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$^{-1}$, 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.

Keywords: LiFePO$_4$; Fluorine doping; Low-temperature
fluorine at the oxygen site of Li[Ni\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}]O\textsubscript{2} can improve high rate capacity and cycle stability, even at high voltage limit of 4.6 V\cite{12}. Zhou et al. synthesized F-doped LiFePO\textsubscript{4} 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 LiFePO\textsubscript{4} at room temperature, it shows a high capacity (146 mAh/g, 137 mAh/g, 122 mAh/g respectively)\cite{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 \cite{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\textsubscript{4}/C and LiFePO\textsubscript{4}/C cathode materials were synthesized by two-step solid-state reaction. It is different from the previous study\cite{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\textsubscript{4}/C especially at low temperature. Powder X-ray diffraction (XRD) measurements, SEM micrographs and FTIR 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.

\section{EXPERIMENTAL}

\subsection{Material preparation}

F-doped LiFePO\textsubscript{4}/C and LiFePO\textsubscript{4}/C samples were synthesized by two-step solid state reaction. The raw materials were LiOH·H\textsubscript{2}O, FeC\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O, NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{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 450 r/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.

\subsection{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\alpha 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\textsubscript{4}.

\subsection{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 1.0 mol/L LiPF\textsubscript{6}/EC+DMC (VEC:VDMC=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 testing rates (0.1C-2C, 1C=140 mAg\textsuperscript{-1}) at 25°C and -20°C. The electrochemical impedance measurements were measured in the frequency range of 10\textsuperscript{5}–0.01 Hz, the amplitude was set as 5 mV. The cyclic voltammetry (CV) tests of the cells were carried out at a scan rates of 0.1 mV/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 6 h before measurement.

\section{RESULTS AND DISCUSSION}

\subsection{Structural characterization}

The effects of different quantity of F on the XRD pattern of LiFe(PO\textsubscript{4})\textsubscript{1-x}F\textsubscript{x}/C (x=0, 0.02) are shown in Fig. 1. All diffraction patterns were collected in the range of 20°-100° with a scanning speed of 2°/min. The crystal structures of LiFePO\textsubscript{4} or LiF standard diagram were used to evaluate the fluorine-doped LiFePO\textsubscript{4}/C samples. The lattice constants of LiFe(PO\textsubscript{4})\textsubscript{1-x}F\textsubscript{x}/C were calculated by the least-squares method.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
x & a/Å & b/Å & c/Å & V/Å\textsuperscript{3} \\
\hline
0 & 10.3610 & 5.9673 & 4.7058 & 290.95 \\
0.02 & 10.3491 & 5.9208 & 4.6997 & 287.97 \\
\hline
\end{tabular}
\caption{Lattice constants of LiFe(PO\textsubscript{4})\textsubscript{1-x}F\textsubscript{x}/C}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{XRD pattern of LiFe(PO\textsubscript{4})\textsubscript{1-x}F\textsubscript{x}/C (x=0, 0.02)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{The infrared spectrograms of LiFe(PO\textsubscript{4})\textsubscript{1-x}F\textsubscript{x}/C (x = 0, x = 0.02)}
\end{figure}
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 1380 cm⁻¹~1465 cm⁻¹[15]) did not exist. The spectral band of LiFe(PO₄)₀.₉₉₃F₀.₀₂/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 = 140 mAg⁻¹) at different temperatures. The discharge platform at 25°C is 0.05 ~ 0.1 V higher than at -20°C, while the charge platform was nearly 0.06V lower than that at the low temperature, 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, 138 mAhg⁻¹ at 25°C while 109 mAhg⁻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)₀.₉₉₃F₀.₀₂/C was 82 mAhg⁻¹, higher than that of undoped material (65 mAhg⁻¹) at the rate of 0.5C, and 50 mAhg⁻¹ (the capacity of undoped material is 28 mAhg⁻¹) at 2C. While previous study[17] showed the capacity of LiFePO₄ was 91 mAhg⁻¹(0.1C) and 65 mAhg⁻¹(0.3C) at -20°C, lower than the F-doped sample. F-doped lithium iron phosphate (LiFe(PO₄)₀.₉₉₃F₀.₀₂/C) showed

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 = 140 mAg⁻¹) at different temperatures. The discharge platform at 25°C is 0.05 ~ 0.1 V higher than at -20°C, while the charge platform was nearly 0.06V lower than that at the low temperature, 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, 138 mAhg⁻¹ at 25°C while 109 mAhg⁻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)₀.₉₉₃F₀.₀₂/C was 82 mAhg⁻¹, higher than that of undoped material (65 mAhg⁻¹) at the rate of 0.5C, and 50 mAhg⁻¹ (the capacity of undoped material is 28 mAhg⁻¹) at 2C. While previous study[17] showed the capacity of LiFePO₄ was 91 mAhg⁻¹ (0.1C) and 65 mAhg⁻¹ (0.3C) at -20°C, lower than the F-doped sample. F-doped lithium iron phosphate (LiFe(PO₄)₀.₉₉₃F₀.₀₂/C) showed
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$_4$)$_{1-x/3}$Fx/C ($x=0,0.02$) are shown in Fig.6 at a density of 140mA g$^{-1}$, potential window: 2.5V-4.2V, recorded at -20°C.

Fig.6. Galvanostatic charge–discharge cycle curves for LiFe(PO$_4$)$_{1-x/3}$Fx/C ($x=0,0.02$)(current density of 140mA g$^{-1}$, potential window: 2.5V-4.2V, recorded at -20°C)

Fig.7 shows the Cyclic voltammograms of doped-F and undoped 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 smaller value of potential interval. 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$_4$)$_{1-x/3}$Fx/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$_{0.3}$Al$_{0.2}$O$_2$[18], LiV$_2$O$_4$[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$_4$)$_{1-x/3}$Fx/C ($x=0,0.02$), which were carried out at room temperature(a) and -20°C(b), in order to compare the impedance pa-

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

Fig.8. Electrochemical impedance spectra of cathodes: LiFe(PO$_4$)$_{1-x/3}$Fx/C ($x=0,0.02$) at 25°C(a) at -20°C(b) amplitude was 5mV in the frequency range of 10$^3$Hz–0.01Hz.)
Research on Low Temperature Performance of the F-doped LiFePO4/C Cathode Materials

J. New Mat. Electrochem. Systems

Figure 9 shows the relationship between $Z_{re}$ and $\omega^{-0.5}$ at low frequencies for LiFePO4/C (x=0,0.02) at different temperatures. The slope of the fitted line is the Warburg coefficient $\delta$. The value of $\delta$ was calculated by using Eq. (1) [21]:

$$Z_{re} = R_s + R_{ct} + \delta \omega^{-0.5}$$  \hspace{1cm} (1)

Both $R_s$ and $R_{ct}$ are kinetics parameters independent of frequency. $\delta$ 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]:

$$D = R^2 T^2 / 2 A^2 F^4 C^2 \sigma^2$$  \hspace{1cm} (2)

Where $R$ is the gas constant (8.314 J mol$^{-1}$ 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):

$$i^0 = RT / nF R_{ct}$$  \hspace{1cm} (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 LiFePO4 are $\sim 10^{-14}$ cm$^2$ s$^{-1}$ [23]. In our results, diffusion coefficient was improved by 10$^2$ by C-coating. On this basis, F$^+$, doped in LiFePO4/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 LiFePO4/C and LiFePO4/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 LiFePO4/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>
<thead>
<tr>
<th>Temperature (K)</th>
<th>x</th>
<th>Rct</th>
<th>$\sigma$</th>
<th>D(cm$^2$·s$^{-1}$)</th>
<th>$i^0$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0</td>
<td>117.1</td>
<td>122.935</td>
<td>1.600E-12</td>
<td>0.219</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>94</td>
<td>79.473</td>
<td>3.828E-12</td>
<td>0.273</td>
</tr>
<tr>
<td>253</td>
<td>0</td>
<td>3181</td>
<td>5475.587</td>
<td>5.813E-16</td>
<td>6.853E-3</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>2223</td>
<td>227.989</td>
<td>3.353E-13</td>
<td>9.807E-3</td>
</tr>
</tbody>
</table>
was 82 mAh g⁻¹, higher than that of undoped material (65 mAh 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 referred 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.

REFERENCES