Non-stoichiometric carbon-coated LiFe$_x$PO$_4$ as cathode materials for high-performance Li-ion batteries†

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A series of non-stoichiometric carbon-coated lithium iron phosphate (LiFe$_x$PO$_4$/C) have been prepared by a solid-state reaction to study the variation of electrochemical performance at different $x$ values.

Characterized by XRD in conjunction with Rietveld refinement, Mössbauer, TEM, Raman, etc., it is indicated that the Li–O bond is elongated in the Fe-poor non-stoichiometric lithium iron phosphate with decreasing $x$ value, while the content of Fe$_2$P and graphitization degree of carbon layer in LiFe$_x$PO$_4$/C samples is associated with the ratio of $x$. The powder electronic conductivity increases from $8.33 \times 10^{-2}$ $\text{S cm}^{-1}$ to $16.67 \times 10^{-2}$ $\text{S cm}^{-1}$ as the $x$ value decreases from 1.04 to 0.98, which is due to a suitable amount of Fe$_2$P and a superior graphitized carbon layer. Among different Fe/Li ratios, LiFe$_{0.98}$PO$_4$/C exhibits the highest rate capability of 163.5 mA h g$^{-1}$ at 0.1C and 93.5 mA h g$^{-1}$ at 20C, as well as the largest diffusion coefficient of $12.6 \times 10^{-14}$ cm$^2$ s$^{-1}$. It is illustrated that the synergy effect of elongated Li–O bonds, moderate Fe$_2$P and graphitized carbon layer results in the high performance of non-stoichiometric LiFe$_x$PO$_4$/C.

LiFe$_{0.98}$M$_{0.02}$PO$_4$ samples with different doped ions M including Mg$^{2+}$, Ni$^{2+}$, Al$^{3+}$, V$^{5+}$, respectively, and found that with the dopant of V$^{5+}$ the average Li–O bond length increased from 2.140 Å of undoped LiFePO$_4$ to 2.157 Å of LiFe$_{0.95}$V$_{0.05}$PO$_4$, which exhibited larger Li-ion diffusion coefficient and higher discharging capacity of 152 mA h g$^{-1}$ at 0.1C and 136 mA h g$^{-1}$ at 1C.$^{28}$ Gao et al. investigated the rate capability of Co-doped LiFe$_{1-x}$Co$_x$PO$_4$ ($x = 0–0.20$) and found that LiFe$_{0.95}$Co$_{0.05}$PO$_4$ with the largest length of Li–O average bonds exhibited the best electrochemical performance of 114.8 mA h g$^{-1}$ at 10C.$^{19}$ Generally, it is considered that the elongation of Li–O bonds can facilitate the Li-ion migration so as to achieve high capacity and decent rate capability.

1. Introduction

Lithium iron phosphate, with the characteristics of high theoretical capacity, inexpensive cost, environmental benignity and safety,$^{1,2}$ except for low electronic conductivity and ionic diffusivity,$^{3,5}$ has attracted much attention as a promising cathode material for Li-ion batteries.$^{6,7}$ Numerous strategies have been adopted to overcome the intrinsic drawbacks of lithium iron phosphate (LiFePO$_4$), involving surface modification with conductive agents,$^{8-10}$ decreasing the particles to nanometer sizes,$^{11-13}$ doping with supervalent ions,$^{14-16}$ etc. In particular, some alien ion dopants have been reported to be capable of tailoring the lattice parameters of LiFePO$_4$ crystals and accelerating the Li-ion migration.$^{17}$ Yang et al. prepared LiFe$_{0.98}$M$_{0.02}$PO$_4$ samples with different doped ions M including Mg$^{2+}$, Ni$^{2+}$, Al$^{3+}$, V$^{5+}$, respectively, and found that with the dopant of V$^{5+}$ the average Li–O bond length increased from 2.140 Å of undoped LiFePO$_4$ to 2.157 Å of LiFe$_{0.95}$V$_{0.05}$PO$_4$, which exhibited larger Li-ion diffusion coefficient and higher discharging capacity of 152 mA h g$^{-1}$ at 0.1C and 136 mA h g$^{-1}$ at 1C.$^{28}$ Gao et al. investigated the rate capability of Co-doped LiFe$_{1-x}$Co$_x$PO$_4$ ($x = 0–0.20$) and found that LiFe$_{0.95}$Co$_{0.05}$PO$_4$ with the largest length of Li–O average bonds exhibited the best electrochemical performance of 114.8 mA h g$^{-1}$ at 10C.$^{19}$ Generally, it is considered that the elongation of Li–O bonds can facilitate the Li-ion migration so as to achieve high capacity and decent rate capability.

The Li-ion diffusion channels in the pristine lithium iron phosphate could be blocked by Li–Fe anti-site defects, as reflected by the atomistic modelling$^{20,21}$ and experimental characterizations including aberration-corrected high-angle annular dark-field STEM,$^{22,23}$ neutron and X-ray diffraction,$^{24}$ etc.$^{25,26}$ To eliminate the negative effect of Li–Fe anti-site defects on the electrochemical performance, the non-stoichiometric lithium iron phosphate have been synthesized recently. For example, Chen et al. prepared Li$_{1.08}$FePO$_4$ by the microwave-assisted hydrothermal method, of which the excess content of Li could inhibit the anti-site defects so as to achieve discharge capacity of 95 mA h g$^{-1}$ at high rate of 10C.$^{27}$ Park et al. synthesized the lithium-excess Li$_{1.05}$Fe$_{0.95}$PO$_4$ by the solid-state reaction, exhibiting 30C rate capability of 78 mA h g$^{-1}$ caused by the elimination of Fe$_2$P defects.$^{28}$ On the other hand, there appeared the literature indicating that the non-stoichiometric lithium

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iron phosphate consisted of certain impurities that played a significant role in the electrochemical performance. For instance, Kang and Ceder reported that the fast ion-conducting surface phase of Li$_3$P$_2$O$_7$ was responsible for the ultrafast charging and discharging performance of LiFe$_{1-\delta}$P$_{1-\gamma}$O$_{4-\sigma}$ (\(\gamma = 0.05\)), which exhibited nearly 100 mA h g$^{-1}$ at 60C. Moreover, Hu et al. prepared LiFe$_{1+2\delta}$P$_{1+2\gamma}$O$_{4+2\sigma}$/C using the solid-state technique, and concluded that the non-stoichiometric sample with 6.5% Fe$_2$P exhibited better rate performance of 73 mA h g$^{-1}$ at 5C, whereas the stoichiometric sample with 4.5% insulating Li$_2$PO$_4$ suffered a rapid decrease of the capacity at 4C. So far no report has been found on the evolution of lattice parameters of the non-stoichiometric lithium iron phosphate crystals, in particular, the variance of Li–O bond length.

In this article, we prepared a series of non-stoichiometric carbon-coated lithium iron phosphate (LiFe$_x$PO$_y$/C) by a solid-state reaction. For the first time, our work is focused on the fine modulation of Li-ion diffusion channels of non-stoichiometric lithium iron phosphate in view of the variation of crystal lattice parameters. In combination with XRD, Mössbauer, TEM, Raman etc., it is indicated that the elongated Li–O bond appears in the Fe-poor non-stoichiometric lithium iron phosphate. Besides, the content of Fe$_3$P and the graphitization degree of carbon layer is associated with the ratio of \(x\). Through analysing the Li-ion diffusion coefficient and the electronic conductivity, it is illustrated that the synergy effect of elongated Li–O bonds, moderate Fe$_3$P and the graphitized carbon layer results in the high performance of non-stoichiometric LiFe$_x$PO$_y$/C.

2. Experimental

2.1. Material preparation

Non-stoichiometric LiFe$_x$PO$_y$/C (\(x = 0.96, 0.98, 1.02, 1.04\)) were synthesized by a solid phase reaction. As a contrast, LiFe$_{1.0}$PO$_4$/C was prepared in the same way. The starting materials of Li$_2$CO$_3$ (99.99%; Shanghai Aladdin Bio-Chem Technology Co., Ltd.), FeC$_2$O$_4$·2H$_2$O (99.99%; Alfa Aesar), NH$_4$H$_2$PO$_4$ (99.99%; Shanghai Aladdin Bio-Chem Technology Co., Ltd.), and glucose (98%; Shanghai Aladdin Bio-Chem Technology Co., Ltd.) were mixed in a mole ratio of \(1 : x : 1 : 0.5\). The glucose was used as a carbon source. In a typical preparation, the reactants were ball-milled in 20 ml of 95 wt% alcohol solution for 6 h then dried under N$_2$ protection at 25°C. The pale yellow sample was ground into powder then preheated at 350°C for 10 h under an N$_2$ atmosphere. Then the obtained black powder precursor was heated at 700°C at a heating rate of 5°C min$^{-1}$, and held for nearly 6 h to form a crystalline phase LiFe$_x$PO$_y$/C. Finally, the prepared powder samples were cooled down to ambient temperature and reground before use. The LiFe$_x$PO$_y$/C samples are denoted in terms of the \(x\) value, e.g., LiFe$_{0.96}$PO$_4$/C is the sample synthesized with the Fe/Li ratio of 0.96. For all the synthesized samples, including LiFe$_{0.90}$PO$_4$/C, LiFe$_{0.98}$PO$_4$/C, LiFe$_{1.0}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C, and LiFe$_{1.04}$PO$_4$/C, the elemental compositions of Li, Fe, P were analysed by Atomic Absorption Spectrometry (AAS), chemical titration, and inductively coupled plasma emission spectrometry (ICP), respectively, as listed in Table S1 in the ESI.† It is indicated that the ratios of Li : Fe : P in all the samples are approximately to the mixing ratio of individual precursor.

2.2. Structural and morphological characterizations

The phase composition were determined by powder XRD (Rigaku D/MAX-2500) in the 2\(\theta\) range from 10° to 65° with a Cu-Kz radiation (\(\lambda = 0.154 \text{ nm}\)) at 40 kV. The scanning step is 4° min$^{-1}$. The refined structural parameters were calculated by GSAS software, which eliminated the effects of impurities. Room-temperature $^{57}$Fe Mössbauer spectra were carried out on a Wissel/MSPCA spectrometer with a $^{57}$Co γ-ray radioactive source. The transmitted photons were measured by a proportional counter. The velocity calibration was conducted with the z-Fe spectrum at room temperature. The morphology of the samples and the thickness of carbon layer were observed by JEM-100CX-II high-resolution transmission electron microscopy (HR-TEM) at 100 kV. Thermogravimetry (TG) analysis was performed on a Netzsch-STA 449C thermal analyser at a heating rate of 10°C min$^{-1}$ from 25°C to 700°C in air to determine the carbon content. Raman spectra were obtained on Renishaw inVia reflex Raman spectrometer equipped with a 532 nm laser. The powder electronic conductivity was detected with four-point probes resistivity measurement system.

2.3. Electrochemical measurements

To test the electrochemical performance, the LiFe$_x$PO$_4$/C powder was mixed with polyvinylidene fluoride (PVDF) and battery grade acetylene black (80:10:10 wt%) in N-methyl pyrrolidone under magnetic stirring for 10 h. Next, the viscous black slurry was spread onto aluminum foil then dried for 12 h at 80°C. The cathode films were punched into 1.3 cm diameter discs after roll-pressing, and dried at 120°C in vacuum oven. The electrolyte was prepared by dissolving 1 M LiPF$_6$ in the mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC). We assembled Li/LiFe$_x$PO$_4$ cells with standard CR2032 coin cell hardware in an argon-filled glove box with H$_2$O and O$_2$ content under 0.1 ppm. The pieces of LiFe$_x$PO$_4$/C cathode were separated by Celgard 2400 from lithium metal anodes. Charge/discharge cycle performance tests were conducted on a LAND-CT2011A battery test system (Wuhan, China) in voltages of 2.0 to 4.2 V at different rates. The electrochemical impedance spectroscopic analysis (EIS) was performed on a CHI660E electrochemical analyser (CH Instruments, China) with a 0.005 V amplitude signal with the frequency range from 0.1 Hz to 100 kHz, and the data was fitted by Z-view software. The cycle voltammetry (CV) test was performed on the electrochemical analyser (CH1604A, CH Instruments, China) at the scan rate of 0.1 mV s$^{-1}$.

3. Results and discussion

3.1. Structural characterization

The XRD patterns (Fig. 1) present the composition of LiFe$_x$PO$_4$/C. For LiFe$_{1.0}$PO$_4$/C with the \(x\) value unequal to 1.0, the major peaks are located similarly to the standard orthorhombic
structure of LiFe$_{1-x}$PO$_4$/C confirmed with ICPDS file (no. 81-1173) except for small peaks of some impurities. In the case of LiFe$_{0.96}$PO$_4$/C, there are peaks of the impurities of Li$_3$PO$_4$ and Fe$_2$P, while other non-stoichiometric samples including LiFe$_{0.98}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C and LiFe$_{1.04}$PO$_4$/C there exist the peaks of Fe$_2$P impurity. Table 1 lists the refined lattice parameters, cell volume $V$, crystal size of particles, and carbon content of LiFe$_{1-x}$PO$_4$/C composites. The crystal size of particles were calculated according to the (311) diffraction peak in Fig. 1 by Scherrer’s equation \(D = \frac{0.9\lambda}{B\cos\theta}\). The average crystalline size is respectively 64.5, 68, 71, 72.3, and 75.1 nm for LiFe$_{0.96}$PO$_4$/C, LiFe$_{0.98}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C, LiFe$_{1.04}$PO$_4$/C, and LiFe$_{1.04}$PO$_4$/C, suggesting that the crystalline size decreases at lower Fe/Li ratio.

To demonstrate the variation in the local structure of LiFe$_{1-x}$PO$_4$/C, the bond length parameters were calculated from Rietveld refinement using powder XRD data at room temperature. Fig. S1 and Table S2† present the detailed results of Rietveld refinement. To make the discussion clear, the oxygen atoms are classified into several groups according to previous literature.\(^{33}\) We focused on the interatomic distances around Fe and Li, displayed in Fig. 2. Table 2 lists the refined bond length parameters of LiFe$_{1-x}$PO$_4$/C. The Li–O(1) bond length of LiFe$_{1.0}$PO$_4$/C is 2.161 Å, whereas it increases to 2.176 Å and 2.184 Å as the x value decreases to 0.98 and 0.96. Similarly, the values of Li–O(2) and Li–O(3) bond lengths rise at x values lower than 1.0. On the other hand, the bond lengths of Fe–O(1), Fe–O(2) and Fe–O(3) decrease with decreasing x values. Combining the results of Tables 1 and 2, it is demonstrated that LiFe$_{0.96}$PO$_4$/C and LiFe$_{0.98}$PO$_4$/C possess the enlarged Li–O bond length as well as the shorter diffusion distance in crystal particles in contrast to LiFe$_{1.0}$PO$_4$/C, which would be promising to achieve enhanced rate capability with improved rate of Li-ion extraction/intercalation.

### 3.2. Mössbauer spectra

In order to determine the amount of impurity phases, the $^{57}$Fe Mössbauer spectra were carried out at room temperature. As shown in Fig. 3, all spectra curves contain two doublets which means two different iron environments in LiFe$_{1-x}$PO$_4$/C. The green curves correspond to octahedral Fe$^{2+}$ in LiFePO$_4$, while the blue curves are due to the presence of Fe$_2$P. For Fe$^{2+}$ in LiFePO$_4$, the isomer shift (IS) of the green symmetrical doublet is 1.23 mm s$^{-1}$, and the quadrupole splitting (QS) is 2.99 mm s$^{-1}$. Compared to the IS and QS values in previous literature, the parameters of the blue doublet are similar to that of Fe$^{3+}$ at 3f site in Fe$_2$P,$^{34,35}$ which is formed due to the following carbon-thermal reduction:

\[
6\text{LiFePO}_4 + 8\text{C} \rightarrow 3\text{Fe}_2\text{P} + 2\text{Li}_3\text{PO}_4 + \text{P}^\uparrow + 8\text{CO}_2 \uparrow \quad (1)
\]

Table 3 lists the Mössbauer parameters and the percentage of iron in different environments. When every mole of Fe$_2$P is generated, there appears 2/3 mole of Li$_3$PO$_4$ according to eqn (1). In order to obtain the accurate content of Fe$_2$P, the fraction of Li$_3$PO$_4$ should be taken into account. The weight and mole percent of Fe$_2$P, Li$_3$PO$_4$ and LiFePO$_4$ in LiFe$_{1-x}$PO$_4$/C samples are listed in Table 4. The calculated weight ratio of Fe$_2$P is 12.82 wt% for LiFe$_{0.98}$PO$_4$/C, 5.34 wt% for LiFe$_{0.96}$PO$_4$/C and 4.95 wt% for LiFe$_{1.02}$PO$_4$/C. Because $^{57}$Fe Mössbauer spectra are highly sensitive to detect both crystalline and non-crystalline phases, the results indicate the existence of small amount of Fe$_2$P impurity in LiFe$_{1.0}$PO$_4$/C, although the peak is not detectable in XRD pattern. Previously, Fe$_2$P was reported to have an amphoteric effect on the electrochemical properties of LiFePO$_4$, suggesting that Fe$_2$P can only serve an electronic conductive function when its concentration is maintained below a critical value.\(^{36}\) Compared to LiFe$_{1.0}$PO$_4$/C, the excessive Fe$_2$P in LiFe$_{1.03}$PO$_4$/C and LiFe$_{1.04}$PO$_4$/C would probably block the one-dimensional diffusion channel and reduce the Li-ion mobility, leading to the degradation of the rate capability and cycle performance, which can be deduced in LiFe$_{0.96}$PO$_4$/C in the same way.
3.3. Morphological characterization

Fig. 4 displays the HR-TEM images of the LiFe\textsubscript{x}PO\textsubscript{4}/C samples. It is indicated that all of the samples consist of similar spherical particles with the particle size distribution around 30–100 nm (Fig. 4(a)–(e)). Some occluded carbon structure appear between particles, which provide a larger contact area on the particle–particle and electrode–electrolyte interface, alleviating the diffusion limitation problems. The thickness of the amorphous carbon coating layer varies between 5–10 nm (Fig. 4(f)–(j)), contributing to improve the electronic conductivity. The carbon content measured by TG analysis are 13.21 wt%, 14.59 wt%, 14.18 wt%, 12.99 wt% and 12.77 wt% for LiFe\textsubscript{0.96}PO\textsubscript{4}/C, LiFe\textsubscript{0.98}PO\textsubscript{4}/C, LiFe\textsubscript{1.0}PO\textsubscript{4}/C, LiFe\textsubscript{1.02}PO\textsubscript{4}/C, and LiFe\textsubscript{1.04}PO\textsubscript{4}/C, respectively (Table S3 and Fig. S2†).

3.4. Raman spectra

Aiming to clarify the conductivity contribution of the carbon layer, Raman spectra were adopted to investigate the degree of carbon disorder on the surface of LiFe\textsubscript{x}PO\textsubscript{4}/C. As Fig. 5 shows, the two dominant peaks around 1350 cm\textsuperscript{-1} and 1580 cm\textsuperscript{-1} represent disorder (D) band and graphitic (G) band, respectively.\textsuperscript{37} The D band is characteristic of the disordered structure ascribed to the breathing vibration at the boundary of graphene sheet, whereas the G band is corresponding to bond stretching of the graphitized carbon atoms.\textsuperscript{38} Graphitized carbon is known to possess better electronic conductivity than disordered carbon. Generally, the peak intensity ratio (I\textsubscript{D}/I\textsubscript{G}) is used to

| Samples                  | Fe\textsuperscript{3+} in Fe\textsubscript{2}P | Li\textsubscript{3}PO\textsubscript{4} | LiFePO\textsubscript{4} |
|--------------------------|---------------------------------------------|--------------------------------------|-------------------------|
|                          | IS (mm s\textsuperscript{-1})                | QS (mm s\textsuperscript{-1})        | \(\Gamma\) (FWHM) mol%  |
| LiFe\textsubscript{0.96}PO\textsubscript{4}/C | 0.5345                                      | 0.5927                               | 0.582                    | 26.1                     | 1.2377          | 2.9951          | 0.408                | 73.9                     |
| LiFe\textsubscript{0.98}PO\textsubscript{4}/C | 0.5474                                      | 0.7505                               | 0.582                    | 11.4                     | 1.2369          | 2.9954          | 0.292                | 88.6                     |
| LiFe\textsubscript{1.0}PO\textsubscript{4}/C  | 0.7761                                      | 0.6655                               | 0.582                    | 10.6                     | 1.2367          | 2.9914          | 0.355                | 89.4                     |
| LiFe\textsubscript{1.02}PO\textsubscript{4}/C | 0.5682                                      | 0.6364                               | 0.582                    | 17.5                     | 1.2370          | 2.9937          | 0.338                | 82.5                     |
| LiFe\textsubscript{1.04}PO\textsubscript{4}/C | 0.6338                                      | 0.6660                               | 0.582                    | 19.4                     | 1.2371          | 2.9936          | 0.394                | 80.6                     |
indicate the graphitization of the carbon layers. As listed in Table 5, the LiFe$_{0.98}$PO$_4$/C shows relatively higher degree of graphitization than the others.

### 3.5. Electrochemical characterizations

Fig. 6 shows the electrochemical performances of LiFe$_x$PO$_4$/C samples. Fig. 6(a) presents the profiles of initial charge/discharge capacity versus potential from 2.2 V to 4.2 V at 0.1C. The flat voltage plateaus from 3.39 V to 3.46 V correspond to the redox reaction between LiFePO$_4$ and FePO$_4$. From the result of Fig. 6(a), the discharge capacities of LiFe$_{0.96}$PO$_4$/C, LiFe$_{0.98}$PO$_4$/C, LiFe$_{0.96}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C, and LiFe$_{1.04}$PO$_4$/C are 157.7 mA h g$^{-1}$, 163.5 mA h g$^{-1}$, 153.7 mA h g$^{-1}$, 148 mA h g$^{-1}$, and 143.5 mA h g$^{-1}$, respectively. The corresponding coulombic efficiencies are calculated as 95.9%, 96.3%, 94.3%, 94.3% and 95%. Furthermore, the rate capability of LiFe$_x$PO$_4$/C are illustrated with five cycles at every rates of 0.1C, 1C, 2C, 5C, 10C and 20C in Fig. 6(b), indicating the superior performance of LiFe$_{0.98}$PO$_4$/C. The loading amount of the active material in the each cathode are 1.07, 1.07, 1.02, 1.06 and 1.08 mg cm$^{-2}$ for LiFe$_{0.96}$PO$_4$/C, LiFe$_{0.98}$PO$_4$/C, LiFe$_{1.0}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C, and LiFe$_{1.04}$PO$_4$/C, respectively. As Fig. 6(c) shows, all of the LiFe$_x$PO$_4$/C samples demonstrate excellent cycle performance at 20C. The capacity retention rates after 100 cycles are 98.8%, 99.2%, 98.7%, 97.4% and 90.2%, respectively. In particular, LiFe$_{0.98}$PO$_4$/C retains 90.9% capacity even after 500 cycles, as shown in Fig. 6(d). It is illustrated that Fe-poor LiFe$_{0.98}$PO$_4$/C exhibits the outstanding discharge capacity, coulombic efficiency and rate capability, which could be attributed to the faster Li-ion migration and enhanced electronic conductivity originated from the elongated Li–O bond lengths, appropriate content of Fe$_2$P and highly graphitized carbon layer on the grain surface. Although LiFe$_{0.96}$PO$_4$/C has the longest Li–O bond length (Table 2), too much content of Fe$_2$P blocks the Li-ion diffusion pathways and hinders Li-ion movement, resulting in an inferior discharge capacity of LiFe$_{0.96}$PO$_4$/C.

The first-around CVs profiles of LiFe$_x$PO$_4$/C are shown in Fig. 7(a). It can be seen that all the CV curves consist of distinct anodic and cathode peaks corresponding to the extraction and insertion process of Li ions, respectively. Among them, LiFe$_{0.98}$PO$_4$/C shows the sharpest redox peaks, implying the superior electrode kinetics. According to the CV curves, it is indicated that the peak potential difference between anodic and cathode peak is 0.145 V for LiFe$_{0.98}$PO$_4$/C, 0.171 V for LiFe$_{0.96}$PO$_4$/C, 0.187 V for LiFe$_{1.0}$PO$_4$/C, 0.201 V for LiFe$_{1.02}$PO$_4$/C, 0.263 V for LiFe$_{1.04}$PO$_4$/C, respectively. Thus, LiFe$_{0.98}$PO$_4$/C exhibits the smallest value of the potential interval and the
The highest peak current in CV curves, suggesting an enhanced electrode reaction reversibility and a better rate capability, which is consistent with the electrochemical performance shown in Fig. 6.

The electrode reaction dynamics and Li-ion diffusion characteristics of LiFe$_x$PO$_4$/C were studied by electrochemical impedance spectroscopy (EIS). Fig. 7(b) displays the concise equivalent circuit model applied to analyse the impedance.
spectra which is shown in Fig. 7(c). Here, $R_\Omega$ refers to the ohmic resistance of electrolyte presented as intercept on the abscissa axis at high frequency. The component CPE (constant phase angle element) reflects the impedance caused by irregular surface structure and energy barrier at mass and charge transfer.

The $R_\text{ct}$ component represents the charge transfer resistance appearing in electrochemical reactions, which includes the resistances derived from particle–particle and electrolyte–electrode contacts, and exhibits as a semicircle within the medium frequency region. The Warburg impedance $Z_W$ is associated with the diffusion kinetics of Li ions in the crystal lattice, corresponding to the inclined line in the low frequency. Furthermore, the Li-ion diffusion coefficient $D$ for each sample can be computed as follows:

$$D = R^2T^2/2A^2n^4F^2C^2\sigma^2$$

where $R$ refers to the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (298 K), $A$ is the surface area of the cathode, $n$ represents the number of electrons per molecule during oxidation, $F$ is the Faraday constant (96 485.333 C mol$^{-1}$), $C$ is the concentration of Li ions, and $\sigma$ represents the Warburg factor connected with $Z'$:

$$Z' = R_\Omega + R_\text{ct} + \sigma\omega^{-1/2}$$

where $R_\Omega$ and $R_\text{ct}$ are the resistance of charge transfer and solution resistance, respectively, and $\sigma$ is the angular frequency ($2\pi$). Fig. 7(d) reflects the relationship between $Z'$ and $\omega^{-1/2}$ in the low-frequency region. The slopes of the individual lines are the outcome of linear least squares fitting, and the scattered points represent the experimental values. The values of $D$ for Li ions in the samples are calculated according to the slope parameters in Fig. 7(d) and eqn (2) and (3). In addition, the powder electronic conductivity were detected by four-point probe methods. Both the simulated and calculated parameters and the value of electronic conductivity of LiFe$_x$PO$_4$/C samples are listed in Table 6.

Table 6 The fitting results of the data given in Fig. 7 using sectionized simulation and the powder electronic conductivity of LiFe$_x$PO$_4$/C detected by four-point probe method

| Sample          | $R_\Omega$ ($\Omega$ cm$^2$) | $R_\text{ct}$ ($\Omega$) | $D_{Li}$ ($\times 10^{-14}$ cm$^2$ s$^{-1}$) | Electronic conductivity ($10^{-2}$ S cm$^{-1}$) |
|-----------------|-------------------------------|---------------------------|--------------------------------------------|-----------------------------------------------|
| LiFe$_{1.0}$PO$_4$/C | 1.077                         | 88.85                     | 8.48                                       | 7.69                                          |
| LiFe$_{0.98}$PO$_4$/C | 1.866                         | 68.78                     | 12.6                                       | 16.67                                         |
| LiFe$_{1.01}$PO$_4$/C | 1.582                         | 101.6                     | 7.38                                       | 14.29                                         |
| LiFe$_{1.02}$PO$_4$/C | 1.700                         | 130.2                     | 7.24                                       | 9.09                                          |
| LiFe$_{1.03}$PO$_4$/C | 1.209                         | 152.3                     | 6.36                                       | 8.33                                          |

Obviously, $R_\text{ct}$ decreases according to the Fe/Li ratio in descending order, except for LiFe$_{0.98}$PO$_4$/C, which shows the lowest charge transfer resistance of 68.78 $\Omega$ and the highest electronic conductivity of 16.67 $\times 10^{-2}$ S cm$^{-1}$. It can be ascribed to the moderate Fe$_2$P and superior graphitization degree of carbon layer. In addition, it was reported that the increase of active sites was represented by a decreasing semicircle diameter and increasing frequency at which the sloping line begins. Here, the EIS data suggest the reason for the better cycle stability and electrochemical performance observed for the LiFe$_{0.98}$PO$_4$/C sample, which exhibits the smallest semicircle diameter. The exchange current density $i_0$ is obtained from $R_\text{ct}$ using eqn (4):

$$i_0 = R\text{f}nF R_\text{ct}$$

where $n$ is the charge transfer number per molecule during intercalation. The value of $i_0$ obtained for the LiFe$_{0.98}$PO$_4$/C sample is 0.37 mA, which is higher than 0.29 mA for LiFe$_{0.96}$PO$_4$/C, 0.25 mA for LiFe$_{1.0}$PO$_4$/C, 0.19 mA for LiFe$_{1.02}$PO$_4$/C and 0.17 mA for LiFe$_{1.04}$PO$_4$/C.

In general, the value of exchange current density is associated with the reversibility of electrode. LiFe$_{0.98}$PO$_4$/C exhibits the higher current density than any of others, which coincides with the optimal battery performance. As shown in Table 6, the value of $D$ for Li ions in the LiFe$_{0.98}$PO$_4$/C sample is calculated as $12.6 \times 10^{-14}$ cm$^2$ s$^{-1}$, which is considerably greater than the values of other samples, which is $8.48 \times 10^{-14}$, $7.38 \times 10^{-14}$, $7.24 \times 10^{-14}$ and $6.36 \times 10^{-14}$ cm$^2$ s$^{-1}$ for LiFe$_{0.98}$PO$_4$/C, LiFe$_{1.0}$PO$_4$/C, LiFe$_{1.02}$PO$_4$/C and LiFe$_{1.03}$PO$_4$/C, respectively. Thus, it is reasonable to conclude that the enlarged Li–O bond lengths in non-stoichiometric Fe-poor LiFe$_{0.98}$PO$_4$/C result in the accelerated Li-ion migration through the LiFePO$_4$ bulk and electrode–electrolyte interface via enhanced Li-ion intercalation/de-intercalation processes, consequently achieving the high electrochemical performance.

4. Conclusions

Non-stoichiometric LiFe$_x$PO$_4$/C ($x = 0.96, 0.98, 1.02, 1.04$) cathode materials have been synthesized by a simple solid-state reaction. Based on the refined lattice parameters, it is indicated that the Fe-poor samples possess the enlarged Li–O bond lengths, facilitating the Li-ion migration. Moreover, Mössbauer spectra show that the content of Fe$_2$P impurity is related to Fe/Li ratio, which enhances the conductivity at low concentration. The graphitization degree of carbon is slightly elevated with high content of carbon. Due to the enlarged Li–O bond length, proper content of Fe$_2$P impurity and relatively high graphitization degree of carbon layer, the Li-ion diffusivity and electronic conductivity of LiFe$_{0.98}$PO$_4$/C are superior to other non-stoichiometric samples. The synergy effect of these factors makes LiFe$_{0.98}$PO$_4$/C exhibit the highest discharge capacity, rate capability, as well as excellent cycle performance. The disclosed
relationship among the crystal lattice parameters, the composition and the electrochemical performance of non-stoichiometric LiFePO4/C provides a pathway to design new material of other type olivine phosphate so as to improve the electrochemical performance.

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