Short communication

Effects of graphite on electrochemical performance of Sn/C composite thin film anodes

L.Z. Zhao [a,b], S.J. Hu [a,c], Q. Ru [a], W.S. Li [a,b,*], X.H. Hou [a,b], R.H. Zeng [a,b], D.S. Lu [a,b]

[a] *Department of Chemistry, South China Normal University, Guangzhou 510006, China*
[b] *Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, Guangzhou 510006, China*
[c] *Department of Mathematics and Physics, Wuyi University, Jiangmen 529020, China*

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ABSTRACT

The composite thin films of tin with 0 wt.%, 3.2 wt.%, 6.0 wt.%, and 11.8 wt.% graphite on the Cu foil were fabricated by magnetron sputtering (MS). The surface morphology, the composition and the electrochemical performance of the composite films were characterized by scanning electron microscopy (SEM), energy disperse spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and galvanostatic charge/discharge (GC) measurements. It is found that the capacity loss of tin can be significantly reduced by its composite with graphite, but its discharge capacity decreases with increasing the content of graphite. The composite with 6.0 wt.% graphite show its good discharge capacity and cyclic stability. Its initial discharge capacity is 750 mAh g^{-1} and it keeps 85% of its initial discharge capacity after 10 cycles, comparing to the 14% for the pure tin.

1. Introduction

Much attention has been paid to the rechargeable thin film lithium ion batteries in recent years, which have great potential for application in mini-portable electronic devices and electrical vehicles. To meet the demands for power sources with high energy density, a great deal of work has been done to find a substitute for graphite that is widely used as the anode in a commercial lithium ion battery. As a very promising anode material, tin has a high theoretical specific capacity, which reaches 990 mAh g^{-1}. However, tin suffers from severe volume variations during lithium intercalation and de-intercalation, leading to pulverization and quick capacity fade. This drawback limits its practical application as anode of lithium ion battery.

It has been reported that, in the case of Sn oxide anode, Sn provides the high discharge capacity and Li$_2$O acts as a matrix that helps to lengthen the cycle life of the electrode [1]. Since then, many efforts have been focused on the selection of proper matrix, which can ease the electrode stress that appears during cycling and extend effectively the cycle life. Many tin-based alloys and composites, such as Sn–Ni [2] and SnO$_2$–carbon [3,4], have been therefore

investigated. The cyclic stability of tin can be improved to a great extent but its capacity is reduced significantly due to the use of the matrix.

The performances of tin as the anode of lithium ion battery are related to the preparation methods [5–7]. Magnetron sputtering (MS) is a simple, manageable and efficient method to fabricate thin film over a large area. It was found in our lab that the tin film electrode prepared by MS has a better cyclic performance than the tin film electrode by electrodeposition [8]. In this paper, MS was used to fabricate the composite thin films of tin with graphite (Sn/C) on the Cu foil, and the effect of graphite content on the performance of the composite as the anode of lithium ion battery was considered.

2. Experimental

Sn/C thin films were prepared onto Cu-foil substrates in a deposition chamber evacuated to 5×10^{-3} Pa by multi-target radio frequency magnetic sputtering-4 (RFMS-4) apparatus. The pure tin target (99.9%, $\varphi 59 \times 4$ mm) and the graphite target (99.95%, $\varphi 52 \times 5$ mm) were used as starting materials. The Cu-foil substrates were cleaned ultrasonically with acetone and fixed onto a rotatable holder at the position 59 mm above the targets. Pure argon (99.999%) was input at 60 ml min^{-1} into the chamber till the vacuum demand in the chamber was reached. Direct current (DC) power with 100 W was used to bombard the substrates for 5 min

before the fabrication of the thin films. Radio frequency (RF) power with 100 W was used to smelt the target for 5 min to eliminate the impurity of the surface. Three samples of composite Sn/C films were fabricated as follows, sputtering tin target with a RF power of 150 W onto the Cu foil for 15 min and then sputtering graphite target with a RF power of 150 W onto the obtained Sn thin film for 5 min, 10 min and 20 min, respectively. The weight of tin on the Cu foil was about 0.27 mg cm^{-2}, which was determined by electronic balance.

The morphologies of the samples were observed with SEM (JSM-6380-LA, JEOL). The electronic state of carbon in the composite thin film was determined by XPS (AXIS Ultra DLD, Kratos). The ratio of graphite to tin was measured by EDS (JSM-6380-LA, JEOL) analysis.

Galvanostatic charge/discharge (GC) measurements were carried out by 8-channel testing system (Solartron1480, England) at room temperature with CR2016 button cells. The cells were assembled in an argon-filled glove box (Mikrouna, Sukei1220/750). Lithium foil was used as both counter and reference electrodes. The electrolyte was 1 M LiPF$_6$ dissolved in a 1:1:1 (vol.) mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). Polypropylene membrane (Celgard 2400) was used as the separator. In the GC test, the current was 0.1 mA cm^{-2} and the potentials were between 0 and 1.5 V. All the potentials in this paper are with respect to Li/Li$^+$. The discharge and charge processes are corresponding to lithium intercalation and lithium de-intercalation, respectively.

3. Results and discussion

3.1. Characterization of thin films

Fig. 1 presents the surface SEM morphologies of tin films with sputtering graphite for 0 min, 5 min, 10 min, and 20 min. It can be seen from Fig. 1a that the pure tin has a compact layered structure in large grain sizes. However, the surface of the films with graphite looks very different from that of the pure tin, as shown in Fig. 1b–d. This indicates that the tin is covered by graphite. It is noted that the boundaries of the pure tin can still be seen for the sample with sputtering graphite for 5 min, as shown in Fig. 1b, indicating that the tin of this sample cannot be covered completely by graphite. As the sputtering time of graphite increases, the morphology of pure tin disappears completely, as shown in Fig. 1c and d, indicating that the tin can be covered completely for the samples with the sputtering time over 10 min.

Fig. 2 presents the EDS of Sn/C films formed with sputtering graphite target for 5 min, 10 min and 20 min. Based on the EDS analysis, it is found that the graphite content of the three samples is 3.2 wt.%, 6.0 wt.% and 11.8 wt.%, respectively.

Fig. 3 presents the XRD pattern of the Sn/C film with 6.0 wt.% graphite on Cu foil. The diffraction peaks of Sn and Cu appear in the XRD patterns of the Sn and Sn/C films. The Cu diffraction should be ascribed to that of the Cu foil. The diffraction of graphite in Sn/C film shows the existence of graphite in the sample. It should be noticed that there is not any diffraction for CuSn alloys. This suggests that during the film fabrication CuSn alloy cannot form or it may form but its content can be neglected.

To identify the electronic state of carbon in the Sn/C film, the Sn/C film with 6.0 wt.% graphite was performed with XPS analysis. The results obtained are shown in Fig. 4. It can be found from Fig. 4a that the film surface is mainly composed of carbon, with small amount of tin and some amount of oxygen. The oxygen should be from sample transfer in the air. Fig. 4b shows the percentage of graphite in total deposited carbon reflected by the
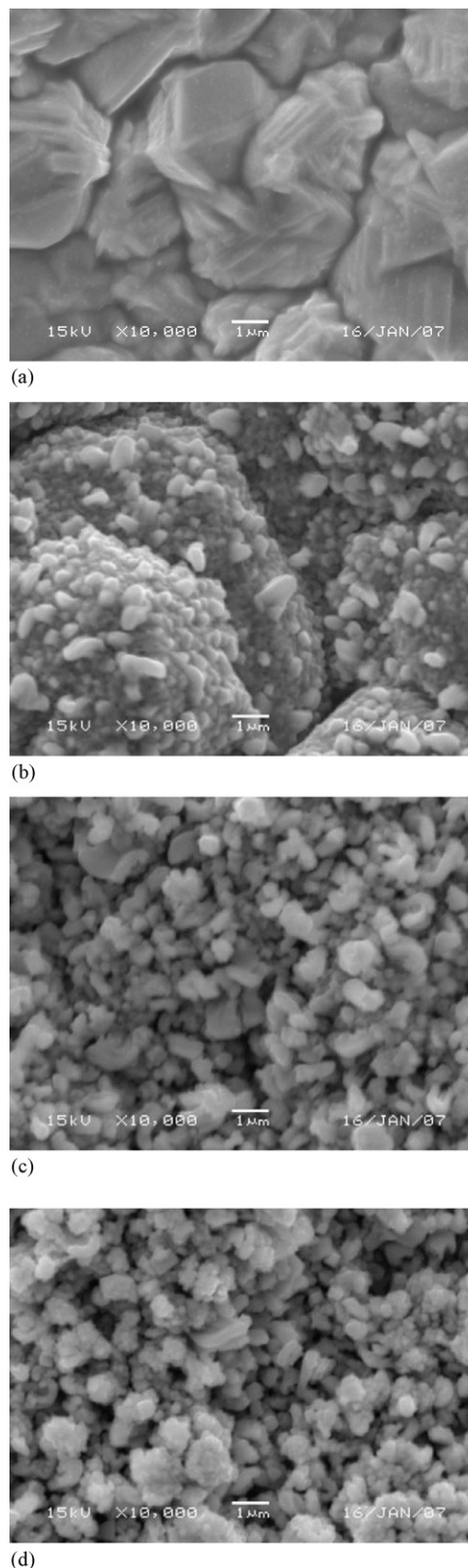

(a)

(b)

(c)

(d)

Fig. 1. Morphologies of Sn/C films with tin films with sputtering graphite for (a) 0 min, (b) 5 min, (c) 10 min, and (d) 20 min.
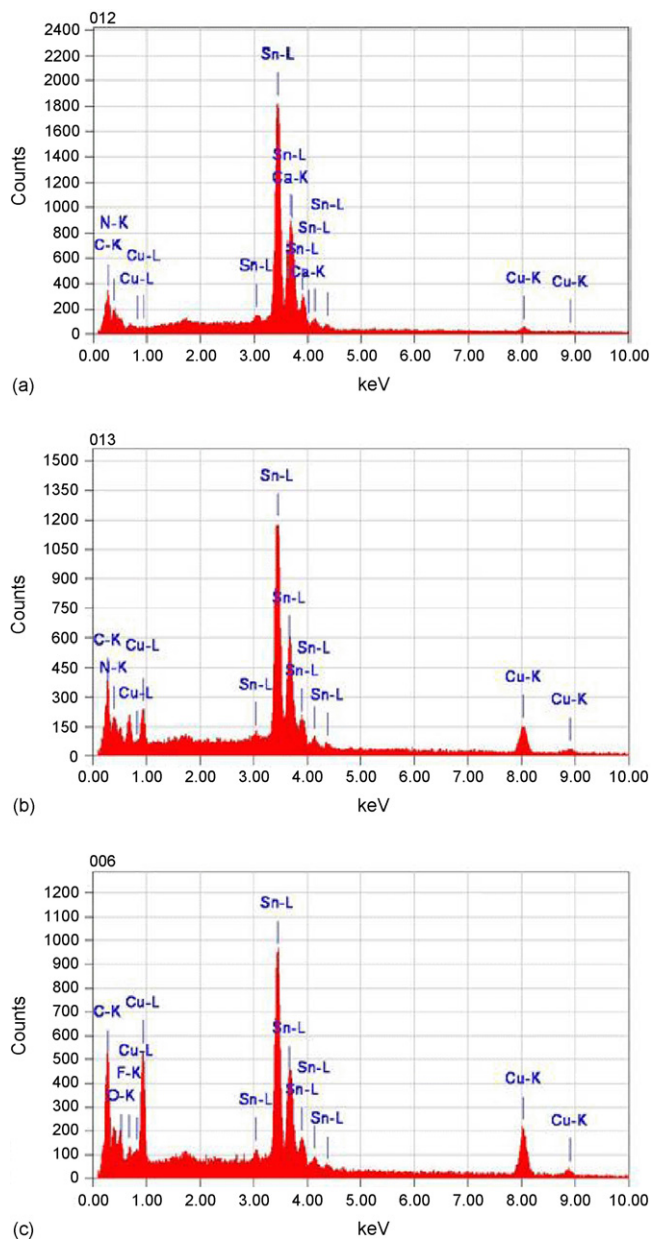
Fig. 2. EDS of Sn/C films with different sputtering time (a) 5 min, (b) 10 min, (c) 20 min.

C1s peak in XPS. It can be found from Fig. 4b that there are several states of carbon. One is at the binding energy of 284.31 eV, corresponding to pure graphite [9], others are at the binding energy of 287.07 eV, corresponding to the carbon in the form of C–C and C–O [10]. The former makes up about 84 at% of the total carbon, indicating the carbon in the Sn/C film is mainly in the form of graphite.

3.2. Charge and discharge behavior

Fig. 5 presents the first charge–discharge curves of Sn/C film electrodes with different graphite content. The discharge (lithium intercalation) and charge (lithium de-intercalation) capacities, the initial capacity loss and the coulombic efficiency of Sn/C film electrodes with different graphite content in the first cycle, obtained from Fig. 5, is listed in Table 1. It can be seen from Table 1 that,
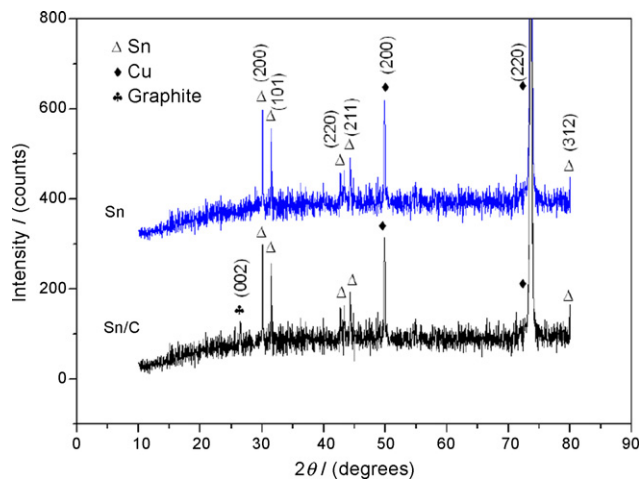

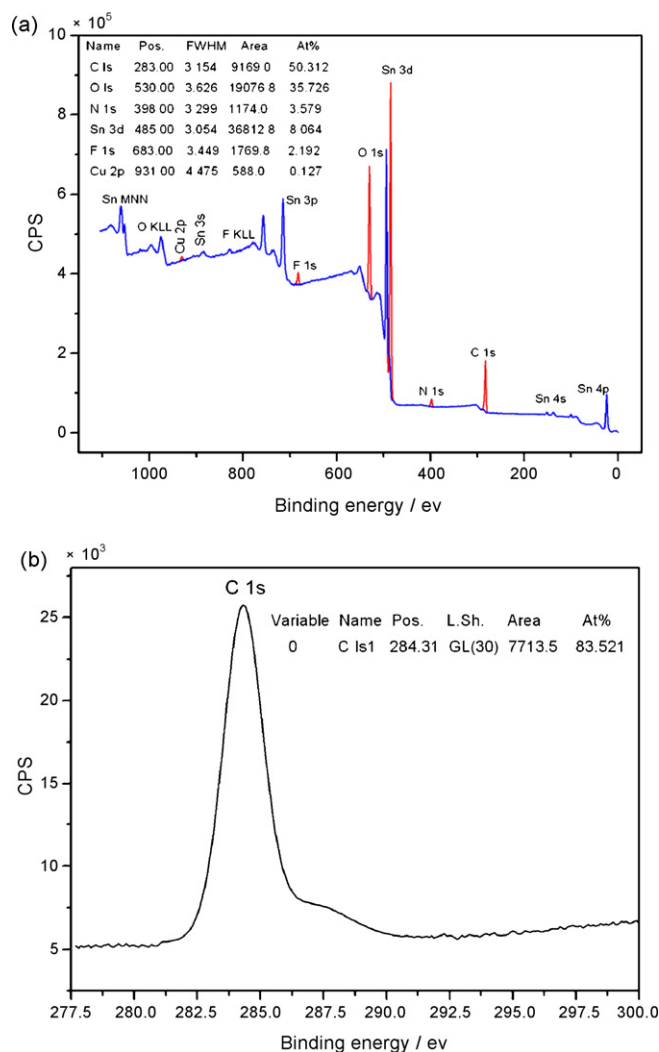**Fig. 3.** XRD patterns of Sn film and Sn/C film with 6.0 wt.% graphite.

Fig. 4. XPS of Sn/C film with 6.0 wt.% graphite, (a) wide survey, (b) the percentage of graphite in total deposited carbon reflected by the C1s peak in XPS.
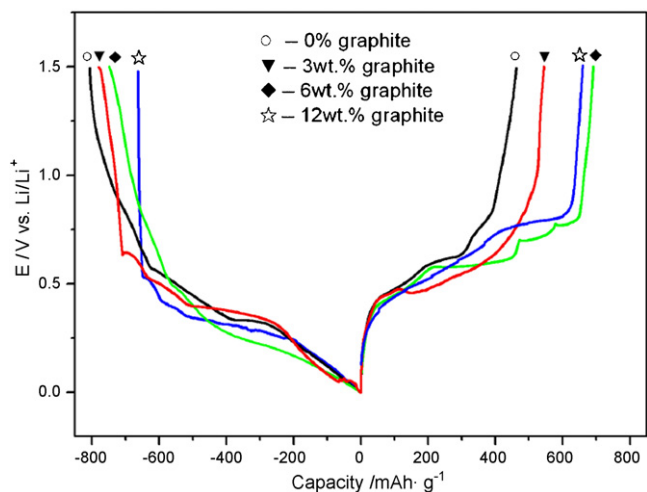
Fig. 5. First charge–discharge curves of Sn/C film electrodes with different graphite content.

as graphite content increases, the discharge capacity decreases gradually, changing from 810 mAh g^{-1} of pure Sn to 670 mAh g^{-1} of composite Sn/C film with 11.8 wt.% graphite. This should be ascribed to the higher theoretical specific capacity of tin than graphite.
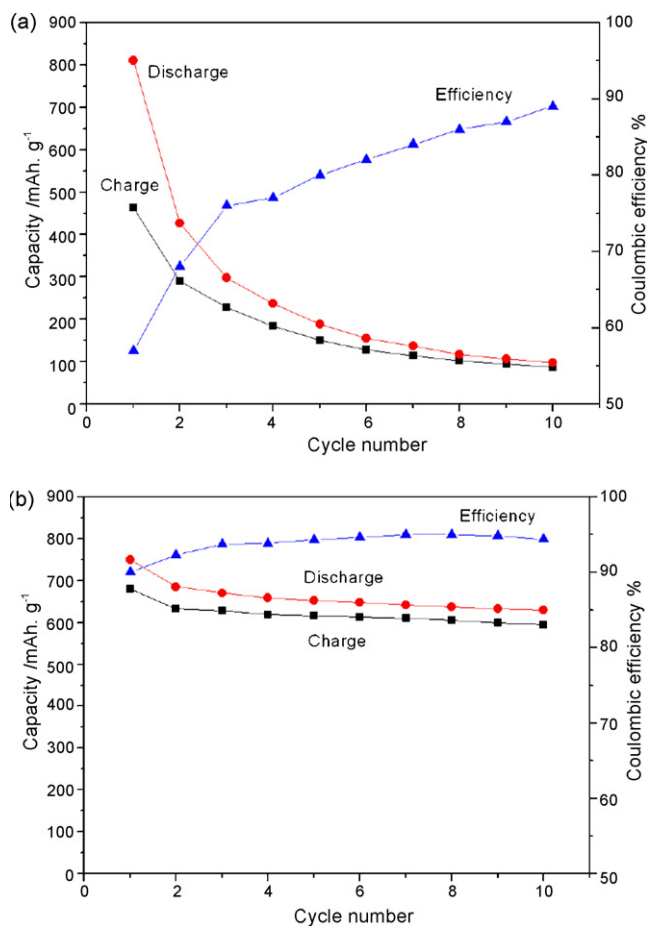

Fig. 6. Cyclic performance of Sn and Sn/C film (a) 0 wt.% graphite and (b) 6 wt.% graphite.

Table 1
Charge/discharge parameter of Sn/C film electrodes with different graphite content in the first cycle

Graphite content (wt.%)	0	3.2	6.0	11.8
Discharge capacity (mAh g^{-1})	810	778	750	670
Charge capacity (mAh g^{-1})	462	545	680	648
Initial capacity loss (mAh g^{-1})	348	233	70	22
Coulombic efficiency (%)	57	71	90	96

However, the initial capacity loss is reduced significantly as graphite content increases, changing from 348 mAh g^{-1} of pure Sn to 22 mAh g^{-1} of composite Sn/C film with 11.8 wt.% graphite. Among all the samples, the Sn/C film with 6.0 wt.% graphite shows its high enough initial capacity (750 mAh g^{-1}) and appropriate initial capacity loss (70 mAh g^{-1}), and therefore is good for the application in lithium ion batteries.

Fig. 6 presents the cyclic performance of Sn and Sn/C (6.0 wt.% graphite) film electrodes. It can be seen from Fig. 6a that the discharge and charge capacities of the Sn film electrode decrease quickly with increasing cyclic number. After 10 cycles, the Sn film keeps only 14% of its initial discharge capacity. However, the Sn/C film shows its good cyclic stability, as shown in Fig. 6b. The Sn/C film keeps 85% of its initial discharge capacity after 10 cycles.

It is obvious the stability of tin as anode can be improved significantly by its composite with graphite. This improvement can be ascribed to the good electrical contact of tin and the alleviation of tin pulverization due to the graphite covering the tin.

4. Conclusions

Composite Sn/C thin films can be fabricated by magnetron sputtering. The composite of tin with graphite can improve its performance as lithium intercalated anode of lithium ion battery. With graphite content increasing in the composite, the capacity loss of the composite is reduced, but its discharge capacity decreases. The composite film with 6.0 wt.% graphite shows its good discharge capacity and cyclic stability.

Acknowledgements

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