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Electrochemical property of tin oxide thin film by photo-CVD process

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Abstract

The tin oxide (SnO_2) films were prepared by a photo-CVD process and characterized by X-ray diffraction (XRD) and electrochemical measurements. The SnO_2 films prepared at 473 and 523 K showed amorphous-like hallow pattern, while the SnO_2 film prepared at 573 K showed a poor crystalline pattern. All the Li/SnO_2 cells showed the reversible capacity of 600 mAh/g in the voltage range of 0.1–0.8 V over 200 cycles. It was clarified that the SnO_2 film showing superior electrochemical performance was prepared at low temperature of 473 K using TMT ($Sn(CH_3)_4$) and O_2 (containing 4 mol.% O_3) as the source material.

Keywords: Tin oxide films; Photo-CVD; Low temperature preparation

1. Introduction

Tin-containing oxides are promising anode materials for secondary lithium ion battery [1]. Most of the recent studies have reported that for bulk samples of amorphous and crystalline tin oxide (SnO_2), a decomposition reaction initially occurs leading to the formation of metallic tin in a Li_2O matrix, followed by subsequent Li–Sn alloy formation [2–6].

A variety of methods have been used to prepare SnO_2 powders and films [3–6]. Brousse et al. reported that the crystalline SnO_2 film prepared at 773 K by a low-pressure chemical vapor deposition (LPCVD) showed the reversible capacity of 500 mAh/g over 100 cycles [3,4]. Liu et al. reported that the SnO_2 powders prepared by a precipitation method from $Sn(OH)_2$ gel showed the reversible capacity of 600 mAh/g with heat treatment temperature above 1073 K, but showed the poor reversible capacity with heat treatment temperature at 423 K [5]. Nam et al. reported that the SnO_2 films prepared by electron-beam evaporation showed the reversible capacity of 350 mAh/g over 100 cycles, depending on heat treatment temperature which influenced to the structure, grain size, and adhesion to the substrate [6]. These SnO_2 films were heat-treated above 573 K. Therefore, it is not clear how the crystal structure and morphology are related for electrochemical performance of SnO_2 prepared at low temperature under 573 K.

In the present study, SnO_2 film was prepared using the tetramethyl tin (TMT) by a photo-CVD process and electrochemical property of films was investigated. Furthermore, it was discussed the relationship between crystal structure, morphology, and electrochemical property.

2. Experimental

The SnO_2 films were prepared on the stainless substrate by a photochemical vapor deposition (photo-CVD) system (UVD-200TS: SAMCO Inc.) [7]. TMT ($Sn(CH_3)_4$) and O_2 (containing 4 mol.% O_3) were used as the source materials and a low-pressure mercury lamp was used as the light sources. The deposition parameters are shown in Table 1. The amount of SnO_2 film deposited was estimated by weighting the substrate before and after deposition.

X-ray diffraction (XRD) patterns of the films were obtained with an X-ray diffractometer (Rigaku RAD-C) with Cu Kα radiation. The diffraction data were collected at each 0.02° step width over a 2θ range from 5 to 80°.

Electrochemical intercalation and deintercalation were carried out using lithium cells with a beaker-type configuration.

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Table 1
Deposition parameters of SnO_2 films

Light intensity (center)	8 mW/cm^2 (254 nm)
TMT flow rate	3 sccm
O_2 (4 mol.% O_3) flow rate	300 sccm
Total pressure	1.33×10^3 Pa
Substrate temperature	473, 523 and 573 K
Deposition time	90 min

The films deposited on the stainless substrate were used as the working electrode and lithium metal was used as both counter and reference electrode. The electrolyte used in these cells was 1 M solution of $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and 1,2 dimethoxycarbonate (DMC) (Tomiyama Petrochemical Company Ltd., battery grade). The cells were constructed in an argon-filled glove box. The current density was calculated based on the area of SnO_2 films. Electrochemical tests were measured galvanostatically using BTS2004 apparatus (Nagano).

3. Results and discussion

3.1. Preparation

Fig. 1 shows the variation of XRD patterns as a function of substrate temperature. The SnO_2 films prepared at 473 and 523 K were amorphous, while the SnO_2 film prepared at 573 K was polycrystalline and showed 110 and 211 peaks, which was good consistent with values reported by JCPDS card 41–1445 [8]. SEM observation of all the samples showed a small grain size of <0.1 μm. The thickness of films increased with increasing substrate temperature. The thickness of the films prepared at 473, 523 and 573 K was about 0.13–0.16, 0.20–0.26, and 0.22–0.42 μm, respectively. The film prepared at 523 K showed the minimum resistivity of 7×10^{-3} Ω cm in our samples.

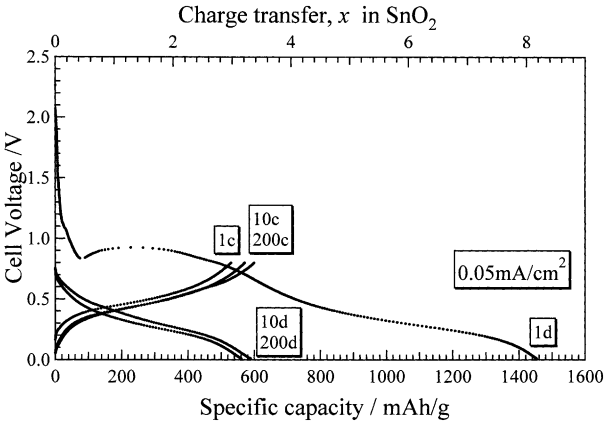

Fig. 2. Charge and discharge curves of the cell, Li/SnO_2 prepared at 473 K, as a function of charge transfer x in SnO_2 (top axis) and specific capacity (bottom axis) with a current density of 0.05 mA/cm^2. Cut-off voltages are between 0 and 0.8 V.

3.2. Electrochemical property

Reversibility of the Li/SnO_2 film cell was examined in the voltage range of 0.01–0.08 V with the current density of 0.05 mA/cm^2. Fig. 2 shows the charge and discharge curves of SnO_2 film prepared at 473 K. The discharge capacity of the first cycle is the capacity of 1450 mAh/g, which is very close to the theoretical value of 1495 mAh/g. After first cycle, these charge and discharge curves show the similar smooth voltage profiles and the cycle capacity of 600 mAh/g, which is close to the theoretical reversible capacity of 711 mAh/g.

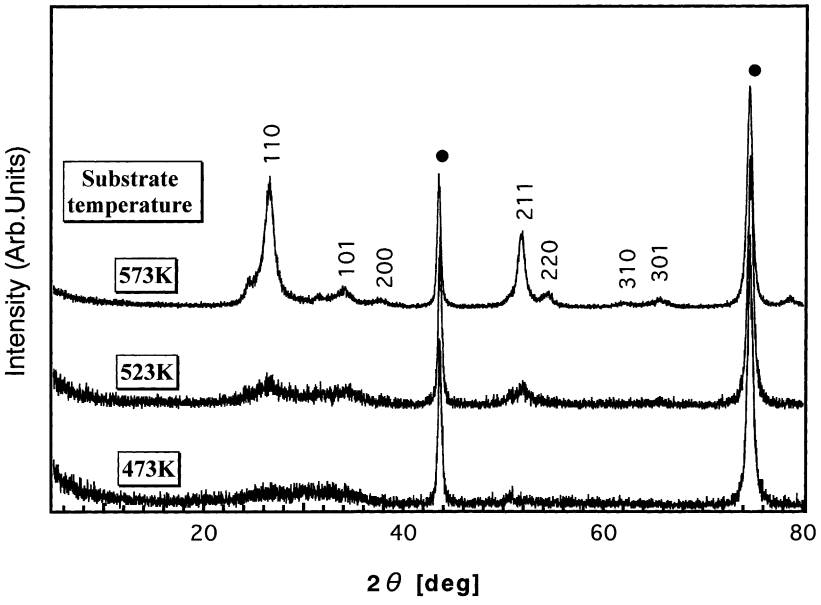

Fig. 1. X-ray diffraction patterns for SnO_2 films prepared by a photo-CVD process.

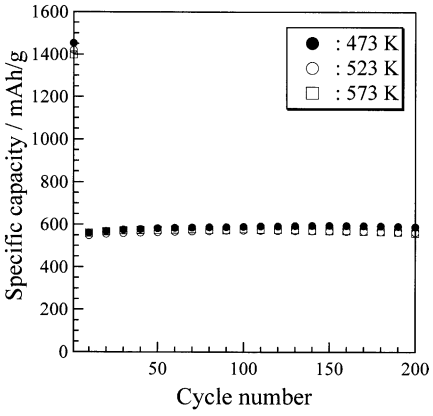

Fig. 3. Cycle capacity of the Li/SnO_2 film cell with a current density of 0.05 mA/cm^2.

A slight decrease of capacity was observed with increasing current density from 0.025 to 0.1 mA/cm^2, corresponding to 1/4*C* to 1*C*, without any conductive additive. This result indicates that the physical properties of SnO_2 films prepared by our photo-CVD process are sufficient for the diffusion of lithium and electronic conductivity. Fig. 3 shows the cycle dependence of discharge capacity for all the SnO_2 films. All of the Li/SnO_2 cells show the reversible capacity of 600 mAh/g with a current density of 0.05 mA/cm^2 after 200 cycles. For all the SnO_2 films, macroscopic crack was observed after 200 cycles.

Reversibility of the Li/SnO_2 film cell was examined by changing the cut-off voltage range. In the voltage range of 0 and 1.3 V, the cycle capacity of 600 mAh/g was observed in the 100 cycles, but the capacity decreased to 400mAh/g after 200 cycles. A slight of decrease in capacity was observed with increasing substrate temperature. These results correspond to the aggregation of metallic Sn above 0.8 V [3]. Our results in this study indicate that SnO_2 with small particle of <0.1 μm improves the cycle performance and the size of particle is more important than the morphology and structure of amorphous and crystalline from the viewpoint of electrochemical property.

4. Conclusions

We have reported that electrochemical cell using SnO_2 film prepared by a photo-CVD process showed superior cycle reversibility of 600 mAh/g after 200 cycles. Our photo-CVD process using TMT as the source material make it possible to prepare the SnO_2 film at a low temperature of 473 K and is promising method to prepare the SnO_2 film on the plastic substrate as the anode material for micro-battery.

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