

Stoichiometry dependence of electrochemical performance of thin-film SnO_x microbattery anodes deposited by radio frequency magnetron sputtering

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Abstract

Thin-film SnO_x microbattery anodes, with various oxygen deficiencies, are deposited from a SnO_2 target on to an ambient temperature substrate by radio frequency (RF) magnetron sputtering. The high reversible capacity and cycle performance characteristics of SnO_x are described. RF power density and process gas pressure during deposition are fixed at 2.5 W/cm^2 and 10 mTorr, respectively. The SnO_x films are characterized by energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Constant-current galvanostatic charge–discharge tests of half cells are also performed. The stoichiometric parameter x increases with the increase in oxygen partial pressure, but decreases when the number of Sn chips placed on the target material in an argon atmosphere are increased. It is observed that SnO_x transforms to lithium oxide and metallic Sn after an initial Li intercalation reaction. The charge–discharge performance of the tin oxide films is found to be dependent on stoichiometry. In the present work, $\text{SnO}_{1.43}$ is the optimum stoichiometry, exhibiting the highest reversible capacity ($498.33 \mu\text{A h/cm}^2 \mu\text{m}$) and the lowest irreversible capacity ($301.79 \mu\text{A h/cm}^2 \mu\text{m}$). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Anode materials; X-ray diffraction; Magnetron sputtering; Tin oxide; Microbattery; Lithium intercalation

1. Introduction

Microbatteries [1–3], in the form of thin films, typically consist of an anode (lithium metal, carbon-based systems [4,5], and lithium alloy systems), a cathode (transition metal oxides such as LiMn_2O_4 [6,7], LiCoO_2 [8], and LiNiO_2 [9,10]), and a solid-state electrolyte (polymeric materials such as lithium phosphorous oxynitride (LiPON) [11,12]). Lithium metal is the most electropositive anode material and has a high specific capacity (3.86 A h/g). The use of metallic lithium as an anode material causes problems, however, due to its reactivity with the electrolyte, which results resulting in the formation of a den-

dritic lithium phase after repeated charge–discharge cycling [13]. Furthermore, precise handling of lithium metal in a dry room filled with argon gas is necessary during all processing due to its instability in normal atmospheres. Carbon-based materials have thus been widely used for the anode instead of metallic lithium, without affecting the mechanical and the electrical properties, since they can reversibly accept and donate significant amounts of lithium (Li:C = 1:6). The maximum theoretical capacity and volumetric capacity of carbon-based materials are reported to be 372 mA h/g and 800 mA h/ml , respectively [14]. Compared with to metallic lithium, these values are quite low.

Recently, tin oxide has been proposed as a promising alternative anode material for microbatteries. It has been reported that its theoretical volumetric capacity is four times larger than that of carbon-based material, while its gravimetric capacity is twice as large [15].

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Tin oxide tends to undergo a transformation from SnO₂ to metallic Sn during the first cycle and substantial irreversibility thus occurs and is considered to be related to the formation of lithium oxide and metallic tin [16]. The formation of lithium oxide is probably due to the large change in density as the metallic Sn transforms to a lithium–tin alloy, which in general results in catastrophic failure of the electrode [16,17]. In the present study, however, lithium oxide formation has been to play a very important role in allowing the electrode to expand and contract reversibly during the cycling process. Remarkably, there have not been any reported studies of the effect of tin oxide composition on the electrochemical charge–discharge performance. Obtaining a better understanding of the influence of film stoichiometry on the performance of tin oxide electrodes is thus essential. In this paper, experimental studies have been directed towards decreasing the irreversible capacity of the lithium oxide that is formed during the first cycle, and towards obtaining the optimum SnO_x electrode of high capacity that can react reversibly.

2. Experimental

Thin films of tin oxide were deposited on a soda lime substrate by radio frequency (RF) magnetron sputtering from a SnO₂ target (2 in. in diameter, 1/4 in. thick, and 99.99% purity) purchased from Cerac. In the deposition procedure, distance between the substrate and the target, the RF power density, and the substrate temperature were fixed at 40 mm, 2.5 W/cm², and ambient temperature, respectively. Titanium as an anode current-collector was also deposited by the same sputtering system. SnO_x films with various stoichiometries were obtained by varying the composition of the process gas mixture, O₂/(Ar + O₂), during sputtering, or by controlling the number of Sn chips (10 mm in diameter and 5 mm thick) placed on the SnO₂ target in an argon atmosphere.

Qualitative analysis of the Sn/O composition of the films was conducted using energy dispersive X-ray spectroscopy (EDS). The phase composition of the deposited SnO_x films was investigated by X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 0.15418$ nm). The chemical composition of the films was also investigated by X-ray photoelectron spectroscopy (XPS). Half cells were assembled with Li foil as the counter and reference electrodes, and 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) as an electrolyte. The cells were used to evaluate the charge–discharge performance of the tin oxide film anodes. Galvanostatic charge–discharge tests (TYS-31TU03) were performed with a constant current of 100 μ A/cm² in the potential range 0.01 to 1.4 V.

3. Results and discussion

The Sn/O composition of SnO_x (determined by EDS) obtained by varying the oxygen partial pressure and the number of Sn chips is presented in Fig. 1. The value of x is in the range 1.43 to 2.0, depending on the oxygen partial pressure. With an O₂/(O₂ + Ar) ratio of 0.5, stoichiometric SnO₂ is obtained. At ratios above 0.5, the value of x saturates at about 2.0. SnO_x films with relatively low oxygen content are obtained when Sn chips placed on a SnO₂ target in an argon atmosphere are used. The value of x decreases as the number of Sn chips increases. In general, SnO_x films with x varying from 0.97 to 2.00 can be readily obtained by varying either the oxygen partial pressure or the number of Sn chips.

XRD patterns of SnO_x films with various stoichiometries are shown in Fig. 2. Three intense XRD peaks from (110), (101), and (211), corresponding to the tetragonal phase of stoichiometric SnO₂ [17], are observed in the case of sample (a), which was deposited with an O₂/(O₂ + Ar) ratio of 0.5 and is thus SnO_{2.00}. Sample (b), SnO_{1.87}, shows less intense diffraction peaks, which indicates a decrease in crystallinity as the oxygen partial pressure decreases. In the case of sample (c), SnO_{1.43}, the diffraction peaks corresponding to SnO₂ are further weakened and new XRD peaks, corresponding to Sn₃O₄ and α -Sn, appear. No diffraction peaks, except those for the Ti substrate peak, can be observed in the case of sample (d), SnO_{1.25}, which was deposited by using Sn chips placed on a SnO₂ target in an argon atmosphere. Sample (e), SnO_{1.01}, shows sharp XRD peaks that correspond to metallic Sn, but no XRD peaks for SnO₂ can be observed.

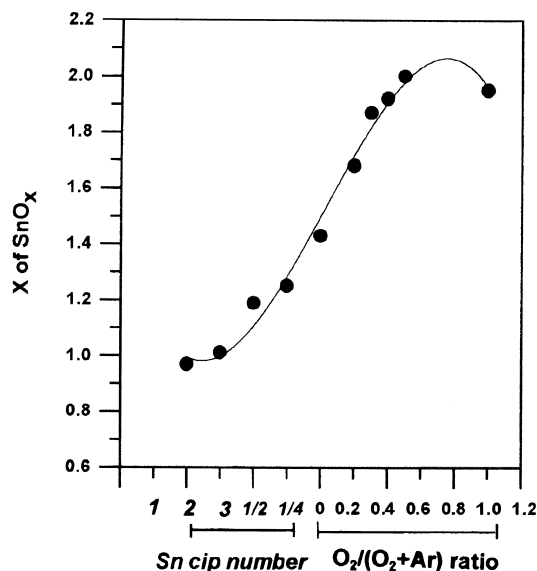


Fig. 1. EDS analysis of Sn/O composition of SnO_x films obtained by varying oxygen partial pressure and number of Sn chips.

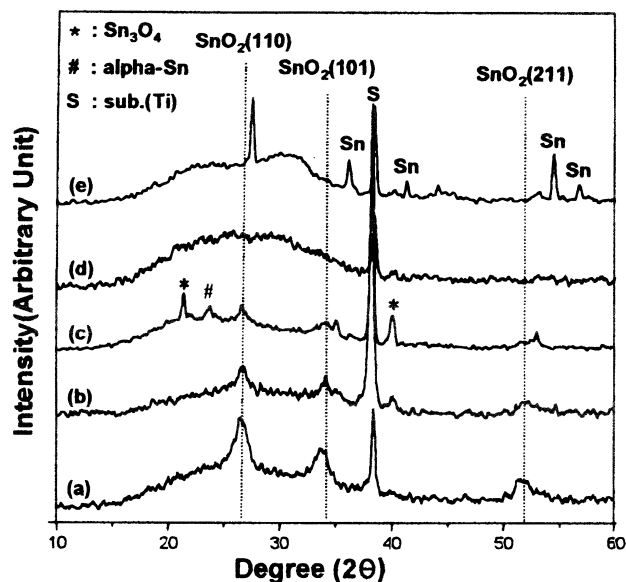


Fig. 2. XRD patterns of SnO_x films with various stoichiometries: (a) $\text{SnO}_{2.00}$, (b) $\text{SnO}_{1.87}$, (c) $\text{SnO}_{1.43}$, (d) $\text{SnO}_{1.25}$, (e) $\text{SnO}_{1.01}$.

The XPS Sn 3d narrow scan spectra of SnO_x films are presented in Fig. 3. All samples show a Sn $3d_{5/2}$ peak with about 8.4 eV splitting between the Sn $3d_{5/2}$ and Sn $3d_{3/2}$. The peak position of the binding energy of the Sn $3d_{5/2}$ peak in the case of sample (a), $\text{SnO}_{2.00}$, is about 487.0 eV, which is almost identical to that of SnO_2 [18]. As the oxygen deficiency increases, the peak position of Sn 3d shifts to a lower binding energy. Sample (d), $\text{SnO}_{1.25}$, which has a high Sn/O ratio, exhibits a shoulder peak at a binding energy close to 485 eV, which corresponds to the Sn–Sn binding energy.

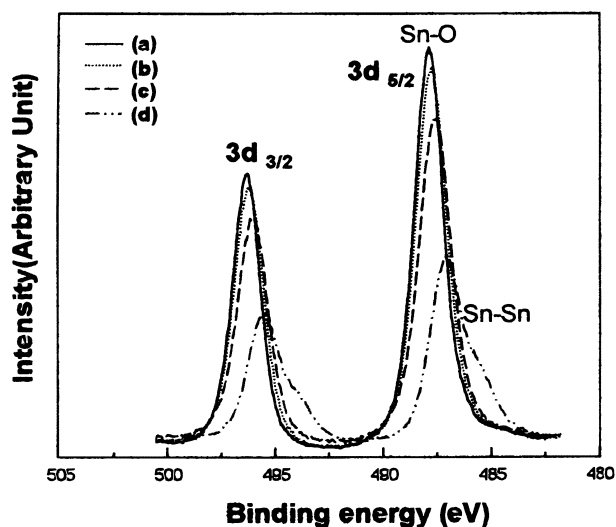


Fig. 3. XPS Sn 3d narrow scan spectra of SnO_x films with various stoichiometries: (a) $\text{SnO}_{2.00}$, (b) $\text{SnO}_{1.87}$, (c) $\text{SnO}_{1.43}$, (d) $\text{SnO}_{1.25}$.

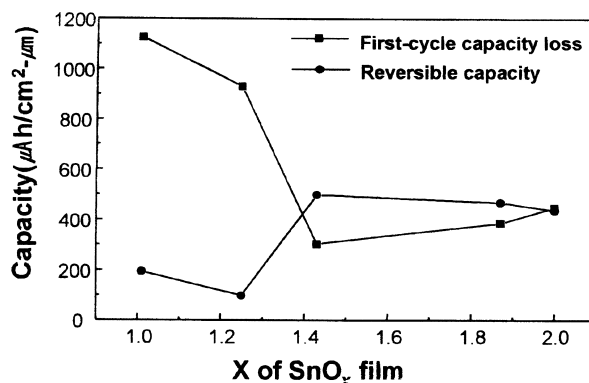


Fig. 4. Reversible capacity and capacity loss of SnO_x films with various stoichiometries.

It was expected that the capacity of the $\text{SnO}_{1.01}$ film would be the highest because of the higher proportion of active material, Sn, which can electrochemically react with Li. The cyclic characteristics of this film, however, give rise to catastrophic failure of the electrode. This can be ascribed to an insufficient amount of lithium oxide being formed in the first cycle of the charge–discharge process. In the case of sample (d), $\text{SnO}_{1.25}$, which has relatively more active material compared with samples (a), (b) and (c), the existence of Sn–Sn bonding can also cause cyclic degradation due to a large change in volume after electrochemical reaction with Li. It is thus concluded that SnO_x , which has both Sn–O bonding and lower oxygen content, is the best electrode material in terms of high capacity and long cycle-life.

The oxygen deficiency dependence of the reversible capacity and first-cycle capacity loss of SnO_x samples are presented in Fig. 4. The maximum reversible capacity is obtained from $\text{SnO}_{1.43}$, which also shows a lower irre-

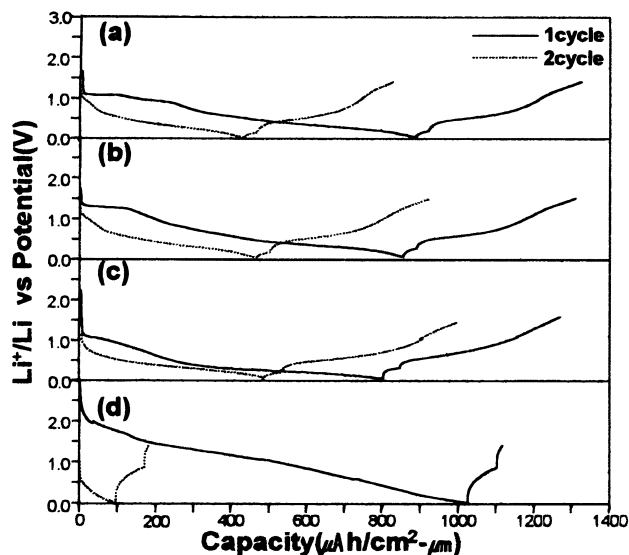


Fig. 5. Insertion capacities of SnO_x films with various stoichiometries: (a) $\text{SnO}_{2.00}$, (b) $\text{SnO}_{1.87}$, (c) $\text{SnO}_{1.43}$, (d) $\text{SnO}_{1.25}$.

versible capacity compared with the other films. Although the samples obtained by controlling Sn chips show high capacities on the first cycle, these samples suffered immediate degradation. It thus appears that the optimum stoichiometry of SnO_x films is $\text{SnO}_{1.43}$, which has a reversible capacity of $498.33 \mu\text{A h/cm}^2 \mu\text{m}$.

The discharge capacities of the SnO_x film electrodes on the first and second cycles are given in Fig. 5. Samples (a), (b) and (c) yield relatively large reversible capacities and cycle without capacity loss. Sample (d), however, does not accept lithium after the first cycle, and thus has a capacity close to zero. As metallic tin transforms to lithium–tin alloy, which has a much lower density, catastrophic failure of the tin oxide electrode occurs as a result of the large change in density. Lithium oxide formation thus plays a very important role in allowing the electrode to expand and contract reversibly during the cycling process. In the present work, $\text{SnO}_{1.43}$ shows lower irreversible lithium oxide formation during the first cycle as well as a higher capacity and a longer cycle-life.

4. Conclusions

Thin films of SnO_x with various oxygen deficiencies have been sputter deposited from a SnO_2 target on to an ambient temperature substrate. The main focus has been on decreasing the irreversible formation of lithium oxide during the first cycle by selecting the proper stoichiometry of SnO_x . A certain amount of lithium oxide must be present to prevent the Li–Sn alloy from suffering mechanical deterioration during repeated discharge–charge cycles. Although the lithium oxide content can be controlled, it is believed that a certain degree of lithium oxide plays an

important role in the reversibility of tin oxide electrodes. From an electrochemical test of SnO_x films, it is concluded that $\text{SnO}_{1.43}$ shows the lowest irreversible capacity of $301.79 \mu\text{A h/cm}^2 \mu\text{m}$ and the highest reversible capacity of $498.33 \mu\text{A h/cm}^2 \mu\text{m}$.

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