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Structure and Electrochemical Performance of $LiFePO_4$/C Cathode Materials Coated with Nano Al_2O_3 for Lithium-ion Battery

ZHAO Shi-Xi[1], LI Ying-Da[1,2], DING Hao[1,2], LI Bao-Hua[1], NAN Ce-Wen[2]

(1. Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China; 2. School of Materials Science and Engineering, Tsinghua University, Beijing100084, China)

Abstract: The structure and electrochemical performance of Al_2O_3-coated $LiFePO_4$ cathode materials were investigated. A nano Al_2O_3 coating on the surface of commercial $LiFePO_4$/C particles (Aleees Inc.) was prepared by using the Sol-Gel method. The effect of the amount of Al_2O_3 coating on the electrochemical performance and structural stability of $LiFePO_4$ electrodes at room temperature (25℃) and elevated temperatures (55℃) was studied. The results show that 2wt% Al_2O_3 coating can effectively enhance the cycling capacity, alleviate capacity fading at high temperature and reduce cell impedance. It is largely attributed to Al_2O_3 coating, which plays a regulatory role of lithium-ion inserting the lattice and preventing direct contact between the cathode material and the electrolyte, and improves the structural stability of $LiFePO_4$ during cycles.

Key words: lithium-ion battery; cathode materials; $LiFePO_4$; nano Al_2O_3 coating

In recent years, the lithium-ion batteries have extended their applications from portable electronic devices to electric vehicles and other power tools that demand better performance such as higher energy density and higher cycling capacity for their power sources[1]. For high power densities (viz. higher rates), the electrode materials in LIBs must possess rapid ionic and electronic diffusion[2]. $LiFePO_4$ was firstly reported by Padhi, *et al*[3-4] as a potential cathode material for lithium-ion batteries. Because of the non-toxicity and high safety and other properties matching the needs mentioned above, intensive investigations on $LiFePO_4$ have been done over years and significant advances have been made[5-9]. However, poor electronic conductivity and low lithium ion diffusivity are two of main problems for the applications of $LiFePO_4$ cathode materials. Structural modification such as doping and surface carbon coating has been proved to be an effective way to solve this problem[10-14]. Except for carbon coating, oxides costing such as TiO_2[15], SiO_2[16], CuO[17], has drawn scholars' attention too. Other coating has also been reported such as Li_3PO_4[18-19], AlF_3[20], and NiP[21]. They all play an important role in preventing $LiFePO_4$ from direct contact with the electrolyte solution, improving the structural stability, and increasing cycling capacity. On the other hand, Al_2O_3 has been used as coating on other cathode materials such as layered $LiCoO_2$[22-23], $LiMnO_2$[24] and $LiMn_2O_4$[25-26] for the same aim. Oh, *et al* [23] reported that Al_2O_3-coated $LiCoO_2$, it was found that $AlF_3{\cdot}3H_2O$ was formed from the Al_2O_3-coating layer by a reaction with HF and H_2O, thereby scavenging H_2O molecules in the electrolyte and consequently decreasing the amount of HF. Huang, *et al*[27] have proved that the modified Al_2O_3 coating process can speed up Li^+ diffusion of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and decrease activation energy of charge transfer reaction.

In this paper, the structure and electrochemical performance of Al_2O_3-coated $LiFePO_4$ were investigated at room temperature (25℃) and elevated temperatures (55℃).

1 Experimental

The $LiFePO_4$ powder (Aleees Inc.) employed had an average grain size of 500 nm and a carbon content of 3.74wt%. Al_2O_3-coated $LiFePO_4$ powder was prepared by using the Sol-Gel method. The amount of Al_2O_3 coated was about 1wt%–5wt% of the $LiFePO_4$ powder. In the preparation, firstly $LiFePO_4$/C powder (Aleees Inc.) was mixed with $Al(C_3H_7O)_3$ in ethanol, then the slurry was stirred at 70℃ until totally dried. Finally, the as-prepared powder was calcined at 500℃ for 1 h in Ar gas flow to prevent the formation of Fe^{3+} compounds.

X-ray diffraction (XRD) was carried out on a

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Biography: ZHAO Shi-Xi (1966–), male, PhD, associate professor. E-mail:zhaosx@sz.tsinghua.edu.cn

diffractometer (Rigaku Co. D/MAX-2500, Japan) with Cu-Kα radiation. The lattice parameters were determined by Rietveld analysis of the diffraction data using the Maud program. The particle morphology was examined by scanning transition electron microscope (JEM-2011, JEOL Japan), and transition electron microscope (JEM-2011, JEOL, Japan). Energy dispersive X-ray spectroscope (EDS) was used to analyze the surface composition and element distribution of cathode materials.

The electrochemical performance was carried out in CR2016 coin-type cells. The cells consisted of a cathode and a lithium foil as anode separated by a microporous polypropylene sheet (Celgard 2400, Celgard Inc., USA). The electrolyte was 1 mol/L $LiPF_6$ in a mixture solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. Composite cathode films were prepared by mixing of 80wt% $LiFePO_4$ active material with and without Al_2O_3 coating, 10wt% acetylene black as a conductive additive and 10wt% polyvinylidene fluoride (PVDF) as a binder, and nmethyl pyrrolidone (NMP) as a solvent. The paste was then coated onto an aluminum foil, and finally was dried under vacuum at 100℃ for 10 h. The coin cells were assembled in glove box filled with pure argon (H_2O, O_2 <0.1×10^{-6}, M. Braun). The cells were placed for 12h before testing. The charge-discharge tests were conducted on a battery test system (C2001A, LAND, China) with cut-off voltages of 2.5–4.3 V (*vs* Li/Li^+) at different rates at 25℃ and 55℃. The electrochemical impedance spectroscope (EIS) was employed to characterize the interfacial resistance of cathode using a Chenhua CHI760B Electrochemical Workstation over the frequency range from 1 MHz to 1 mHz with an amplitude of 10 mV at room temperature.

2 Results and discussion

The XRD patterns of the Al_2O_3-coated $LiFePO_4$ powders are the same as that of the sample without Al_2O_3 coating, and no Al_2O_3 peaks occur as shown in Fig. 1. A possible explanation is that the lower processing temperature of 500℃ would result in low crystalline or amorphous-like Al_2O_3.This may be due to the little amount of the Al_2O_3 coating, and the coating consists of nano amorphous particles. The lattice constants of uncoated $LiFePO_4$ and Al_2O_3-coated $LiFePO_4$ (in Table 1) are obtained by Rietveld refinement analysis. The Al_2O_3 coating does not cause the change of the lattice constants, which indicates that nano Al_2O_3 particles adhere on the surface of $LiFePO_4$ particles instead of diffusing into $LiFePO_4$ lattice.

TEM images of the uncoated $LiFePO_4$ and 2wt% Al_2O_3-coated $LiFePO_4$ samples are shown in Fig. 2. The $LiFePO_4$ particles are of nearly orbicular shape, the uncoated particles exhibit almost smooth surfaces as shown in Fig. 2(a), whereas the surface of the Al_2O_3-coated particles are covered with a thin amorphous layer as shown in Fig. 2(b, c), which should be the Al_2O_3 coating.

SEM and EDS mapping images of 2wt% Al_2O_3-coated $LiFePO_4$ show that the product particles consist of the uniform fine grains with the average size of about 300–500 nm. Al_2O_3 coating on the surface of $LiFePO_4$ particle could not be observed clearly (Fig. 3(a)) because of the low content and small particle size of Al_2O_3 powder. The EDS mappings of Al, Fe (Fig. 3(c) and Fig. 3(d)) match with the SEM micrograph of the corresponding particles shown in Fig. 3(b), which clearly reveal that Al_2O_3 is uniformly distributed on the surface of $LiFePO_4$ particles, which is consistent with the TEM analysis shown in Fig. 2.

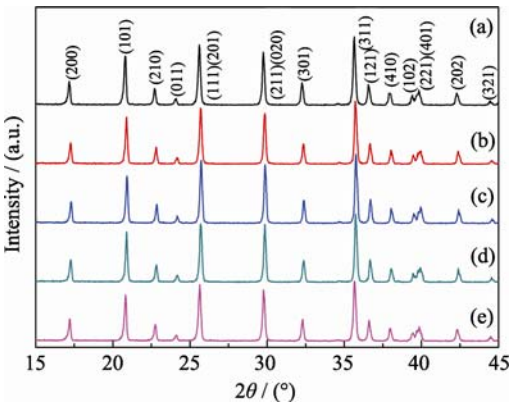

Fig. 1 XRD patterns of pristine $LiFePO_4$ (a) and the coated $LiFePO_4$ powders with Al_2O_3 content of 1wt% (b), 2wt% (c), 3wt% (d) and 5wt% (e), respectively

Table 1 Lattice constants of pristine $LiFePO_4$ and Al_2O_3-coated $LiFePO_4$ by Rietvelt refinement

Sample	Lattice constants/nm			Volume of unit/nm^3	Space group
	a	*b*	*c*		
Pristine $LiFePO_4$	1.03301(3)	0.60049(2)	0.46932(2)	0.29112(4)	Pmnb
1wt% Al_2O_3	1.03306(4)	0.60034(3)	0.46893(1)	0.29082(4)	Pmnb
2wt% Al_2O_3	1.03323(2)	0.60035(1)	0.46912(2)	0.29099(4)	Pmnb
3wt% Al_2O_3	1.03304(1)	0.60021(2)	0.46910(4)	0.29086(1)	Pmnb
5wt% Al_2O_3	1.03330(1)	0.60035(1)	0.46920(2)	0.29106(4)	Pmnb

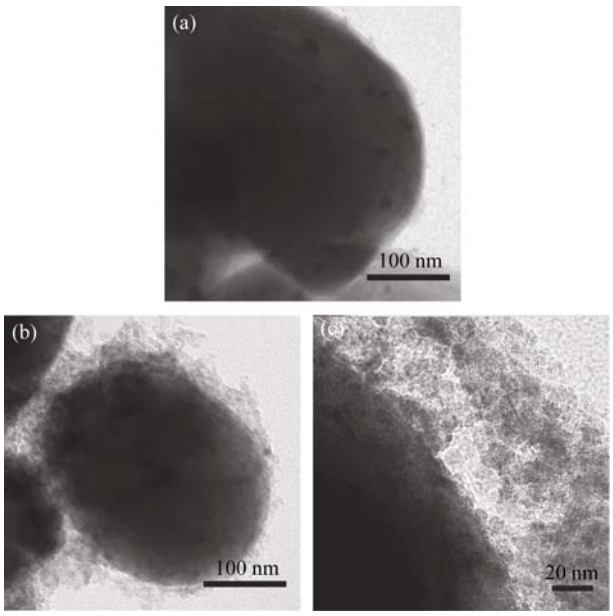

Fig. 2 TEM images of pristine $LiFePO_4$ (a) and 2wt% Al_2O_3-coated $LiFePO_4$ (b), (c)

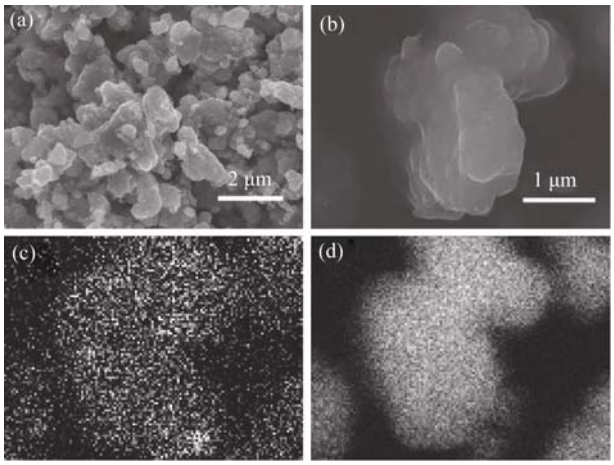

Fig. 3 SEM images of Al_2O_3-coated $LiFePO_4$ (a, b) and the corresponding EDS mapping of Al (c) and Fe (d) element

The discharge capacity and cycling performance of the uncoated $LiFePO_4$ and the Al_2O_3-coated $LiFePO_4$ cathode materials were tested between 2.5 V and 4.3 V at 25℃. Figure 4(a, b) show the curves of discharge capacity *vs* cycle numbers at rate of 0.1*C* and 5*C*, respectively. The results show the discharge capacities of the uncoated $LiFePO_4$ are nearly 150 mAh/g at 0.1*C* and 110 mAh/g at 5*C*, whereas the capacity of the 2wt% coated $LiFePO_4$ cell get nearly 155 mAh/g at 0.1*C* and 123 mAh/g at 5*C*. The higher capacities of Al_2O_3-coated $LiFePO_4$ derive from improving of the orderliness of lithium-ion intercalation/de-intercalation and accelerating the lithium-ion diffusion. This result also can be verified from the impedance measurement as shown in Fig. 5. As the coating amount increases, however, the capacity of 5.0wt% Al_2O_3 coated samples drops. This might result from the thick coating layer to obstruct from Li-ion diffusion.

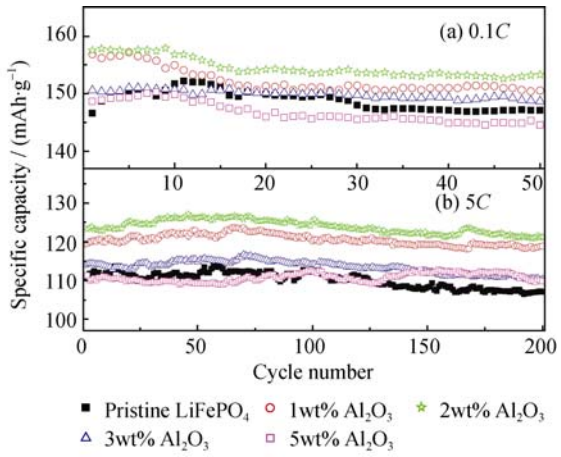

Fig. 4 Comparison of cycling behaviors of pristine $LiFePO_4$ and Al_2O_3-coated $LiFePO_4$ at rate of 0.1*C* (a) and 5*C* (b)

The electrochemical impedance spectroscopy (EIS) of the uncoated $LiFePO_4$ and 2wt% Al_2O_3-coated $LiFePO_4$ are shown in Fig.5. After the first cycle, the cathode impedance shifts from 39 Ω to 24 Ω (Fig. 5(a)). After 100 cycles, the impedance of the uncoated $LiFePO_4$ cathode increases to 94 Ω, while the impedance of the Al_2O_3-coated $LiFePO_4$ cathodes only has 40 Ω. It indicates that the interfacial resistance is significantly suppressed for the Al_2O_3-coated $LiFePO_4$, as depicted in Fig. 5(a). The increase of the interfacial resistance with cycle numbers has also been restrained significantly. This means that the lithium-ion diffusion is enhanced in the Al_2O_3-coated $LiFePO_4$. Similar results were also found for SiO_2-coated $LiFePO_4$[16]. This outcome suggests that the degradation at the $LiFePO_4$/electrolyte interface is restrained by the metal oxide coating, which seems to improve the interfacial properties on the $LiFePO_4$ surface. In order to investigate the cycling behavior of $LiFePO_4$ with the Al_2O_3 coating at the elevated temperature, the cycling has been carried out between 2.5 V and 4.3 V at 55℃ and 1*C* rate. The capacity retention curve is shown in Fig. 6. As a result, the capacity retention rate of the $LiFePO_4$ without Al_2O_3 coating is only about 85% of the initial capacity after 100 cycles, while that of the $LiFePO_4$ with 3wt% Al_2O_3 coating increases significantly and reach 95%. But the capacity retention of 5wt% Al_2O_3 coated $LiFePO_4$ is less than that of 3wt% coated sample as shown in Fig. 6. The improvement of the cycle performance of the $LiFePO_4$ with Al_2O_3 coating is largely due to the nano Al_2O_3 coating, which helps to prevent $LiFePO_4$ particles from having direct contact to the electrolyte, and thus reduces iron dissolution of $LiFePO_4$ during cycle.

But when the amount of Al_2O_3 coating layer is more than 3wt%, the increase of the interfacial resistance results to the capacity and capacity retention decrease.

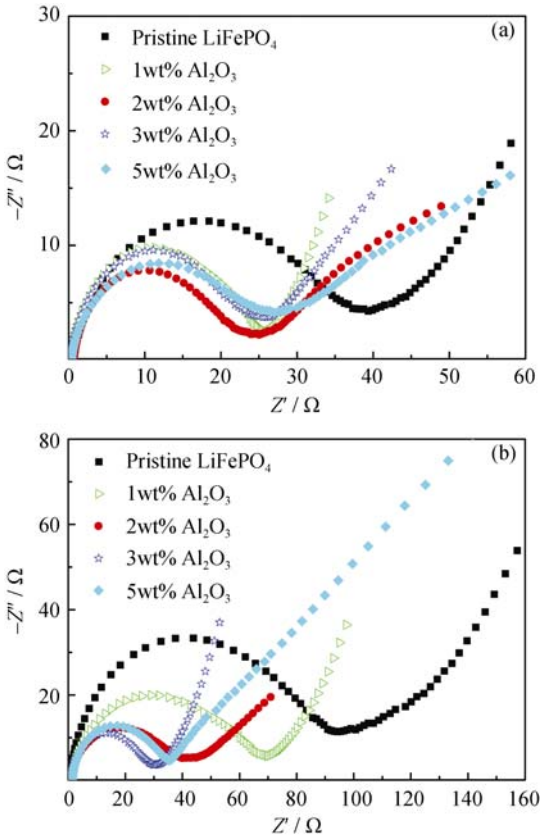

Fig. 5 Electrochemical impedance spectroscopy (EIS) of the cells discharged to 2.5 V after 1 and 100 cycles with testing frequency from 1 MHz to 1 mHz at room temperature

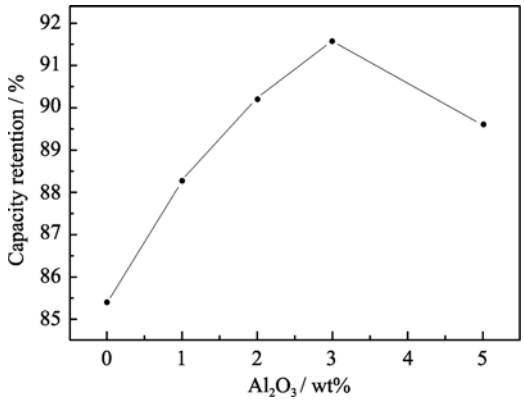

Fig. 6 Capacity retention rates of the cells *vs* weight ratio of Al_2O_3 after 100 cycles at 55℃ and 1*C*

3 Conclusions

The electrochemical performance of $LiFePO_4$ cathode can be improved by nano Al_2O_3 coating, which significantly increases the capacity and cycle ability of the coated $LiFePO_4$ electrode. About 2wt% Al_2O_3 coating results in a higher cycling capacity and lower cell impedance and excellent capacity retention of the cell. The reason for the improved electrochemical performance of the Al_2O_3-coated $LiFePO_4$ could be that the Al_2O_3 coating effectively prevents the $LiFePO_4$ particles from having direct contact with the electrolyte solution, improving the structural stability, increasing the order of lithium-ion diffusion, and reducing the interfacial resistance. Therefore, nano Al_2O_3 surface modification for the $LiFePO_4$ particle is a promising route for preparing $LiFePO_4$ based cathode materials.

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纳米 Al_2O_3 包覆 $LiFePO_4$/C 正极材料的结构和电化学性能

赵世玺[1], 李颖达[1,2], 丁 浩[1,2], 李宝华[1], 南策文[2]

(1. 清华大学 深圳研究生院, 深圳 518055; 2. 清华大学 材料科学与工程学院, 北京 100084)

摘 要: 主要研究了纳米氧化铝包覆对 $LiFePO_4$/C 复合正极材料结构和电化学特性的影响。采用溶胶–凝胶方法把纳米氧化铝包覆在商业 $LiFePO_4$/C 颗粒表面。研究了 Al_2O_3 包覆层的量对 $LiFePO_4$ 电极在室温和高温充放电性能的影响。结果显示：2wt%Al_2O_3 包覆层能有效增加电池的循环容量, 能延缓电池在高温条件下充放电的容量衰减, 减小电极的界面阻抗。这归因于氧化铝包覆层对磷酸铁锂晶粒的表面起保护作用, 减少电解液对磷酸铁锂晶粒表面的腐蚀, 从而改善循环过程中磷酸铁锂的表面结构的完整和稳定, 确保锂离子扩散通道的畅通。

关 键 词: 锂离子电池; 正极材料; 磷酸铁锂; 纳米氧化铝包覆

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