Short communication

Structural and electrochemical properties of Cl-doped LiFePO$_4$/C

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A B S T R A C T

Cl-doped LiFePO$_4$/C cathode materials were synthesized through a carbothermal reduction route, and the microstructure and electrochemical performances were systematically studied. Cl-doped LiFePO$_4$/C cathode materials presented a high discharge capacity of ∼90 mAh g^{-1} at the rate of 20 C (3400 mA g^{-1}) at room temperature. Electrochemical impedance spectroscopy and cyclic voltamperometry indicated the optimized electrochemical reaction and Li$^+$ diffusion in the bulk of LiFePO$_4$ due to Cl-doping. The improved Li$^+$ diffusion capability is attributed to the microstructure modification of LiFePO$_4$ via Cl-doping.

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1. Introduction

Among the phosphate-based olivine compounds – LiMPO$_4$ (M = Fe, Mn, Co and Ni), LiFePO$_4$ has been attracting substantial attention as a promising substitute for LiCoO$_2$ [1,2]. LiFePO$_4$ has many advantages over LiCoO$_2$, such as low price, high capacity (∼170 mAh g^{-1}), flat discharge plateau (3.45 V), structural stability during charge and discharge, and low toxicity [1,3,4]. Therefore, LiFePO$_4$ has great potential to be used in Li ion batteries as power sources for electric vehicles (EV), hybrid electric vehicles (HEV), etc. However, it is known that the high-rate performances of pure LiFePO$_4$ are rather poor due to the low intrinsic electrical conductivity [5–10] and the sluggish Li$^+$ diffusion in the bulk of the materials. Various approaches have been adopted to optimize the electrical conductivity and Li$^+$ diffusion capability of LiFePO$_4$ by reducing the particles to sub-micron and even nanoscale [11–14] or doping cations in Fe-sites [15,16].

Up to now, most of efforts have focused on cation doping; however, anion doping is also important for Li ion battery materials. Yin et al. [17] proposed that layered Li$_5$M(PO$_4$)$_2$F$_2$ (M = V or Cr) could be synthesized from α-Li$_3$M$_2$(PO$_4$)$_3$ via F-doping. Sorensen et al. [18] reported that Li was intercalated into Ag$_4$V$_2$O$_6$F$_2$ at 3.5 V, which was 0.25 V higher than that of its counterpart AgV$_3$O$_8$. The voltage increase is ascribed to the presence of fluorine in the structure.

Liao et al. [19] studied the effects of fluorine substitution on the electrochemical performances of LiFePO$_4$/C cathode materials. The F-doped samples showed a discharge capacity of 110 mAh g^{-1} at 10 C. Very recently, Yang et al. [20] have reported the electrochemical performances of Cl-doped LiFePO$_4$/C at 15 C at a high Cl-doping level, which presented a capacity of ∼90 mAh g^{-1}. Accordingly, anion doping is also effective to optimize the electrochemical performances of LiFePO$_4$/C. In the present work, we systematically investigated the structural and electrochemical properties of Cl-doped LiFePO$_4$/C to clarify the origin of the improvement LiFePO$_4$/C due to the Cl-doping.

2. Experimental

2.1. Material preparation

Cl-doped LiFePO$_4$/C was prepared via carbothermal reduction route (CTR) [21]. The starting materials, 0.6895 g LiNO$_3$, 4.0400 g Fe(NO$_3$)$_3$·9H$_2$O, 0.0054 g NH$_4$Cl, 1.1388 g NH$_4$H$_2$PO$_4$ and 1.3077 g glucose, were dissolved in purified water under stirring condition, and then the mixture was dried in an oven at 100 °C. The molar ratio of Li:Fe:P:Cl in the precursor was 1.05:1:0.99:0.01. The synthesis process of Cl-doped LiFePO$_4$/C is similar to that of V-doped LiFePO$_4$/C [22]. Carbon converted from glucose acted as reducing agent in the synthesis process and conducting agent in the resulting sample, whose amount was ca. 5 wt%. The pristine LiFePO$_4$/C sample was also prepared for comparison through the same procedure except the addition of NH$_4$Cl.
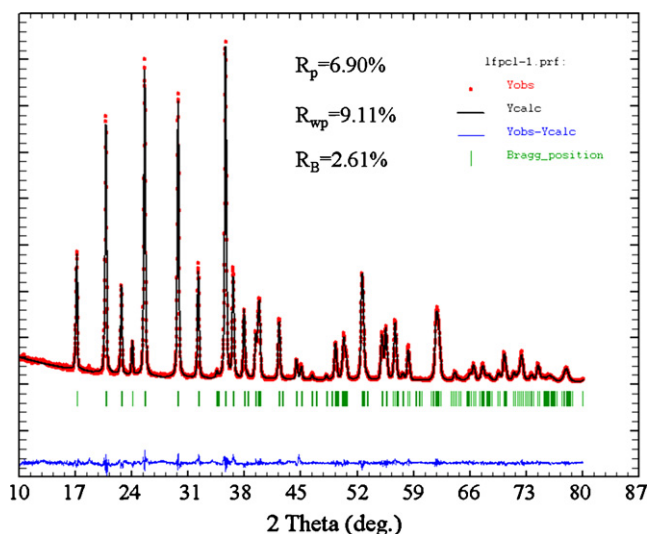
Fig. 1. Rietveld refinement of Cl-doped LiFePO$_4$/C using space group *Pnma*.

2.2. Structural and morphological characterization

The crystalline phases of pristine and Cl-doped LiFePO$_4$/C samples were identified through X-ray diffraction (XRD) under the Rigaku D/MAX III diffractometer with a Cu Kα radiation. For both samples, Rietveld refinement was carried out with the Fullprof program [23]. The morphology of the samples was also observed by using a Hitachi S-3500N scanning electron microscopy (SEM).

2.3. Electrochemical tests

Test cathodes were prepared by mixing 85 wt% active materials with 10 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder. After rolling, the obtained sheets were cut into circular strips of 8 mm in diameter, and about 5.0 mg cm^{-2} active material was loaded on an Al foil. The strips were dried at 100 °C for 8 h. Electrochemical measurements were conducted in Li test cells with lithium foil as counter and reference electrodes. All test cells contained 1.0 mol L^{-1} LiPF$_6$ in ethylene carbonate (EC)–ethyl methyl carbonate (EMC)–dimethyl carbonate (DMC) (1:1:1, v/v/v) as electrolyte and were assembled in an argon-filled glove box. Charge/discharge tests were performed between 2.5 and 4.2 V within a Land CT2001 battery tester at 25 °C.

Cyclic voltammograms (CVs) were performed with the scanning rate from 50 μV s^{-1} to 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was conducted under a Zahner-Elektrik IM6e electrochemical workstation with the frequency range of 10^4 to 10^{-2} Hz and the potential amplitude of 5 mV. The electrical conductivity was measured through linear polarization [22].

3. Results and discussion

3.1. Structural characterization

The Rietveld refinement of Cl-doped LiFePO$_4$/C was performed, and the result is shown in Fig. 1; the doped material is well crystallized in orthorhombic structure without any unexpected phase. Due to the Cl-doping, the lattice parameters of *a*, *b* and *c* are shrunken by 0.25%, 0.17% and 0.28%, respectively (Table 1), implying that Cl$^-$ ions were successfully introduced into LiFePO$_4$ matrix.

Fig. 2 shows the morphologies of the Cl-doped and pristine LiFePO$_4$/C samples. Although the size of primary particles was 100–200 nm for both samples, the pristine LiFePO$_4$/C particles

Table 1
Lattice constants of pristine and Cl-doped LiFePO$_4$/C.

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
LiFePO$_4$/C	10.336	6.006	4.697	291.58
Cl-doped LiFePO$_4$/C	10.310	5.996	4.684	289.56

(Fig. 2a) slightly congregated together compared with the doped ones (Fig. 2b).

3.2. Galvanostatic charge/discharge tests

Fig. 3 shows the galvanostatic charge/discharge curves of the pristine and Cl-doped LiFePO$_4$/C materials measured at 0.1 C (17 mA g^{-1}) between 2.5 and 4.2 V vs. Li$^+$/Li^0. The pristine LiFePO$_4$/C presents a discharge capacity of 132.1 mAh g^{-1}; in contrast, Cl-doped LiFePO$_4$/C exhibits 162 mAh g^{-1}. The galvanostatic charge/discharge cycling capabilities of two samples are shown in Fig. 4. At 20 C rate, a specific capacity of ∼90 mAh g^{-1} was recorded for Cl-doped LiFePO$_4$/C, 54 mAh g^{-1} higher than that of the pristine one. To clarify the improvement of rate performances of LiFePO$_4$/C via Cl-doping, EIS and CV tests were performed.

3.3. EIS and CV measurements

The EIS plots of the pristine and Cl-doped LiFePO$_4$/C are shown in Fig. 5. An equivalent circuit is also constructed to interpret
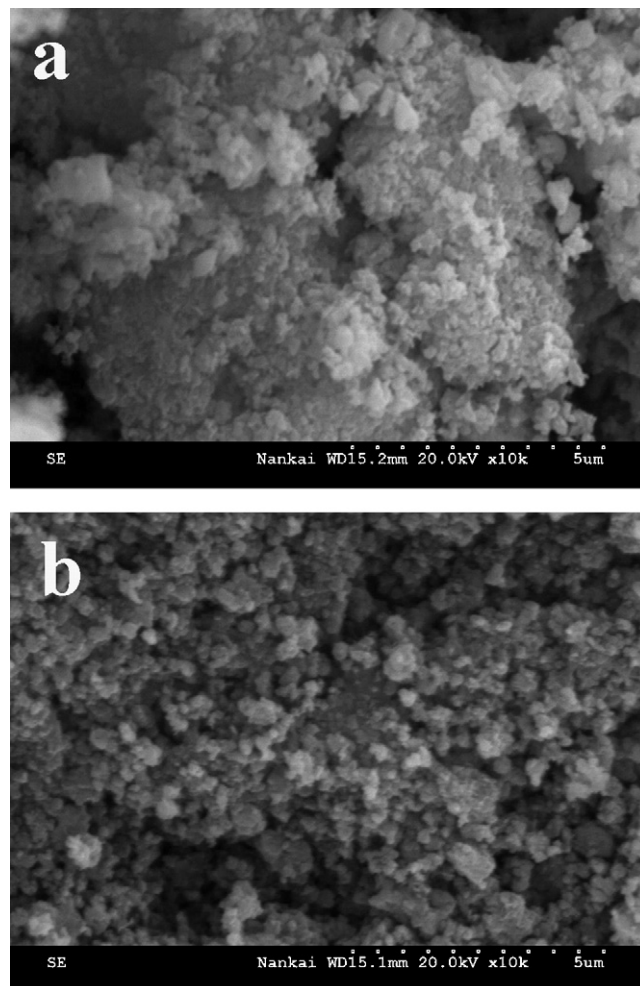

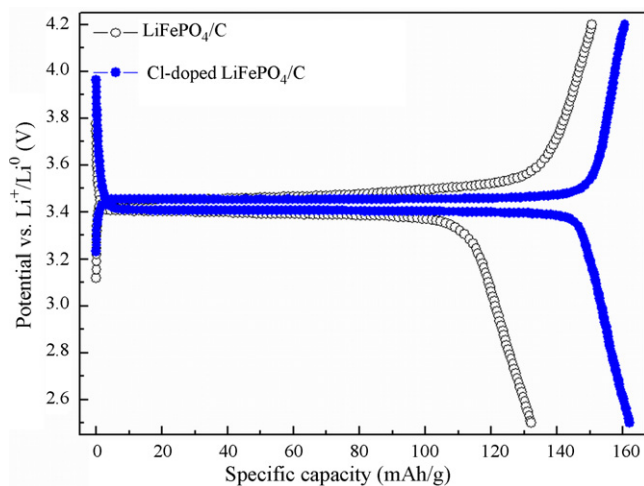**Fig. 2.** SEM images of pristine (a) and Cl-doped LiFePO$_4$/C (b).

Fig. 3. Charge/discharge curves of pristine and Cl-doped LiFePO₄/C cathodes at 0.1 C rate in the range of 2.5–4.2 V at 25 °C.
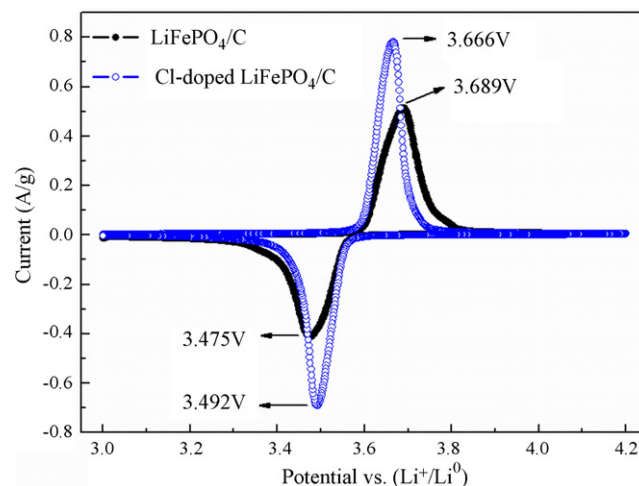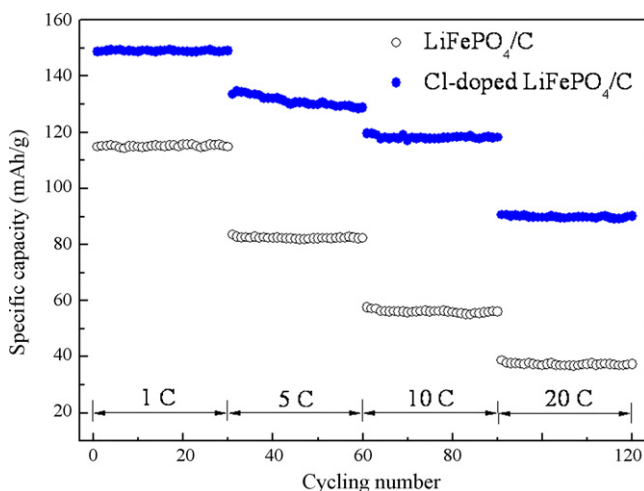

Fig. 4. Cycling performances of pristine and Cl-doped LiFePO₄/C cathodes with different rates in the voltage range of 2.5–4.2 V at 25 °C.
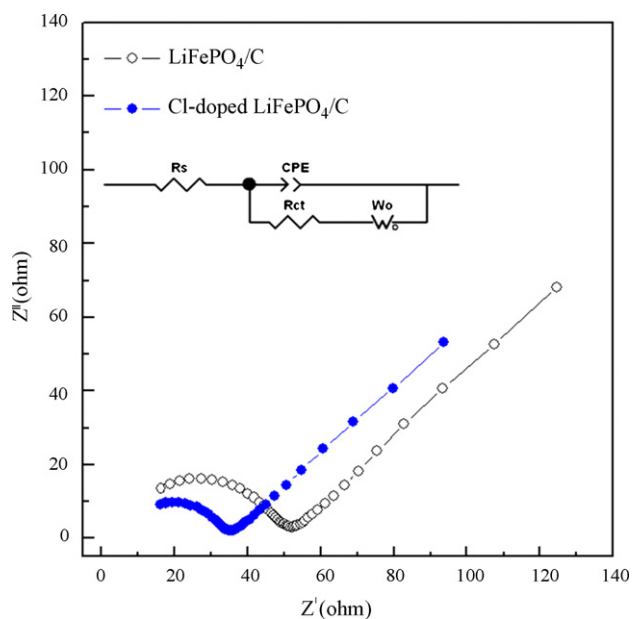

Fig. 5. Electrochemical impedance spectroscopy (EIS) of pristine and Cl-doped LiFePO₄/C within the frequency range of 10^4 Hz to 10 mHz at 25 °C.

Fig. 6. CV curves of pristine and Cl-doped LiFePO₄/C measured with a scanning rate of 100 μV s⁻¹ between 3.0 and 4.2 V at 25 °C.

the impedance spectra (inset in Fig. 5). R_s, R_{ct}, CPE, and W_o denote the solution resistance, the charge-transfer resistance, the constant phase angle element, and Warburg impedance, respectively. Among them, R_{ct} corresponds to the semicircle in the high frequency region, and W_o is related to the straight line in the low frequency region. The EIS plots indicate that the impedance of electrochemical reaction was depressed after Cl-doping. The impedance fitting for Li⁺ diffusion was also depressed from 640.8 to 331.5 Ω via Cl-doping. The depressed impedances of electrochemical reaction and Li⁺ diffusion are both favorable for the improvement of rate performances of LiFePO₄.

Fig. 6 shows the CV curves of the pristine and Cl-doped LiFePO₄/C. The CV profile of the Cl-doped LiFePO₄/C shows sharper oxidation–reduction peaks. After Cl-doping, the peak current density of reduction reaction increased from 0.412 to 0.692 A g⁻¹. Meanwhile, the potential difference between oxidation and reduction peak is depressed from 0.214 to 0.174 V, which implies the improvement of reversibility. The results of CV tests convince us that the kinetics of electrochemical reaction of LiFePO₄/C is improved by Cl-doping. This is in agreement with the EIS results.

It is known that the low electrical conductivity and sluggish Li⁺ diffusion in LiFePO₄ bulk are the main origin of the poor electrochemical performances [1,2,24]. To further clarify the origin of the improved rate capacity, linear polarization and CVs at different scanning rates were performed to determine the electrical conductivity and the Li⁺ "effective" diffusion coefficient of two samples [22,25]. It was reported that the electrical conductivity and the Li⁺ ion "effective" diffusion coefficient in olivine LiFePO₄ are $\sim 10^{-9}$ S cm⁻¹ and $\sim 10^{-14}$ cm² s⁻¹, respectively [26]. As for our results, the electrical conductivity was improved to 10^{-3} to 10^{-2} S cm⁻¹ due to carbon coating on the particles. The electrical conductivity of the doped one is 1.01×10^{-2} S cm⁻¹, a little greater than that of the pristine one (8.51×10^{-3} S cm⁻¹). Meanwhile, the Li⁺ ion "effective" diffusion coefficient of the Cl-doped LiFePO₄/C was optimized to 1.05×10^{-9} cm² s⁻¹, also higher than that of the pristine one (5.55×10^{-10} cm² s⁻¹). Therefore, the electrical conductivity and Li⁺ ion diffusion in the bulk of LiFePO₄ can both be optimized via Cl-doping.

The above results suggest that Cl-doping can further enhance the electrical conductivity of LiFePO₄ on the basis of carbon coating, and optimize the ability of Li⁺ diffusion in the bulk of materials. One explanation for the promotional effects is the enhanced intra-crystal electronic conductivity due to the Cl-doping. As pointed in our previous paper [22], the electrochemical reaction dynam-

Table 2
The atomic coordinates of Cl-doped LiFePO$_4$ from Rietveld refinement.

Atom	x	y	z
Li	0.00000	0.00000	0.00000
Fe	0.28221	0.25000	0.97403
P	0.09529	0.25000	0.41755
O1	0.09736	0.25000	0.74559
O2	0.45491	0.25000	0.21017
O3	0.16607	0.45452	0.28186

Note: Cl can be substituted for O1, O2 or O3 randomly.

Table 3
Interatomic distances in pristine and Cl-doped LiFePO$_4$/C according to Rietveld refinement.

LiFePO$_4$/C				Cl-doped LiFePO$_4$/C			
Atom 1	Atom 2	Counts	$d_{1,2}$ (Å)	Atom 1	Atom 2	Counts	$d_{1,2}$ (Å)
	O2	2×	2.0744		O2	2×	2.0801
Li	O1	2×	2.1616	Li	O1	2×	2.1819
	O3	2×	2.1785		O3	2×	2.1952
	O3	2×	2.0431		O3	2×	2.0634
Fe	O2	1×	2.0962	Fe	O2	1×	2.1127
	O1	1×	2.1879		O1	1×	2.1996
	O3	2×	2.2514		O3	2×	2.2382
	O1	1×	1.5484		O1	1×	1.5068
P	O2	1×	1.5622	P	O2	1×	1.5379
	O3	2×	1.5805		O3	2×	1.5525

ics may not be dominated by the electrical conductivity when it has been improved to as high as 10^{-3} to 10^{-2} S cm^{-1}, and Li$^+$ diffusion in the bulk of materials may play a more important role of rate performances.

To clarify the improvement of Li$^+$ diffusion in Cl-doped LiFePO$_4$/C, Rietveld refinements were conducted. The atomic coordinates of LiFePO$_4$ are shown in Table 2. In the crystal lattice, O tends to be replaced by Cl [27], but there are three kinds of O sites in the lattice; therefore, the three kinds of O-sites may be occupied by Cl separately or randomly. The atomic coordinates of LiFePO$_4$ changed little after Cl-doping. The result of the refinement with random O-site occupation was better than others, which means that the three kinds of O may be replaced randomly by Cl. The interatomic distances between Atom 1 (Li, Fe, P) and Atom 2 (O1, O2, O3) are listed in Table 3 for the Cl-doped LiFePO$_4$/C with random O-site doping and the pristine one. The distances of Li–O vary from 2.074 to 2.195 Å, and those of P–O vary from 1.507 to 1.580 Å. The interatomic distances of Li–O are enlonged by 0.27%, 0.94% and 0.77% for Li–O1, Li–O2 and Li–O3, respectively. This indicates that the extraction of Li from the lattice of LiFePO$_4$ could be facilitated via Cl-doping, since the interaction between Li and O is weakened. Meanwhile, after Cl-doping the lengths of P–O decreased by 2.69%, 1.56% and 1.78% for P–O1, P–O2 and P–O3, respectively, indicating that the framework of LiFePO$_4$ becomes more stable.

4. Conclusion

Cl-doped LiFePO$_4$/C and LiFePO$_4$/C were both prepared via carbothermal reduction route. The relationship between the elec-

trochemical performances and the microstructure changes was investigated through XRD, SEM, EIS and CV. EIS and CV indicated that Cl-doping facilitated the electrochemical reaction during cycling and thus improved the high-rate capability, which mainly resulted from the improvement of the Li$^+$ ion diffusion in the bulk of the material. The optimized Li$^+$ ion diffusion could be attributed to the introduction of Cl$^-$ into the lattice of olivine structure, which resulted in the weakness of Li–O bonds. Similar to the supervalent cation substitution in Li-site or Fe-site, anion doping may be another effective way for optimizing the high-rate electrochemical performances of LiFePO$_4$/C.

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