



Tunable synthesis of nanoporous tin oxide structures on metallic tin by one-step electrochemical anodization



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ABSTRACT

Nanoporous tin oxide structures were synthesized by electrochemical anodization of tin substrates at various anodizing conditions, including electrolyte species and concentration, anodizing potential, anodizing temperature and duration of the process. The influences of anodizing conditions on the structure features of anodized oxide films were investigated in detail. It is worth stressing that the correlation of the morphologies and current density virtue time curves (*i-t* curves) was analyzed in our work. The structure features of as-prepared tin oxide layers were found to be strongly related to anodizing conditions. Significant increases of average pore diameter occurred with the increase of anodizing potential, temperature and time. In addition, it is noteworthy that strong linear dependences between average steady-state current density and electrolyte concentration, anodizing potential as well as temperature were observed. It indicates the anodizing process is limited by mass transfer in electrolyte. Moreover, growth mechanisms in both kinetics and thermodynamics were established to elaborate the growth process of porous structures during anodization.

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1. Introduction

In recent years, nanoporous structures have received much attention for their unique physical and chemical properties, such as huge specific surface area and quantum size effect [1,2]. Owing to these extraordinary properties, they are widely applied in many fields, especially in photocatalysts [3,4], solar cells and electrodes [5–8]. The most widely studied nanoporous structure is alumina fabricated by electrochemical anodization. And it is widely applied as template in nanofabrication for its highly ordered one-dimensional nanoporous structure [9–12]. Therefore, nanoporous structures synthesized by electrochemical anodization attracted much attention for their special open-framework structures and unique properties.

Tin monoxide (SnO) and tin dioxide (SnO₂), as two important oxide phases of metallic tin, have shown *p*-type and *n*-type properties respectively [13–15]. Both of them have been investigated as materials in gas sensors [16,17], lithium-ion batteries [18,19], supercapacitors [20,21], solar cells and photoelectrochemical

devices [22,23]. The optical band gap of SnO₂ is about 3.6 eV, which is corresponding to absorption onset of 340 nm [24]. It was reported that SnO₂ had much higher electron mobility than that of TiO₂ [25], which seems to be a new choice for many electronic devices. Moreover, the charge injection of SnO₂ under the light irradiation seems to be possible as its conduction band energy level is more negative than anatase TiO₂ [26].

Nanoporous tin oxide layers have been synthesized on the surface of metallic tin via a simple anodization process, which were carried out in an alkaline [9,27,28] or acidic electrolyte [29–32], even in a mixed electrolyte of sulfide and fluoride [33]. The main role of these resulting thin films was amorphous tin oxide (SnO) [34,35]. As the tin oxide crystallized in phase of SnO₂ is more stable than SnO in thermodynamics, as-prepared oxide layers can be easily oxidized to SnO₂ when the temperature is upon 500 °C [29,31]. It is commonly believed that the intriguing properties and potential application of tin oxide are extensively related to the morphology. For example, it is no doubt that tin oxide layers with dense nanopores would have more efficiently practical use in gas sensors than that of bulk materials [34]. Moreover, the discontinuity between adjacent layers would result in more efficient gas evolution, mass transfer and wide applications in photocatalysis and adsorption, on the contrary, lower mechanical stability and higher resistance would also occur [33].

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Comparing with the wide study of oxalic acid electrolyte, only few works adopted sodium hydroxide as electrolyte in anodization of tin oxide [9,27,28]. In this work, through the comparison of the structure features of tin oxides that carried out in two different electrolytes (0.3 M oxalic acid and 0.3 M sodium hydroxide), we chose sodium hydroxide as electrolyte for our further investigation. It is reported that the morphology and composition of nanoporous tin oxides formed by anodization have strong dependence on anodizing parameters, such as electrolyte concentration, applied potential, anodizing temperature and time [31]. Therefore, we performed series of anodizing experiments to investigate the influences of anodizing parameters on morphologies of anodic tin oxide, including the species of electrolytes.

In this study, we synthesized five series of tin oxide layers on the surface of Sn foils via electrochemical anodization under different conditions. The work has investigated the influences of different anodizing conditions on the structure features of resulting samples, assisting with current density versus time curves for the analysis of electrocrystallization processes at different conditions. Moreover, the growth mechanisms in both kinetics and thermodynamics for nanoporous tin oxide structures were established according to FESEM images and *i*-*t* curves in time series. Our work would provide an inner sight to the correlations between anodizing conditions and structure features of tin oxide layers carried out in NaOH electrolyte.

2. Experimental

2.1. Materials

Sodium hydroxide, oxalic acid, acetone and absolute ethyl alcohol used in this work are analytically pure and purchased from Sino-pharm Chemical Reagent Co., Ltd. The water we used in the experiments is deionized water. Tin foils of 99.99% purity used in this work were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd.

2.2. Sample preparation

Anodizing experiments were carried out in a two-electrode electrolytic cell as shown in Fig. 1. Sn foil and Ti foil with the dimension of 40 mm × 10 mm × 0.5 mm were used as anode and cathode in each anodizing process respectively. Prior to an anodization, the high purity Sn foil was polished to remove oxide layer on surface. In a typical polish procedure, Sn foil was firstly polished with a 1500 abrasive paper in two perpendicular directions alternately for 30 min. Then, an iterative process was performed on an abrasive paper in 2000 meshes to get mirror polish. Then, the foils were ultrasonically cleaned in acetone, ethanol and deionized water respectively for three times. Various anodizing conditions were applied in each experiment, including species (oxalic acid and sodium hydroxide) and concentrations of electrolyte (0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M), applied potentials (4 V, 8 V, 12 V, 16 V and 20 V), anodizing temperatures (25 °C, 35 °C and 45 °C) and time (5 min, 15 min, 30 min, 50 min and 80 min). After anodizations, the samples were rinsed with deionized water and then dried at 60 °C in air-blower-driver for 12 h.

2.3. Characterization

The morphologies of anodized samples were characterized by field emission scanning electron microscope (FESEM, HITACHI SU8010). Current density versus time curves were recorded during each anodization. The average pore diameters of the porous structures were determined by analyzing the FESEM images using Nano Measure software.

3. Results and discussion

3.1. Tin oxide films obtained via anodization at NaOH and H₂C₂O₄ electrolytes

Tin oxide films were formed on the surface of Sn foils during the anodization at the potential of 12 V at 25 °C for 50 min, independently of the species of electrolytes. As-prepared samples were amorphous (no significant peaks of SnO and SnO₂ were found in the PXRD spectrum), and the color of the anodic films was dark. These results were also reported in other literature, indicating the resultant films are tin oxide [28,29,31].

The morphologies of as-synthesized tin oxide films are shown in Fig. 2(a) and (b) respectively. It is interesting that dense and irregular nanoporous structures are formed on the two anodic surfaces, independently of the species of electrolyte. There are plenty of interconnections between individual nanopores. Moreover, it is obvious that the porous structures consist of nano-channels oriented along the thickness, indicating that the growth pattern of the obtained two tin oxide films is perpendicular to the substrate. The porous layered structures allowed a more efficient transport for the reactant molecules, which is beneficial to contribute the electrochemical responses from the exposed part of the electrode into the electrolyte. As there was no phenomenon about the peeling of oxide film, and no precipitate or suspended solid appeared in the electrolyte during anodization, we supposed the anodic films that synthesized in our work adhered strongly to the tin substrates. Thus they may not need any supporting material or binder while they are in other electrochemical investigations [36].

The average pore diameters of the two porous structures are about 50.08 nm and 52.17 nm, which were derived by images analysis of the as-shown FESEM images using Nano Measure. Accordingly, the pore diameter histograms are presented in Fig. 2(c) and (d). This fact, in conjunction with the porous structures observed in Fig. 2(a) and (b), indicate a large porosity and specific surface area are contained in as-prepared tin oxide films.

Current density vs. time curves are serviceable for the investigation of electrocrystallization process. Fig. 3 shows the *i*-*t* curves recorded during anodizations. The curve recorded during anodization in 0.3 M NaOH is similar to that found by Yang et al. for anodization in 4 M NaOH for 10 min with the potential of −1.54 V (see Refs. [28], Fig. 3). There is a three-step growth process for the anodic tin oxide in NaOH electrolyte. Firstly, just at the beginning of the anodization, anodic dissolution of Sn in high current densities occurs, which is accompanied by a heterogeneous nucleation and growth of tin oxide. With the continuation of these processes, the surface of anode Sn is gradually passivated as a result of in situ formation of tin oxide passivation layer, leading to the rapid decrease of anodic current density in second stage. During the

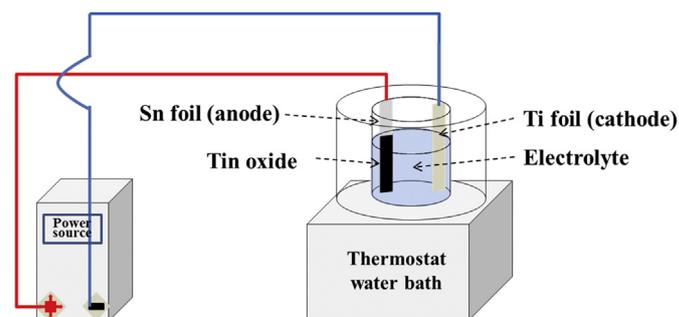


Fig. 1. Schematic diagram of electrochemical anodization system.

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