

Synthesis and characterization of core–shell F-doped LiFePO_4/C composite for lithium-ion batteries

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Abstract Core–shell LiFePO_4/C composite was synthesized via a sol–gel method and doped by fluorine to improve its electrochemical performance. Structural characterization shows that F^- ions were successfully introduced into the LiFePO_4 matrix. Transmission electron microscopy verifies that F-doped LiFePO_4/C composite was composed of nano-sized particles with a ~ 3 nm thick carbon shell coating on the surface. As a cathode material for lithium-ion batteries, the F-doped LiFePO_4/C nanocomposite delivers a discharge capacity of 162 mAh/g at 0.1 C rate. Moreover, the material also shows good high-rate capability, with discharge capacities reaching 113 and 78 mAh/g at 10 and 40 C current rates, respectively. When cycled at 20 C, the cell retains 86% of its initial discharge capacity after 400 cycles, demonstrating excellent high-rate cycling performance.

Keywords Nanocomposite · Core–shell · LiFePO_4 · Li-ion batteries · F doping

Introduction

Ever since Padhi et al. [1] reported in 1997 that LiFePO_4 could be used as a cathode material, olivine compound LiFePO_4 has been considered as one of the most likely candidates for the cathode material of large-scale lithium-ion batteries owing to its advantages such as low cost, high energy density, high theoretic capacity, and environmental friendliness. However, inherent low electronic and ionic

conductivities prevent LiFePO_4 olivine materials from large-scale commercial utilization [1–3]. A great deal of efforts have gone into overcoming these drawbacks and improve its electrochemical performance, mainly including carbon coating [4, 5], lattice doping [6–9], and reducing particle size [10, 11]. Carbon coating has been one of the most extensively studied approaches because carbon addition could hinder particle growth and limit grain size and thus help increasing the lithium-ion diffusion rate and greatly improve the electron conduction of LiFePO_4 materials, leading to an increase of conductivity of LiFePO_4 . Recent research progress has indicated that nanosized LiFePO_4 materials possess enhanced power performance than micro-sized LiFePO_4 materials. Wang et al. [5] reported that core–shell LiFePO_4/C nanomaterials prepared with an in situ polymerization restriction method could have a discharge capacity of 96 mAh/g at 60 °C. As for lattice doping, the effort to date has focused on cation doping, while anion doping has received much less attention [8, 12]. However, studies have shown that anion doping is also important for lithium-ion battery materials. Fluorine substitution at the oxygen site has been reported to be effective for improving cycle life and rate performance of the cathode active materials for lithium-ion batteries. Zhong et al. [9] reported enhanced rate capability of F-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Liao et al. [8] investigated the effects of F substitution on the electrochemical behavior of LiFePO_4/C and report that $\text{LiFe}(\text{PO}_4)_{0.9}\text{F}_{0.3}/\text{C}$ delivered a discharge capacity of 110 mAh/g at 10 C rate, showing that F doping is effective to optimize the electrochemical performances of LiFePO_4/C . Based on the previous research work, we believe that F doping combined with carbon coating which not only enhance conductivity but also simultaneously minimize particle size could optimize the electrochemical performance of LiFePO_4 . In the present

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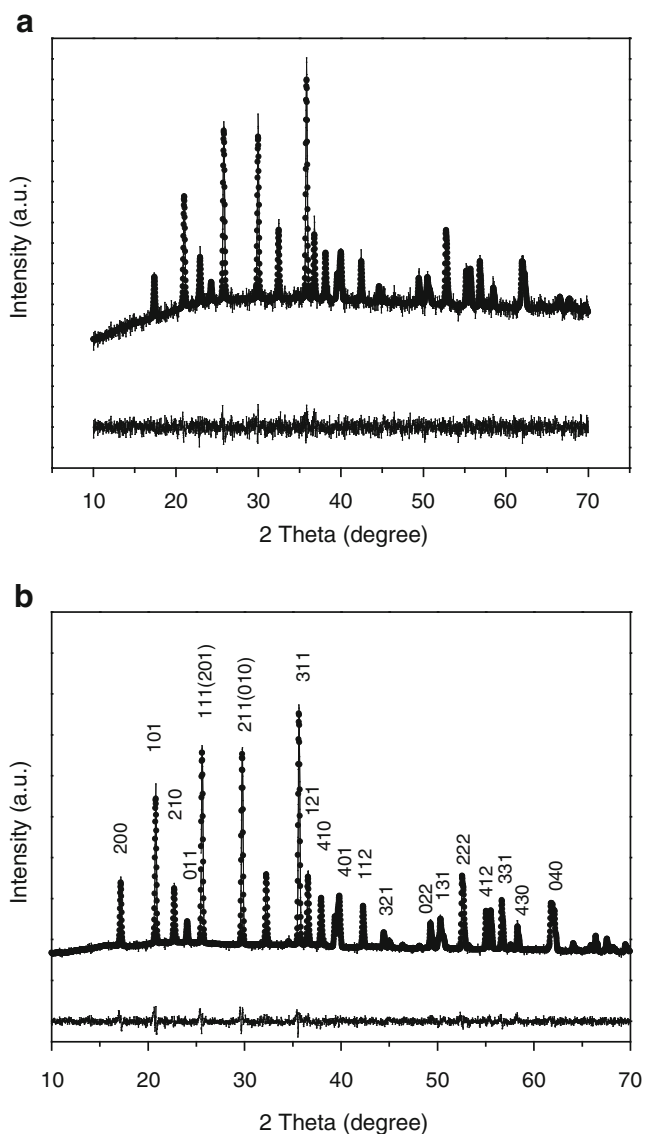


Fig. 1 Rietveld refinement of LiFePO_4/C (a) and F-doped LiFePO_4/C (b) using space group $Pnma$

work, a sol–gel-based technique was adopted to prepare core–shell F-doped LiFePO_4/C cathode material with nano-sized fine particles. Structural and electrochemical properties after F doping were investigated in detail.

Experimental

F-doped LiFePO_4/C was prepared with a sol–gel method using ferric citrate, ammonium dihydric phosphate

($\text{NH}_4\text{H}_2\text{PO}_4$, AR), and lithium hydroxide (LiOH, AR) as starting materials and lithium fluoride (LiF, AR) as doping agent. Ferric citrate was dissolved in distilled water at 60°C with continuous stirring to yield a 0.2 M solution. Separately, an equimolar aqueous solution was prepared from $\text{NH}_4\text{H}_2\text{PO}_4$, LiOH (95%), and LiF (5%). The solutions were mixed and heated at 40°C under vigorous stirring until a viscous gel was formed. The as-formed gel precursor was heat treated in an inert (pure nitrogen) atmosphere at 650°C for 7 h to obtain F-doped LiFePO_4/C composites. LiFePO_4/C was prepared following the same procedure without the addition of LiF.

The crystalline phases were identified by powder X-ray diffraction which was carried out on a Philips X'Pert Pro X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54178$) in the 2θ range from 10° to 80° at room temperature. Morphology of the composites was observed by transmission electron microscope (TEM, JEOL-2010, Japan) equipped with electron diffraction. Carbon content was determined by elemental analyzer (Vario ELIII).

The positive electrodes were prepared by pressing a mixture of the active materials, acetylene black, and binder (polyvinylidene fluoride, dissolved in *N*-methyl-2-pyrrolidone) in a weight ratio of 80:15:5 on aluminum foil followed by a drying procedure in a vacuum at 120°C for 8 h. The Li metal was used as the counter and reference electrodes. Each individual electrode has an area of 0.785 cm^2 and contains $4\text{--}6\text{ mg/cm}^2$ of active materials. One molar LiPF_6 in a 1:1 mixture of ethylene carbonate/diethyl carbonate was used as electrolyte. The cell was assembled in an argon-filled box. Charge and discharge performance was tested on a multi-channel battery tester (Shenzhen Neware, BTS, China) in the voltage range of 2.0–4.3 V at different current densities. Cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI660C) with a three-electrode system.

Results and discussion

The Rietveld refinement of LiFePO_4/C (profile residual (Rp), 3.60; weighted profile residual (Rwp), 2.84; expected residual factor (Rexp), 3.30) and F-doped LiFePO_4/C (Rp, 1.53; Rwp, 2.01; Rexp, 2.23) was performed, and the results are shown in Fig. 1. Both pristine and doped materials have an olivine structure well indexed to the orthorhombic $Pnma$ space group without any unexpected

Table 1 Lattice parameter, cell volume, and average particle size of LiFePO_4/C and F-doped LiFePO_4/C

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	Particle size (nm)
LiFePO_4/C	10.3363	6.0100	4.6988	291.9	102.4
F-doped LiFePO_4/C	10.3191	6.0118	4.6900	290.5	107.2

phase. Due to the F doping, the lattice parameters of LiFePO₄/C decrease compared to LiFePO₄/C as shown in Table 1, implying that F⁻ ions were successfully introduced into LiFePO₄ matrix. The crystallite size calculated using Jade 5.0 software from the most intense peaks in Fig. 1 is 107.2 nm, which is slightly larger than that of LiFePO₄/C (102.4 nm), indicating that the incorporation of fluorine catalyzes the growth of the primary particles [8]. The interatomic distances between Atom 1 (Li, Fe, and P) and Atom 2 (O1, O2, and O3) are listed in Table 2 for the F-doped LiFePO₄/C with random O-site doping and LiFePO₄/C. The distances of Li–O vary from 2.036 to 2.115 Å. The interatomic distances of Li–O increase by 1.09%, 0.98%, and 2.61% for Li–O1, Li–O2, and Li–O3, respectively. This indicates that the extraction of Li from the lattice of LiFePO₄ could be facilitated via F doping, since the interaction between Li and O is weakened.

Figure 2a shows a typical low-magnification TEM image of F-doped LiFePO₄/C sample, where the LiFePO₄ grains are connected together through carbon nano-interconnects, which could provide good grain-to-grain electronic contact while reducing the grain-to-grain contact resistance. Carbon content in the F-doped LiFePO₄/C composite determined by Elementar (Vario ELIII) was 3.65%. Figure 2b–e are TEM images of individual particles as indicated by circles in Fig. 2a and their corresponding electron diffraction patterns. TEM images of particle A and particle B clearly show a core–shell structure with the coexistence of two phase, LiFePO₄ core and amorphous carbon shell. The carbon layer is uniformly covering the whole surface of the LiFePO₄ particle, and the thickness of the carbon film is about 3 nm. From the electron diffraction patterns of the particle A and particle B, it is showed that both particles are

highly crystalline and oriented along the same crystallographic direction.

Figure 3a shows the charge/discharge profiles of F-doped LiFePO₄/C composite at various discharge rates ranging from 0.1 to 40 C. Inset is the charge/discharge profiles of LiFePO₄/C at 0.1 and 5 C. The pristine LiFePO₄/C and F-doped LiFePO₄/C each presents a discharge capacity of 157 and 162 mAh/g (including the mass of carbon) at 0.1 C rate. As the discharge current rate increases to 5 C, the pristine LiFePO₄/C delivers a discharge capacity of 90 mAh/g, and the F-doped LiFePO₄/C, however, exhibits a much higher capacity of 120 mAh/g, indicating significantly enhanced rate capability after F doping. Even at 40 C, a discharge capacity reaching 78 mAh/g was also recorded for F-doped LiFePO₄/C, confirming F doping can improve the kinetics of LiFePO₄ cathode materials. Cycling performance is shown in Fig. 3b, from which we can see that F-doped LiFePO₄/C shows excellent capacity retention after 500 cycles at 1 and 2 C rates. When cycled at 20 C, the cell still retains 86% of its initial discharge capacity after 400 cycles with coulombic efficiency maintaining over 97% for each cycle, demonstrating good high-rate cycling performance.

To further understand the improved high-rate performance, cyclic voltammograms measurements on LiFePO₄/C before and after F doping were performed and the results are presented in Fig. 4a, where anodic and cathodic peaks appear at ~3.5 and 3.35 V vs. Li/Li⁺ for both materials, respectively. The increased peak current of F-doped LiFePO₄/C results from its higher utilization because of its good electronic conductivity and lithium-ion diffusivity. Generally, low electrical conductivity and Li-ion diffusion in the bulk are the main factors impeding the high-rate performance in

Table 2 Interatomic distances in pristine and F-doped LiFePO₄/C according to Rietveld refinement

LiFePO ₄ /C				F-doped LiFePO ₄ /C			
Atom 1	Atom 2	Counts	Interatomic distances (Å)	Atom 1	Atom 2	Counts	Interatomic distances (Å)
Li	O1	2×	2.115 (12)	Li	O1	2×	2.138 (6)
	O2	2×	2.036 (9)		O2	2×	2.056 (5)
	O3	2×	2.110 (12)		O3	2×	2.165 (7)
Li–O average distance 2.087				Li–O average distance 2.120			
Fe	O1	1×	2.246 (18)	Fe	O1	1×	2.198 (9)
	O2	1×	2.116 (21)		O2	1×	2.086 (11)
	O3	2×	2.272 (10)		O3	2×	2.252 (5)
	O3	2×	2.089 (13)		O3	2×	2.058 (7)
Fe–O average distance 2.181				Fe–O average distance 2.151			
P	O1	1×	1.550 (12)	P	O1	1×	1.550 (6)
	O2	1×	1.666 (23)		O2	1×	1.640 (13)
	O3	2×	1.555 (13)		O3	2×	1.574 (8)
P–O average distance 1.582				P–O average distance 1.585			

Fig. 2 **a** TEM image of F-doped LiFePO_4/C ; **b**, **c** typical TEM of particle *A* as indicated in **a** and its corresponding electron diffraction pattern; **d**, **e** typical TEM of particle *B* as indicated in **a** and its corresponding electron diffraction pattern

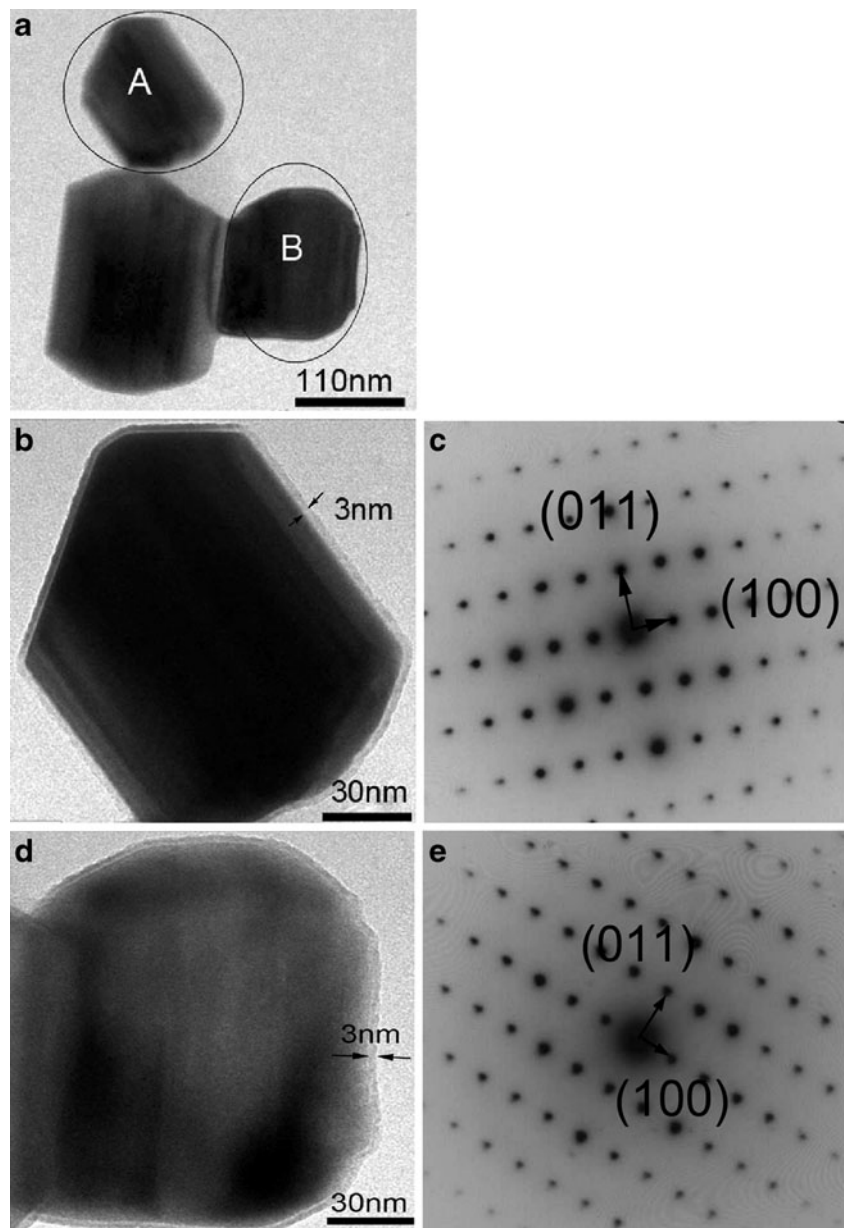


Fig. 3 **a** Charge/discharge curves of F-doped LiFePO_4/C composite at various rates (0.1, 1, 2, 2.5, 5, 7.5, 10, 15, 20, 30, and 40 C). *Inset* Charge/discharge curves of LiFePO_4/C at 0.1 and 5 C rates. **b** Cycling performance of F-doped LiFePO_4/C at 1, 2, and 20 C

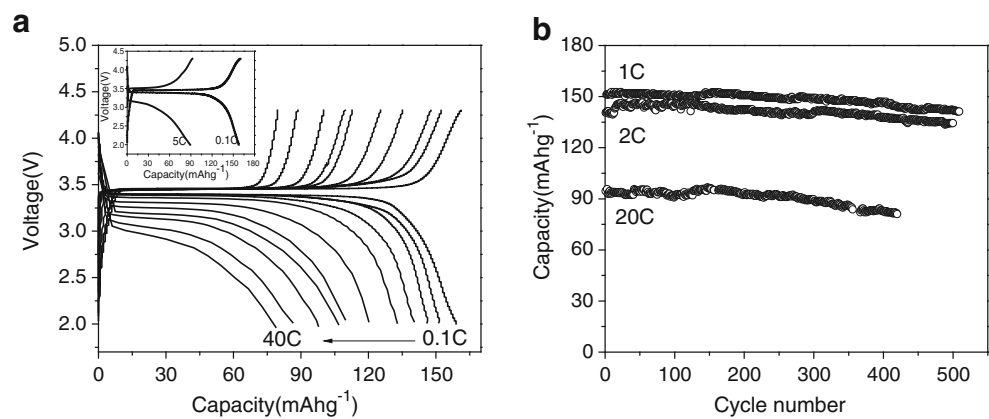
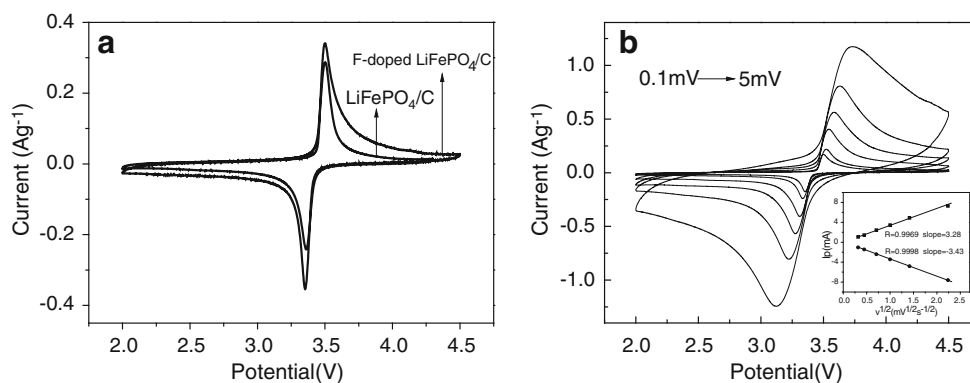


Fig. 4 **a** Cyclic voltammograms of LiFePO₄/C and F-doped LiFePO₄/C at the scan rate of 0.1 mV s⁻¹; **b** Cyclic voltammograms of F-doped LiFePO₄/C under different scan rates



LiFePO₄. The combination of carbon coating and F doping helps improve electrical conductivity and Li-ion diffusion, which is why F-doped LiFePO₄/C shows enhanced high-rate performance. The CV profiles with different scan rates are presented in Fig. 4b for the F-doped LiFePO₄/C. Peak separation increases with increasing scan rate, and all CV profiles overlap regardless of the scan rate at the beginning of charging and discharging. There is a clear linear dependence between i_p and $v^{1/2}$, indicative a diffusion-controlled process. The apparent diffusion constant calculated for F-doped LiFePO₄/C with the slope of the i_p vs $v^{1/2}$ is $\sim 10^{-10}$ cm² s⁻¹, higher than that of the pristine one ($\sim 10^{-11}$ cm² s⁻¹). The results of CV tests indicate that the kinetics of electrochemical reaction of LiFePO₄/C is improved by F doping, which agrees with the improved electrochemical performance of F-doped LiFePO₄/C.

Conclusions

Core-shell F-doped LiFePO₄/C composite was successfully prepared by a sol-gel method. Electrochemical characterization indicated that F doping can improve high-rate capability and cycling performance of LiFePO₄/C. The combination of F doping, achieving nanosized particles and

an efficient surface carbon coating is an effective approach for enhancing the electrochemical performance of LiFePO₄ cathode materials.

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