Journal of Alloys and Compounds 509 (2011) 957–960

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Electrochemical performance of SiO_2-coated $LiFePO_4$ cathode materials for lithium ion battery

Ying-Da Li[a,b], Shi-Xi Zhao[a,*], Ce-Wen Nan[b], Bao-Hua Li[a]

[a] Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China
[b] Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 23 April 2010
Received in revised form 26 August 2010
Accepted 27 August 2010
Available online 23 October 2010

Keywords:
Lithium ion battery
Cathode material
SiO_2 Coating
LiFePO4

ABSTRACT

The surface of $LiFePO_4$/C particles was coated with SiO_2 via a sol–gel method, and the electrochemical performance of SiO_2-coated $LiFePO_4$ cathode materials at room temperature and 55 °C was investigated. Compared with pristine $LiFePO_4$, the structure of $LiFePO_4$ with SiO_2 coating had no change, the existence of SiO_2 coating effectively enhanced the cycling capacity, reduced capacity fading at high temperature and alleviated the cell impedance. The SiO_2 coating played a regulatory role for Li-ion inserting the lattice, by increasing the order of lithium ion intercalating the outer lattice of the particle. As a consequence, capacity retention improves significantly.

1. Introduction

$LiFePO_4$, as a potential cathode material for the lithium ion batteries, was first reported by Goodenough and co-workers in 1997 [1,2], which has a high lithium intercalation voltage of 3.4 V compared with lithium metal and a high theoretical capacity of 170 mA h g^{-1}. Subsequently, $LiFePO_4$ has received much attention as a next-generation cathode material in lithium ion batteries because of the non-toxicity and high safety and the abundance of its raw materials, the intensive investigations on $LiFePO_4$ have been done over years and significant advances have been made [3–7]. However, the main problems with this material are low electronic conductivity and low lithium diffusivity, which prevent its large-scale application in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [8–10].

Thus far, much effort has been made to improve the electric and ionic conductivities of $LiFePO_4$ by reducing the particle size [11–14] and surface modification and doping, especially carbon coating is the most common surface modified method [15–20]. So far, there have been few reports on oxide or other coating on the $LiFePO_4$ particle surface [21–27]. But for other cathode materials such as layered $LiCoO_2$, $LiNiO_2$, spinel $LiMn_2O_4$, oxides coating has been proved to be an effective method to improve the performance of cathode materials such as preventing the direct contact with the electrolyte solution, improving the structural stability, increasing Li-ion conductivity, reducing capacity fading and so on [26–34].

SiO_2 protective layer is efficient in decreasing by more than 50% the exothermic reaction of the cathode material $LiNi_{0.8}Co_{0.2}O_2$ in the charged state with the electrolyte [34]. Silica, as a good additive used in battery industry, has been proved to effectively enhance the ionic conductivity when it used in organic electrolytes [35–36]. To our knowledge, no publications about SiO_2 coating on the $LiFePO_4$ particle are seen. In this paper, SiO_2 was coated onto the surface of $LiFePO_4$ particles by a sol–gel method. The results demonstrate the electrochemical performance of $LiFePO_4$ cathode materials is enhanced by the SiO_2 coating.

2. Experimental

The $LiFePO_4$ powder (Aleees Inc.) was mixed with tetraethylorthosilicate (TEOS, 99%) in a molar ratio of TEOS: $LiFePO_4$ = 5:100 in ethanol. Then the slurry was stirred for 5 h and dried at 70 °C. Finally, the dried materials were fired at 500 °C for 1 h in a purified Ar gas flow to prevent the formation of Fe^{3+} compounds and the SiO_2-coated $LiFePO_4$ were obtained.

The powder were characterized by X-ray powder diffraction analysis (XRD, D/MAX-2500, Rigaku Co., Japan) with Cu K_α radiation and the structural parameters were determined by Rietveld analysis of the diffraction profiles, using the Maud program. The particle morphology was observed using a scanning electron microscope (Ultra-high Resolution SEM S-4800, Hitachi Company) and transition electron microscope (JEM-2011, JEOL, Japan), and EDS mapping analysis was used to analyze the composition and element distribution of the particle surface.

The electrochemical performance of both pristine $LiFePO_4$ and SiO_2-coated $LiFePO_4$ cathode materials were evaluated using coin-type cells (CR2016). A lithium metal foil was used as the anode. Composite cathode films were prepared by mixing of 80 wt% $LiFePO_4$ active material, 10 wt% acetylene black as a conductive additive and 10 wt% polyvinylidene fluoride (PVDF) as a binder, and *N*-methyl pyrrolidone (NMP) as a solvent. The paste was then coated onto an aluminum foil, and finally

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[*] Corresponding author. Tel.: +86 0755 26036372; fax: +86 0755 26036372.
E-mail address: zhaosx@sz.tsinghua.edu.cn (S.-X. Zhao).

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doi:10.1016/j.jallcom.2010.08.154

Table 1
Lattice constants of u-LFP and Si-LFP by Rietvelt refinement.

Sample	Lattice constants (Å)			Volume of unit (Å^3)	Space group
	a	*b*	*c*		
u-LFP	10.3301(3)	6.0049(2)	4.6932(2)	291.12(1)	*Pmnb*
Si-LFP	10.3243(5)	6.0004(3)	4.6883(3)	290.44(2)	*Pmnb*

dried under vacuum at 100 °C for 10 h before electrochemical evaluation. The electrolyte was a solution of 1 M $LiPF_6$ dissolved in the mixture solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with ratio of 1:1. A microporous polypropylene sheet (Celgard 2400, Celgard Inc., USA) was used as the separator. The cells were assembled in a dry glove box filled with pure argon. All the cells were allowed to age for 10 h before testing. The charge-discharge tests were conducted on a battery test system(C2001A, LAND, China) with cut-off voltages of 2.5 V and 4.3 V (versus Li/Li+) at different current rate at room temperature and 55 °C. The electrochemical impedance spectroscopy (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_{rms} at room temperature. Electrochemical impedance spectroscopy (EIS) of the $LiFePO_4$ with SiO_2 coating and the $LiFePO_4$ without SiO_2 coating were measured by using same coin cells in same conditions. The relative difference of EIS should reflect the difference of the cathode materials.

3. Results and discussion

Fig. 1 shows the XRD patterns of the uncoated pristine $LiFePO_4$ (abbreviated as u-LFP) and the SiO_2-coated $LiFePO_4$ (abbreviated as Si-LFP) powders. From both patterns, only $LiFePO_4$ was detected and there were not peaks of SiO_2. This may be due to the low content and amorphous state of SiO_2. The lattice constants of u-LFP and Si-LFP obtained by Rietveld refinement analysis was tabulated in Table 1. The results show that surface modification using SiO_2 did not cause the change in the lattice constants. This indicates Si atoms adhered on the surface of $LiFePO_4$ particles as SiO_2 coating rather than diffused into $LiFePO_4$ lattice.

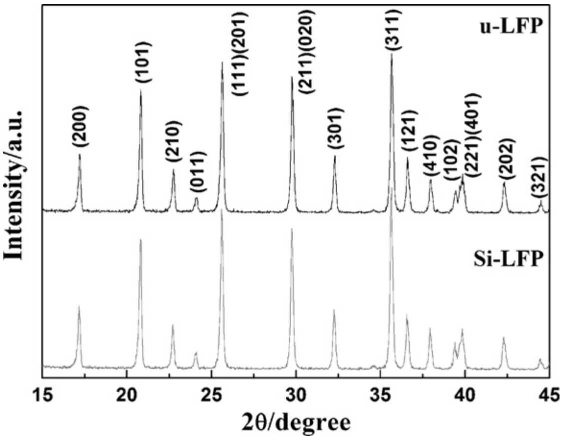

Fig. 1. XRD patterns of u-LFP and Si-LFP powders.

Fig. 2 shows the SEM and TEM images of u-LFP and Si-LFP samples. The SEM micrographs show that the product particles are uniform and particle size is about hundreds of nanometers. The TEM micrographs show the surface of u-LFP (as shown in Fig. 2b) was covered with a thin layer which should be the carbon coating, whereas the surface of Si-LFP (as shown in Fig. 2d) was covered with a denser and thicker amorphous layer, which should be the mixture of carbon and SiO_{2-x}, as supported by EDS mapping analysis shown in Fig. 3. The amount of SiO_2 was too small to form a film, it only was a thin layer nano SiO_2 particles. The EDS mapping of Si, O, P, as shown in Fig. 3b–d, match with the SEM micrograph of the corresponding particles shown in Fig. 3a, which gives unequivocal evidence to the presence of SiO_{2-x} coating on the surface of $LiFePO_4$ particles. The EDS mapping of Si on individual Si-LFP particles gives fairly uniform Si distribution on the surface of particles.

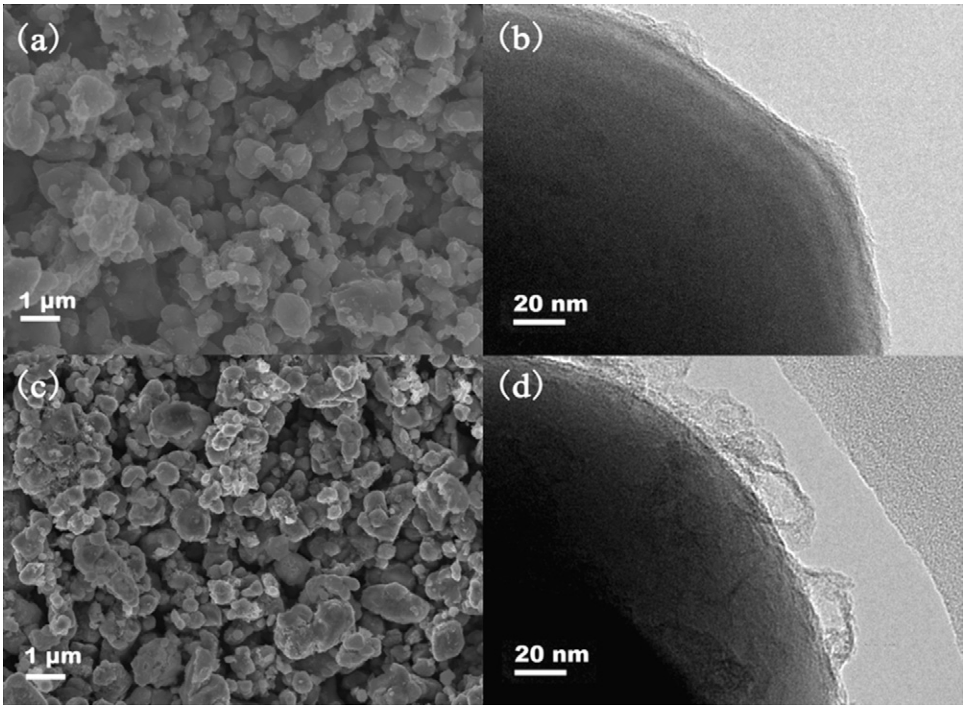

Fig. 2. SEM and TEM images of u-LFP (a) and (b) and Si-LFP (c) and (d).

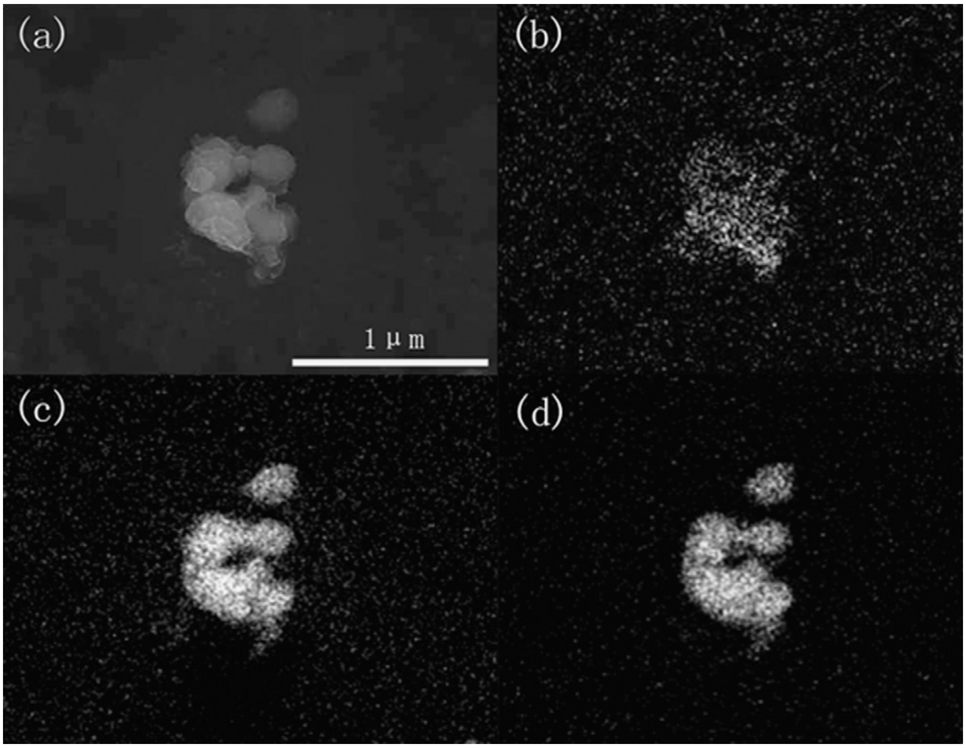

Fig. 3. (a) SEM image of Si-LFP powders; and (b)–(d) the corresponding EDS mapping of Si, O and P element respectively.

Fig. 4 shows the discharge capacity and cycling performance at 0.1 C and 1 C charge–discharge rate, respectively, between 2.5 V and 4.3 V at room temperature. The u-LFP cell shows a capacity of near 150 mAh g^{-1} at 0.1 C and 140 mAh g^{-1} at 1C, whereas the capacity of Si-LFP cell reaches nearly 160 mAh g^{-1} at 0.1 C and 145 mAh g^{-1} at 1 C. The higher capacity of Si-LFP should be derived from improving of the structural stability of $LiFePO_4$ grains coated by amorphous SiO_{2-x} layer, increasing the orderliness of Li-ion intercalation/de-intercalation. The amorphous SiO_{2-x} networks layer may accelerate the Li^+ diffusion, which can be supported by the impedance measurement results shown in Fig. 5.

Fig. 5 shows the electrochemical impedance spectroscopy (EIS) profiles of u-LFP and Si-LFP cathodes at selected cycles. The EIS measurements were carried out at the fully discharged state and room temperature. The total interfacial resistance can be derived from the resistance of the semi-circle within the curves. It can be seen that the interfacial resistance of the Si-LFP cell shifts from 29 Ω to 33 Ω after 30 cycles, while the interfacial resistance of the u-LFP cell shifts from 39 Ω to 77 Ω after 30 cycles. This implies the SiO_{2-x} coating modification has effectively enhanced the Li-ion diffusion and restrained the increasing of the interfacial resistance among particles during the cycles. Silica as a good additive was used in polymer electrolytes; it has been proved able to effectively enhance the ionic conductivity [35,36]. Although SiO_2 is an isolator, but in this study, nano-SiO_2 layer was formed in reducing atmosphere, it may be amorphous nano-SiO_{2-x}. Another electrolyte seeps into these amorphous nano-SiO_{2-x} to form solid electrolyte. So the SiO_2 coating can reduce the electrochemical impedance of cathode.

The discharge potential curves at selected cycles of the two cells are showed in Fig. 6. Before the capacity reaches 130 mAh g^{-1}, the discharge curves match with each other per-

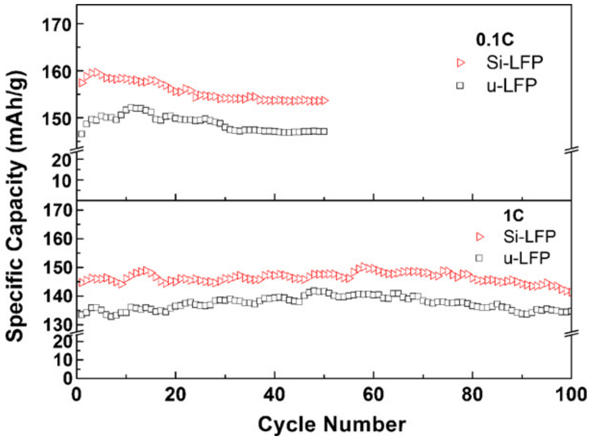

Fig. 4. Comparison of cycling behaviors of u-LFP and Si-LFP at 0.1 C (up) and 1 C (down).

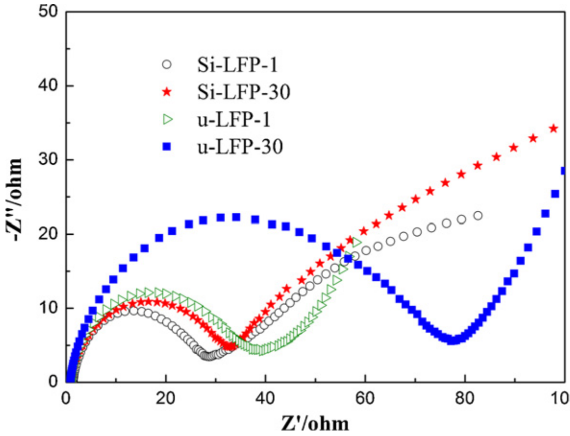

Fig. 5. Electrochemical impedance spectroscopy (EIS) of the cells discharged to 2.5 V after 1 and 30 cycles with testing frequency from 1 MHz to 1 mHz at room temperature.

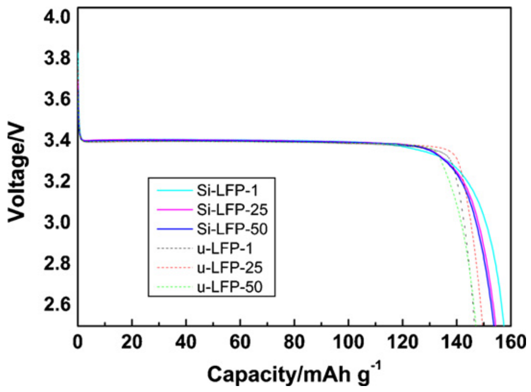

Fig. 6. Comparison of discharge potential curves after 1, 25 and 50 cycles of the cells.

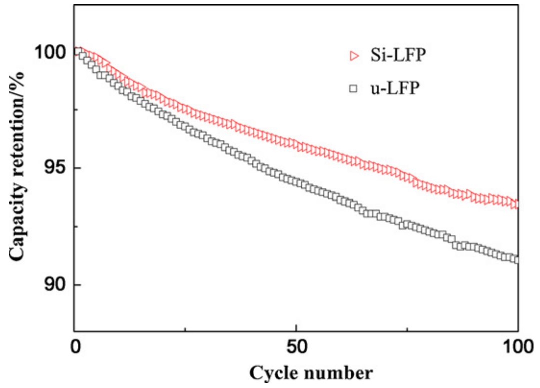

Fig. 7. Comparison of capacity retention rates of the cells after 100 cycles at 55 °C and 0.5 C.

fectly, which indicates that the fundamental nature of the Li-ion intercalation/de-intercalation $LiFePO_4$ lattices in the early stages of charge/discharge was not affected by the coating. However, after the capacity reaches 130 mAh g^{-1}, the discharge potential of the Si-LFP cell slowly reduces and its discharge capacity could reach higher. For instance, at the first cycle, the capacity of the Si-LFP cell finally reaches 158 mAh g^{-1}, as shown in Fig. 6. We infer that the SiO_2 coating played a regulatory role for insertion of the Li-ion into the lattice in later discharge stage, it may have increased the order of lithium ions that occupy the outer lattice sites of the $LiFePO_4$ grains and increase the number of lithium ion into the lattice, thus resulting in voltage drop delay, and capacity increases.

Fig. 7 shows the cycle performance of the $LiFePO_4$ cathode materials with and without SiO_2 coating at 55 °C. The cycling was carried out between 2.5 V and 4.3 V at 0.5 C charge–discharge rate. The capacity retention rate of the Si-LFP cell is near to 94% of the initial capacity after 100 cycles, while the capacity retention of the u-LFP cell is about 91%. This result demonstrates that the SiO_2 coating can improve the cycling stability of $LiFePO_4$ cathode materials at high temperature. Such an improvement in the cycle performance of the Si-LFP over the u-LFP cell is largely due to the presence of the SiO_2 coating that helps to prevent direct contact between the $LiFePO_4$ particles and the electrolyte, and thus reduces erosion of $LiFePO_4$ upon cycling. This is consistent with the observation that the Si-LFP/Li cell has a lower increasing rate in interfacial resistance than the u-LFPO/Li, as shown in Fig. 5.

4. Conclusions

The $LiFePO_4$ coated with SiO_2 shows improved electrochemical performance such as higher cycling capacity and lower cell impedance. This is attributed to the presence of SiO_2 on the particle surface which effectively prevents the $LiFePO_4$ particles from the direct contact with the electrolyte solution, improving the structural stability, reducing the interfacial resistance and increasing Li-ion conductivity. The SiO_2 coating plays a regulatory role for Li-ion inserting the lattice, increasing the order of lithium ion occupied the outer lattice of the particle.

Acknowledgement

This work was supported by Shenzhen-Hong Kong Innovation Circle project (Shenzhen Science and Technology Plan Foundation, No. 08LH-03).

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