Short communication

Surface modification of aluminum with tin oxide coating

Xuefeng Lei, Jiangfeng Xiang, Xiaoling Ma, Chiwei Wang, Jutang Sun [*]

Department of Chemistry, Wuhan University, Wuhan 430072, PR China

Abstract

Tin oxide (SnO) was coated on the surface of aluminum spherules with an average particle size of 37 μm by a chemical deposition method to improve the electrochemical properties. The samples were characterized by particle size analysis, X-ray diffraction (XRD), scanning electron microscope (SEM), ac impedance spectroscopy and galvanostatic cycling. Pure aluminum electrode delivers an initial reversible capacity of 779 mAh g^{-1}, whose capacity loss is 58% after 10 cycles. In comparison, 10 wt% SnO–Al composite delivers an initial reversible capacity of 806 mAh g^{-1} with the capacity loss of 28% after 10 cycles. Results show that SnO coating plays an important role in the improvement of the electrochemical performances. It could not only reinforce the mechanical stability of aluminum particles, but also provide better electronic contacts to the electrode.

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1. Introduction

Lithium-ion batteries have been widely used as power sources in modern electronic devices, and it is well known that carbon materials are commercially used as anode material. However, the researches aimed at finding new high-performance electrode materials have been performing to meet the market expansion and diverse needs. Previous research suggested that aluminum could be a possible candidate as a negative electrode for lithium ion batteries [1]. However, the use of this metal in lithium ion batteries has faced the problem of particle cracking and crumbling as well as consequent loss of capacity [1,2].

As reported in literature, intermetallic and composite were employed to improve the cycling behavior of lithium alloys by forming three kinds of composites: (i) active/inactive composites. This kind of composites has an active component as reactant storing lithium, whereas the other less active or inactive component as a matrix buffering the volume expansion of the reactant during charge–discharge process [2–6]. (ii) Inactive/active composites. For these composites, the active component act as matrix and the inactive component was embedded homogeneously in the active matrix [7]. (iii) All-active composites. All the compo-

nents are active to react reversibly with lithium. Improvements in the cycling behavior of these all-active composites can be related to the fine dispersion of the small size reactant in the phase of electric polymer matrix [8,9]. It is believed that the existence of intermetallic and composite strengthens the mechanical stability of lithium alloys and enhances the resistance to crack initiation and propagation.

In this work, active SnO was used to improve the electrochemical performance of aluminum matrix.

2. Experimental

The aluminum spherules (37 μm) were used as received. All other chemicals were AR grade. Three grams Al spherules were dispersed in DMF solvent forming slurry, to which 0.5 ml LiOH aqueous solution (2.3 M) was added. The mixture was ultrasonicated for 15 min to reach the aim of metallic external corrosion. After ultrasonicating, the slurry was diluted by DMF, and then 2.5 ml LiOH aqueous solution (2.0 M) was added entirely with vigorous stirring, subsequently, 5 ml SnCl$_2$ solution of DMF including 0.558 g SnCl$_2$·2H$_2$O was added drop by drop to precipitate Sn(OH)$_2$. The amount of SnCl$_2$ was strictly controlled to obtain a uniform precipitation of Sn(OH)$_2$. The solid phase was filtrated, washed with distilled water, and dried in vacuum at 180 °C overnight to obtain 5 wt% SnO–Al product. The content of tin oxide was calculated by strict molar ratio. The amount

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[*] Corresponding author. Tel.: +86 27 87218494; fax: +86 27 68754067.
E-mail address: jtsun@whu.edu.cn (J. Sun).

of SnCl$_2$ was varied during the precipitation to obtain other SnO–Al composites.

Coin cells were used for electrochemical tests. Slurries prepared were consisted of 60 wt% active materials, 25 wt% acetylene black and 15 wt% polytetrafluoroethylene (PTFE) binder. Lithium metal was used as a counter electrode, and 1 M LiPF$_6$ solution in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The cells were assembled in an argon-filled glove box (Mikrouna-China Super 1220/750). Cells were charged and discharged galvanostatically with current density 100 mA g^{-1} in the range of 0.001–1.5 V at 25 °C. The electrochemical properties were examined using Neware cell test system.

The particle size was measured by Malvern Mastersizer 2000. The X-ray power diffraction (XRD) measurements were carried out with a Shimadzu XRD6000 diffractometer with Cu Kα_1 radiation ($\lambda = 1.54056$ Å). The scanning electron microscope (SEM) images were observed by means of Hitachi 400 SEM. Ac impedance measurements were performed using CHI660A by applying an ac voltage of 5 mV amplitude in the frequency range 1 MHz to 10 mHz.

3. Results and discussion

The particle size and particle size distribution of aluminum matrix is shown in Fig. 1, whose average particle size is 36.682 μm. Fig. 2 gives the XRD patterns of pure aluminum and Al–SnO composites with different contents. The four strong diffraction peaks at 2θ values of 38.57, 44.81, 65.21 and 78.33° are characteristic of metallic aluminum [JCPDS No. 89-4037]. Weak peaks of tetragonal tin oxide at 2θ values of 30.01, 33.56, 51.01 and 57.62° are observed in Fig. 2c and d [JCPDS No. 85-0712]. However, no obvious SnO peaks appear in Fig. 2b due to a small amount of SnO.

Fig. 3 illustrates the SEM photograph of pure aluminum and all composites. It is observed that the aluminum powders are smooth with spherical morphology (Fig. 3a). In comparison, the metal keeps the shape of spherule but the surface becomes coarse
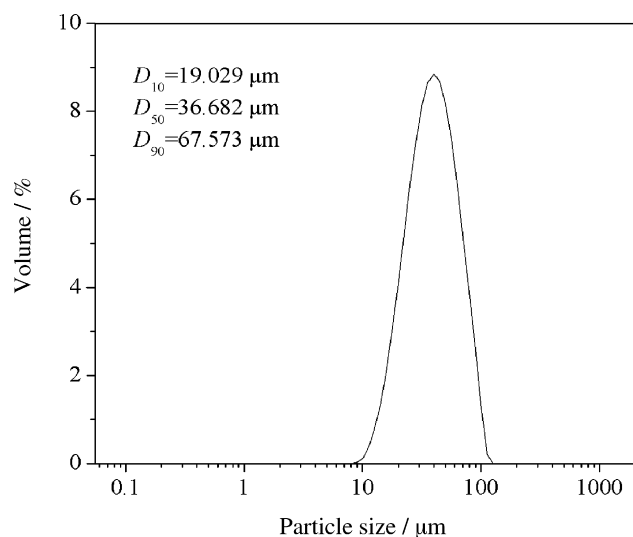

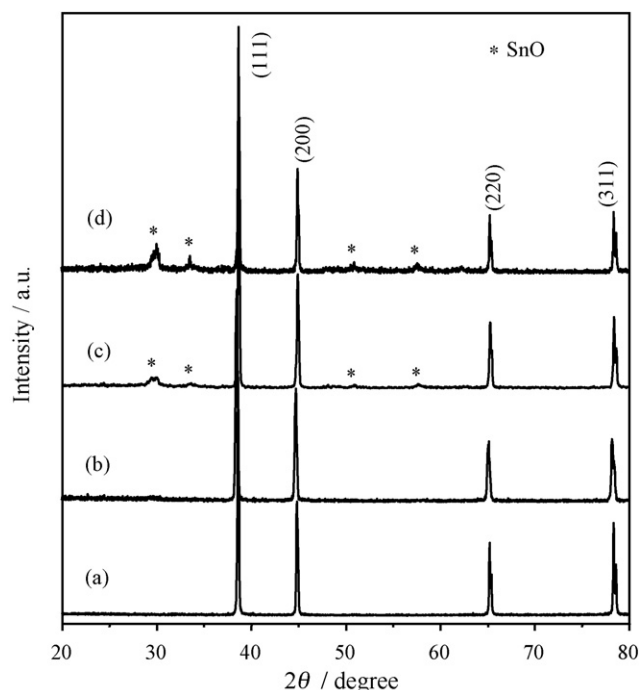Fig. 1. The particle size distribution of aluminum matrix.

Fig. 2. XRD patterns of pure aluminum and SnO–Al composites: (a) pure aluminum, (b) 5 wt% SnO coating, (c) 10 wt% SnO coating and (d) 20 wt% SnO coating.

after dealing with alkali; meanwhile, tin oxide small particles confirmed by the XRD patterns are dispersed and deposited on the surface of aluminum.

Fig. 4 shows the first cycle discharge and charge profiles of various composites (here the lithiation and de-lithiation are, respectively, defined discharge and charge according to a half cell). The first cycle discharging curve of aluminum electrode mainly consists in three regions [1]: the initial lithium insertion occurs between 1.5 and 0.2 V (region I); the following wide plateau at 0.2 V is the specific characteristic for aluminum, indicating the formation of LiAl alloy (region II); a final insertion occurs between 0.2 and 0.001 V (region III). For SnO–Al composites, the capacities of region I enhance with the increase of SnO content, at the same time, all composites inherit the low and flat potential plateau in region II.

Fig. 5 shows the cycle performances and coulombic efficiencies of pure aluminum and SnO–Al composites electrodes. Although all samples show irreversible capacity losses, the SnO–Al composites, especially the 10 wt% SnO–Al composite, exhibits higher capacity retention and better cyclability compared with pure aluminum. Simultaneously, it is noticeable that all composites maintain higher coulombic efficiencies than pure aluminum after the fourth cycle.

Electrochemical performances of the electrodes are listed in Table 1. In the table, $R_{10/1}$ is the ratio of charge capacity in the 10th cycle relative to the 1st, which indicates the material cyclability [10]. Results show that the pure aluminum electrode has a high coulombic efficiency of 76% in the first cycle, but the charge capacity rapidly decreases to 323 mAh g^{-1} after 10 cycles, whose capacity retention ($R_{10/1}$) is only 42%. The first coulombic efficiencies of 5 wt% SnO–Al, 10 wt% SnO–Al and
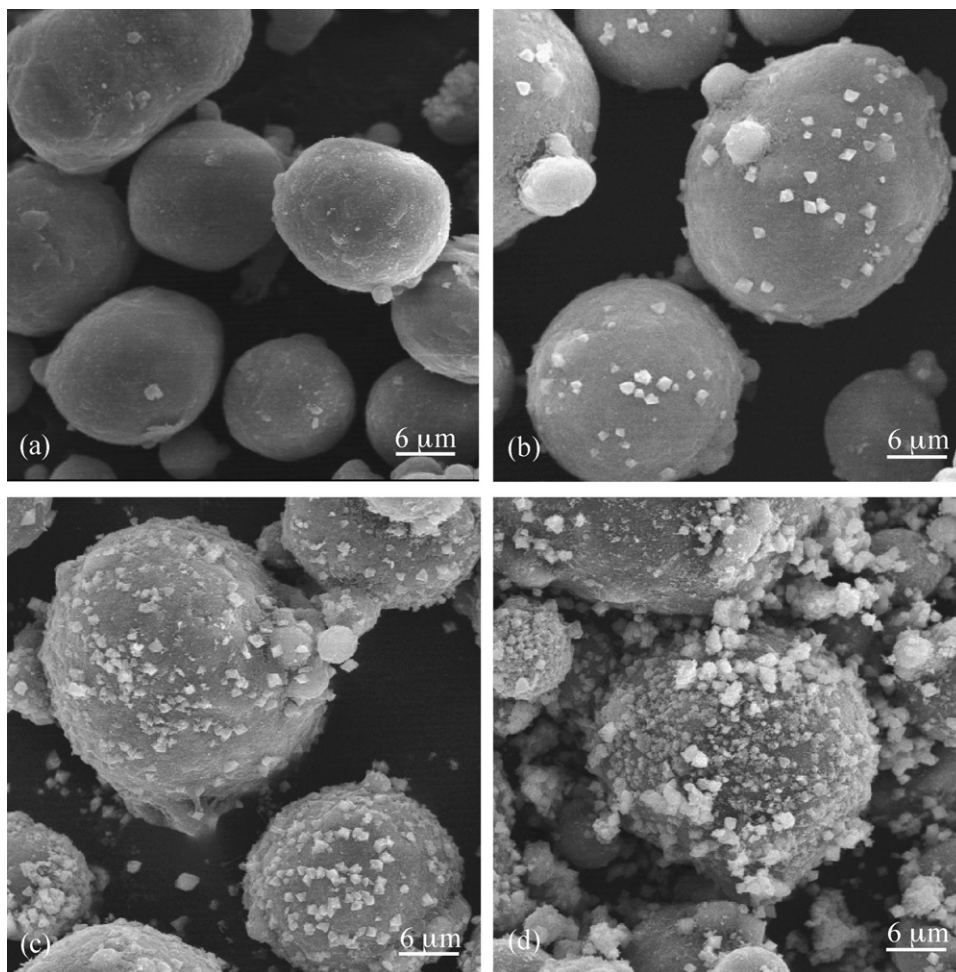
Fig. 3. SEM images of pure aluminum and SnO–Al composites: (a) pure aluminum, (b) 5 wt% SnO coating, (c) 10 wt% SnO coating and (d) 20 wt% SnO coating.

20 wt% SnO–Al composites are 73, 66 and 64%, respectively. Compared with pure aluminum electrode, the coulombic efficiencies decrease due to the irreversible reduction process of SnO. However, the capacity retentions ($R_{10/1}$) of these composites significantly increase to 70, 72 and 71%, respectively. For example, 10 wt% SnO–Al composite delivers the charge capacity of 582 mAh g^{-1} after 10 cycles, which is almost twice than that of pure aluminum electrode. It is obvious that the coating of SnO has improved the cyclability.
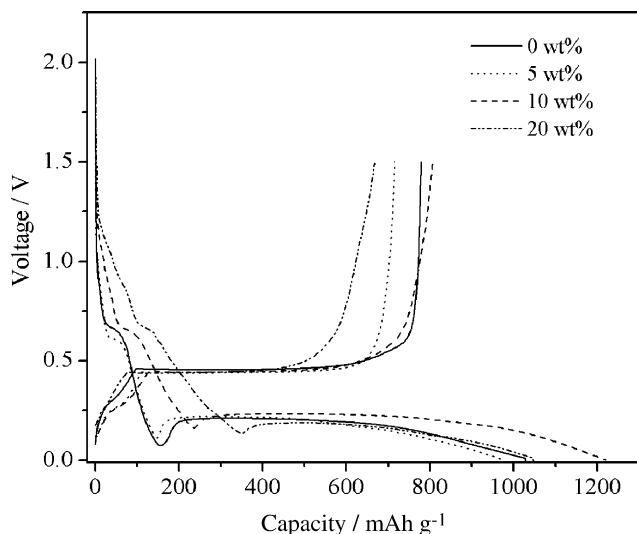

Fig. 4. First cycle profiles of pure aluminum and SnO–Al composites cycled between 0.001 and 1.5 V at a current density of 100 mA g^{-1}.
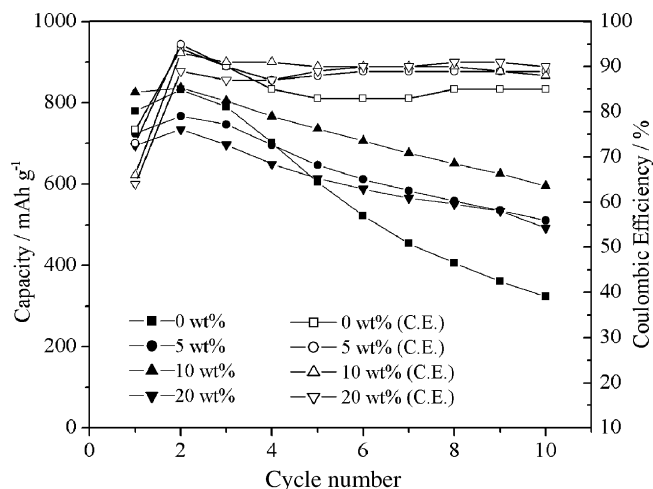

Fig. 5. The the cycleability of pure aluminum and SnO–Al composites cycled between 0.001 and 1.5 V at a current density of 100 mA g^{-1}.
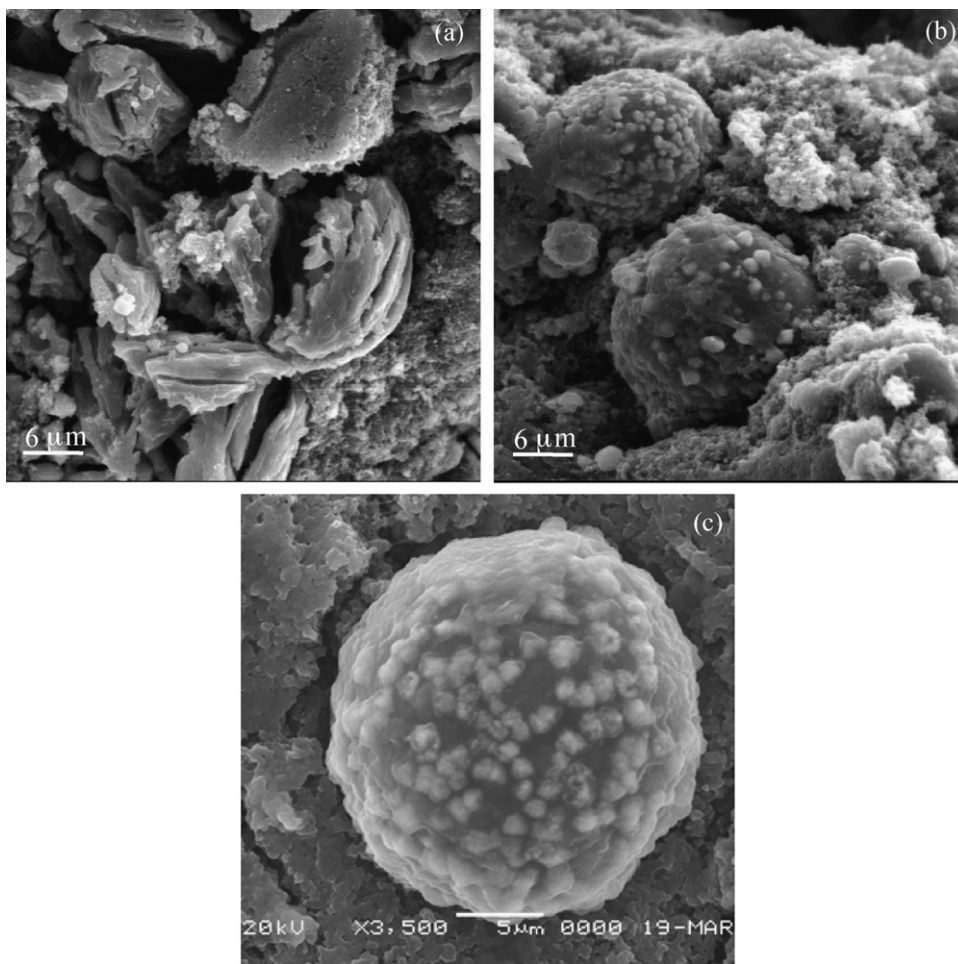
Fig. 6. SEM images of pure aluminum (a) and 10 wt% SnO–Al composite (b and c) electrodes after one cycle.

To understand the effects of SnO on cycling behavior, the morphology of pure aluminum and 10 wt% SnO–Al composite electrodes after one cycle were obtained (Fig. 6). The aluminum spherules show severe pulverization in pure aluminum electrode, whereas the spherical shape maintains in SnO–Al electrode, which demonstrates that the existence of SnO buffers the volume expansion and restrains the pulverization efficiently. The ac impedance of pure aluminum and 10 wt% SnO–Al composite electrodes were also performed on fully lithiated state in the first cycle (Fig. 7). Two semicircles were observed in the spectrum. The first semicircle appearing at high frequencies is related to the resistance of surface film, and the second observed in the middle frequencies corresponds to the charge transfer resistance. Both of the semicircles of 10 wt% SnO–Al

composite electrode are distinctly decreased compared to the impedance of pure aluminum electrode, indicating the lower resistance of surface film and charge transfer reaction, namely better electronic connection. Based on above investigation, it may be concluded that SnO plays important role via two ways:

Table 1
Electrochemical performances of Al and various Al–SnO samples

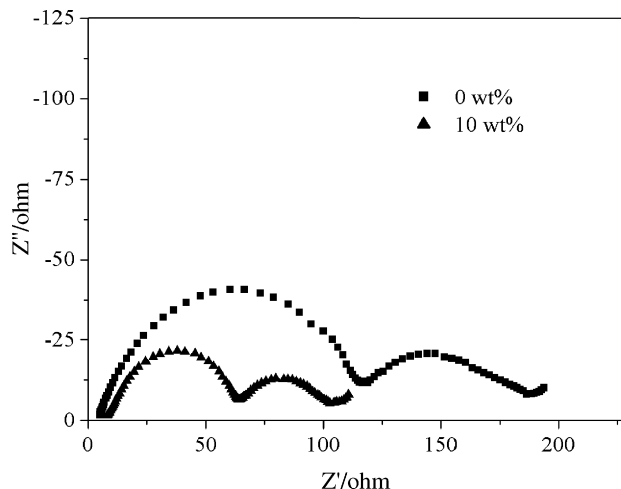|	SnO content (wt%)			
	0	5	10	20
1st discharge capacity (mAh g^{-1})	1029	977	1220	1048
1st charge capacity (mAh g^{-1})	779	716	806	669
Coulombic efficiency (%)	76	73	66	64
$R_{10/1}$	42	70	72	71

Fig. 7. The ac impedance spectra of pure aluminum and 10 wt% SnO–Al composite electrodes at fully lithiated state in the first cycle.

first, for only aluminum particles, their mechanical stabilities are reinforced through SnO coating. It was reported that the particulate-reinforced aluminum composite has a higher elastic modulus, greater tensile strengthen, and more resistance to crack initiation and propagation than the unreinforced one [7,11–13]. SnO decomposes into a mixture of metallic tin and LiO_2 during the first discharging process, the mixture tends to become a homogeneously coating layer on the surface of aluminum particles to form a core/shell structure, which can be clearly observed in Fig. 6c. This coating layer should be made to accommodate the volume expansion of aluminum particles, thus making the particles possess more resistance to pulverization. Second, the electronic contacts of the electrode are improved by SnO coating. SnO reacts with lithium in the first Li insertion process, the formed metallic Sn can provide better electronic contacts between aluminum particles and the carbon black, thus increasing the amount of "connected" active material. The assumption has been confirmed by the ac impedance.

4. Conclusion

Small particles of SnO were coated on the surface of aluminum spherules by chemical deposition method to obtain SnO–Al composites. Despite the coating of tin oxide decreases the initial reversible capacities of composites, the capacity retention and cycleability are improved. The volume expansion and pulverization of the aluminum particles are buffered significantly by forming a core/shell structure during the first lithiation process, which reinforces the mechanical stability of aluminum particles. Simultaneously, the metallic Sn reduced from SnO provides better electronic contacts to the composite electrode.

Results indicate that it is feasible to coat aluminum with active particles, and it is possible to obtain new types of aluminum based composites with good performance if the active particles are chosen preferably.

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