

Synthesis and Electrochemical Characterizations of Zinc-doped LiFePO_4/C by Carbothermal Reduction

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Abstract: Alien atom doping has been adopted to modify the electrochemical performance of olivine type LiFePO_4 for cathode material. Here, we report that zinc-doping can improve the performance of LiFePO_4/C immensely by a simple method. LiFePO_4/C and Zn-doped LiFePO_4/C cathode materials were firstly synthesized by carbothermal reduction method. Physical-chemical characterizations were done by X-ray diffraction, scanning electron microscope and transmittance electron microscope. Electrochemical behavior of the cathode materials were analyzed by using cyclic voltammetry, and galvanostatic measurements were employed to characterize the reaction of lithium ion insertion and de-insertion. ICP and XRD analyses indicate that Zn ions were sufficiently doped in LiFePO_4 and did not alter its crystal structure. During de-intercalation and intercalation process of lithium ions, the doped zinc atoms protect the LiFePO_4 crystal from shrink. Consequently, the conductivity is enhanced after doping. It is noted that zinc ions doping can improve performance of LiFePO_4 , especially on the aspect of stable cycle-life at higher C rate.

Key words: LiFePO_4 ; doping zinc; lithium ion battery; cycle performance

Since the olivine structure LiFePO_4 could be used as cathode material for lithium ion batteries in 1997^[1-2], it has appeared to be a promising cathode candidate because of its high theoretical capacity (170 mAh/g), low cost, excellent cycling stability, low toxicity and environmentally benign nature^[3-5]. However, there are still some drawbacks of this material, such as poor electronic conductivity and low Li ion motion ability^[2,6-8], which need to be improved before its commercial applications. The ways of doping supervalent cations, synthesis of nanocrystalline grains and electronic conductive carbon coating have been regarded as effective methods to enhance its electronic conductivity and Li-ion diffusivity rate^[9-13].

The olivine LiFePO_4 can be synthesized by different synthesis techniques including solid-state reaction, Sol-Gel^[14], hydrothermal^[15], co-precipitation^[16], microwave heating^[4], etc. All of alternative synthesizing routes have performed to prepare LiFePO_4 with fine and homogeneous particle sizes. Barker *et al*^[17] and Mi *et al*^[18] reported that LiFePO_4 can be synthesized by carbothermal reduction method. The carbon during the synthesis process ensured the reduction of Fe^{3+} to Fe^{2+} , controlled the morphology and sizes of the powder, and improved the con-

ductivity of the material with coated carbon film on the LiFePO_4 particles.

To alleviate the poor conductivity and slow diffusion, various research groups have adopted different strategies, including substitution of a small quantity of Li^+ or Fe^{2+} by supervalent metal ions^[17,19]. Thereby, it is found that doping alien cations is another feasible way to enhance the intrinsic conductivity. Liu *et al*^[20] reported on zinc-doped $\text{LiFe}_{0.99}\text{Zn}_{0.01}\text{PO}_4$, which was synthesized using iron (II) and ZnO by the solid state route. Both discharge capacity and rate capacity were greatly ameliorated. Shenouda *et al*^[21] prepared Zn-doped LiFePO_4 through mechanical mixing of nanoscale precursors to obtain small particles of LiFePO_4 coated with ZnO. The initial specific discharge capacity was about 177 with little decrease after 150 cycles.

Here we have reported for the first time that, through a reformative carbothermal reduction method, Zn ions were doped to pursue a kind of sufficient and homogenous doping way. Besides, a novel reducing agent polyethylene glycol (PEG; mean molecular weight of 10,000) had also been selected, by mixing it with precursor and ball milling together at room temperature. And the doping effect was investigated.

Received date: 2010-02-22, Modified date: 2010-04-01, Published online: 2010-05-10

Foundation item: Xinjiang High-Technology Research & Development Program (200716117)

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1 Experimental

Original and zinc-doped LiFePO_4 samples were prepared by a carbothermal reduction route. All the starting material like Li_2CO_3 (AR, Tianjin Fuchen), Fe_2O_3 (AR, Tianjin Jizhun), $\text{NH}_4\text{H}_2\text{PO}_4$ (AR, Tianjin Fuchen), $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (AR, Shanghai) and 20 wt% PEG (AR, Tianjin) were mixed in ratio of $n(\text{Li}): n(\text{Fe}+\text{Zn}): n(\text{PO}_4)=1:1:1$. The precursor was grinded by a planet mixer (QM-BP) for 15 h. Liquid medium of ethyl alcohol was employed. After milling, the mixtures were dried in oven at 60°C for 12 h in the air. Then they were transferred to a temperature-controlled tube furnace equipped with flowing argon and heated at 350°C for 2 h, whereafter heated at 700°C and held for 12 h. The products were removed from the furnace after cooling.

The structures of the as-prepared materials were characterized by XRD (D8-Advance, Bruker) using $\text{CuK}\alpha$ radiation in the range of 15° – 60° with a scanning rate of $2^\circ/\text{min}$. The content of Zn ion was investigated by inductively coupled plasma (ICP, IRIS intrepid XSP, Thermo Electron Corporation). The morphologies and microstructure of powder particles were observed by SEM (LEO-1430VP) and TEM (H-600, Hitachi Limited).

The cathodes were prepared by mixing with 85 wt% of active material, 10 wt% of acetylene black as a conducting material, and 5 wt% of polyvinylidene difluoride as a binder in N-methyl-2-pyrrolidinone solvent to form homogeneous slurry. Then the slurry was coated onto an aluminum foil and cut into 10 mm diameter and then dried by vacuum oven at 120°C for 12 h. Finally, coin-type cells were assembled in a glove box, which used lithium foil as the counter electrode, celgard 2400 as the separator, and LiPF_6 (1 mol/L) mixed with 1:1:1 (V/V/V) ratio of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC). The electrochemical properties of the cells were characterized by cyclic voltammetry at a scan rate of 0.1 mV/s (CHI660) and galvanostatic

charge and discharge studies over a voltage rang of 2.3–4.3 V (BTS-5V/1 mA).

2 Results and discussion

The ICP result of zinc-doped precursor shows that the content of zinc ion is 2.47 at%. It is clear that Zinc ion content of sample is highly close to the target value 2.5 at%, which demonstrates our method could hold the content of dopant accurately.

The carbothermal reduction process is used extensively in the extraction metallurgy industry to reduce metal oxides to the pure metal state and relies on the application of the two carbon oxidation reaction. Barker *et al*^[17] found that the ease of reduction for a particular metal oxide depends on the affinity of that metal for the oxide lattice, a property characterized by the standard free energy of formation for the oxide. They also found that reaction ($2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$) is expected to dominate at higher than 650°C . So we used 700°C to synthesize the composite.

Figure 1(a) shows the X-ray diffraction patterns of the original and Zn-doped LiFePO_4 . All peaks can be indexed as an olivine phase with an ordered orthorhombic structure belonging to the phase group $Pnma$. The absence of any other signals indicates there are no unwanted impurity phases, such as Zn^{2+} or Fe^{3+} related compounds because of the low doping concentration. There is no evidence of carbon diffraction peaks, indicating the carbon phase is amorphous. In this work, Fe^{3+} in the precursor was reduced to Fe^{2+} with the help of strong reductive agent, which was generated by PEG decomposition and the polymer sticks particles of the reactant together so there was no need to pelletise. The synthesis has then been made possible only by the hydrogen that is the common ingredient present in the polymer we have used here and all the other organic compounds that have already proved their efficiency for that purpose^[22]. At the same time, the residual carbon coated on the LiFePO_4 particles to form

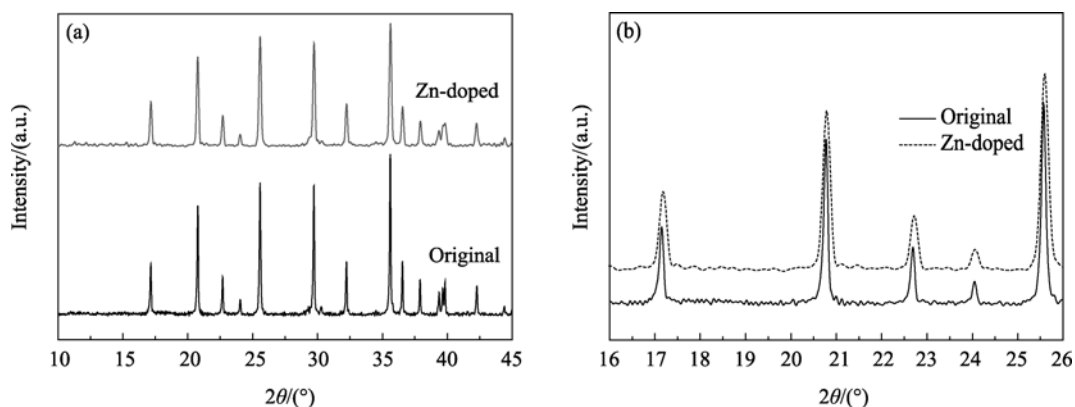


Fig. 1 (a) XRD patterns of original and Zn-doped LiFePO_4/C , (b) amplified patterns in the 2θ range of 16° – 26°

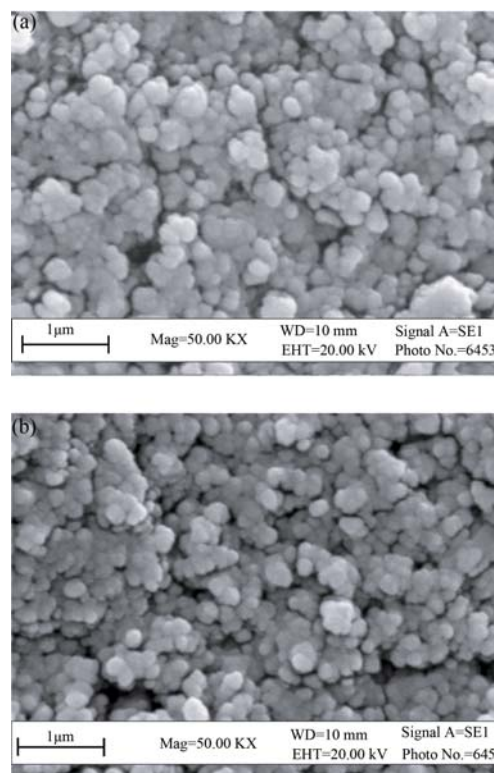
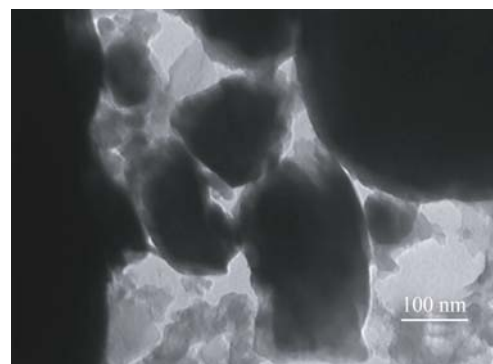
Table 1 crystal cell parameters of original and Zn-doped samples

Sample	Original	Zn-doped
a/nm	1.029	1.033
b/nm	0.599	0.601
c/nm	0.467	0.469
V/nm^3	0.2878	0.2912

LiFePO₄/C composite. Figure 1(b) exhibits the amplified patterns in the 2θ range of 16° – 26° . A slightly shift to the higher 2θ angle of the diffraction peaks was observed as the Zn-doped. According to the Prague equation and Scherrer formula, when the sites of peak deflected to high angle, interplanar spacing d would like to decrease; besides, the crystallite size D of these dopant solid solutions decreased gradually on increasing the breadth of half high of diffraction peaks.

For further study, lattice parameters and calculated crystallite size of Zn-doped samples are shown in Table 1. It is clear that the lattice parameters of Zn-doped LiFePO₄ have changed, that is, the value of a , b , c and V are both increased. It indicates the unit cell parameters of Zn doping are enlarged compared to original one. The expansion in the crystal lattice could provide more space for lithium insertion and de-insertion. The possible reason is that some Zn²⁺ permeated into the lattice of LiFePO₄/C and substituted Fe²⁺ as substitution ions when Zn(Ac)₂ was intermingled and diffused permeated into the precursor. The ionic radius of Zn²⁺ is 0.083 nm and little larger to 0.078 nm of Fe²⁺. The reported unit cell parameter of LiZnPO₄ are $a=1.730$, $b=0.977$, $c=1.620$ nm and $V=2.705$ nm³. Enlargement is known to occur due to the doping^[23]. During the de-insertion process, the lattice would be prevented from shrinking by the Zn²⁺ dopant ions, due to the unchangeable radius of Zn²⁺.

The surface morphology and particle size of the original and Zn-doped LiFePO₄ samples are shown in Fig. 2 and Fig. 3. The particle morphologies of samples are near-spherical, more than one hundred nanometer size. But there is slight agglomeration of original sample and the particles of Zn-doped one are more uniform, indicating that the Zn ions in the solid solution inhibit particles to conglomerate and form secondary particles during calcinations, which is conducive to shorten the lithium diffusion distance. Moreover, the shorter lithium ions diffusion distance, will also benefit lithium insertion and de-insertion. Therefore, both the conductivities of electrons and lithium ions would like to increase more or less, and a better electrochemical performance and cycle ability at various C rates of samples should be expected. The TEM micrograph of Zn-doped sample is represented in Fig. 3. It can be seen clearly that LiFePO₄ grain disperse

**Fig. 2** SEM micrographs of (a) original and (b) Zn-doped samples**Fig. 3** TEM micrograph of Zn-doped sample

in the carbon, most of the grains are wrapped and connected with carbon. The coating of amorphous carbon decomposed from PEG is uniform and characterized by a single morphology with approximately globular structure. This type of morphology will greatly improve the electrochemical applications of LiFePO₄ as it increases contact surface between the particles and electrolyte. Besides, the smaller particle size and more homogeneous carbon coating result in less electrode polarization associated with electronic and/or ionic resistance at the boundary of crystallites^[24].

The charge/discharge voltage profiles of LiFePO₄/C and Zn-doped one are shown in Fig. 4(a) and (b). Initial charge and discharge capacity of original sample have 125 and 122 mAh/g, respectively. For Zn-doped sample, the charge capacity increases from 125 to 140 mAh/g, and the

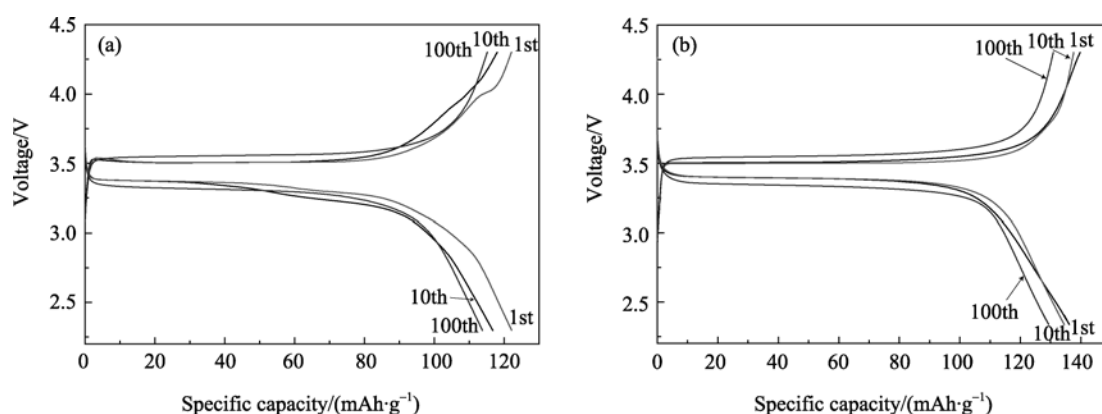


Fig. 4 Charge and discharge studies of 1st, 10th and 100th cycles over a voltage range of 2.3–4.3 V at 1 C rate for (a) original (b) Zn-doped samples

discharge capacity from 122 to 137 mAh/g. The charge voltage plateau is 3.51–3.56 V for original LiFePO_4/C and 3.52–3.56 V for Zn-doped one, while the discharge voltage plateau is 3.33–3.29 V for original sample and 3.39–3.35 V for Zn-doped sample, which is identified as the single-phase transition process between LiFePO_4 and FePO_4 phase. The lower electrochemical polarization of the Zn-doped sample suggests that the increased conductivity is induced by Zn^{2+} doped into the LiFePO_4/C .

The cycling performances of the original and doped samples were evaluated in the voltage range of 2.3 to 4.3 V at different C rates in the cell configuration $\text{Li}/\text{LiFePO}_4$, and the results are shown in Fig. 5. The related date of electrochemical performance was listed in Table 2.

Both samples perform excellent cycling performance but Zn-doped sample exhibits higher discharge capacity and lower fading rate at various C-rates. It is found that original sample exhibits a capacity of 135 mAh/g for the first cycle at 0.1 C and then obviously increases to 140 mAh/g for 20th cycle. Its' initial capacities are 125, 122, 115 and 92mAh/g, at current rate of 0.5 C, 1 C, 2 C and 5 C, respectively. The initial specific capacities of Zn-doped sample are 158, 143, 137, 126 and 95mAh/g corresponding to the current rate of 0.1 C, 0.5 C, 1 C, 2 C and 5 C, which are higher than former sample. The excess of initial capacity in Table 2 was obtained due to the initial activation process and the influence of test temperature.

From these results, it is obvious that appropriate Zn-doped sample exhibited better performance on the aspects of discharge voltage, capacity and cycle-life with various rates than original one, which is consistent with we had expected.

Typical cyclic voltammograms of the original and Zn-doped samples are given in Fig. 6. The curves indicated that the potential range in which the lithium de-insertion/insertion occurs and the phase transition also formed during this process. All data were taken at room temperature at a scan rate of 0.1 mV/s and the voltage range from 2.8 to 4.2 V vs Li/Li^+ . They both exhibit a pair of redox peaks around 3.5 V vs Li^+/Li , but the peak profiles of Zn-doped sample are more symmetric and

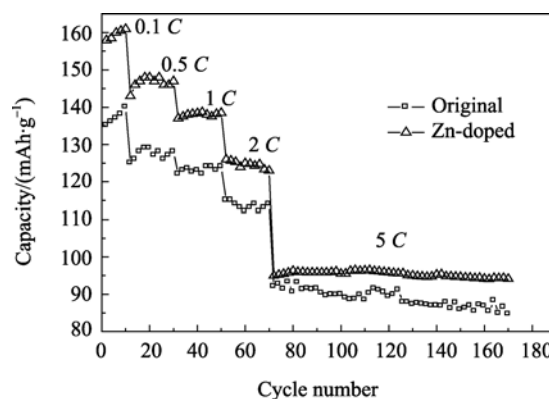


Fig. 5 Cycling performance of original and Zn-doped samples at various rates

Table 2 Electrochemical performance of original and Zn-doped samples

Current rate/C	1st discharge capacity/(mAh·g ⁻¹)		The last discharge capacity/(mAh·g ⁻¹)	
	Original	Zn-doped	Original	Zn-doped
0.1	135	158	141	162
0.5	125	143	129	148
1	122	137	122	138
2	115	126	113	123
5	92	95	86	92

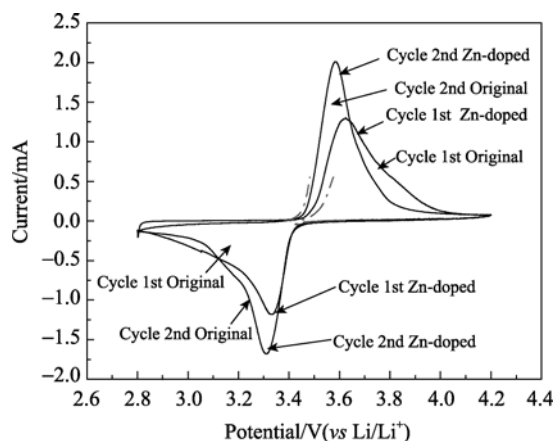


Fig. 6 C - V curves of original and Zn-doped samples at scan rate of 0.1mV/s

spiculate. As shown in Fig. 6, the original and Zn-doped samples both gave a single anodic and cathodic peak during the charge/discharge process. This corresponds to single-step lithium ion removal/reinsertion from the materials. As for C - V curves, it suggests that the Zn-doping has good reversibility of Li^+ between LiFePO_4 and FePO_4 structure.

3 Conclusion

In this study, pure phase LiFePO_4/C and Zn-doped LiFePO_4/C cathode materials were successfully synthesized by carbothermal reduction method using a novel carbon source, PEG. ICP and XRD analyses indicate that Zn ions were sufficiently doped in LiFePO_4 and did not alter its crystal structure. It is noted that Zn doping increases in the unit cell parameters and provides more space for lithium ion insertion/de-insertion. The morphology of original and Zn-doped LiFePO_4/C powders is similar and average particle size is about 100-200 nm. In addition, Zn-doped LiFePO_4/C has higher charge/discharge capacities, and the reversibility of lithium insertion into and removal from materials may be due to enhancement of the electrical conductivity, especially on aspect of stable cycle-life at high C rates. The C - V curves of Zn-doped LiFePO_4/C indicate the two-phase nature of Lithium extraction and insertion reaction between LiFePO_4 and FePO_4 . The benign electrochemical performance indicates that the reported high efficiency synthesis method is promising for developing a cheaper and safer cathode material for fabrication of large scale lithium ion batteries.

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碳热还原法制备 Zn 掺杂的 LiFePO_4 及其电化学性能

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摘 要: 利用碳热还原法制备了 LiFePO_4/C 以及 Zn 掺杂的 LiFePO_4/C . 通过 X 射线衍射、扫描电镜、透射电镜、恒流充放电、循环伏安法等手段对其物化性质进行了分析. 结果表明: 少量 Zn 掺杂不改变 LiFePO_4 的晶体结构. 在充放电过程中, Zn^{2+} 可以减少晶体体积收缩, 为锂离子的扩散提供较大的空间, 使其充放电性能特别是较高倍率下的循环特性得到提高.

关 键 词: LiFePO_4 ; Zn 掺杂; 锂离子电池; 循环性能

中图分类号: TM912

文献标识码: A