, and then test its impedance and get the value of conductivity through the equation of $\rho = R \times S/L$ (ρ represents conductivity, R represents tested impedance, S and L represent the square area and the thickness of the pellet, respectively). Cyclic voltammetry (CV) tests were performed on a CHI660B electrochemical workstation at a scan rate of 0.1 mV/s on the potential interval 2.5–4.2 V (vs. Li⁺/Li). AC impedance experiments were carried out using a CHI660B electrochemical workstation. The AC perturbation signal was 5 mV, and the frequency range was from 10 mHz to 10⁵ Hz. All tests were performed at room temperature.

Results and discussion

The XRD patterns of LiFePO₄/C and LiFe_{0.99}Mn_{0.01}(PO₄)_{2.99/3}F_{0.01}/C are shown in Fig. 1. As can be observed in the figure, all the peaks of the cathode materials can be indexed to LiFePO₄ with an ordered olivine structure, with no impurity phases detected by X-ray diffraction. We magnified the field of 35–36.5°, and take peak (131) as an example, it is clear that there is a very slight shift to lower two theta angles in doped sample. It is worth pointing out that other peaks take the similar situation. This shift indicates that Mn and F were successfully incorporated into LiFePO₄ lattice without altering its structure.

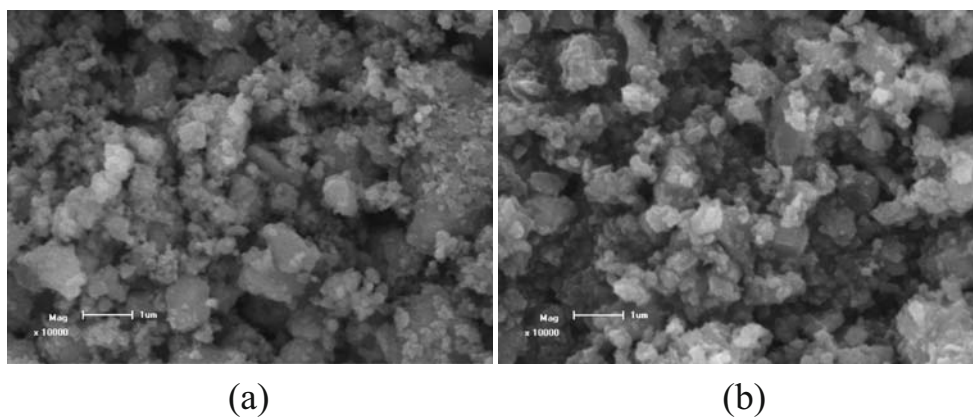
The lattice parameters calculated from JADE 5 were listed in Table 1. The lattice parameters were increased with the co-dope of Mn²⁺ and F⁻, which indicates that Mn²⁺ and F⁻ were incorporated into the lattice successfully. Besides, the cell volume of doped sample is also larger than undoped one, which implies good electrochemical properties because it can provide larger diffusion pathway for Li ion. On the other hand, the doping of Mn and F causes defects in the crystal structure and, therefore, enhances the electronic conductivity of the sample, the conductivity of LiFe_{0.99}Mn_{0.01}(PO₄)_{2.99/3}F_{0.01}/C is $3.2 \times 10^{-2} \text{ S cm}^{-1}$, which is increased by a factor of 3 than the undoped sample ($4.4 \times 10^{-5} \text{ S cm}^{-1}$).

SEM images of the samples are shown in Fig. 2. They both have average crystal size about 1–2 μm , implying that the particle size and morphology of LiFePO₄ were almost insensitive to the Mn–F co-dope. Both the samples are in a small grain size around micrometer range without aggregation. Consequently, we assumed that the improvements in the electrochemical performances in the doped sample were attributed to the intrinsic properties, such as conductivity,

Table 1 Lattice parameters of the samples

Sample	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>V</i> /Å ³
LiFePO ₄ /C	5.9829	10.3008	4.6821	288.55
LiFe _{0.99} Mn _{0.01} (PO ₄) _{2.99/3} F _{0.01} /C	6.0058	10.3190	4.6999	291.27

Fig. 2 SEM images of LiFePO_4/C (a) and $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ (b)



rather than the extrinsic properties such as morphology and grain size.

Figure 3 shows the Fourier transform infrared (FT-IR) spectrum of prepared samples. Using FT-IR spectrum can investigate the local environment of cations in a lattice of close-packed oxygen atoms. Here, we found that no LiF (as starting material) peaks (normally centered at approximately $1,380$ and $1,465\text{ cm}^{-1}$) in Fig. 3, that is LiF was successfully incorporated into the lattice, and no LiF was left unreacted; besides, the peaks shift to slightly higher band numbers which indicate that fluorine has an inductive effect in the lattice due to its high electronegativity. It will induce the rearrangement of electric cloud in P—O bond and, therefore, enhance the conductivity. F^- ion does not likely replace the O^{2-} because the high stability of PO_4^{3-} and also be justified in reference [13], the kind of sites that F^- takes is unclear, but the role the anion plays in lattice is generally understood.

Figure 4 shows the XPS analysis of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ sample. The X-ray photoelectron spectroscopy (XPS) spectra in the region of $\text{Fe } 2p$ is shown in Fig. 4a; the main and the satellite binding energy positions of the $\text{Fe}2p$ peaks match with the B.E. positions reported in

literature and are characteristic for Fe^{2+} cations. The two main peaks center at 710.41 and 723.45 eV , which attribute to $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$, respectively. Figure 4b shows the XPS spectra of $\text{Mn } 2p$. We fitted it here because the doping

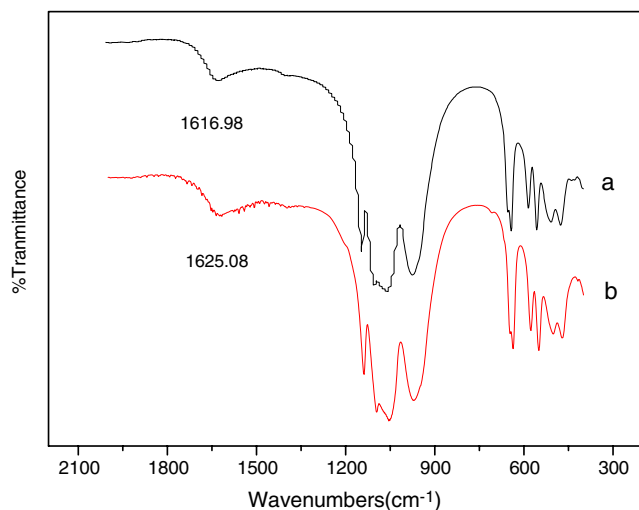


Fig. 3 FT-IR spectrum of prepared samples

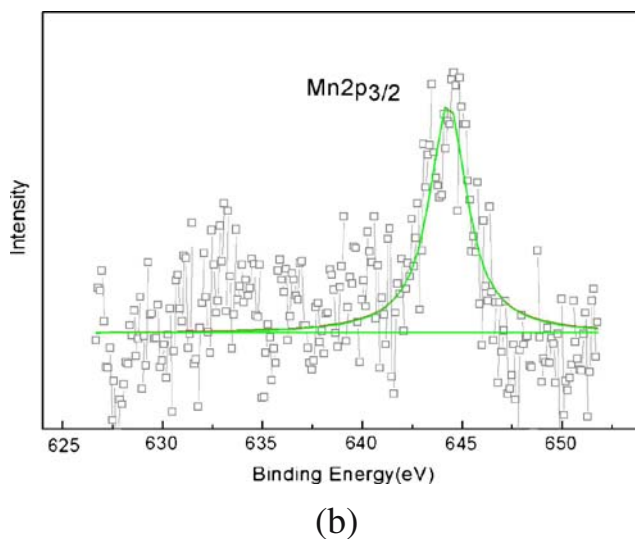
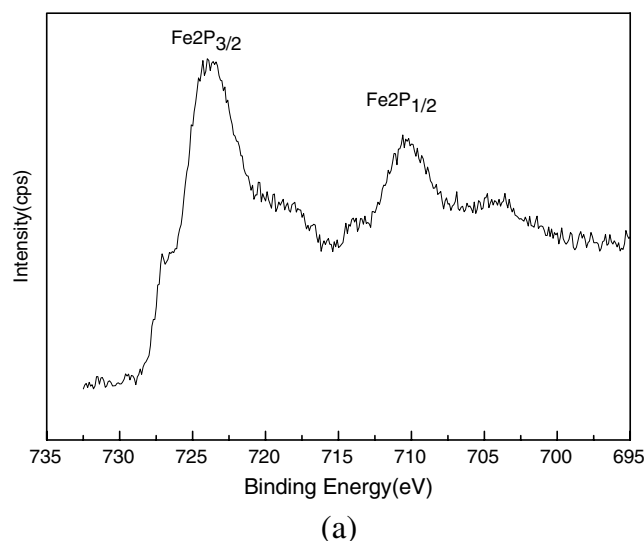


Fig. 4 XPS analysis of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$

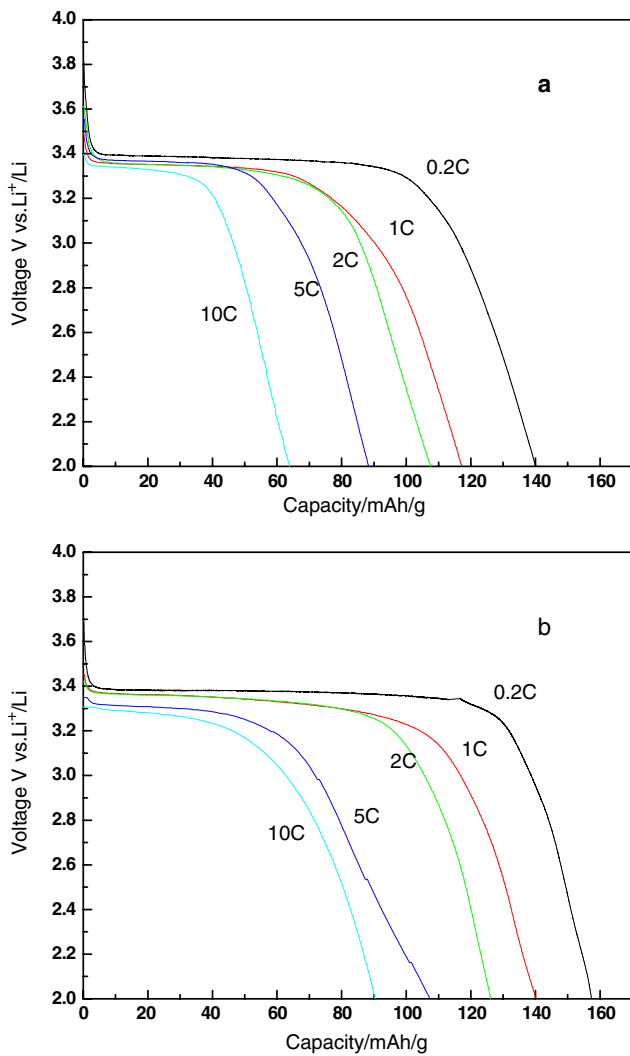


Fig. 5 Discharge profiles of LiFePO₄/C (a) and LiFe_{0.99}Mn_{0.01}(PO₄)_{2.993}F_{0.01}/C (b) samples at different C rates

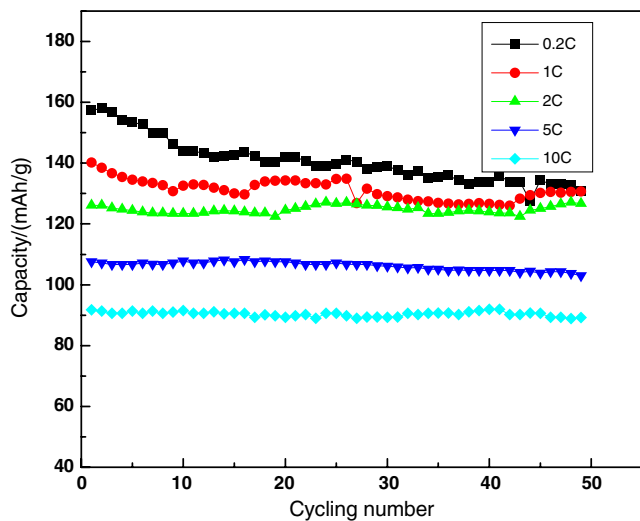


Fig. 6 Cycling performance of LiFe_{0.99}Mn_{0.01}(PO₄)_{2.993}F_{0.01}/C between 2.0 and 4.2 V

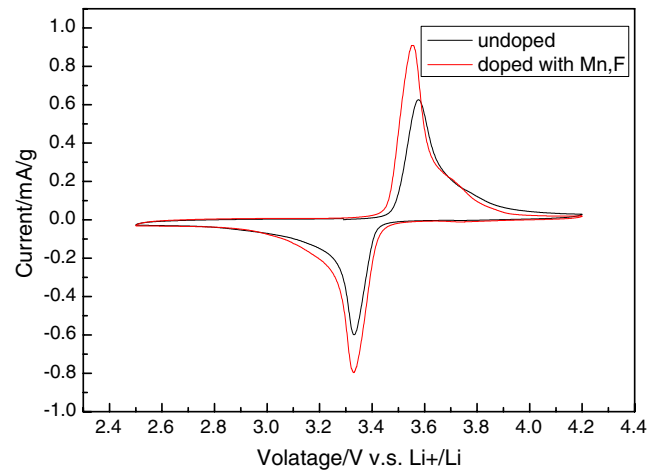


Fig. 7 Cyclic Voltammograms of LiFePO₄/C (a) and LiFe_{0.99}Mn_{0.01}(PO₄)_{2.993}F_{0.01}/C (b)

amount of Mn is relatively small (1%), and the peak is disturbed by noise. It can be observed that a main peak centered at 644.30 eV which can be attributed to Mn 2p_{3/2} in the typical form of Mn²⁺. From the analysis of XPS, we

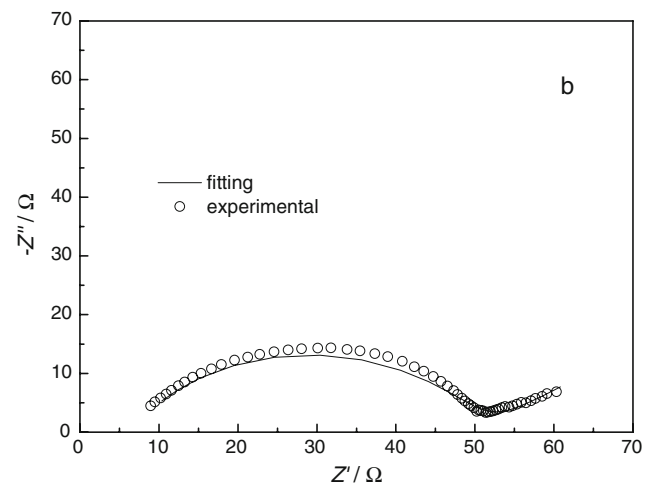
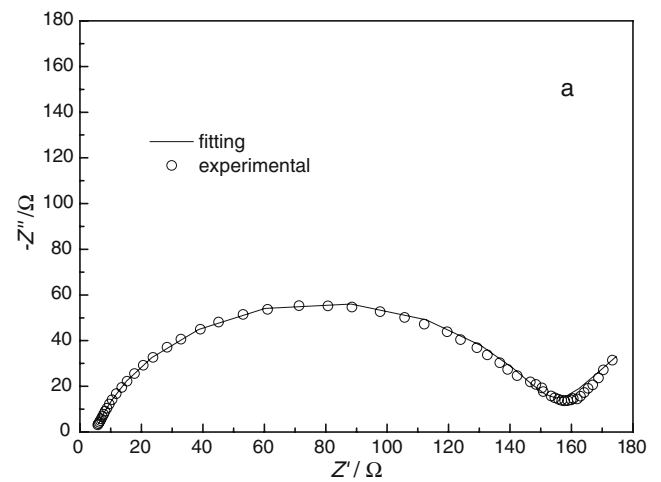


Fig. 8 EIS of LiFePO₄/C (a) and LiFe_{0.99}Mn_{0.01}(PO₄)_{2.993}F_{0.01}/C (b)

confirm that Mn^{2+} has been incorporated into the lattice and remained the valence as in the starting material.

Figure 5 compares the rate performance of LiFePO_4/C with $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ samples. The discharge curves were tested at various C rates from 0.2C to 10C at a cutoff voltage of 2.0 V (1C = 150 mA/g). The cells were then recharged at the same rate as the discharge rate. It can be seen that the discharge performance of LiFePO_4/C was strongly affected by the C rate. In particular, the initial discharge capacity dropped sharply with the increase in rate. However, the co-doped sample exhibited better performance under all current densities tested. The discharge capacities at different rates were 157.4 (0.2C), 140.2 (1C), 126.1 (2C), 107.6 (5C), 91.8 (10C) mAh/g, respectively. In the co-doped samples, carbon coating which comes from decomposition from sucrose under argon atmosphere can increase the bulk electronic conductivity; on the other hand, the co-doping could increase intrinsic electronic conductivity which resulting good rate capability, so the degree of Li^+ intercalation and deintercalation at high rate could be deepened because of the expanded diffusion pathway of Li^+ caused by the addition of Mn^{2+} and F^- .

Figure 6 shows the life cycle at different rates of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$. There is only a small amount of fading observed in the figure, especially in high-rate tests. The capacity retention rates of the samples up to 50 cycles at different rates were 84.4% (0.2C), 93.2% (1C), 100.5% (2C), 95.7% (5C), 97.2% (10C), respectively. The improved cycling performance may be due to the stable olivine structure. It can also approve that co-doping do not affect material's basic structure.

The effect of the co-doping on the electrochemical performance of the samples can be further investigated by cyclic voltammograms. Figure 7 shows the CV curves of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ samples tested between 2.5 and 4.0 V at a scan rate of 0.1 mV/s. The two samples show that similar CV curves with only one pair of redox peaks respond to a two-phase reaction between lithiated phase LiFePO_4 and delithiated phase FePO_4 . It can be observed that the peak currents of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ sample (0.92 and 0.79 mA/g respond to oxidative and reductive processes, respectively) are higher than those of LiFePO_4/C (0.61, 0.59 mA/g). It implies that the poor conductivity of LiFePO_4 was increased by both doping and carbon coating. The peak area of $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ sample is larger than that of LiFePO_4/C , so we expect that the co-doped sample can intercalate and deintercalate more Li ions in accordance with demonstration in Fig. 5. What is more, the peak separation of the co-doped sample (0.22 V) is smaller than LiFePO_4/C (0.25 V); it implies that the polarization was alleviated by Mn and F co-doping, so the rate performance of the sample was improved which are shown in Fig. 6.

The Nyquist plots for undoped and doped samples are presented in Fig. 8. The charge–discharge process of LiFePO_4 was controlled by the step of charge transfer. The high-frequency semicircle represents the charge transfer resistance (R_{ct}) caused by charge transfer across the electrode–electrolyte interface. The low-frequency line represents Warburg resistance caused by diffusion of lithium ion in the electrode matrix. The R_{ct} of doped sample has a much lower value of 45.3 Ω than undoped one which is 146.4 Ω . It indicates that Mn and F co-doping can reduce R_{ct} and increase the conductivity of the sample; the kinetics of charge–discharge process was improved.

Conclusion

Olivine typed LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ samples were prepared by solid-state reaction, and the effects of Mn–F co-doping on the structure and electrochemical behaviors of LiFePO_4/C were investigated. Mn^{2+} and F^- addition made the lattice parameter and the cell volume expanded which can facilitate the Li^+ diffusion between LiFePO_4 phase and FePO_4 phase. The $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$ sample delivered higher discharge capacity under various C rates than undoped ones. As a result, the co-substitution of Mn^{2+} and F^- was effective to improve the electrochemical properties of LiFePO_4 .

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