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ORIGINAL PAPER

Electrochemical performance of $LiFePO_4$/C doped with F synthesized by carbothermal reduction method using NH_4F as dopant

Maosen Pan · Xuehao Lin · Zhentao Zhou

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Abstract The effect of fluorine doping on the electrochemical performance of $LiFePO_4$/C cathode material is investigated. The stoichiometric proportion of $LiFe(PO_4)_{1-x}F_{3x}$/C (x=0.01, 0.05, 0.1, 0.2) materials was synthesized by a solid-state carbothermal reduction route at 650 °C using NH_4F as dopant. X-ray diffraction, scanning electron microscope, energy-dispersive X-ray, and X-ray photoelectron spectroscopy analyses demonstrate that fluorine can be incorporated into $LiFePO_4$/C without altering the olivine structure, but slightly changing the lattice parameters and having little effect on the particle sizes. However, heavy fluorine doping can bring in impurities. Fluorine doping in $LiFePO_4$/C results in good reversible capacity and rate capability. $LiFe(PO_4)_{0.95}F_{0.15}$/C exhibits highest initial capacity and best rate performance. Its discharge capacities at 0.1 and 5 C rates are 156.1 and 119.1 mAh g^{-1}, respectively. $LiFe(PO_4)_{0.95}F_{0.15}$/C also presents an obviously better cycle life than the other samples. We attribute the improvement of the electrochemical performance to the smaller charge transfer resistance (R_{ct}) and influence of fluorine on the PO_4^{3-} polyanion in $LiFePO_4$/C.

Keywords Electrochemical performance · Carbothermal reduction method · Ammonium fluoride · F-doped lithium iron phosphate · Dopant

M. Pan · Z. Zhou (✉)
College of Materials Science and Engineering,
South China University of Technology,
Guangzhou 510640, People's Republic of China
e-mail: mcztzhou@scut.edu.cn

M. Pan
e-mail: p_ms@163.com

X. Lin
Shenzhen Meixin Electronics Co. Ltd,
Shenzhen 518000, People's Republic of China

Introduction

Olivine-typed $LiFePO_4$ has attracted much attention in the past decades because of its low toxicity, low cost, high safety, and excellent reversibility of electrochemistry [1]. However, the low electronic and ion conductivities of pristine $LiFePO_4$ result in poor electrochemical performance especially under moderate and high rates, which poses a great challenge for its practical applications such as electric vehicles and hybrid electric vehicles [2]. So, numerous methods, mainly including carbon coating [3–5], particle size reduction [6, 7], and heteroatom doping [2, 8–11], have been developed to overcome these drawbacks.

In recent years, anion doping has been considered as an established approach to improve the electrochemical performance of $LiFePO_4$ cathode material [11–15]. Especially, fluorine doping at the oxygen site or substituting for PO_4^{3+} polyanion can improve obviously the rate capability and cyclic performance [12, 13]. Unfortunately, their research results show that some impurities such as LiF and $Fe_2(PO_4)F$ existing in the $LiFePO_4$ product which could cause a capacity loss and fluorine waste. Moreover, the LiF dopant was generally regarded as a stable compound even at high temperature [16]. Compared with LiF, NH_4F is not only facilely decomposed at lower temperature but also cheaper. What is more, it also can be completely utilized. Therefore, NH_4F is preferred to be used as F dopant.

On the other hand, synthesis route significantly affects the cathode material's electrochemical performance and the cost [17, 18]. Recently, the solid-state carbothermal reduction (CTR) method has been successfully applied in the preparation of $LiFePO_4$ [17–20]. This method has many advantages, such as low cost of raw material and simple

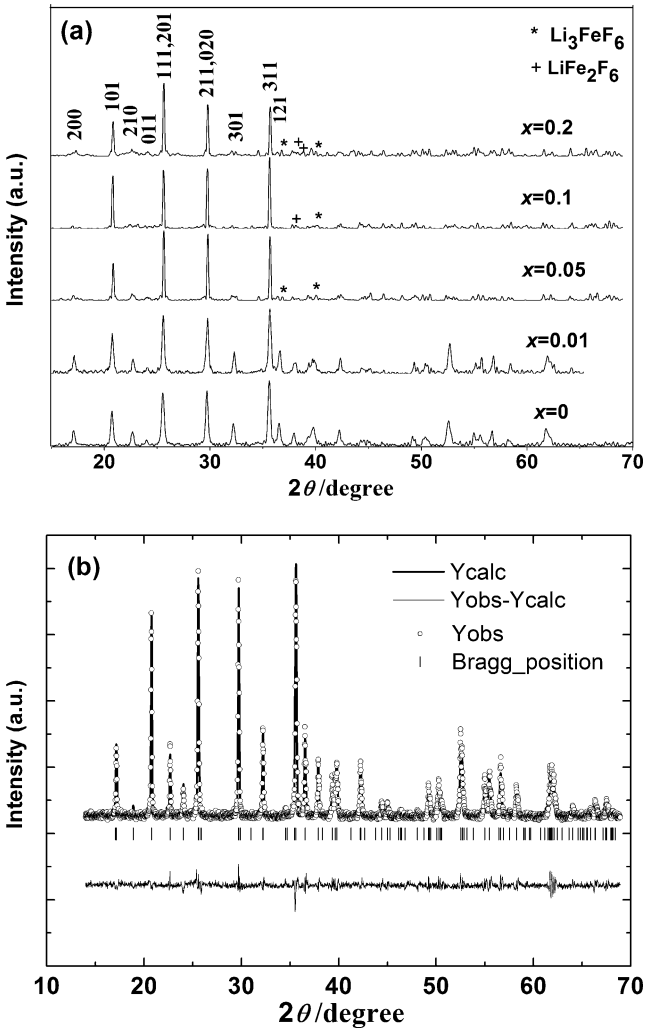

Fig. 1 **a** XRD patterns of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.01, 0.05, 0.1, 0.2) materials and **b** the Rietveld refinement of $LiFe(PO_4)_{0.95}F_{0.15}/C$

synthesis process. However, there is no literature about it being used in the synthesis of F-doped $LiFePO_4$ material. In this investigation, we prepared the $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) cathode materials by CTR method using NH_4F as the dopant, and the effect of fluorine doping on the electrochemical performance of $LiFePO_4$/C cathode material was studied in details.

Experimental

$LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) materials were synthesized by a solid-state CTR route of stoichiometric amount of Fe_2O_3, $(NH_4)_2HPO_4$, Li_2CO_3, and NH_4F, using soluble starch (25.0 g starch/1 mol Fe_2O_3) as reducing agent and carbon source. The starting materials were mixed by planetary ball-milling for 6 h in ethanol absolute medium. The resulting mixture was heated at a rate of 1 °C/min to 300 °C and kept for 10 h, followed by sintering at 650 °C for 24 h. The whole heating procedure was under nitrogen atmosphere. After the temperature was cooled down to room atmosphere, the products were ground by hand until the powder size was below 400 meshes. Finally, $LiFe(PO_4)_{1-x}F_{3x}/C$ samples (x=0, 0.01, 0.05, 0.1, 0.2) were obtained. The carbon content in the $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) powder is about 5.4 (±0.2) wt.% as determined by a chemical analysis [21].

The samples were verified by powder X-ray diffraction (XRD; Bruker D8 ADVANCE, Germany) using Cu K_1 radiation. The morphology and microstructure of this material were observed by scanning electron microscope (SEM; LEO-1530VP, Germany). Energy-dispersive X-ray analysis (EDX) was performed by using a Roentec EDX detector mounted on the LEO-1530VP scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was obtained for the $LiFePO_4$/C and $LiFe(PO_4)_{0.95}F_{0.15}/C$ under Kratos Axis Ultra DLD spectrometer with monochromatic Al Kα radiation (hv=1,486.6 eV).

Electrochemical testing was performed by assembling coin-typed cells with a cathode and a lithium foil anode separated by a Celguard 2300 micro-porous membrane and with 1 M $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate as electrolyte. For cathode fabrication, the as-synthesized $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) was mixed with acetylene black and polytetrafluoroethylene binder with a weight ratio of 85:10:5. Then, the mixture was pressed onto a stainless mesh (current collector) and dried at 120 °C for 24 h in a vacuum oven. The assembly of the cell was carried out in a dry N_2-filled glove box. The charge and discharge test of the cells were examined by a Qintian BS-9300 electrochemical test

Table 1 The lattice parameters and refinement factors of the samples with different fluorine content

F content[a]	a/Å	b/Å	c/Å	V/Å^3	R_p (%)	R_{wp} (%)
0	10.3298	6.0059	4.6974	291.43	5.24	4.08
0.01	10.3327	6.0058	4.6953	291.37	6.31	4.97
0.05	10.3320	5.9852	4.6942	290.29	8.57	6.71
0.1	10.3356	6.0028	4.6949	291.28	9.63	8.32
0.2	10.3373	6.0104	4.6955	291.74	11.46	10.05

[a]F content is the variable x in the formula of $LiFe(PO_4)_{1-x}F_{3x}/C$ ($0 \le x < 0.5$)

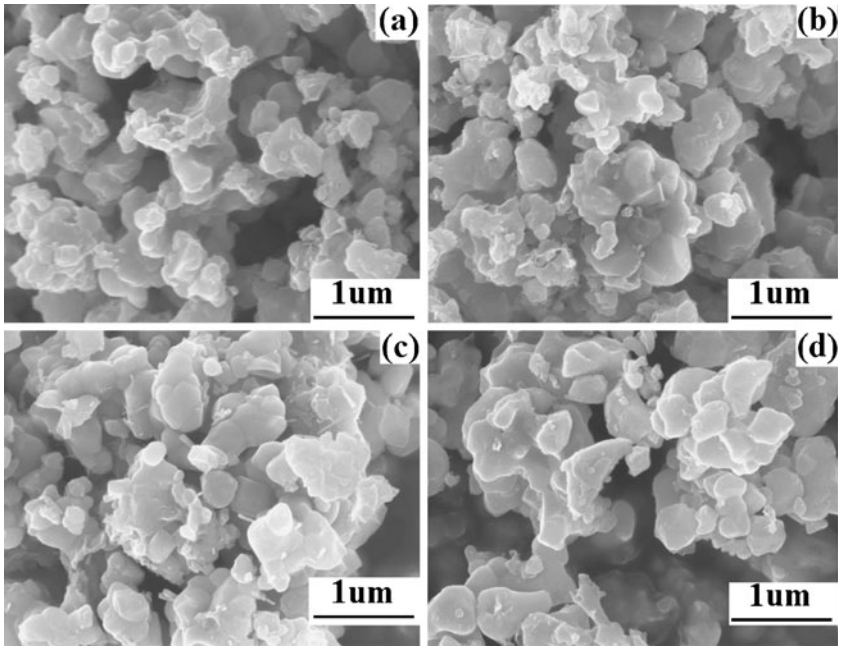

Fig. 2 SEM images of LiFe $(PO_4)_{1-x}F_{3x}$/C materials: **a** x=0.01, **b** x=0.05, **c** x=0.1, **d** x=0.2

instrument between 2.5 and 4.2 V at an ambient temperature. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed on a CHI660B (Chenhua, Shanghai) electrochemical workstation. The scan rate of CV was 0.1 mV s^{-1} over a voltage range of 2.5–4.2 V while the amplitude of EIS was 5 mV in the frequency range of 10^{-2} –10^{5} Hz.

Results and discussion

Figure 1 shows the XRD patterns of $LiFe(PO_4)_{1-x}F_{3x}$/C (x= 0, 0.01, 0.05, 0.1, 0.2) samples and the Rietveld refinement of $LiFe(PO_4)_{0.95}F_{0.15}$/C. The main diffraction peaks of these materials can be indexed to $LiFePO_4$ with an ordered olivine structure (orthorhombic *Pnmb* group given by

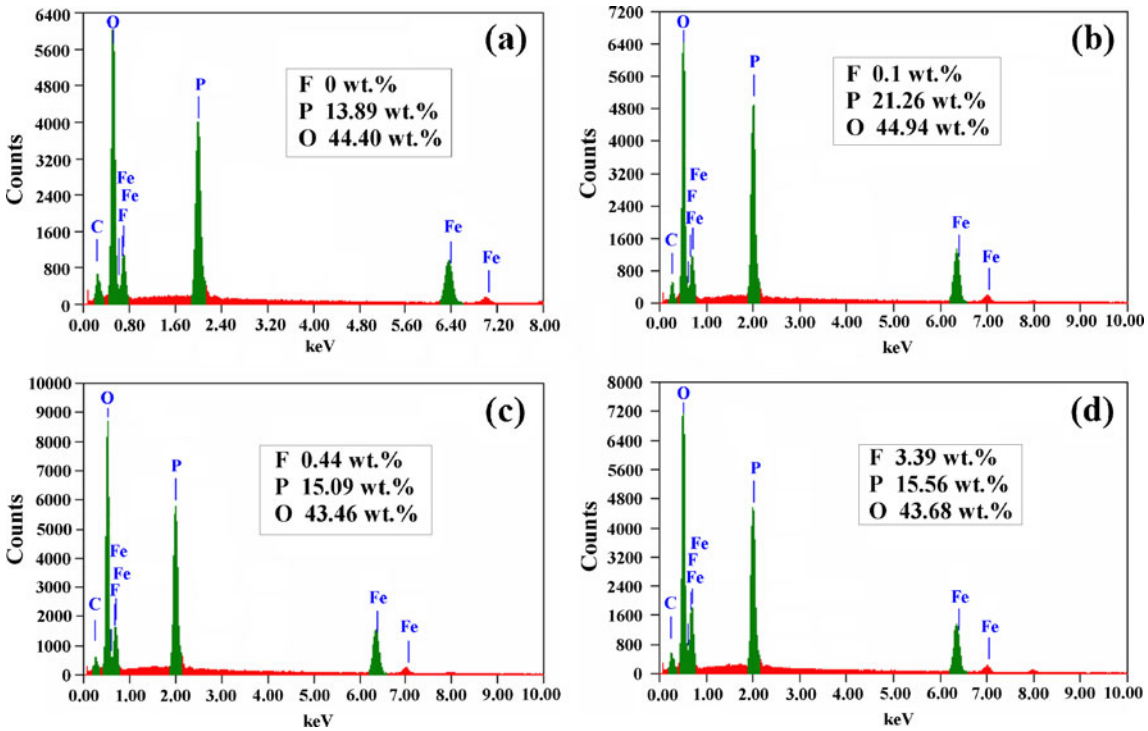

Fig. 3 EDX analysis of $LiFe(PO_4)_{1-x}F_{3x}$/C materials: **a** x=0.01, **b** x=0.05, **c** x=0.1, **d** x=0.2

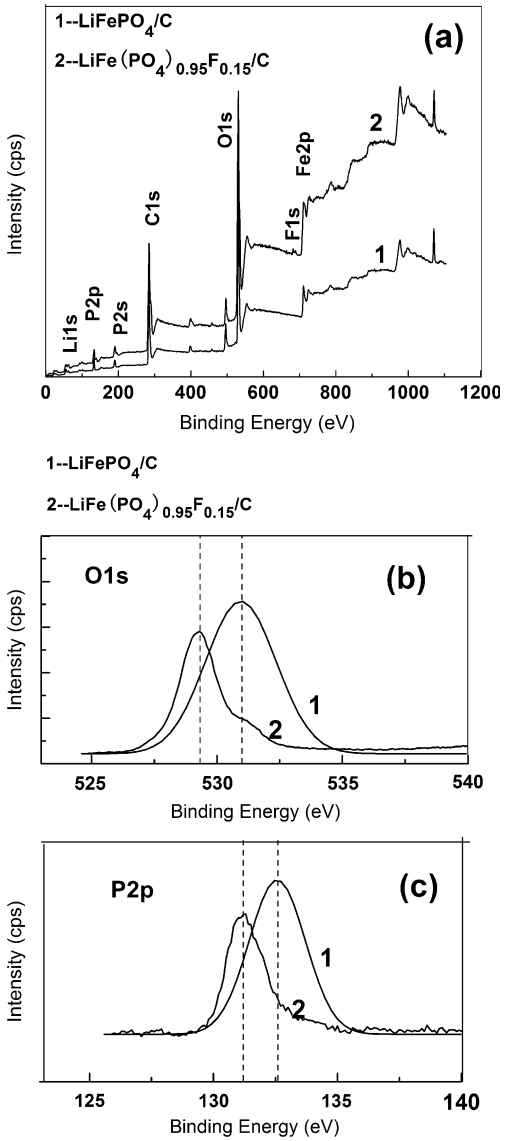

Fig. 4 XPS spectra of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.05) materials: **a** wide-range scanning spectrum; high resolution spectra of **b** O and **c** P

JCPDS 83–2092). The diffraction peaks varied obviously with the increase of F content added in $LiFePO_4/C$ composite, namely, the location of which shifting to the higher or lower 2θ angles as well as the fading of weak diffraction peaks (seen in Fig. 1a). Even some impurities such as Li_3FeF_6 and $LiFe_2F_6$ appeared when the fluorine content was more than 0.05. The refined lattice parameters of five samples were obtained by Rietveld method, as shown in Table 1, and the Rietveld profile refinement of the typical sample of $LiFe(PO_4)_{0.95}F_{0.15}/C$ was presented in Fig. 1b. It can be seen from Table 1 that the lattice parameters decreased with the increase of F content up to 0.05. However, a further increase of the F content resulted in the increase of lattice parameters. The refinement factors of the samples except $LiFe(PO_4)_{0.8}F_{0.6}/C$ were lower than 10%, which indicated the reliance of the refinement data. All of the above results suggest that fluorine has been successfully incorporated into the lattice of $LiFePO_4/C$ without altering its olivine structure, but slightly changing the lattice parameters [9, 12].

The morphology of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.01, 0.05, 0.1, 0.2) materials are shown in Fig. 2. It can be seen that the F-doped $LiFePO_4/C$ materials had the sphere-like surface, the particle sizes of which were about 250–400 nm. The content of fluorine introduced into the $LiFePO_4/C$ matrix structure has little effect on the growth of the particle sizes.

In order to clarify F distribution on the surfaces of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.01, 0.05, 0.1, 0.2) materials, energy-dispersive X-ray analysis was used to scan the samples. The results are shown in Fig. 3. From the EDX spectra, it can be estimated that the F content of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.01, 0.05, 0.1, 0.2) materials was about 0, 0.1, 0.44 and 3.39 wt. %, while the corresponding P/O ratios were 0.162, 0.244, 0.179, and 0.185, respectively. These data indicate that F element exists in these $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.05, 0.1, 0.2) materials. More importantly, the P/O ratio of $LiFe(PO_4)_{0.95}F_{0.15}/C$ composite is nearest approach to the ideal state of $LiFePO_4$ (its P/O ratio is 0.25, namely, one P atom combining with four O atoms in $LiFePO_4$ formula), which means that the destruction of fluorine to the PO_4^{3-} polyanion in $LiFePO_4$ formula can be reduced to the lowest level when the F content was about 0.05. This point is very important for the F-doped $LiFePO_4/C$ cathode material to get good electrochemical performance.

To get more information about the substitution of fluorine, the binding energy of oxygen and phosphorous ions in both $LiFePO_4/C$ and $LiFe(PO_4)_{0.95}F_{0.15}/C$ was investigated by XPS. The results were exhibited in Fig. 4. From Fig. 4a, it can be found that one F_{1s} peak centered at 682.7 eV appeared in the wide-range scanning spectra of $LiFe(PO_4)_{0.95}F_{0.15}/C$, while only Li, Fe, P, O, and C element existed in the sample $LiFePO_4/C$. This indicates

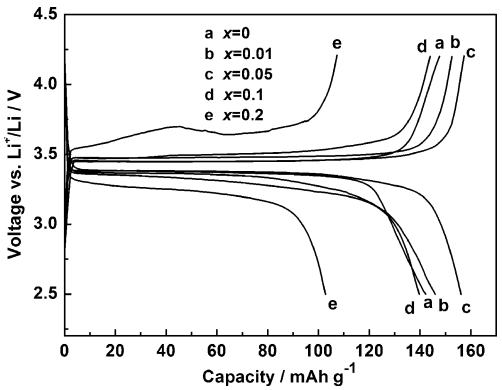

Fig. 5 Charge–discharge curves of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) materials at 0.1 C rate

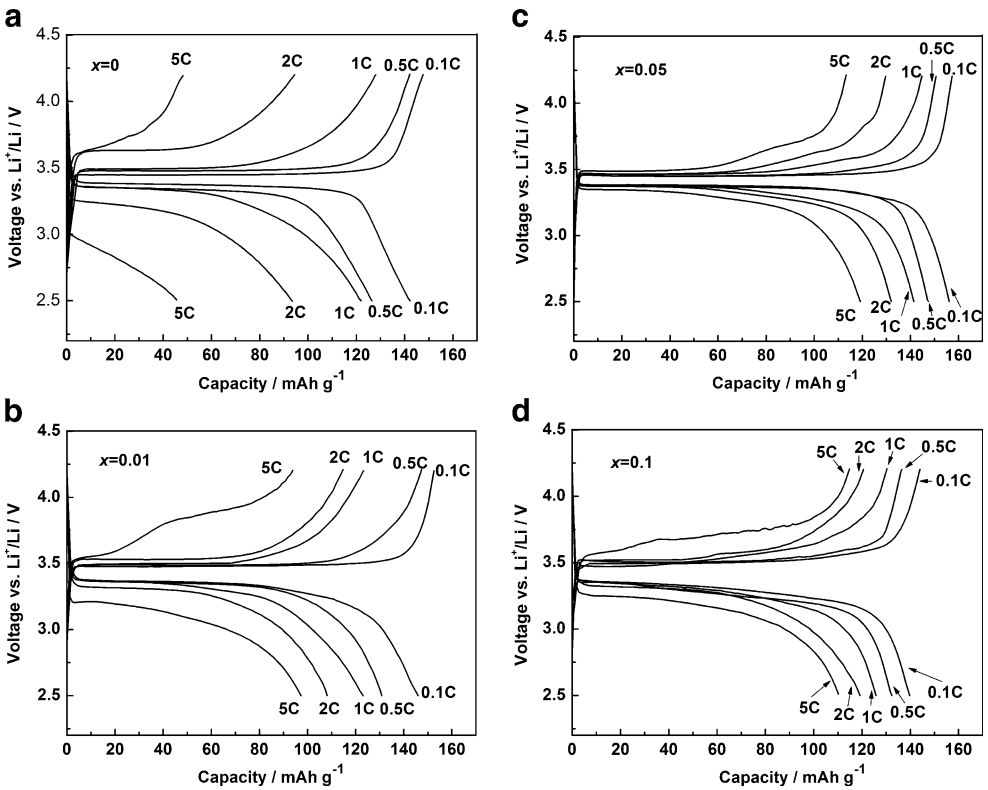

Fig. 6 Charge–discharge profiles of $LiFe(PO_4)_{1-x}F_{3x}/C$ materials: **a** x=0, **b** x=0.01, **c** x=0.05, **d** x=0.1 at 0.1–5 C rates

introduction of fluorine into the $LiFePO_4/C$. More interesting things happened in the high-resolution spectra of O and P (Fig. 4b, c). Not only the O_{1s} peak but also the P_{2p} peak of $LiFe(PO_4)_{0.95}F_{0.15}/C$ had a chemical shift compared to that of $LiFePO_4/C$. This suggests the influence of fluorine incorporated into $LiFePO_4/C$ on both O and P element, namely, the PO_4^{3-} polyanion of $LiFePO_4/C$. Therefore, we concluded that fluorine substituted for PO_4^{3-} polyanion of $LiFePO_4/C$.

Figure 5 presents the charge–discharge profiles of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1, 0.2) at 0.1 C (1 C= 170 mA g^{-1}) rate. F-doped $LiFePO_4/C$ materials remained in the same shape of charge–discharge profiles as the un-doped one. The $LiFe(PO_4)_{0.95}F_{0.15}/C$ material delivered the highest discharge capability of 156.1 mAh g^{-1} among all of the samples, and the other samples $LiFe(PO_4)_{1-x}F_{3x}/C$ (x= 0, 0.01, 0.1, 0.2) showed a capacity of 142.2, 146.0, 139.7, and 102.8 mAh g^{-1}, respectively. It can be seen that the reversible capacities of these cathode materials increased with the increase in fluorine content. However, excess fluorine in the $LiFePO_4/C$ powder caused a capacity loss due to the appearance of impurities and the influence of fluorine on the PO_4^{3-} polyanion. These data suggest that fluorine introduced into $LiFePO_4/C$ improves the reversible capacity of the cathode materials, but the fluorine content needs to be controlled to some extent.

Figure 6 compares the rate performance of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1) samples at 0.1–5 C rates. Both charge and discharge performances of $LiFePO_4/C$ were strongly affected by charge and discharge rates. The discharge voltage plateau decreased obviously from 3.37 V (0.1 C) to 2.8 V (5 C) with increased C rates, while the charge voltage plateau increased from 3.45 V (0.1 C) to 3.8 V (5 C). Both charge and discharge capacities also faded sharply when the C rates increased. Even at 5 C rates, its discharge capacity decreased to 45.6 mAh g^{-1}. On the other hand, F-doped $LiFePO_4/C$ materials showed higher initial discharge voltage and lower charge voltage than the un-doped one under all charge and discharge rates. Furthermore, reversible capacities also were improved greatly, especially when the rate was above 2 C. This indicates that

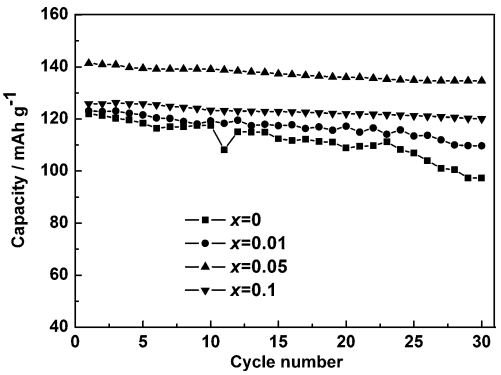

Fig. 7 Cycle performance of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1) materials at 1 C rate

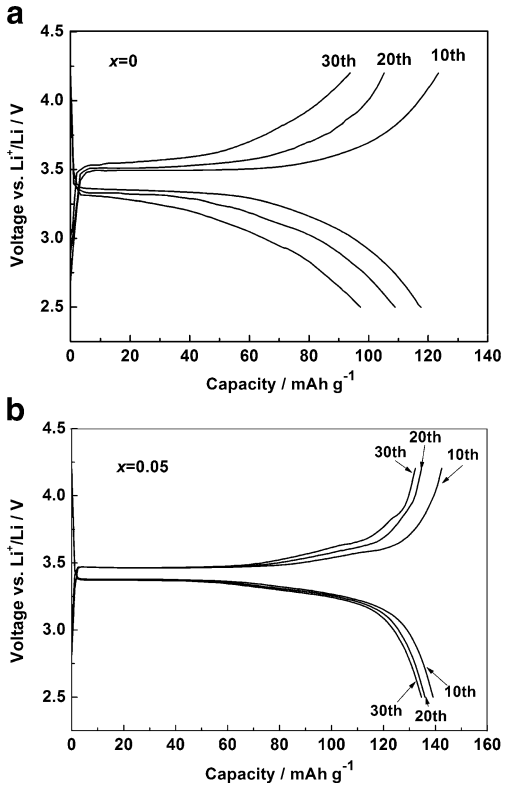

Fig. 8 Charge–discharge profiles of $LiFe(PO_4)_{1-x}F_{3x}/C$ materials: **a** x=0, **b** x=0.05 at 1 C rate

fluorine doping improves the ion conductivities of these cathode materials and alleviates its polarizations. It should be noticed that the $LiFe(PO_4)_{0.95}F_{0.15}/C$ material exhibited the best electrochemical performance among all the F-doped $LiFePO_4/C$ materials. Its discharge capacity at 0.1, 0.5, 1, 2, and 5 C rates was 156.1, 147.5, 141.4, 132.0, and 119.1 mAh g^{-1}, respectively. The charge and discharge voltage varied from 3.45 V (0.1 C) to 3.55 V (5 C) and from 3.38 V (0.1 C) to 3.3 V (5 C), respectively. Comparably, the discharge capacity of $LiFe(PO_4)_{0.99}F_{0.03}/C$ at 0.1, 0.5, 1, 2, and 5 C was 146.0, 130.9, 123.1, 108.1, and 97.3 mAh g^{-1}, respectively, while 139.7, 132.3, 125.8, 119.1, and 110.2 mAh g^{-1} for the $LiFe(PO_4)_{0.9}F_{0.3}/C$. Both of them showed significant polarization, which resulted in lower discharge voltage and higher charge voltage than the $LiFe(PO_4)_{0.95}F_{0.15}/C$ sample. The reason for this can be attributed to two aspects. One is the shortage or excess of fluorine. The shortage of fluorine cannot afford enough F^- that improves the motion of lithium ions [9, 12]. By contrary, the excess of fluorine would produce impurities (confirmed by the XRD in Fig. 1), which were inactive in the cathode materials. It should be pointed out that a few impurities had no effect on the electrochemical performance of the F-doped $LiFePO_4/C$ material, such as $LiFe(PO_4)_{0.95}F_{0.15}/C$. The other aspect is the influence of fluorine on the PO_4^{3-} polyanion in the $LiFePO_4/C$ material. $LiFe(PO_4)_{0.95}F_{0.15}/C$ material has the perfect P/O ratio (namely, a little damage to the PO_4^{3-} polyanion). Consequently, $LiFe(PO_4)_{0.95}F_{0.15}/C$ material shows the best electrochemical performance.

Figure 7 exhibits the cycling characteristics of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1) materials at 1 C rate for 30 cycles. It is easy to find that the $LiFe(PO_4)_{0.99}F_{0.03}/C$ sample has a similar cycle stability to the un-doped $LiFePO_4/C$ material. The other samples, $LiFe(PO_4)_{0.95}F_{0.15}/C$ and $LiFe(PO_4)_{0.9}F_{0.3}/C$, presented obviously better cycle life and higher cycling capacity than that of the un-doped one. The capacity of 30th cycle for the $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.01, 0.05, 0.1) samples was 97.3, 109.7, 134.6, and 120.0 mAh g^{-1}, respectively. After 30 cycles, the capacity retention of $LiFePO_4/C$ was only 79.8% of the initial capacity. However, the $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0.01, 0.05, 0.1) materials kept 89.1%, 95.2%, and 95.4% of the initial capacity, respectively. This indicates that fluorine doping does not change the olivine structure of $LiFePO_4/C$ but enhances its cycling performance. In order to know more details about the cycling performance of $LiFe(PO_4)_{0.95}F_{0.15}/C$ sample, voltage profiles from cycles 10, 20, and 30 for $LiFePO_4/C$ and $LiFe(PO_4)_{0.95}F_{0.15}/C$ were compared in Fig. 8. It is clear to observe that the charge–discharge profiles of $LiFe(PO_4)_{0.95}F_{0.15}/C$ material main-

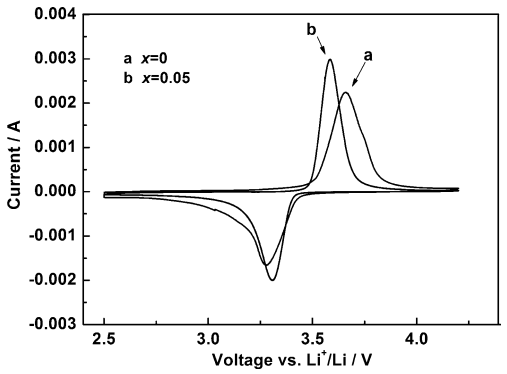

Fig. 9 Cyclic voltammetry curves of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.05) materials

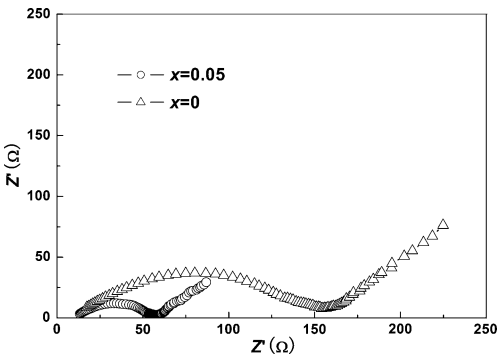

Fig. 10 EIS spectra of $LiFe(PO_4)_{1-x}F_{3x}/C$ (x=0, 0.05) materials

tained almost the same shape after 30 cycles. The capacity also faded slowly. However, the curves of $LiFePO_4$/C changed greatly with the cycles. Significant polarization happened after 10 cycles and the voltage polarization became more severe as the cycling proceeded. Besides, the capacity of $LiFePO_4$/C decreased sharply with the cycling. All these results suggest that fluorine doped in $LiFePO_4$/C reduced both inner resistance and voltage polarization of these cathode materials, which resulted in good cycling performance of the cells.

In order to have a further study on the effect of fluorine on the electrochemical performance of $LiFePO_4$/C and $LiFe(PO_4)_{0.95}F_{0.15}$/C, cyclic voltammetry was carried out. The CV curves of $LiFe(PO_4)_{1-x}F_{3x}$/C (x=0, 0.05) samples are shown in Fig. 9. It can be observed that the two samples have similar redox peaks. The redox peaks of $LiFe(PO_4)_{0.95}F_{0.15}$/C and $LiFePO_4$/C were centered at 3.585/3.309 and 3.656/3.281 V, respectively. Obviously, the peak separation of $LiFe(PO_4)_{0.95}F_{0.15}$/C was narrower and the peak shape was sharper than that of $LiFePO_4$/C. These results demonstrate that easier lithium insertion and extraction happened in the $LiFe(PO_4)_{0.95}F_{0.15}$/C material.

Figure 10 presents the Nyquist plots for $LiFe(PO_4)_{1-x}F_{3x}$/C (x=0, 0.05) materials. The intercept to real axis at the high frequency end of semicircle corresponds to the electrolyte ions transportation barrier (R_e). The high frequency semicircle is related to the charge transfer process, the diameter of which is equal to the charge transfer resistance (R_{ct}). The low frequency straight line predicts a typical Warburg behavior that provides the Li^+ diffusion process from the surface to the interior of the crystalline $LiFe(PO_4)_{1-x}F_{3x}$/C . The R_e of both samples are about 13–17 Ω. The R_{ct} of F-doped material is ca. 44 Ω, much lower than that of the un-doped one (ca. 137 Ω). This indicates that F-doping reduced the R_{ct}, namely, increasing the conductivity of the $LiFePO_4$/C material. Therefore, the kinetics of the charge–discharge process was improved, resulting in good electrochemical performance.

Conclusions

In summary, $LiFe(PO_4)_{1-x}F_{3x}$/C (x=0.01, 0.05, 0.1, 0.2) cathode materials were synthesized by a CTR method at 650 °C using NH_4F as dopant. XRD, SEM, EDX, and XPS analyses demonstrated that fluorine could be incorporated into $LiFePO_4$/C without altering the olivine structure but slightly changing the lattice parameters and having little effect on the particle sizes. However, heavy fluorine (F content was more than 0.05) brought in impurities. Fluorine doping can improve the reversible capacity and rate capability of the cathode materials. $LiFe(PO_4)_{0.95}F_{0.15}$/C exhibited highest initial capacity and best rate performance. Its discharge capacities at 0.1 and 5 C rates were 156.1 and 119.1 mAh g^{-1}, respectively. $LiFe(PO_4)_{0.95}F_{0.15}$/C also presented obviously better cycle life than the other samples. All of these are mainly attributed to the smaller charge transfer resistance (R_{ct}) and influence of fluorine on the PO_4^{3-} polyanion in $LiFePO_4$/C.

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