Research on Low Temperature Performance of the F-doped LiFePO$_4$/C Cathode Materials

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Abstract: *F-doped LiFePO$_4$/C cathode materials were synthesized by two-step solid-state reaction route. The F-doped LiFePO$_4$/C increases the intrinsic conductivity, the diffusion of lithium ions, also improves the high-rate and low-temperature performances of LiFePO$_4$. The SEM images reveal some small morphology changes of the two kinds of the materials, so the improved properties may not due to grain size changes but crystal structure changes. The F-doped material has a higher capability at low temperature. At -20°C, with the rate of 0.5C, the discharge capacity was 82mAhg^{-1}, higher than that of undoped material(65mAhg^{-1}) and the result is better than the previous study[17](65mAhg-1 at the rate of 0.3C), and the disparity would enlarge with the rate increased. The CV plots indicate that the doped material reveals less degree of polarization. F-doping sample improves the electrical conductivity of material, accelerating the process of Li$^+$ deintercalation, therefore, improving the electrochemical performances at low temperature.*

1. INTRODUCTION

As a promising cathode material for lithium-ion batteries, olivine structure LiFePO$_4$ was first introduced by Goodenough et al. in 1997[1]. The overwhelming advantages of iron-based compounds are that, in addition to being inexpensive and naturally abundant, they are safer and less toxic[2]. LiFePO$_4$ is a very attractive material in the field of electric vehicles power application and its commercial use has already started.

Compared to LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$, the Fe resource is much richer, safer and less toxic than Co, Ni, Mn, V. The theoretical capacity of LiFePO$_4$ is up to 170 mAhg^{-1}, and the charge and discharge voltage plateau is 3.4 V(vs.Li$^+$/Li), which is lower than the voltage of the decomposition of most electrolytes. In addition, lithium iron phosphate has excellent cyclability and thermal stability, especially at high temperature[3,4]. However, a main drawbacks of mass LiFePO$_4$ production are its low intrinsic electronic conductivity and chemical diffusion coefficient of lithium irons. Therefore, there is a great need for increasing the intrinsic conductivity and the diffusion of lithium ions to improve the high rate performance of LiFePO$_4$.

Nowadays the researches of the synthesis and modification of lithium iron phosphates mainly focus on adding electronically conductive materials like carbon[5], doping with supervalent cations[6], and limiting particle size [7][8]. Kuppan Saravanan et al. [8] synthesized nanoplates of LiFePO$_4$ with a uniform coating of a 5 nm thick amorphous carbon layer by the solvothermal method, and the thickness along b axis was 30-40 nm, which would shorten diffusion lengths for Li$^+$ ions. Doping LiFePO$_4$ with impurity ions may lead to lattice defects, which would improve the diffusion of lithium ions. The most successful approaches are cation substitution, namely doping LiFePO4 with metal ions at the lithium or iron site. On the other hand, anion substitution, is less often attempted.

Doping fluorine at the oxygen site of the cathode active materials for lithium ion batteries has attracted much attention in recent years[9]. Kubo et al. reported that fluorine doping at the oxygen site of LiNiO$_2$ can improve cycling life for layered structure cathode materials effectively[10]. Furthermore, the crystal structure of these materials was stabilized and the phase transitions during charge and discharge are partially inhibited after fluorine doping. Amatacci et al. observed that doping fluorine at the oxygen site of LiAl$_{0.2}$Mn$_{1.8}$O$_{3.8}$F$_{0.2}$ resulted in improvements in capacity and its retention during 300 cycles [11]. Kim et al. reported that doping

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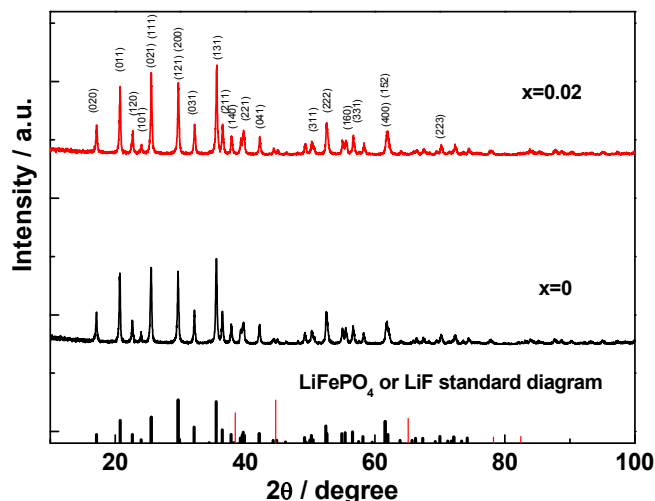Phone: Tel./Fax: +86-10-68918828

Figure 1. XRD pattern of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C (x=0,0.02)

Figure 2. The infrared spectrograms of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C(x = 0,x = 0.02)

fluorine at the oxygen site of Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ can improve high rate capacity and cycle stability, even at high voltage limit of 4.6V[12]. Zhou et al. synthesized F-doped LiFePO4 by using Fe(III) compound as the iron source and polypropylene as the reductive agent and carbon source. they researched on the rate performance(1C,2C,3C) of F-doped LiFePO4 at room temperature, it shows a high capacity(146mAhg^{-1},137 mAhg^{-1},122 mAhg^{-1} respectively)[13]. Besides, fluorine- doping catalyzes the growth of the primary particles, which in turn results in high tap density as well as high volumetric capacity [14].

Therefore, we can see that fluorine-doping is an effective way to improve the electrochemical performance of the cathode materials for lithium ion batteries. In this work, F-doped LiFePO$_4$/C and LiFePO$_4$/C cathode materials were synthesized by two-step solid-state reaction. It is different from the previous study[13] that using Fe(II) compound as the iron source and sucrose as carbon source(traditional carbon source). In order to investigate the influences of fluorine doping on the electrochemical performances of LiFePO$_4$/C especially at low temperature. Powder X-ray diffraction (XRD) measurements, SEM micrographs and FITR were carried out. Charge-discharge tests, cyclic voltammetry tests and ac impedance measurements were used to evaluate the electrochemical performances at room and low temperature.

2. EXPERIMENTAL

2.1. Material preparation

F-doped LiFePO$_4$/C and LiFePO$_4$/C samples were synthesized by two-step solid state reaction. The raw materials were LiOH·H$_2$O, FeC$_2$O$_4$·2H$_2$O, NH$_4$H$_2$PO$_4$ and LiF, and mixed in a stoichiometric ratio. Some sucrose was added in the raw materials as carbon source, whose mass was 10% of the final product. The raw materials were milled (Pulverisette 6, Fritsch) at 450r/min for 12 hours with ethanol as dispersant, then dried and calcined. The precursors were first calcined at 300°C for 5 hours, and then heated at 650°C for 10 hours in a nitrogen atmosphere.
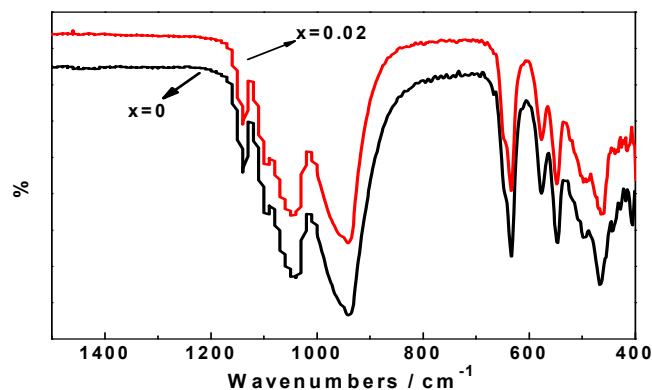
2.2. Structural and morphological characterization

The crystalline phase of the synthesized samples was analyzed by powder x-ray diffraction(XRD, UltimaIV-185 Rigaku) with Cu K radiation. XRD patterns were collected in the range of 10°-80° with a scanning speed of 10°/min. The particle morphology was observed by a scan electron microscopy (SEM, S-3500N Hitachi). fourier transform infrared spectroscopy spectrometer (FTIR, Nicolet 6700 Netzsch) was applied to test whether F- was successfully doped into LiFePO$_4$.

2.3. Electrochemical tests

A mixture of synthesized sample, acetylene black, and PVDF binder with a weight ratio of 75:15:10 was used as the cathode. During electrochemical measurements, lithium metal foil was used as the counter electrode, Celgard 2400 as separator, and 1.0mol/L LiPF$_6$/EC+DMC[V$_{EC}$:V$_{DMC}$=1:1] as the electrolyte solution All cells above were assembled in an argon-filled glove box.

Charge/discharge tests with the range of 2.5 and 4.2V were performed by Land CT2001A battery tester with various texting rates(0.1C-2C ,1C=140 mAg^{-1}) at 25°C and -20°C. The electrochemical impedance measurements were measured in the frequency range of 10^{5}Hz~0.01Hz, the amplititude was set as 5mV. The cyclic voltammetry (CV) tests of the cells were carried out at a scan rates of 0.1mV/s, between 2.2 and 4.5 V. EIS and CV analysis were both conducted on a CHI660C electrochemical work station (Chenhua, Shanghai). For the low temperature performance of the cells, which were first put in the constant temperature box at -20°C for 6h before measurement.

3. RESULTS AND DISCUSSION

3.1. Structural characterization

The effects of different quantity of F on the XRD pattern of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C (x=0, 0.02) are shown in Fig.1. All diffraction

Table 1. Lattice constants of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C

x	a/Å	b/Å	c/Å	V/Å^3
0	10.3610	5.9673	4.7058	290.95
0.02	10.3491	5.9208	4.6997	287.97

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(a)

(b)
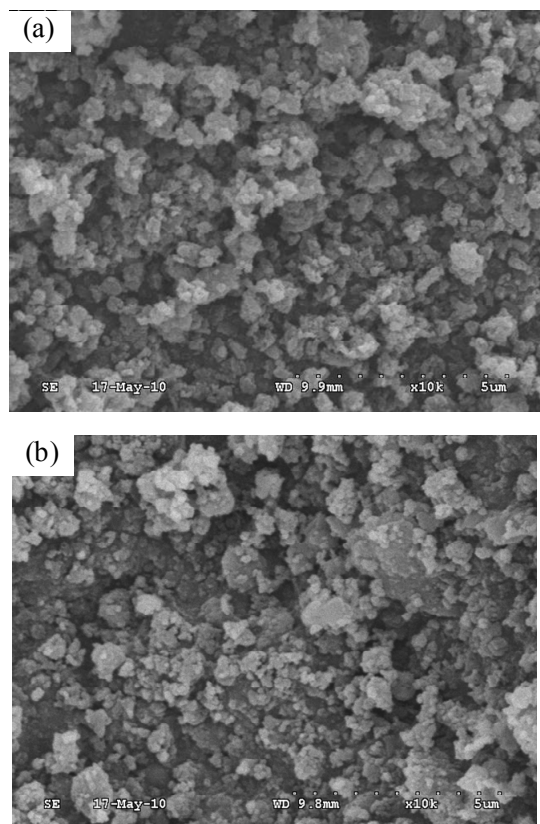
Figure 3. SEM images of LiFe(PO₄)$_{1-x/3}$F$_x$/C (a)x=0; (b)x=0.02

Figure 4. Initial Galvanostatic charge–discharge curves of LiFe-PO4/C at 25°C and -20°C with the rate of 0.1C
(1C = 140mAg^{-1},under the potential window of 2.5-4.2V)

Figure 5. Cycling performances of LiFe(PO₄)$_{1-x/3}$F$_x$/C(x=0,0.02) cathodes with different rates in the voltage range of 2.5- 4.2V at -20°C.

peaks can be well fitted to the standard pattern of LiFePO₄ (PDF Card No.40-1499) without any unexpected phase. Due to F⁻ doped in LiFePO₄ the lattice parameters of a, b and c were shrunken by 0.11%, 0.78% and 0.13% , respectively (Table 1), that is because F ionic radius is smaller than that of O, indicating that F was successfully doped into LiFePO₄ matrix. Another certification of doping successfully is infrared spectroscopic analysis. From Fig.2, the peaks of the set of infrared spectrograms were performed consistently. The characteristic peaks of LiF (at the range of 1380cm^{-1}~1465cm^{-1}[15]) did not exist. The spectral band of LiFe(PO₄)$_{0.993}$F$_{0.02}$/C slightly became strong, indicating that strong electronegativity of F⁻ causes inductive effect which leaded to P-O electron cloud rearrangement, thus improving the intrinsic conductivity. Fig.3 reveals the morphologies of the undoped LiFePO₄/C and F-doped sample, which showed some small morphology changes. So we can get the conclusion that the improved electrochemical performances maynot result from morphology.

3.2. Electrochemical properties

Compared to other cathode materials, LiFePO₄ shows poor electrochemical properties at low temperature. And it is a real challenge to improve it. That maybe related to the structure characteristics [16]. Fig.4 shows the charge and discharge curves with the rate of 0.1C (1C = 140mAg^{-1}) at different temperatures. The discharge platform at 25°C is 0.05 ~ 0.1V higher than at -20°C, while the charge platform was nearly 0.06V lower than that at the low tem-
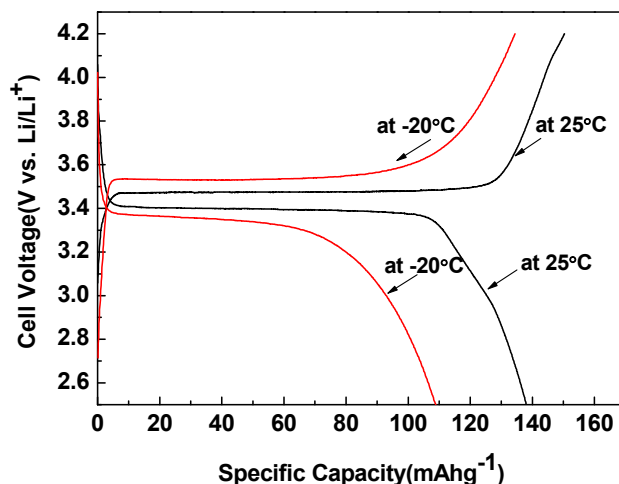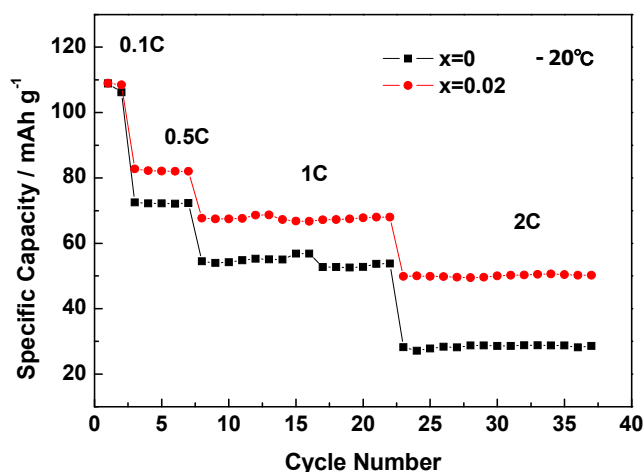
perature, it is because of the increasing of polarization resistance. And that may also affect the initial charge-discharge efficiency (92% at 25°C and 79% at -20°C), the initial discharge capacity of the two conditions showed discrepancy, 138mAhg^{-1} at 25°C while 109mAhg^{-1} at -20°C. That is to say, the capacity of 79% was obtained at low temperature.

From Fig.5 it can be clearly seen that the F-doping can improve the specific capacity especially at the high rates. At -20°C, the capacity of LiFe(PO₄)$_{0.993}$F$_{0.02}$/C was 82mAhg^{-1}, higher than that of undoped material(65mAhg^{-1}) at the rate of 0.5C, and 50mAhg^{-1} (the capacity of undoped material is 28mAhg^{-1}) at 2C. While previous study[17] showed the capacity of LiFePO₄ was 91mAhg^{-1}(0.1C) and 65mAhg^{-1}(0.3C) at -20°C, lower than the F-doped sample. F-doped lithium iron phosphate (LiFe(PO₄)$_{0.993}$F$_{0.02}$/C) showed

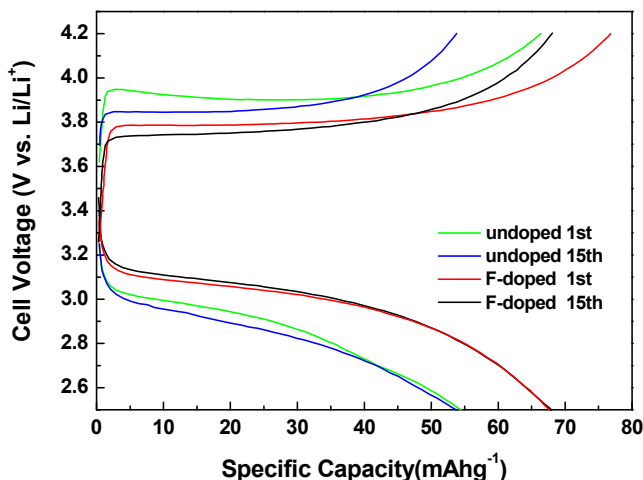Figure 6. Galvanostatic charge–discharge cycle curves for LiFe(PO4)1-x/3Fx/C(x=0,0.02)(current density of 140mAg^{-1}, potential window:2.5V-4.2V, recorded at -20°C)

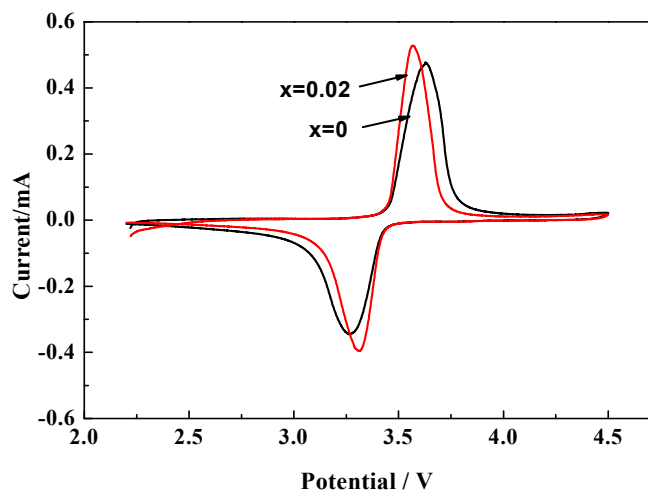Figure 7. Cyclic voltammograms at 25°C of Li cells with cathodes of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C (x=0, 0.02) Scan rate: 0.1mVS^{-1}, voltage range: 2.2–4.5V.

Figure 8. Electrochemical impedance spectra of cathodes: LiFe(PO4)1-x/3Fx/C (x=0, 0.02) at 25°C(a) at -20°C(b)(amplititude was 5mV in the frequency range of 10^5Hz~0.01Hz)

higher capacity than the undoped at the same rate, and revealed a more excellent performance at the aspects of low-temperature and high-rates. Galvanostatic charge–discharge cycle curves (the first cycle and the fifteenth cycle) of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C(x=0,0.02) are shown in Fig.6 at a density of 140mAg^{-1}(1C), under the voltage range of 2.5 ~ 4.2V. Between charge and discharge platform, the polarization of the F-doped sample was lower than undoped one. After 15 cycles of LiFe(PO$_4$)$_{0.993}$F$_{0.02}$/C, the polarization was less and the discharge capacity nearly unchanged(68mAhg^{-1}), while unlike the doped one, the discharge platform of LiFePO$_4$/C at the fifteenth cycle was higher than the one at the first cycle and the discharge capacity was only 54 mAhg^{-1}. So the F doped in LiFePO$_4$ can obviously decrease the polarization and improve the low temperature performance.
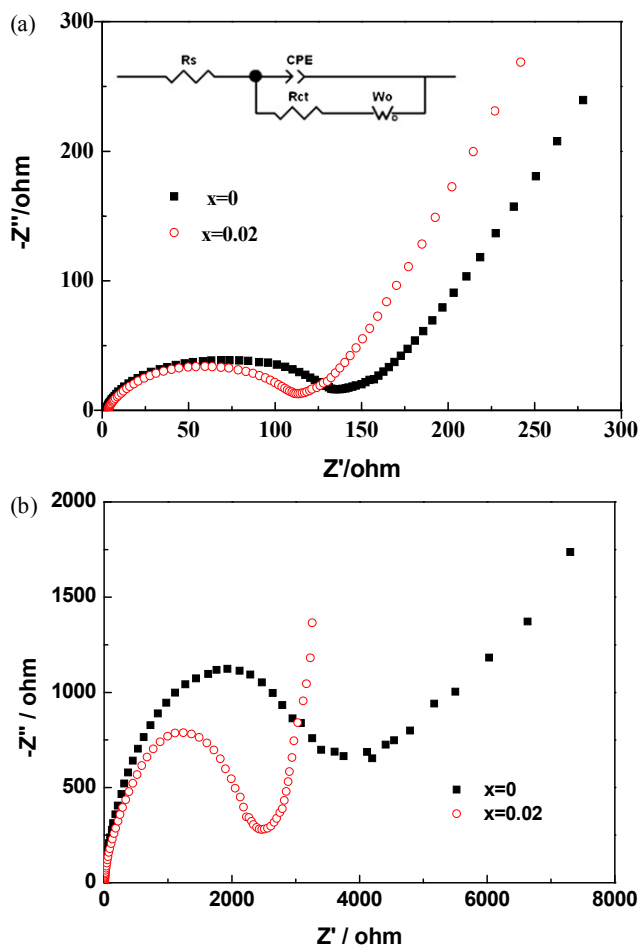
Fig.7 shows the Cyclic voltammograms of doped-F and un-doped LiFePO$_4$/C. The two had the similar and well-symmetrical redox peaks, corresponding to the intercalation and deintercalation of Li$^+$ process respectively. The CV plot of doped material revealed higher peak value, sharper peak shape and maller value of potential interval. The area under the oxidation peak was similar to the reduction one and thus showed that near the same quantity of lithium ions could be reversibly extracted and inserted into the crystal. And as the value of potential interval decreasing, the reversibility was increasing and polarization decreasing. It is in agreement with the electrochemical cycling performance of the LiFe(PO$_4$)$_{1-x/3}$F$_x$/C (x=0,0.02) cathode materials.

Electrochemical impedance spectroscopy (EIS) can be used as a technique to study the electrode kinetics of the cathode. In the literatures, EIS studies have been carried out on LiNi$_{0.5}$Co$_{0.5}$O$_2$,LiNi$_{0.5}$Co$_{0.4}$Al$_{0.1}$O$_2$[18], LiV$_3$O$_8$[19] and LiVPO$_4$F[20], these impedance parameters exhibit a variation as a function of voltage during charge-discharge cycling. Fig.8 presents the Nyquist plots of LiFe(PO$_4$)$_{1-x/3}$F$_x$/C (x=0,0.02), which were carried out at room temperature(a) and-20°C(b), in order to compare the impedance pa-

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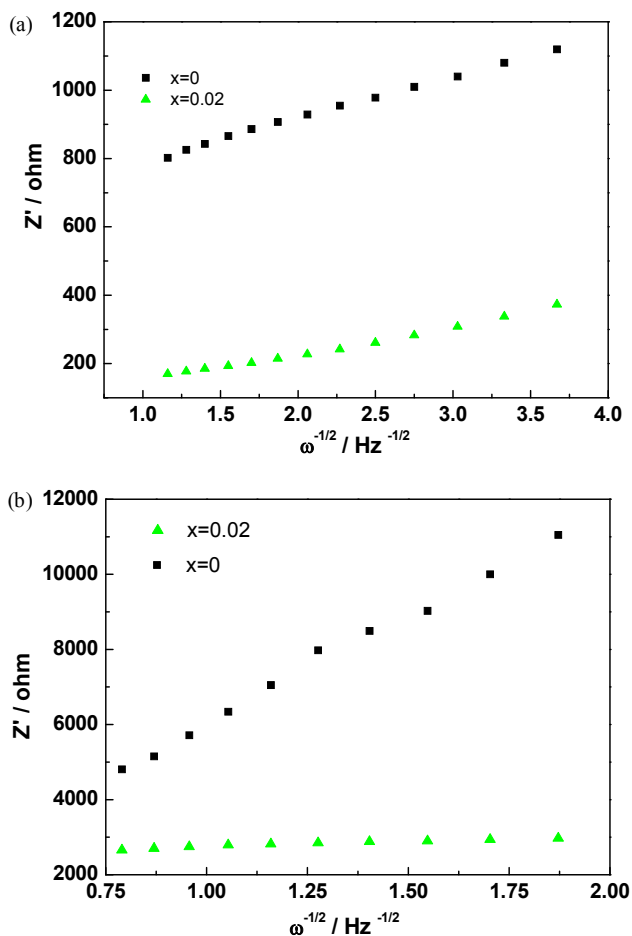/ J. New Mat. Electrochem. Systems*

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(a)

(b)

Figure 9.The relationship between Z_{re} and $\omega^{-1/2}$ at low frequencies for $LiFe(PO_4)_{1-x/3}F_x/C$ (x=0,0.02) at 25°C (a) and at -20°C(b)

rameters in the same condition, the test voltage was set 3.3V. Rs, Rct, CPE, and Wo denote the solution resistance, the charge-transfer resistance, the constant phase angle element and Warburg impedance, respectively. Both of the two sets of EIS all consist of a depressed semicircle at high frequency and a inclined line at low frequency, revealing that the two kinds of materials had the similar impedance characteristic. The resistance of the semicircle was caused by the charge transfer process, which represents the charge transfer resistance. The straight line was attributed to the diffusion of the lithium ions into the bulk of the electrode material, the so-called Warburg diffusion [21]. From Fig.8 (a), the value of Z' was depressed from 117.1Ω to 94Ω via the F-doping. It is obviously that F-doping decrease the electrochemical impedance that may improve the conductivity of electrode material.

By contrast, the impedance value sharply increased when the temperature decreased from 25°Cto -20°C. That is because the SEI film, ionic conductivity and some other factors are sensitive to temperature. The problem may directly affect the low-temperature property. From Fig.8 (b), we can get the same conclusion as Fig.8 (a) that doped lithium iron phosphate showed a lower electrochemical impedance. It is known that the low electrical conductivity and sluggish Li^+ diffusion in $LiFePO_4$ bulk are the main origin of the

poor electrochemical performances [1,22].

Fig.9 shows the relationship between Zre and $\omega^{-0.5}$ at low frequencies for $LiFe(PO_4)_{1-x/3}F_x/C$ (x=0,0.02) at different temperatures. The slope of the fitted line is the Warburg coefficient δ_ω. The value of δ_ω was calculated by using Eq. (1) [21]:

$$Z_{re} = R_e + R_{ct} + \delta_\omega \omega^{-0.5} \tag{1}$$

Both R_e and Rct are kinetics parameters independent of frequency. So δ_ω is the slope for the value of Z_{re} vs. $\omega^{-0.5}$. From the parameters we get above, the diffusion coefficient values of the lithium ions (D) can be obtained from Eq. (2) [21]:

$$D = R^2 T^2 / 2 A^2 F^4 C^2 \sigma^2 \tag{2}$$

Where R is the gas constant (8.314 $Jmol^{-1}K^{-1}$), T is the temperature (K), A is the area of the electrode surface, F is the Faraday's constant (96,500 C mol^{-1}) and C is the molar concentration of Li^+ ions in the electrolyte. Also, the values of the exchange current density (i^0) are calculated with Eq. (3):

$$i^0 = \frac{RT}{nFR_{ct}} \tag{3}$$

The values calculated above are shown in Table 2.

Table 2 shows the parameter varying with temperatures. There is an obvious trend that F-doping sample can perform a better electrochemical properties especially at low temperature. It was reported that the Li^+ ion "effective" diffusion coefficient in olivine $LiFePO_4$ are $\sim 10^{-14}$ cm² s⁻¹ [23]. In our results, diffusion coefficient was improved by 10^{-2} by C-coating. On this basis, F^-, doped in $LiFePO_4/C$, also bettered the diffusion coefficient. And the same trend was happened on the values of exchange current density. The improved Li^+ diffusion may be resulted by high degree of F⁻ ionization.

4. CONCLUSION

The properties of F-doped $LiFePO_4/C$ and $LiFePO_4/C$ at different temperatures have been investigated. XRD analysis shows the formation of phase-pure materials, does not detect the existence of LiF. The infrared spectrograms also support the results. The SEM images reveals some small morphologies changes of the two kinds of the material.

From the comparison of charge and discharge tests at different temperatures, results show that the experimental temperature has an effect on the material capacity. As an example, the capability of $LiFePO_4/C$ decreased from 138mAh g⁻¹ at 25°C to 109mAh g⁻¹ at -20°C at 0.1C. The F-doped material has a higher capability at low temperature, at -20°C, with the rate of 0.5C, the discharge capacity

Table 2. Kinetic parameter of $LiFe(PO_4)_{1-x/3}F_x/C$ (x=0,0.02) at room and low temperature.

Temperature (K)	x	Rct	σ	D(cm²·s⁻¹)	i^0 (mA)
298	0	117.1	122.935	1.600E-12	0.219
	0.02	94	79.473	3.828E-12	0.273
253	0	3181	5475.587	5.813E-16	6.853E-3
	0.02	2223	227.989	3.353E-13	9.807E-3

was 82mAh g^{-1}, higher than that of undoped material(65mAh g^{-1}), and the disparity would increase with the rate of charge-discharge capacity . The Galvanostatic charge–discharge cycle curves reveal that F^{-} doping could decrease the potential difference between the charge and discharge plateau and improve the low temperature performance, which is in agreement with the CV plots. The EIS results were used to determine a series of values such as impedance parameters, Li^{+} diffusion coefficient and exchange current density. All of these reffered above prove that the F-doping improved the electrical conductivity of the material. This doping also decreased the polarization effect and accelerated the process of Li^{+} de-intercalation, therefore, improved the capacity especially at high charge-discharging rate at low temperature.

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