

Investigation of Tin Oxide Based Nanocomposites for Li–Ion Batteries

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In this work, tin oxide (SnO_2) films were deposited on multiwall carbon nanotube buckypaper using a rf magnetron sputter process in a mixed oxygen/argon (1/9) gas environment. Conditions for the growth of SnO_2 thin films on multiwall carbon nanotube buckypaper by rf sputtering are: target composition SnO_2 (99.999 wt%); total system pressure 1 Pa; sputtering power (rf) 75, 100 and 125 W, respectively; O_2/Ar (1/9) gas mixture. The surface morphology of the SnO_2 multiwall carbon nanotube composite films was investigated by scanning electron microscopy. The crystallographic structure of the sample was determined by X-ray diffraction. The electrochemical properties of SnO_2 multiwall carbon nanotube composite anodes were investigated by galvanostatic charge-discharge experiments.

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1. Introduction

Tin oxide (SnO_2) is an *n*-type semiconductor oxide with wide band gap energy [1]. Tin oxide thin films were prepared using various methods, e.g., spray pyrolysis [2, 3], reactive magnetron sputtering [4], reactive ion assisted deposition [5], chemical vapor deposition (CVD) [6], and by filtered vacuum arc deposition (FVAD) [7, 8]. Tin oxide is an attractive material as a potential substitute for the conventional graphite anode in lithium ion batteries, because the theoretical capacity of SnO_2 (1494 mAh g^{-1}) has been estimated to be superior to that of graphite (372 mAh g^{-1}) [9] but also owing to the reasonably low potentials and high volumetric and gravimetric capacities [10].

However, the application of tin-based anodes is significantly hampered by poor cycling performance, which is caused by the significant volume change during the alloying and dealloying processes of Li–Sn [11, 12]. The use of these SnO_2 nanostructures can solve the above-mentioned problem to a large extent due to their high surface area and large surface-to-volume ratio [12].

Carbon nanotubes (CNTs) have become amazing nanostructured materials. Because of their high specific surface area and hollow interior, CNTs can be served as nanometer sized capillaries, mould, or template in material fabrication. The high surface area of CNTs with narrow pore size distribution is also very important to applications used as substrates for external coating. Functional carbon nanotubes can act in several ways to improve electrochemical performance of anodes: (1) increasing conductivity leading to less charge-transfer resistance and improved high rate capability; (2) using as the catalyst support for nanosized tin oxide particles formation; (3) increasing the stability and cycle life of anodes [13].

2. Experimental

Multiwall carbon nanotubes (MWCNTs, catalytic carbon vapour deposition method, 95%) were purchased from Arry International (Germany). MWCNTs were heated in air at 350°C for 2 h and then soaked in hydrochloric acid for 24 h. The precipitate was rinsed with deionized water and dried at 40°C . MWCNTs were chemically functionalized by ultrasonication in a mixture of sulfuric acid and nitric acid (3:1) for 8 h. Functionalized multiwall carbon nanotubes (fMWCNTs) were washed with deionized water and dried at 40°C for 24 h. fMWCNTs (20 mg) was dispersed with 100 mg of SDS in 50 mL of deionized water and sonicated for 1 h. PVDF membranes with a pore size of 220 nm were used in vacuum filtration. Then the MWCNT buckypapers were separated from the PVDF membrane, further compacted, and dried at 40°C for 24 h. The average thickness of the produced MWCNT buckypapers is approximately $100 \mu\text{m}$ and their diameter about 16 nm.

The coating process has been performed in a multifunctional magnetron sputtering PVD unit equipped with rf units. SnO_2 thin films were deposited on MWCNT buckypaper using rf magnetron sputtering. The target was a SnO_2 disc ($\text{SnO}_2 = 99.999\%$ in weight) of a diameter of 50.8 and 6.35 mm thick. The rf powers were 75, 100 and 125 W. SnO_2 thin films were deposited under O_2/Ar (1/9) gas mixture at a constant working pressure of 1.0 Pa. The flow rate of Ar and O_2 gases was fixed by a TDZM-III mass flow controller. The substrate was not heated deliberately and not measured. The crystalline structure of SnO_2 films was characterized by X-ray diffraction (XRD) technique. The XRD patterns of the deposited SnO_2 thin films were obtained by an X-ray diffractometer (Rigaku D/MAX 2000 with a multipurpose attachment) using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$).

The electrochemical performance was studied using 2016-type coin cells assembled in a nitrogen-filled glove

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box. The electrochemical performance of SnO₂ thin films deposited on MWCNT buckypaper was evaluated by galvanostatic discharge–charge measurement using a computer-controlled battery tester at a 1.0 C rate between 0.2 and 3.0 V.

3. Results and discussion

The surface SEM images of uncoated MWCNT buckypaper and SnO₂ thin films deposited with different rf powers on MWCNT buckypaper are shown in Fig. 1.

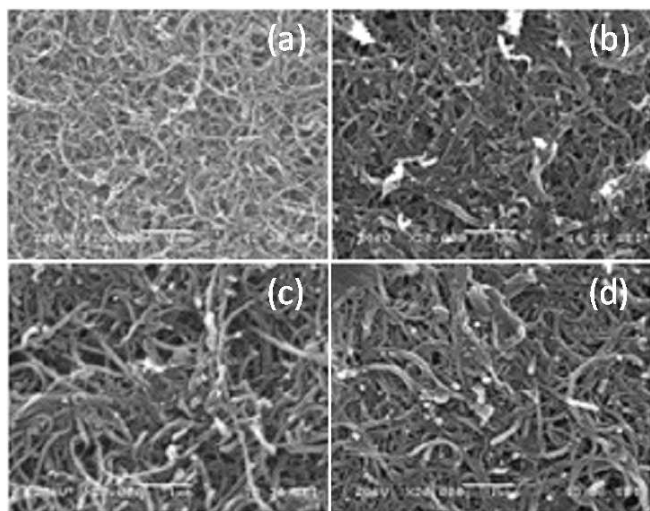


Fig. 1. The surface SEM images of (a) uncoated MWCNT buckypaper and SnO₂ thin films deposited with (b) 75 W, (c) 100 W and (d) 125 W and SnO₂ rf powers on MWCNT buckypaper.

EDS map analyses of the surfaces of SnO₂ thin films deposited with different rf powers on MWCNT buckypaper are shown in Fig. 2. It is observed that very fine tin oxide particles are dispersed well on the surface of MWCNT buckypapers.

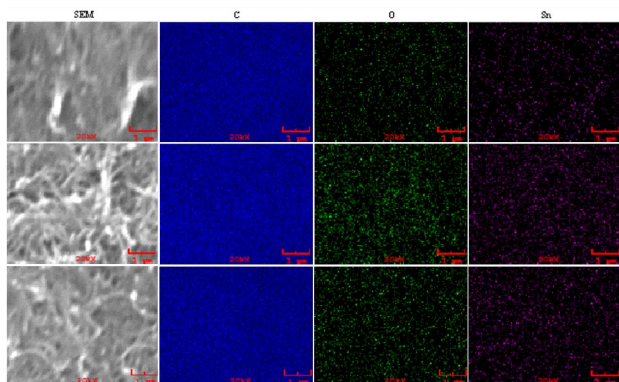


Fig. 2. EDS map analyses of the surfaces of SnO₂ thin films deposited with different rf powers on MWCNT buckypaper.

X-ray diffraction patterns of SnO₂ thin films deposited with different rf powers on MWCNT buckypaper in O₂/Ar (1/9) gas mixture are shown in Fig. 3. The diffraction patterns in Fig. 3 that the (110), (101), (211), (301) and (321) crystal faces have obvious diffraction peaks. The rest of the diffraction peaks of the other crystal faces are absent. The face diffraction peak of the (110) crystal is the most obvious. This indicates that the SnO₂ thin films have good orientation of preferred growth.

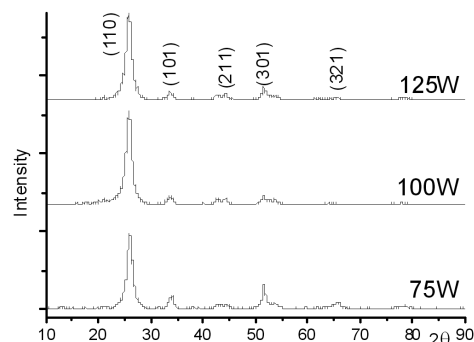


Fig. 3. X-ray diffraction patterns of SnO₂ thin films deposited with different rf powers on MWCNT buckypaper.

The discharge/charge curves of SnO₂ thin films deposited with different rf power on MWCNT buckypaper for the 30 cycles at a 1.0 C rate between 0.2 and 3.0 V are shown in Fig. 4. When comparing the SnO₂ thin films deposited at different rf powers on MWCNT buckypaper, it is obvious that the SnO₂ thin films deposited at 125 W rf power exhibit higher discharge and charge capacities.

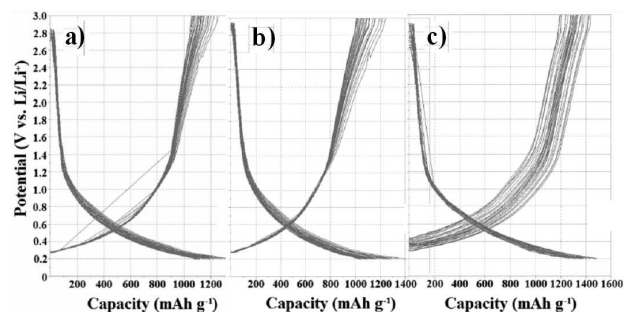


Fig. 4. The discharge/charge curves of SnO₂ thin films deposited on MWCNT buckypaper in O₂/Ar (1/9) gas mixture: (a) 75 W rf power, (b) 100 W rf power, (c) 125 W rf power.

The comparison of the cycling performance of SnO₂ thin films deposited at different rf powers is shown in Fig. 5. The test cells were cycled at a 1.0 C rate between 0.2 and 3.0 V. The profiles show that despite the initial discharge capacities of SnO₂ thin films deposited at 125 W rf power are slightly lower than that of SnO₂ thin films deposited at 75 and 100 W rf powers.

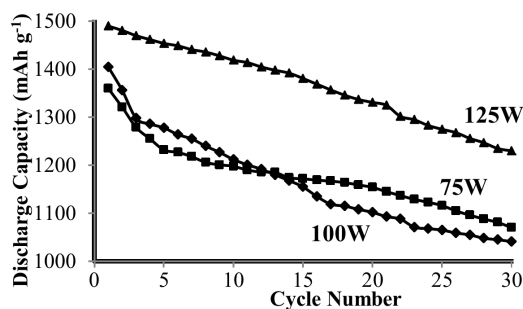


Fig. 5. Cycling behavior of SnO₂ thin films deposited on MWCNT buckypaper in O₂/Ar (1/9) gas mixture.

4. Conclusions

MWCNT buckypaper's role as a buffer in containing the mechanical stress arises from the volume changes in electrochemical lithium insertion and extraction reactions. Higher surface area of nanosized tin oxide particles could lead to higher catalytic efficiency of anodes. It is considered that the finer the size of catalyst particles the better performance. The advantage of using MWCNT buckypaper for a battery is not only their extremely large surface area, but also it is easy for liquid to permeate to the inside. Therefore, electrolyte could access to the entire tin oxide nanoparticles through the porous network readily, which could lead to high catalytic efficiency for electrochemical reactions. Another major function of MWCNT buckypaper is to improve the stability and cycle life of the anode in a lithium ion battery.

Acknowledgments

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