# Synthesis and Characterization of Ti⁴⁺-Doped LiFePO₄ Composite Cathode Materials

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$LiFe_{0.98}Ti_{0.02}PO_4$/C composite cathode material was synthesized from nanocrystalline $Fe_2O_3$ through mechanical activation process, followed by carbothermal reduction reaction in the presence of $Li_2CO_3$ and $NH_4H_2PO_4$. The composition, crystalline structure and morphology of the prepared powders were investigated with XRD and SEM. Electrochemical tests indicated that the Ti-doping of carbon-coated $LiFePO_4$ did not affect the olivine structure of the lithium iron phosphate but obviously improve its discharge capacity and rate capability, which would be ascribed to the increased and larger lattice parameters and electronic conductivity.

Keywords: Carbothermal method, $LiFePO_4$, $Fe_2O_3$, Ti-doping.

## INTRODUCTION

Olivine-type $LiFePO_4$ has been recognized as one of the most promising cathode materials for large format lithium batteries, due to its high theoretic capacity (170 mAh/g), less expensive, better security and environmental benign characteristics[1]. However, there are still some drawbacks of this material, such as low electronic conductivity and poor performance of high-rate capability, which are in need to be improved before its industrialization. The ways of doping supervalent cations, synthesizing nanocrystalline grains and coating electronic conductive carbon have been regarded as effective methods to improve electronic conductivity and Li⁺ diffusion rate[2,3] of $LiFePO_4$.

It is reported that Ti-doped $LiFePO_4$ exhibits a high-rate lithium electrode performance and good cycle ability, because the doped Ti converts the structure of $LiFePO_4$ to a two-phase material[4]. In present study, Ti-doped $LiFePO_4$/C composite powder was synthesized by a combination of mechanical activation method and carbothermal reduction reaction. The results indicated that the $LiFe_{0.98}Ti_{0.02}PO_4$/C materials exhibited improved electroche- mical performances.

## EXPERIMENTAL

Ti-doped $LiFePO_4$ composite cathode materials were synthesized with the starting materials of nanocrystalline $Fe_2O_3$ (99.9 %), $Li_2CO_3$ (97.5 %), $NH_4H_2PO_4$ (99.5 %), nano-size $TiO_2$ (99.9 %) and sucrose (35 wt % to the total amount of $LiFePO_4$ materials) being both the organic carbon source and

reducing agent. All the starting materials were put into a stainless steel cylindrical container with zirconia ball (ball-to-powder weight ratio of 10:2) and ground in a Fritsch Pulversette-6 planetary ball mill for 4 h in absolute ethanol condition at a rotation speed of 350 rpm. The mixture was initially dried at 80 °C, grounded in an agate pestle and mortar by hand and then calcined at 700 °C for 18 h in a tube furnace under flow argon atmosphere with the heating rate of 10 °C/min.The $LiFePO_4$/C was synthesized according to following the same technique but without $TiO_2$ added.

The phases in the product were characterized by X-ray diffraction analysis (XRD, X'Pert PRO) with the CuK$_\alpha$ radiation. The microstructure of the product was observed by scanning electron microscopy (SEM, QUANTA-2000).

The composite cathodes were prepared by mixing with the prepared powders, carbon black (99.99 %) and polyvinylidene flouoride (PVDF) in the weight ratio of 85:10:5 and with adequate amount of N-methyl-2-pyrrolidone (NMP) for turning into slurries. After being coated on Al foil, cathode disks with diameter of 10 mm were prepared by drying and punching. The prepared cathodes were assembled into coin-type cells with Li anode, the Celgard 2400 being the separator and 1 M LiPF6 in EC-PC-DEC (volume ratio of 1:1:1) electrolyte (Tomiyama, Japan) in an argon-filled glove box. The coin-type cell was then measured by Land-CT2001A (Land, Wuhan). Electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) performance of the cell were measured and recorded *via* PARSTAT 2273 (Priceton, USA). The amplitude of AC signal was 5 mV within the frequency

range between 100 kHz and 0.1 Hz and the scan rate of cyclic voltammogram was 0.10.1 mV/s.

## RESULTS AND DISCUSSION

Fig. 1A shows the XRD patterns of the samples $LiFe_{0.98}Ti_{0.02}PO_4/C$. The XRD patterns of the samples agree very well with that of phospho-olivine $LiFePO_4$ (JCPDS 019-0721) and no Ti entity or other impurity phase was detected. The product has narrow diffraction peaks indicating a good crystallinity degree. Gravimetric analysis result shows that the carbon content is 3.83 wt % in $LiFe_{0.98}Ti_{0.02}PO_4/C$. Nevertheless, there is no evidence of carbonaceous or carbon phase in the diffraction patterns, probably due to its low content and/or its amorphous attributes.
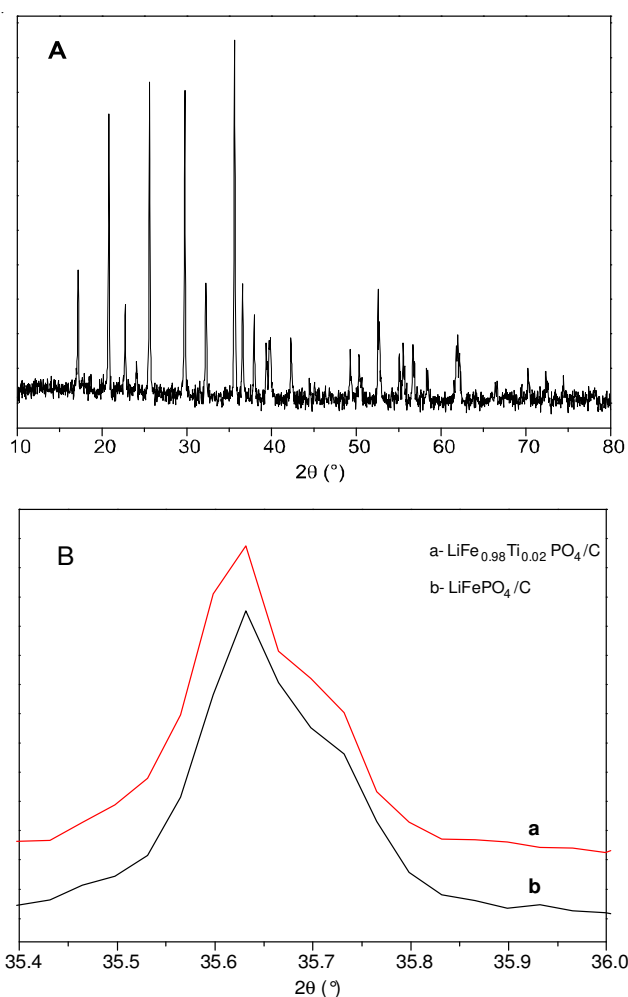


Fig. 1.  XRD patterns of (A) $LiFe_{0.98}Ti_{0.02}PO_4/C$ and (B) amplifed (131) peak of $LiFe_{0.98}Ti_{0.02}PO_4/C$ and $LiFePO_4/C$

Fig.1B exhibits the amplifed patterns in the $2\theta$ range of 35.4-36° for the Ti doping materials and $LiFePO_4/C$ without Ti doping process. A slightly shift to the higher $2\theta$ angle of the diffraction peaks was observed as the Ti doped, compared with the $LiFePO_4/C$ without Ti doping process. According to the equation of Prague and Sherrer, when the sites of peak shifted to high angle, interplanar spacing d would like to decrease; besides, the crystallite size D of the dopant solid solutions may decreased, which was indicated by the increase of breadth of half high of diffraction peaks.

The calculated lattice parameters of $LiFe_{0.98}Ti_{0.02}PO_4/C$ are shown in Table-1. Significant increases in parameters a, b and c are found when 2 mol % of $Fe^{2+}$ ions are substituted by $Ti^{4+}$ ions. These results seems not to be consistent with the expected results that the lattice parameters decrease with $Ti^{4+}$ substitution for $Fe^{2+}$ ions[4], but may support the suggestion of Islam *et al.*[5] that $LiFePO_4$ is not tolerant with aliovalent doping on energetic grounds. $Ti^{4+}$ ions do not occupy $Fe^{2+}$ sites and the occupancy of $Ti^{4+}$ ions is still not clear but results in the enlargement of lattice parameters, which may enhance the diffusivity of $Li^+$ ions in olivine structure, as suggested by previous reports[5,6].

TABLE-1
LATTICE PARAMETERS OF $LiFe_{0.98}Ti_{0.02}PO_4/C$
AND $LiFePO_4/C$ POWDERS

| Sample | A(Å) | B(Å) | C(Å) |
|---|---|---|---|
| $LiFePO_4/C$ | 5.989 | 10.297 | 4.670 |
| $LiFe_{0.98}Ti_{0.02}PO_4/C$ | 6.0349 | 10.374 | 4.693 |

Fig. 2 shows SEM images of $LiFePO_4/C$ (Fig. 2a) and $LiFe_{0.98}Ti_{0.02}PO_4/C$ (Fig. 2b). SEM result indicates that the surface of particle turns sleeker and less granular and displays similar spheric particle with a good dispersion. Besides, the distribution of particle size of the samples is uniform. It is obvious that these factors are helpful to increase the tap density of the powder materials. Furthermore, the size of single grain has a great effect on the electrochemical performance of $LiFePO_4$ in the diffusion mechanism of lithium ion and electron through the interface of $LiFePO_4/FePO_4$ in the electrode process. Thus, for the pure $LiFePO_4$ samples, the reversible capacity would be decreased rapidly with the increase of single crystal size. The powders of b are composed of well-dispersed secondary particles which are slightly agglomerated and show a small quantity of fragments, where the residual carbon introduced by the decomposition of sucrose is distributed around the powders. The average particle size of two samples is less than 300 nm. The reduction of particle size can be related to the nanocrystalline precursor materials produced by ball milling and carbon introduced *in situ* able to interfere with the coalescence of the grains[7], which is conducive to shorten the lithium diffusion distance.
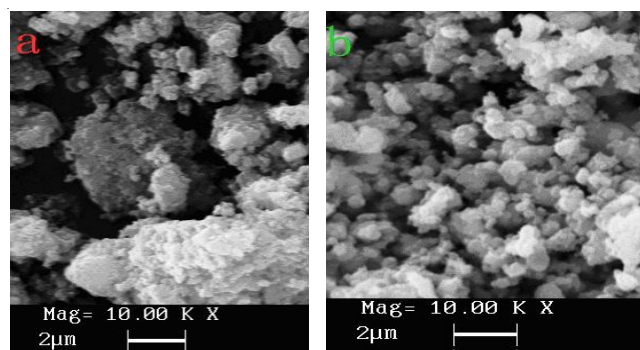


Fig. 2. SEM images of: (a) $LiFePO_4/C$ and (b) $LiFe_{0.98}Ti_{0.02}PO_4/C$

**Electrochemical characterization:** Fig. 3 shows the initial charge and discharge curves of $LiFe_{0.98}Ti_{0.02}PO_4/C$ sample and the relationship between capacity and discharge

rate of the LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C. The electrode exhibits a very flat charge and discharge plateaus and the initial discharge capacity is 158.63 mAh/g at 0.2 C rate. At a high rate of 2C, 81.6 % of the theoretical capacity is accessible to doped sample, so it is clear that the Ti-doped composite material not only increases the specific capacity, but also greatly improves the rate capability. The increase of electrochemical properties should be probably related to the improved mobility of Li$^+$ ion resulting from weakened Li-O interaction as well as to the enhanced Fe-O and P-O by doping. The better lattice structures and smaller particle size may also result in good cycle life.

The cyclic voltammograms of the LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C composite are shown in Fig. 4. Only a pair of anodic and cathodic peaks is observed due to the Fe$^{2+}$/Fe$^{3+}$ redox reaction accompanying Li$^+$ insertion and extraction. The anodic peak represents the oxidation of Fe$^{2+}$ to Fe$^{3+}$, while the cathodic peak is due to the reduction of Fe$^{3+}$ to Fe$^{2+}$. The symmetrical sharp redox peaks imply that kinetics of the lithium diffusion is powerful in the LiFePO$_4$ structure with better reversibility for lithium intercalation/deintercalation, demonstrating less ohmic polarization.
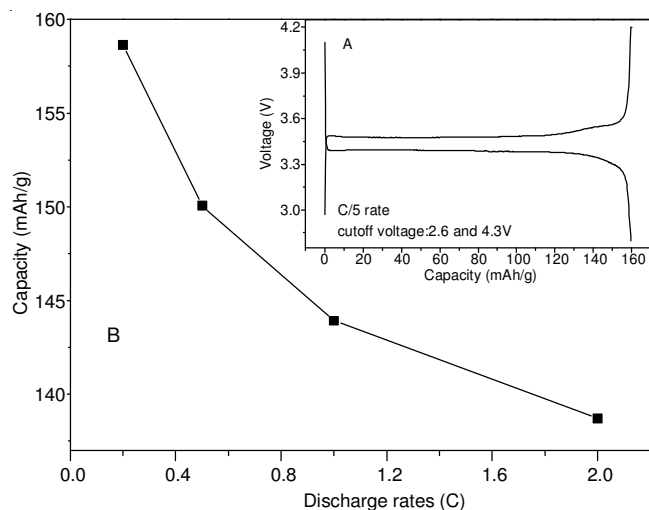
The cyclic voltammetric peak currents (I$_p$) during anodic scans are used to evaluate the Li$^+$ diffusion coefficient[8] (D) and applied to the following eqn:

$$I_p = 0.4463 \times F^{3/2} \times S \times n^{3/2} \times CLi \times R^{-1/2} \times T^{1/2} \times D^{1/2} \times v^{1/2} \quad (1)$$

In the equation, F is the Faraday constant, S is the electrode area (cm$^2$), n is the charge transfer number (1 in our case), CLi is the Li-ion concentration in LiFePO$_4$ (mol/cm$^3$), R is the gas constant, T is the absolute temperature (K), v is the potential scan rate (V/s ), I$_p$ is for units of amperes and (D) is for units of cm$^2$/s. The scan rates used to calculate (D) are 0.1,0.25,0.5,1 and 1.5 mV/s and the peak current (I$_p$) shows a linear relationship with square root of the scan rates(v$^{1/2}$), indicating a diffusion-controlled process. Using the above equation, the Li$^+$ diffusion coefficient of the LiFe$_{0.98}$Ti$_{0.02}$PO$_4$ composite is $6.9 \times 10^{-10}$ cm$^2$/s, whose order of magnitude is four more than bare LiFePO$_4$ ($10^{-14}$ cm$^2$/s).

Fig. 5 exhibits the Nyquist plots of LiFePO$_4$/C and LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C samples synthesized at 700 °C. Both Nyquist plots are comprised of a depressed semicircle in high frequency region and a straight line in low frequency region. An intercept at Z'-axis in the high frequency region identifies the ohmic resistance (R$_s$) of the electrolyte and electrodes. The radius of the semicircle at high frequency region at the Z'-axis is related to the charge transfer resistance (Rct). The slope of inclined line in low frequency represents the Warburg impedance (W), which is associated with lithium-ion diffusion in LiFePO$_4$ cathode.
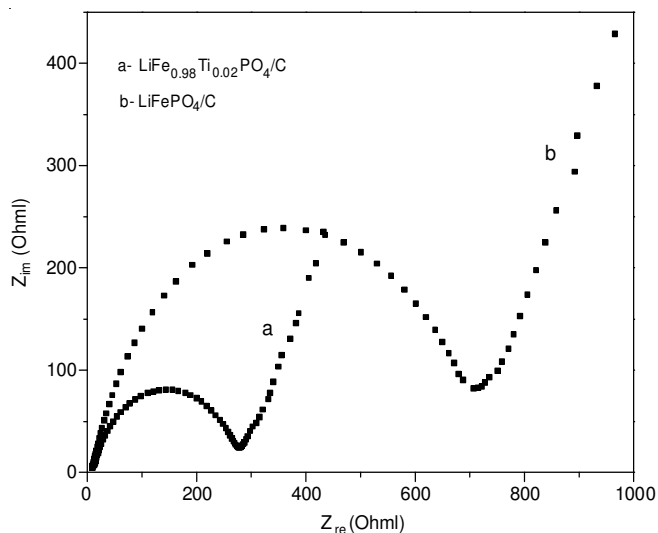


Fig. 3.   (A) Initial charge and discharge curves of LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C sample; (B) Relationship between capacity and discharge rate of the LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C



Fig. 5.  EIS spectra of LiFePO$_4$/C and LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C

It is clear that the resistance of Ti$^{4+}$-doped LiFePO$_4$ cathode (280 Ω) from charge transfer is much smaller than the undoped one (700 Ω), which should be attributed to the Ti$^{4+}$ doping. Furthermore, Ti$^{4+}$-doped LiFePO$_4$ cathode has a higher slope of the inclined line in low frequency, which indicates lower Warburg impedance. The charge-transfer impedance of LiFePO$_4$/C cathode is much bigger than that of LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C cathode, which further supports the above conclusion of the Ti-doped improving the redox kinetics of Fe$^{3+}$/Fe$^{2+}$ couple.



Fig. 4.   Cycle voltammograms of LiFe$_{0.98}$Ti$_{0.02}$PO$_4$/C electrodes between 2.8 and 4.0 V at different scanning rate

## Conclusion

Olivine $LiFe_{0.98}Ti_{0.02}PO_4/C$ has been synthesized successfully by a carbothermal reduction reaction *via* mechanical activation method using sucrose as a carbon source and reducing agent. The charge/discharge tests show that its initial discharge capacity is 158.63 mAh/g at a 0.2C rate between 4.5 and 2.6 V. $LiFe_{0.98}Ti_{0.02}PO_4/C$ sample shows higher reversible capacity and markedly improved rate capability. It may be attributed to it having larger lattice parameters than those of other samples in this study.

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