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ORIGINAL PAPER

Improvement of electrochemical properties of $LiFePO_4$/C cathode materials by chlorine doping

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Abstract The olivine-type cathode materials of $LiFePO_4$ were prepared via solid-state reaction under argon atmosphere and doped by chlorine to improve their electrochemical performances. The crystal structure, morphology, and electrochemical properties of the prepared samples were investigated using thermogravimetry–differential scanning calorimetry, X-ray diffraction, Fourier transform infrared, scanning electron microscopy, cyclic voltammetry, and charge–discharge cycle measurements. The result showed that the electrochemical performance of $LiFePO_4$ had been improved by chlorine doping, and the effect of chlorine in lattice was discussed. The heavily doped samples show better electrochemical performance in relative high rates.

Keywords $LiFePO_4$ · Cathode · Lithium ion battery · Dope

Introduction

The emergence of olivine-type cathode materials for lithium ion batteries shed light on researches on novel positive electrode materials to replace $LiCoO_2$. $LiFePO_4$, developed by Goodenough and coworkers in 1997 [1] as a new generation of cathode materials, is one of the most promising candidates. Its advantages include low cost, environmental friendly, good cycle stability, and a relatively high theoretical capacity (170 mAh/g). However, $LiFePO_4$ is still in no position to replace $LiCoO_2$ as the dominant cathode material in commercial world due to its low electric and ion conductivities, which limit the high rate performance of $LiFePO_4$. Several methods have been proposed to improve the electrochemical diffusion kinetics of $LiFePO_4$, such as coating it with conductive particles, doping it with heteroatom, and reducing its size [2–7]. Among these methods, element doping has been considered as an effective way to improve the electronic conductivity of $LiFePO_4$. Many elements have been used to dope $LiFePO_4$ as $Li_{1-X}M_XFePO_4$, and the mechanism has been extensively studied. Similarly, Mg, Mn, Co, and Ni have been used to dope $LiFePO_4$ as $LiFe_{1-X}M_XO_4$ [8–11]. What is more, doping $LiFePO_4$ with anion such as F^- has been carried out and reported satisfactory results in enhancing its electrochemical performance [12], and Cl doping was found to be effective in enhancing electrochemical performance of cathodes such as $LiNi_{0.7}Co_{0.3}O_2$ [13]. In this paper, $LiFe(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03) has been synthesized via low-temperature solid-state method, and the effects of doping on the crystal structure and electrochemical properties of $LiFePO_4$ have been studied in detail.

Experiment

$LiFePO_4$/C was synthesized using CH_3COOLi H_2O, FeC_2O_4 $2H_2O$, and $NH_4H_2PO_4$ as the raw materials in the mole ratio based on the formula of $LiFePO_4$. The starting materials, with certain amount of sucrose, were mixed and ground using pestle and mortar to get a pasty precursor. After that, the materials were decomposed at 350 °C for 5 h in a flow of Ar atmosphere. The decomposed precursor was then pressed into pellets and sintered at different temperature in the same

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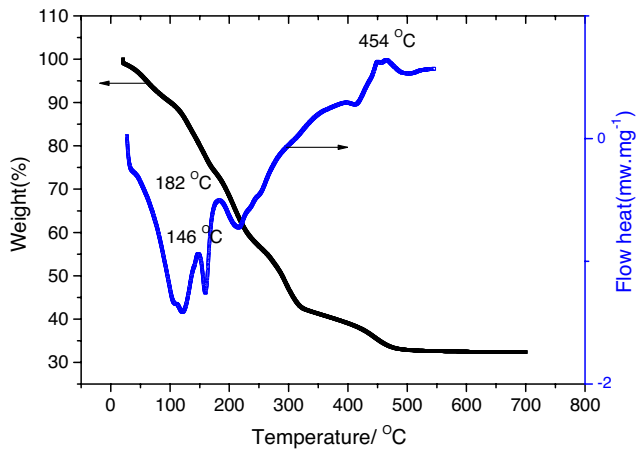

Fig. 1 TG/DSC curves of the $LiFePO_4$/C precursor phase recorded over the temperature range from ambient to 700 °C at a heating rate of 10 °C min^{-1} under argon atmosphere

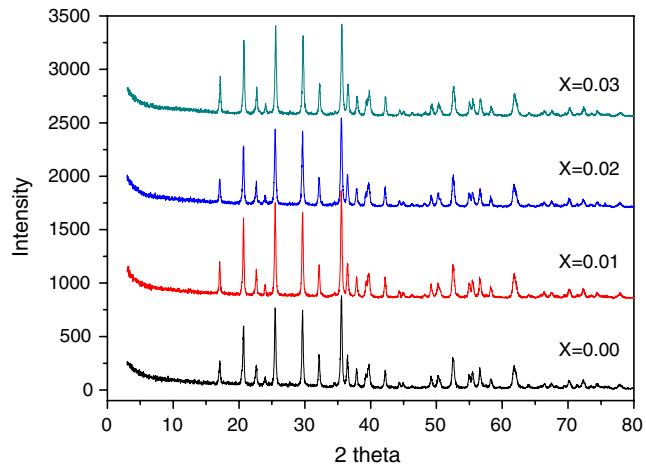

Fig. 3 XRD patterns of LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03)

atmosphere for 12 h. Following the same procedure, LiFe $(PO_4)_{1-X}Cl_{3X}$/C was prepared using LiCl as doping agents, with all agents of analytical reagent degree.

Thermal characterization was performed by thermogravimetry–differential scanning calorimetry (TG/DSC; Netzsch STA 449C, Germany). Heating rate was 10°C min^{-1} from ambient to 700°C in an argon flow using α-Al_2O_3 as the reference material.

The X-ray diffraction (XRD) pattern was obtained by employing D/Max-2500 with Cu Kα radiation at room temperature. The surface morphology of the materials was observed by scanning electron microscopy (JSM 6400, JEOL, Japan).

Fourier transform infrared (FTIR) spectroscopic study was performed on a Perkin-Elmer paragon-500 FTIR spectrophotometer using KBr pellets in the region of 400–2,250 cm^{-1}.

The composite positive electrodes were prepared by pressing a mixture of the active materials, conductive material (acetylene black), and binder (PTFE) in a weight ratio of 85:10:5. The electrolyte was 1 M $LiPF_6$ in a 6:3:1 (volume ratio) mixture of ethylene carbonate, propylene carbonate, and dimethyl carbonate. The cells were assembled in an argon-filled dry box. Charge–discharge tests were performed between 2.0 and 4.2 V. Cyclic voltammetry experiments were performed using a CHI600 Electrochemical Workstation at a scan rate of 0.1 mV/s. All tests were performed at room temperature.

Result and discussion

Figure 1 shows the thermal analysis of the transformation from precursor to $LiFePO_4$/C. TG/DSC curves show that

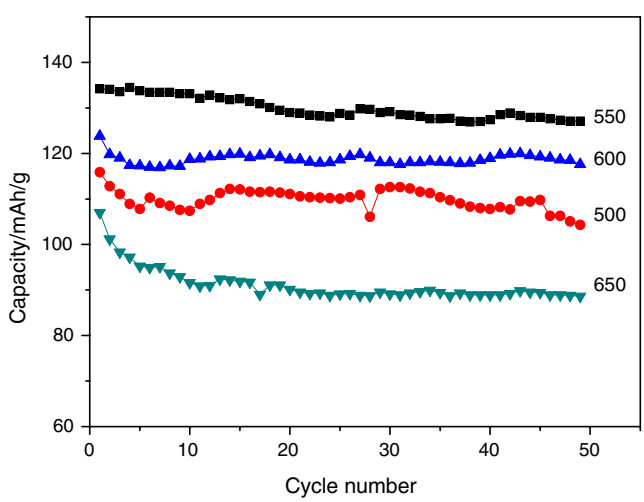

Fig. 2 Cycle performance of $LiFePO_4$/C sintered at different temperatures

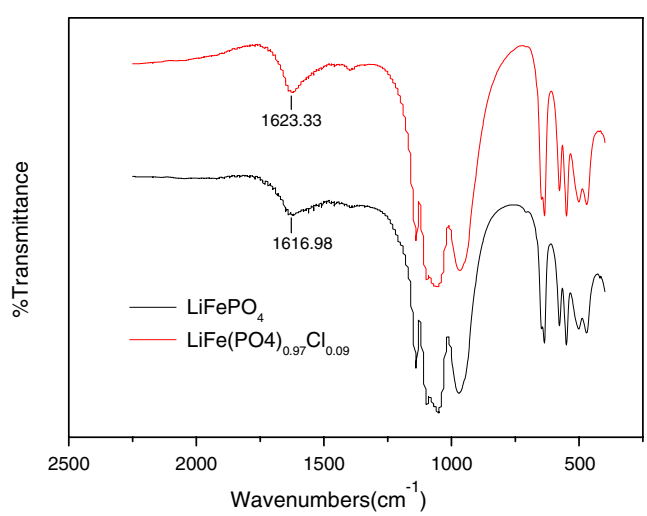

Fig. 4 FTIR spectrum of $LiFePO_4$/C and LiFe $(PO_4)_{0.97}Cl_{0.09}$/C

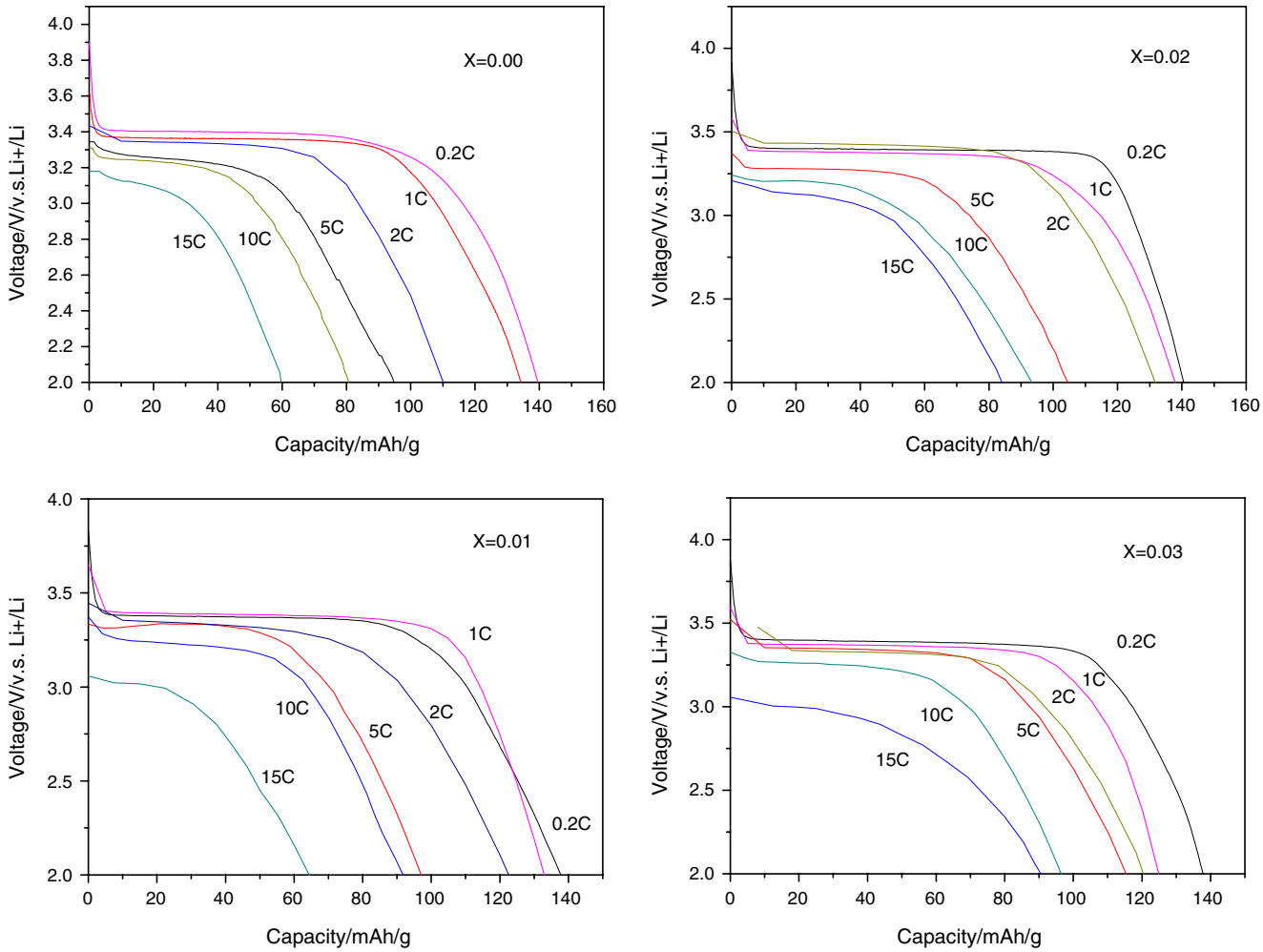

Fig. 5 First discharge curves at various C rates of the LiFe $(PO4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03)

the weight loss of the precursor started from room temperature and continued until 460 °C, which indicates that the reaction can be completed before 460 °C. The weight loss between room temperature and 320 °C (Δm= 58%), which accounts for the major weight loss of the precursor, is due to the evaporation of crystal water in the mixed precursor and the decomposition of salts. The large amount of water evaporation and gas generated during this stage prevent small particles from agglomeration. The weight loss between 320 °C and 460 °C (Δm=19.5%) might be ascribed to the formation of $LiFePO_4$/C. The endothermic peak which appeared at 454 °C was lower than that of the traditional solid state method, which implies that the pasty precursor can reduce the synthesis temperature.

Figure 2 shows the cycling performances of the samples obtained from different sintering temperatures at 1C rate (1C=150 mAh/g). The sample sintered at 550 °C exhibited the best performance—the initial discharge capacity was 134.2 mAh/g and was 127.1 mAh/g after 50 cycles. On the other hand, samples obtained from 500 °C, 600 °C, and 650 °C showed initial discharge capacities of 115.9, 123.8, and 107 mAh/g and after 50 cycles dropped to 104.3, 117.6, and 88.6 mAh/g, respectively. The fading in capacity can be explained as follows: relatively high sintering temperatures (600 °C, 650 °C) allow $LiFePO_4$ particles to

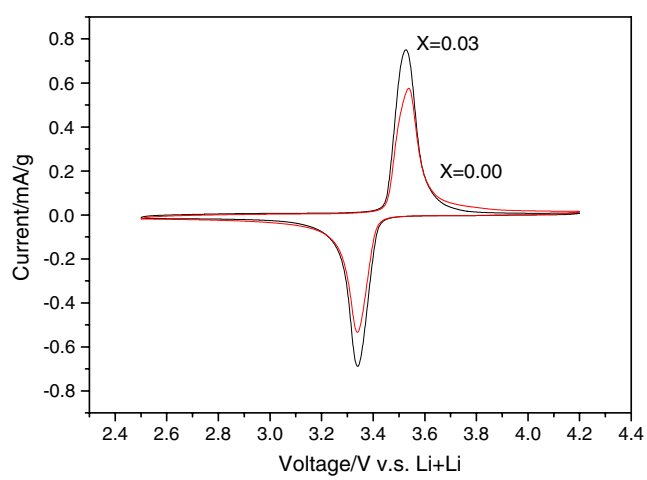

Fig. 6 Cyclic voltammograms for the LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.03)

grow into bigger particles, therefore limiting lithium ion's intercalation and deintercalation. However, relatively low sintering temperature (500 °C) cannot promise a complete crystallization of olivine-type $LiFePO_4$ and therefore resulted in low discharge capacity. As a result, we choose 550 °C as sintering temperature and synthesize LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03).

Figure 3 shows the X-ray diffraction (XRD) patterns of the prepared LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03) samples. All the peaks of the samples fit the olivine structure very well without any impurity detected. For the Cl substitution samples, there is a slight shift to the lower 2θ angle of the diffraction peaks, which indicate larger lattice parameters. The observations above prove that chlorine was incorporated into the structure without altering its structure.

The FTIR spectra of $LiFePO_4$/C and LiFe $(PO_4)_{0.97}Cl_{0.09}$/C are shown in Fig. 4. The local environment of cations in a lattice of close-packed oxygen atoms can be studied by FTIR spectrum because of the sensitivity of vibration modes of cations [14]. Here, this method was used to investigate the effect of chlorine doping on the structure of $LiFePO_4$, and several observations could be made. Firstly, the characteristic peaks of LiCl (as starting material) of 460 and 335 cm^{-1} are not found in Fig. 4, which indicates that LiCl was incorporated into the lattice in the synthesis of $LiFePO_4$ and not left unreacted as a single molecular. Furthermore, the chlorine's effect in lattice can be analyzed. The tetrahedral PO_4^{3-} ion has its fundamental stretching vibrational frequencies between 1,600 and 1,300 cm^{-1}. LiFe $(PO_4)_{0.97}Cl_{0.09}$/C has a peak at 1,623.33 cm^{-1} which attributes to PO_4^{3-} (ν_1), while the pristine $LiFePO_4$/C has a peak at 1,616.98 cm^{-1}. The red shift indicates that chlorine has an inductive effect in lattice; this may introduce rearrangement of electric cloud in PO_4^{3-} ion and therefore enhance the conductivity of the material.

Figure 5 compares the first discharge capacity at various C rates of the LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03) samples. The cells were tested between 2.0 and 4.2 V and recharged at 1C rate. From the curves, it can be seen that the discharge capacity of the undoped sample was severely affected by C rates—the capacity dropped from 137.8 mAh/g (1C) to 60 mAh/g (15C). When X=0.02, the sample delivered 138 mAh/g at 1C rate, which is the highest discharge capacity among these samples. When the rate increased, the heavily doped samples showed better electrochemical performance. For instance, when X=0.03, the sample delivered 97.6 mAh/g at 10C and 92.3 mAh/g at 15C, but a lower initial discharge capacity of 124.9 mAh/g at 1C rate compared to that of the sample with X=0.02. These results are in line with those from [12]. The rate performance was better in doped samples where the polarization was alleviated by chlorine doping. This assumption can be proven by the CV test below.

The electrochemical properties of the samples can be further understood by cyclic voltammetry curves. The CV profiles of LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.03) in the first cycle (shown in Fig. 6) show that anodic and cathodic peak intensities of $LiFe(PO_4)_{0.97}Cl_{0.09}$/C are higher than those of $LiFePO_4$/C. The peak separation of former (0.18 V) is also closer than that of the latter (0.21 V). It can be concluded that the doping of chlorine can increase the conductivity of $LiFePO_4$/C and facilitate the intercalation and deintercalation of lithium ions.

Conclusions

Olivine-type LiFe $(PO_4)_{1-X}Cl_{3X}$/C (X=0.00, 0.01, 0.02, 0.03) samples were prepared by low-temperature solid-state method, and the effects chlorine doping have on the electrochemical behaviors of $LiFePO_4$/C were investigated. Low sintering temperature reduces the particle size and chlorine doping increases conductivity which can facilitate the Li^+ diffusion between $LiFePO_4$ phase and $FePO_4$ phase.

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