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Electrochemical performance of Ti^{4+}-doped $LiFePO_4$ synthesized by co-precipitation and post-sintering method

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Abstract: Ti^{4+}-mixed $FePO_4{\cdot}xH_2O$ precursor was prepared by co-precipitation method, with which Ti^{4+} cations were added in the process of preparing $FePO_4{\cdot}xH_2O$ to pursue an effective and homogenous doping way. Ti^{4+}-doped $LiFePO_4$ was prepared by an ambient-reduction and post-sintering method using the as-prepared precursor, Li_2CO_3 and oxalic acid as raw materials. The samples were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), electrochemical impedance spectroscopy (EIS), and electrochemical charge/discharge test. Effects of Ti^{4+}-doping and sintering temperature on the physical and electrochemical performance of $LiFePO_4$ powders were investigated. It is noted that Ti^{4+}-doping can improve the electrochemical performance of $LiFePO_4$ remarkably. The Ti^{4+}-doped sample sintered at 600 ℃ delivers an initial discharge capacity of 150, 130 and 125 mA·h/g with 0.1*C*, 1*C* and 2*C* rates, respectively, without fading after 40 cycles.
Key words: lithium-ion battery; cathode material; $LiFePO_4$; Ti^{4+}-doping; co-precipitation

1 Introduction

$LiFePO_4$ has been one of the most promising cathode materials for rechargeable lithium-ion batteries because of its low cost, low toxicity, high theoretical capacity (170 mA·h/g), excellent cycling stability and thermal stability, etc[1]. The performance of $LiFePO_4$, however, is limited by its poor electronic conductivity and the inability of lithium ions to diffuse easily through the $LiFePO_4/FePO_4$ interface, which can result in a significant loss of capacity at high currents[1−2]. Several effective ways have been proposed to improve the electronic conductivity, including synthesis of $LiFePO_4$/electronic conductor composites (carbon or metal nano-particles)[3−5] and substitution of a small quantity of Li^+ by supervalent metal ions[6−10]. To reduce the limitation of lithium-ion diffusion, the main way is to prepare $LiFePO_4$ powders with fine particles[11]. Recently, it is found that the porous structure of powders could also facilitate the lithium-ion diffusion[12].

It was reported that doping a small amount of Ti^{4+} cations into $LiFePO_4$ could improve its rate performance and cycling stability[6]. Ti^{4+}-doped $LiFePO_4$ powders are usually prepared via conventional solid-state reaction of mechanically mixed lithium compounds (typically Li_2CO_3 or $LiOH{\cdot}H_2O$), iron compounds (typically $FeC_2O_4{\cdot}2H_2O$ or Fe_2O_3), titanium compounds (typically TiO_2 or $Ti(OCH_3)(CH_3OH)_2$) and phosphates (typically $NH_4H_2PO_4$ or $(NH_4)_2HPO_4$)[6, 13−14]. However, the titanium compounds are hard to be mixed homogenously with other starting materials via mechanical mixing, due to the fact that the titanium contents are usually very low (less than 5%, molar fraction). Furthermore, the solid-state route generally contains several grindings, high temperature and long-time calcinations, which usually results in the formation of larger particles with poor electrochemical properties. In order to improve the doping effect, WANG et al[15] prepared Ti^{4+}-doped $LiFePO_4$ via sol-gel method and obtained good results. Nevertheless, the sol-gel method is impractical because of its high cost and complicated synthesis routes.

In this study, we introduced a novel and simple synthesis method for Ti^{4+}-doped $LiFePO_4$. Namely, titanium compound was added to the process of preparing $FePO_4{\cdot}xH_2O$ precursor to pursue a homogenous doping way, by which the ingredient Fe^{3+},

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Ti^{4+} and PO_4^{3-} were mixed on the atomic scale in water-based solution. Therefore, Ti^{4+} could be evenly brought into $FePO_4{\cdot}xH_2O$ particles while they grew. Then, Ti^{4+}-doped $LiFePO_4$ was prepared by an ambient-reduction and post-sintering method using the as-prepared precursor as raw material. The effects of Ti^{4+}-doping and sintering temperature on physical and electrochemical performance of $LiFePO_4$ powders were investigated.

2 Experimental

2.1 Sample preparation

Ti^{4+}-mixed $FePO_4{\cdot}xH_2O$ precursor was synthesized by the following procedure. 1) $FeSO_4{\cdot}7H_2O$ (AR), H_3PO_4 (AR) and $Ti(SO_4)_2{\cdot}H_2O$ (CP) in a molar ratio of 1: 1: 0.03 were dissolved in de-ionized water to obtain 0.5 mol/L (Fe) solution; 2) Concentrated hydrogen peroxide (30%, mass fraction) was added to the solution under vigorous stirring; 3) $NH_3{\cdot}H_2O$ (2 mol/L, AR) was dropped into the solution to control the pH to be 2.1± 0.1; subsequently, a white precipitate formed immediately; 4) After being stirred for 10 min, the precipitates were filtered, washed several times with de-ionized water and dried in an oven at 120 ℃. Thus, Ti^{4+}-mixed $FePO_4{\cdot}xH_2O$ powders were obtained. For comparison, pure $FePO_4{\cdot}xH_2O$ precursor was prepared with the same procedure.

The as-prepared precursors, Li_2CO_3 (AR) and oxalic acid (AR) in stoichiometric ratio (Fe:C:Li=1:1:(1−4x), where x means titanium content) were mixed by high-energy ball milling. The milling was performed at a speed of 200 r/min for 3 h at ambient temperature. The as-obtained mixtures were sintered at different temperatures (550, 600 and 650 ℃) for 12 h with flowing argon. After being cooled to room-temperature, the crystalline $LiFePO_4$ samples were obtained. More details about the ambient-reduction and post-sintering method can be found in Ref.[16].

2.2 Characterization of synthesized samples

The phase structure of $LiFePO_4$ powders was analyzed by X-ray diffractometry (XRD, Rint−2000, Rigaku) using Cu K_α radiation, and the crystal cell parameters were calculated by WINPLOTR. The powder morphology was observed by scanning electron microscopy (SEM, JEOL, JSM−5600LV). The metal content of $FePO_4{\cdot}xH_2O$ powders was analyzed using inductively coupled plasma emission spectroscopy (ICP, IRIS intrepid XSP, Thermo Electron Corporation).

2.3 Electrochemical measurement

The electrochemical performance was performed using a two-electrode coin-type cell (CR2025) of Li | $LiPF_6$ (EC:EMC:DMC=1:1:1 in volume ratio) | $LiFePO_4$. The working cathode is composed of 80% $LiFePO_4$ powders, 10% acetylene black as conducting agent, and 10% poly (vinylidene fluoride) as binder. After being blended in *N*-methyl pyrrolidinone, the mixed slurry was spread uniformly on a thin aluminum foil and dried in vacuum for 12 h at 120 ℃. A metal lithium foil was used as anode. Electrodes were punched in the form of disks with 14 mm in diameter. A polypropylene micro-porous film was used as the separator. The assembly of the cells was carried out in a dry argon-filled glove box. The cells were charged and discharged over a voltage range of 2.5−4.1 V versus Li/Li^+ electrode at room temperature. Electrochemical impedance measurements were conducted on a CHI660A Electrochemical Workstation (0.01 Hz−100 kHz, 5 mV).

3 Results and discussion

3.1 Structure and morphology

ICP results show that the x(Ti)/x(Fe) value of Ti^{4+}-mixed $FePO_4{\cdot}xH_2O$ precursor, 2.97%, is highly close to the target value, 3.0%. This demonstrates that depositing Ti^{4+} in $FePO_4{\cdot}xH_2O$ powders by the co-precipitation method is very efficient.

X-ray diffraction (XRD) patterns of $LiFePO_4$ and Ti^{4+}-doped $LiFePO_4$ synthesized at 600 ℃ are shown in Fig.1. All diffraction peaks are indexed to an orthorhombic crystal structure (space group *Pnma*), and no impurity phases are detected. Previous studies[6, 8, 13] found that Ti^{4+} tend to occupy M1 sites to form solid solutions without any impurity phase, owing to the fact that the ionic radius of Ti^{4+} in octahedral coordination (0.061 nm) is quite consistent with the radius of Li^+ (0.068 nm). In contrast, if Ti^{4+} cations occupy M2 sites, some impurities such as Li_3PO_4, Fe_3P and $Li_3Fe_2(PO_4)_3$ would be detected[14−15]. Hence, we believe that Ti^{4+} cations have successfully doped into M1 sites. The lattice

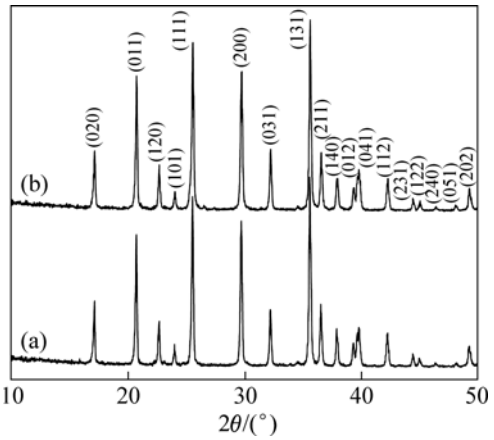

Fig.1 XRD patterns of $LiFePO_4$ (a) and Ti^{4+}-doped $LiFePO_4$ (b) synthesized at 600 ℃

parameters of $LiFePO_4$ samples were calculated: a=1.032 2 nm, b=0.600 2 nm, c=0.469 5 nm, and V=0.290 9 nm^3, while the Ti^{4+}-doped $LiFePO_4$ has slightly varied lattice parameters: a=1.031 7 nm, b=0.600 0 nm, c=0.469 3 nm, and V=0.290 5 nm^3. The unit cell of the crystal lattice was slightly diminished along x, y, and z directions, which should be attributed to the existence of Li^+ vacancies caused by Ti^{4+} doping.

The primary particle size, d, was calculated from the XRD pattern using the Scherrer formula. The d value of Ti^{4+}-doped $LiFePO_4$, 44.1 nm, is smaller than that of the undoped sample (46.3 nm), indicating that dopant Ti^{4+} could restrain the growth of $LiFePO_4$ crystal.

Fig.2 shows the influence of Ti^{4+}-doping on the morphologies of $LiFePO_4$ powders. Primary particles in the size of 200−800 nm can be observed in both samples, but the Ti^{4+}-doped sample owns less agglomeration and scatters more uniformly than the undoped one. This demonstrates that the dopant Ti^{4+} could effectively inhibit the particles aggregation. Reducing the particle size could enhance the lithium-ion diffusion speed cross the $LiFePO_4/FePO_4$ interface and, consequently, would improve the electrochemical properties of $LiFePO_4$ at high current rates[11].

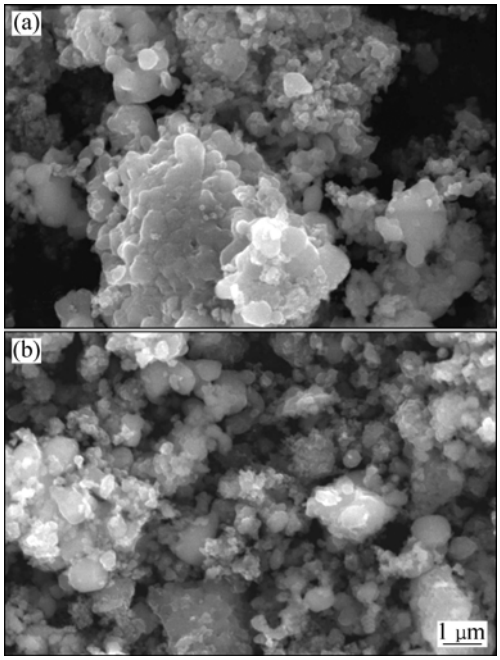

Fig.2 SEM images of $LiFePO_4$ (a) and Ti^{4+}-doped $LiFePO_4$ (b) synthesized at 600 ℃

Fig.3 represents the XRD patterns of Ti^{4+}-doped $LiFePO_4$ synthesized at different temperatures. The intensity of diffraction peaks of $LiFePO_4$ powders are gradually enhanced with the increase of sintering temperature. It is clear that increasing sintering temperature could improve the crystallinity of $LiFePO_4$; nevertheless, high temperature also results in the increase of particle size. The primary particle sizes of Ti^{4+}-doped $LiFePO_4$ synthesized at 550, 600 and 650 ℃ are 41.0, 44.1 and 49.4 nm, respectively.

SEM images of Ti^{4+}-doped $LiFePO_4$ synthesized at various temperatures are shown in Fig.4. The sample

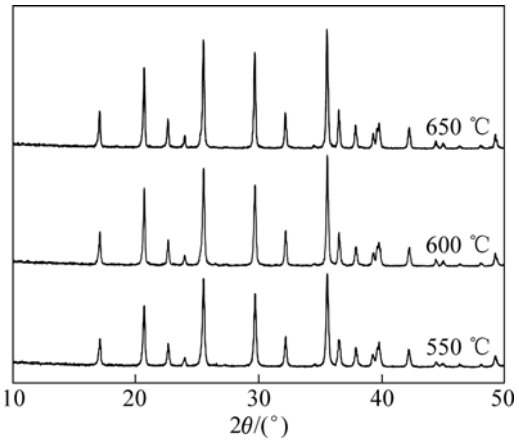

Fig.3 XRD patterns of Ti^{4+}-doped $LiFePO_4$ synthesized at different temperatures

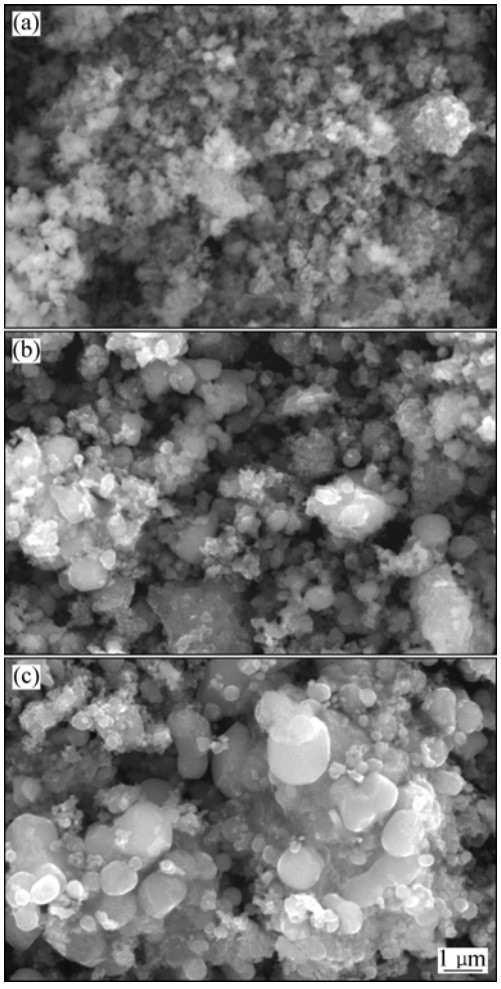

Fig.4 SEM images of Ti^{4+}-doped $LiFePO_4$ synthesized at different sintering temperatures: (a) 550 ℃; (b) 600 ℃; (c) 650 ℃

synthesized at 550 ℃ exhibits a uniform fine-grained microstructure with secondary particle size of 100−500 nm. As mentioned above, the small particle size could improve the electrochemical performance of $LiFePO_4$. However, this sample also exhibits a relatively low crystallinity (Fig.3), which would probably make against its electrochemical properties. On the contrary, the material synthesized at 650 ℃ is well crystallized but serious aggregation exists. In contrast, the sample synthesized at 600 ℃ shows not only little aggregation but also good crystallinity; therefore, a better electrochemical performance should be expected.

3.2 Electrochemical characteristics

Fig.5 exhibits the Nyquist plots of $LiFePO_4$ samples synthesized at 600 ℃. 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 very high frequency region identifies the ohmic resistance (R_s) of the electrolyte and electrodes. The radius of the semicircle at high frequency region on the Z'-axis is related to the charge transfer resistance (R_{ct}). The slope of inclined line in low frequency represents the Warburg impedance (W), which is associated with lithium-ion diffusion in $LiFePO_4$ cathode. It is clear that the charge transfer resistance of Ti^{4+}-doped $LiFePO_4$ cathode (130 Ω) is much smaller than the undoped one (830 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, indicating lower Warburg impedance.

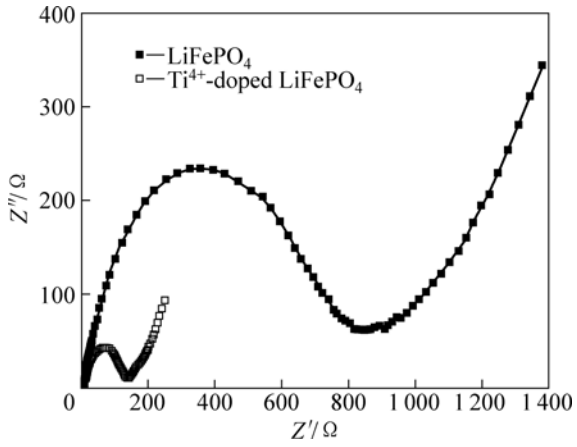

Fig.5 EIS spectra of $LiFePO_4$ and Ti^{4+}-doped $LiFePO_4$ synthesized at 600 ℃

Fig.6 presents the initial discharge curves and cycling performance of $LiFePO_4$ samples at various current rates. As shown in Fig.6(a), at the discharge rate of 0.1C, 1C and 2C, $LiFePO_4$ shows a capacity of 144, 113 and 98 mA·h/g, respectively, while the Ti^{4+}-doped sample delivers a capacity of 150, 130 and 125 mA·h/g,

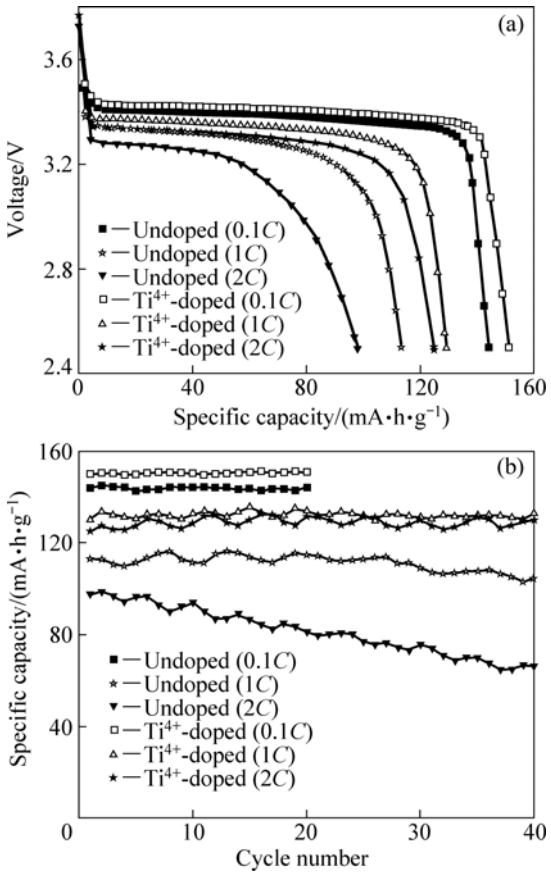

Fig.6 Initial discharge curves (a) and cycling performance (b) of $LiFePO_4$ and Ti^{4+}-doped $LiFePO_4$ synthesized at 600 ℃

respectively. From Fig.6(b), it is clear that both samples exhibit excellent cyclic stability at 0.1C rate, but at higher current rates, the Ti^{4+}-doped sample shows much better cycling performance. After 40 cycles, Ti^{4+}-doped $LiFePO_4$ shows a capacity of 133 and 130 mA·h/g at 1C and 2C rate, respectively, and retains 102.3% and 104.0% of its initial discharge capacity, while $LiFePO_4$ only maintains 92.0% (104 mA·h/g) and 67.3% (66 mA·h/g) of its initial discharge capacity. From analysis above, Ti^{4+}-doped $LiFePO_4$ with better electrochemical properties can be attributed to the following reasons: 1) Ti^{4+} doping intrinsically improves the bulk electronic conductivity of $LiFePO_4$ material by inducing an increased p-type semi-conductivity[6]; 2) Ti^{4+} doping effectively inhibits the particles aggregation and, consequently, enhances the lithium-ion diffusion speed cross the $LiFePO_4/FePO_4$ interface; 3) Ti^{4+} doping reduces the charge transfer resistance (R_{ct}) and Warburg impedance (W) of $LiFePO_4$ cathode.

The influence of sintering temperature on electrochemical performance of Ti^{4+}-doped $LiFePO_4$ is shown in Fig.7. The samples synthesized at 550, 600 and 650 ℃ deliver initial discharge capacities of 107, 130 and 121 mA·h/g, respectively, and maintains a capacity of 100 (93.5% of its initial value), 132 (101.5% of its

initial value) and 116 mA·h/g (95.9% of its initial value) after 40 cycles, respectively. The sample synthesized at 550 ℃ exhibits the lowest discharge capacity and the worst cyclic stability, which are ascribed to the poor crystallinity. Also, the electrochemical properties of Ti^{4+}-doped $LiFePO_4$ synthesized at 650 ℃ are not satisfactory, due to the serious particles aggregation. The sample synthesized at 600 ℃ shows the most impressive performance, owing to its good crystallinity and little aggregation.

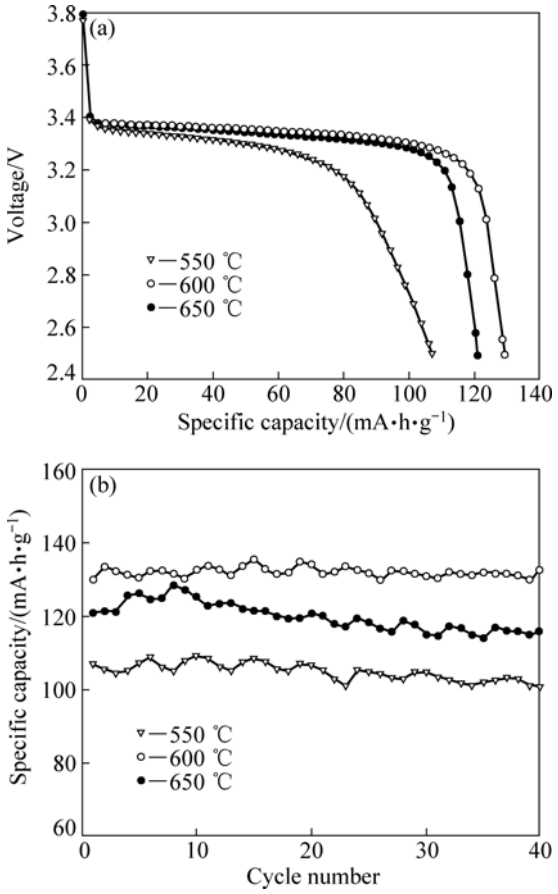

Fig.7 Initial discharge curves (a) and cycling performance (b) of Ti^{4+}-doped $LiFePO_4$ synthesized at different temperatures (Charge/discharge at 1*C* rate)

4 Conclusions

1) Olive-type Ti^{4+}-doped $LiFePO_4$ is synthesized by co-precipitation and post-sintering method. XRD results indicate that Ti^{4+} ions enter into the lattices of $LiFePO_4$ crystal and do not obviously change its structure.

2) Ti^{4+} doping can effectively inhibit the $LiFePO_4$ particles aggregation and consequently enhances the Li^+ diffusion speed cross the $LiFePO_4/FePO_4$ interface. And Ti^{4+} doping can reduce the charge transfer resistance and Warburg impedance of $LiFePO_4$ electrode.

3) The Ti^{4+}-doped $LiFePO_4$ synthesized at 600 ℃ shows the most impressive electrochemical performance with the initial discharge capacity of 150, 130 and 125 mA·h/g at 0.1*C*, 1*C* and 2*C* rate, respectively, and without capacity fading after 40 cycles.

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