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Synthesis and characterization of $LiFePO_4$ coating with aluminum doped zinc oxide

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Abstract: Aluminum doped zinc oxide (AZO), as an electrically conductive material, was applied to coating on the surface of olivine-type $LiFePO_4$ synthesized by solid-state method. The charge−discharge test results show that the rate performance and low-temperature performance of $LiFePO_4$ are greatly improved by the surface treatment. Even at 20*C* rate, the discharge specific capacity of 100.9 mA·h/g was obtained by the AZO-coated $LiFePO_4$ at room temperature. At −20 °C, the discharge specific capacity at 0.2*C* for un-coated $LiFePO_4$ and the coated one are 50.3 mA·h/g and 119.4 mA·h/g, respectively. It should be attributed to the electrically conductive AZO-coating which increases the electronic conductivity of $LiFePO_4$. Furthermore, the surface-coating increases the tap-density of $LiFePO_4$. The results indicate that the AZO-coated $LiFePO_4$ is a good candidate of cathode material for applying in lithium power batteries.

Key words: lithium ion battery; $LiFePO_4$; coating; cathode material; aluminum doped zinc oxide

1 Introduction

Olivine-type $LiFePO_4$, as a replacement of $LiCoO_2$, has attracted attention since the significant report in 1997 by good enough [1] in which it was proposed to be used as cathode material for lithium ion batteries. It has the advantages of environment benign, inexpensive, thermal stable and good cycling stability [2−4]. However, its immanent disadvantages of low electronic conductivity and low diffusion rate of lithium ion during the charge−discharge process destroy the rate performance [5−7], and the capacity decreases rapidly even at moderate current density.

Many reports have discovered that the electrical performance of $LiFePO_4$ can be improved by ion doping [8], carbon coating [9,10] and metal oxide coating [11−13]. Especially, coating carbon which is an electrically conductive material has been wildly applied in industry with advantages of facie, inexpensive and good effect to control the particle size of $LiFePO_4$. However, the electrically conductive carbon reduces the tap-density of $LiFePO_4$, which is being harmful to the energy density of the lithium ion battery [14]. Furthermore, the low-temperature performance of carbon-coated $LiFePO_4$ is also needed to be improved [11].

In this work, the electrically conductive material of aluminum doped zinc oxide(AZO) is firstly applied to coating on the surface of $LiFePO_4$. It is reported that the insulated pure zinc oxide can be changed to be electrically conductive with doping appropriate metals such as indium, gallium and aluminum [15,16]. And the resistivity of the AZO film even can be decreased to 10^{-4} Ω·cm [16]. Besides, the solid density of zinc oxide (5.7 g/cm^3) is even higher than that of the $LiFePO_4$ (3.6 g/cm^3). Therefore, both the electrochemical properties and tap density of $LiFePO_4$ would be greatly improved by coating with the electrically conductive AZO. The low-temperature performance of the AZO-coated $LiFePO_4$ powders is also investigated.

2 Experimental

$LiFePO_4$ was synthesized by solid-state method using $FeC_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$ and Li_2CO_3 as the raw materials. Stoichiometric $FeC_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$ and Li_2CO_3 were full-mixed in isopropanol by ball milling for 2 h. Then the obtained slurry was dried at 80 °C. The

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resulted powders were calcined at 700 °C for 8 h in a purified N_2 flow and the uncoated $LiFePO_4$ was obtained, which is signed as Un-LFP.

$C_4H_6ZnO_4\cdot 2H_2O$ and $C_8H_{12}A_{l2}O_9\cdot 4H_2O$ in the molar ratio of 43.7:1 were initially dissolved in distilled water. The Un-LFP was then added and the mixtures were stirred for 1 h in order to make the Un-LFP disperse homogeneously in the solution. The resultant solution was then dried at 120 °C to get the powder precursor. The powder precursor was calcined at 500 °C for 1 h in a purified N_2 flow and the $LiFePO_4$ coating with AZO was finally obtained (m(AZO):[m($LiFePO_4$)+ m(AZO)]=2%), signed as AZO-LFP.

All the reagents used in the experiment were of analytical purity and were used without further purification. Powder X-ray diffraction (XRD) analysis using Cu K_α radiation was employed to identify the crystalline phase of the prepared powder with a Bruker D8-advance (German) at room temperature in the range of $10°\le 2\theta \le 70°$. The morphology was investigated with a field emission scan electron microscope (SEM, S−4800, Japan). The tap-density meter (BT−300, Dandong Bettersize Instruments Ltd., China) was applied to measuring the tap-density of the prepared powder. The coin cells were assembled by using lithium foil as anode in an argon-filled glove box, the as-prepared powders mixed with 12% acetylene black and 8% PVDF as the cathode and 1 mol/L $LiPF_6$ in a 1:1(V/V) mixture of ethylene carbonate (EC) and dimethylcarbonate(DMC) as the electrolyte, Celgard 2300 membrane as the cell separator. The charge−discharge cycle was performed in a voltage range of 2.0−3.8 V using the coin cells. All the electrical measurements were carried out by a battery testing system (Landet−5 V/10 mA, Landet Electronic Corporation, China) at room temperature.

3 Results and discussion

Figure 1 shows the XRD patterns of the Un-LFP and AZO-LFP powders. All diffraction lines can be index for the orthorhombic olive structure with *pmnb* space group (JCPDS card No. 40—1499) [11]. No peaks corresponding to AZO were observed, indicating that the low content of AZO compound cannot be detected by XRD. The lattice constants of the Un-LFP and AZO-LFP powders have been refined and tabulated in Table 1. It is consistent with that of the standard $LiFePO_4$ and the results obtained in other reports [11,13]. The result also confirms that the surface modification with AZO did not cause the change in lattice constants. This indicates that the Al^{3+} and Zn^{2+} ions are adhere on the surface of the $LiFePO_4$ powders as AZO coating rather than diffuse into $LiFePO_4$ lattice. And more, the tap-densities of the Un-LFP and AZO-LFP powders were also measured and tabulated in Table 1. It is obvious that the tap density of $LiFePO_4$ is improved by the AZO coating. The result is different from that of the carbon coating and is significant for applying in lithium power batteries.

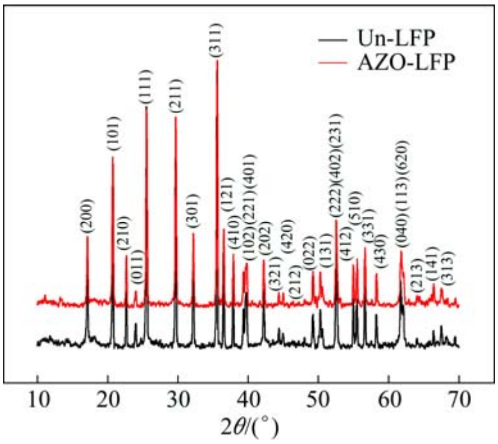

Fig. 1 XRD patterns of Un-LFP and AZO-LFP powders collected by steps of 0.02° in $10°\le 2\theta \le 70°$

Table 1 Calculated structure parameters and tap-densities of Un-LFP and AZO-LFP powders

Production	a/nm	b/nm	c/nm	V/nm^3	Tap density/ (g·cm^{-3})
Un-LFP	1.0327	0.6007	0.46961	0.2910	0.9
AZO-LFP	1.0319	0.6006	0.46913	0.2908	1.5

The SEM images of the Un-LFP and AZO-LFP powders are shown in Fig. 2. It can be clearly seen in Fig. 2(a) that the surface of Un-LFP powder is smooth with little sponge-like material coating on and between the particles. It can be attributed to the decomposition of $C_2O_4^{2-}$ in $FeC_2O_4\cdot 2H_2O$ in purified N_2 flow, which causes little carbon remain. As seen in Fig. 2(b), the surfaces of $LiFePO_4$ particles are covered by some well-distributed nano-particles, which should be the AZO material. It proves that the AZO material has been successfully coated on the surface of $LiFePO_4$, which is consistent with the XRD result mentioned above.

The initial charge−discharge curves of the Un-LFP and AZO-LFP powders tested at different current densities are shown in Fig. 3(a). The cells were firstly charged to 3.8 V at the constant current density, then charged until the charge current density decreased to 0.05C, and finally discharged to 2.0 V at the constant current density. All these curves have the smooth plateaus, indicating the well-crystallized structure of the both samples. The initial charge−discharge specific capacities of the Un-LFP powders at 0.1C and 1C are 156.3/150.3 mA·h/g and 145.5/130.9 mA·h/g, respectively. For the AZO-LFP powders, 165.8/160.1 mA·h/g and 158.1/148.0 mA·h/g were obtained at 0.1C

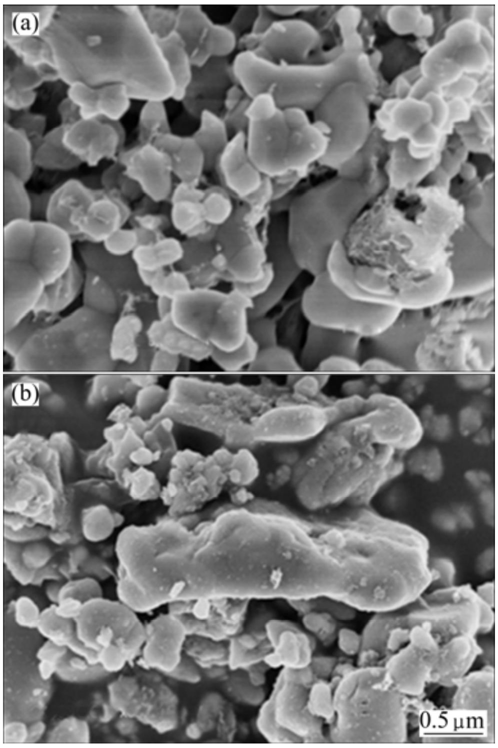

Fig. 2 SEM images of Un-LFP (a) and AZO-LFP powders (b)

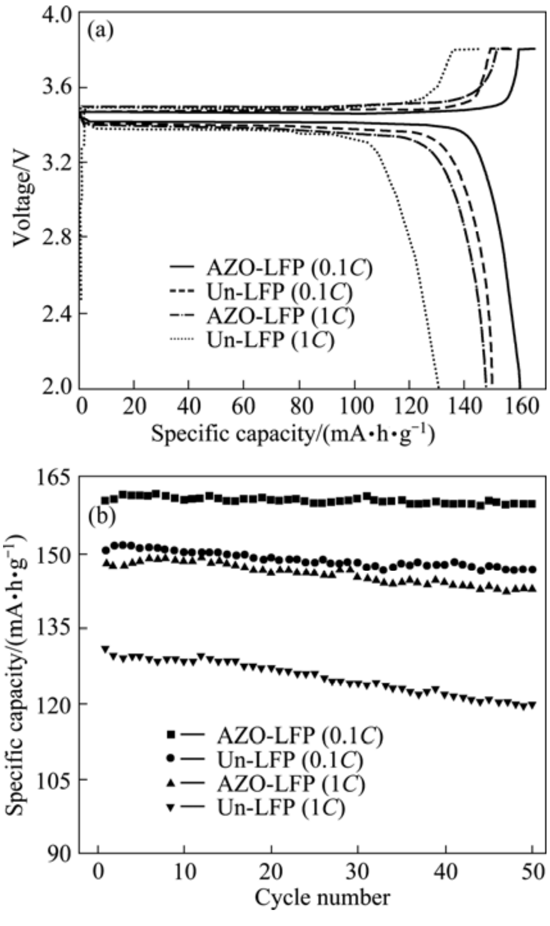

Fig. 3 Initial charge−discharge curves (a) and cycling properties (b) of Un-LFP and AZO-LFP powders tested at room temperature

and 1*C*, respectively. Furthermore, it is obvious that lower discharge plateau is obtained for the curves of the Un-LFP powders, which attributes to the more sever polarization caused by the poor electronic conductivity of $LiFePO_4$ particles. The results well prove that the electrically conductive AZO coating increases the electronic conductivity of $LiFePO_4$, and then improves the specific capacities especially at a high rate.

Figure 3(b) shows the cycle performance of the Un-LFP and AZO-LFP powders. Good results at 0.1*C* are obtained for the both samples. About 99.5% and 97.4% of the initial capacities are retained for the AZO-LFP and Un-LFP powders. When the current density is increased to 1*C*, 96.5% of the initial specific capacity is retained for the AZO-LFP powders, but only 91.3% for the Un-LFP powders. This result demonstrates that the AZO coating can improve the cycling stability of $LiFePO_4$. This improvement is largely due to the presence of AZO which could impede the reaction between the cathode particles and electrolyte [10].

To evaluate the rate capability of the Un-LFP and AZO-LFP, the discharge curves tested at different rates are shown in Fig. 4. For the Un-LFP (Fig. 4(a)), the discharged specific capacity decreases dramatically with increasing the discharge rate. When the rate increases to

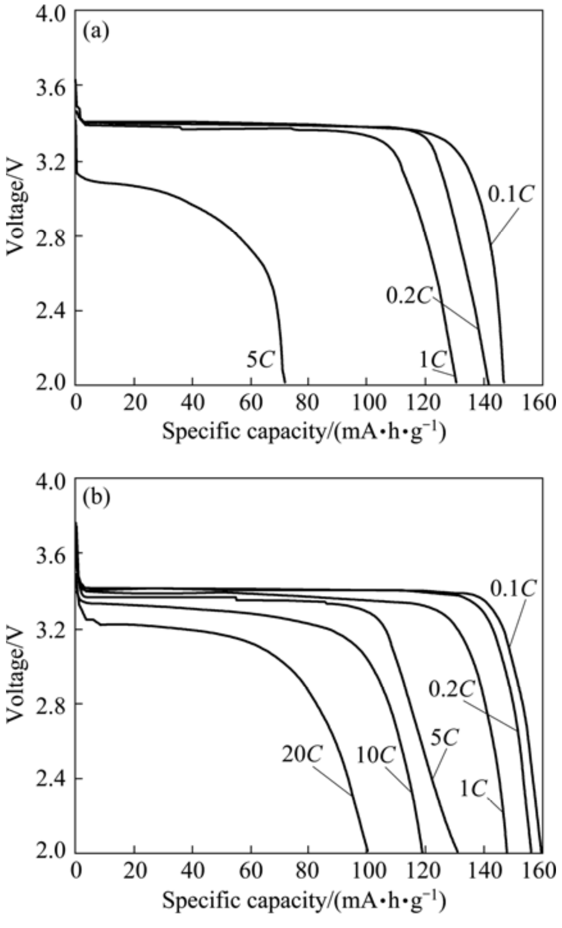

Fig. 4 Rate performance of Un-LFP (a) and AZO-LFP (b) powders at room temperature

5*C*, only 72.0 mA·h/g of the specific capacity is retained for the Un-LFP. However, good rate performance is obtained for AZO-LFP, as shown in Fig. 4(b). The discharge specific capacity can reach 100.9 mA·h/g even at 20*C* rate, indicating that the AZO-LFP is a good candidate of cathode material for lithium power batteries.

Figure 5 displays the initial discharge curves of the Un-LFP and AZO-LFP (0.2*C*) tested at −20 °C. Apparently, the Un-LFP has a bad low-temperature performance shown in Fig. 5. After coating the AZO material, a smooth plateau appears in the discharged process and the specific capacity increases to 119.4 mA·h/g, which indicates that the reaction of Li ions extration/insertion and electron transfer can well proceed at −20 °C. It was reported that the surface reaction kinetics is slowed down with the drop of operation temperature [11]. The obtained results of AZO-LFP should be attributed to the surface treatment which increases the electrode kinetics at −20 °C. Moreover, the improved electrode kinetics can also be beneficial to the rate performance of $LiFePO_4$, which is consistent with the result in Fig. 4.

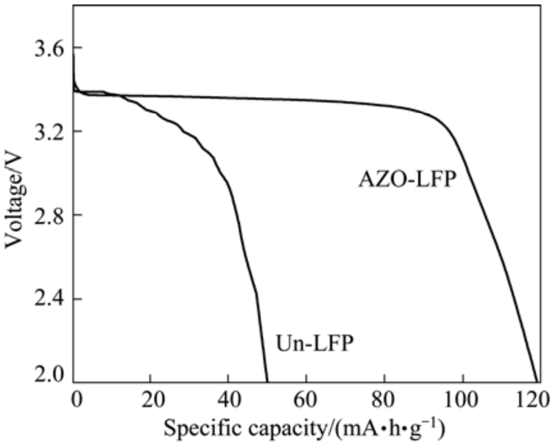

Fig. 5 Initial discharge curves of Un-LFP and AZO-LFP powders tested at −20°C

4 Conclusions

AZO was successfully coated on the surface of $LiFePO_4$ synthesized by solid-state method. Discharge specific capacity of 100.9 mA·h/g can be retained by AZO-coated $LiFePO_4$ testing in the current density of 20*C* at room temperature, whereas the un-coated $LiFePO_4$ can only reach 72.0 mA·h/g even at 5*C* rate. At −20 °C, the discharge specific capacities at 0.2*C* for un-coated $LiFePO_4$ and the coated one are 50.3 mA·h/g and 119.4 mA·h/g, respectively. The surface treatment of AZO-coating greatly improves the rate performance and low-temperature performance of $LiFePO_4$, which indicates that the AZO-LFP is a good candidate of cathode material for lithium power batteries.

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掺铝氧化锌包覆 $LiFePO_4$ 的合成与性能

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摘 要：以简单的固相法合成了橄榄石结构 $LiFePO_4$，并以导电掺铝氧化锌材料(AZO)对其表面进行包覆。充放电结果显示，表面包覆大幅度改善了 $LiFePO_4$ 材料的倍率和低温性能。在 20*C* 高倍率条件下，AZO 包覆 $LiFePO_4$ 的放电比容量可达 100.9 mA·h/g；在低温−20 °C 时进行 0.2*C* 充放电，未包覆 $LiFePO_4$ 和 AZO 包覆 $LiFePO_4$ 的放电比容量分别为 50.3 mA·h/g 和 119.4 mA·h/g。经分析，这可能是由于采用导电 AZO 包覆措施而增加了 $LiFePO_4$ 材料的电导率，从而极大地提高了其比容量。另外，导电 AZO 包覆措施还增加了 $LiFePO_4$ 材料的振实密度。这些结果表明 AZO 包覆 $LiFePO_4$ 材料是一种很好的适用于锂离子动力电池的正极材料。

关键词：锂离子电池；$LiFePO_4$；包覆；正极材料；掺铝氧化锌

(Edited by Hua YANG)