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Tin/Tinoxide (Sn/SnO_2) Nanocomposites Thin Films as Negative-Electrode Materials for Li-Ion Batteries

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In this study, tin/tinoxide (Sn/SnO_2) nanocomposites thin films were produced by thermal evaporation and plasma oxidation as anode materials for Li-ion batteries. To produce Sn/SnO_2 thin films, pure metallic tin (Sn) was thermally evaporated on the stainless steel substrates in argon atmosphere. The Sn films were subjected to plasma oxidation process at oxygen/argon gas mixture. Three different plasma oxidation times (30, 45, and 60 min) were used to investigate oxidation kinetics and physical and microstructural properties. The surface properties were studied by scanning electron microscopy and atomic force microscopy. For structural analysis, X-ray diffraction measurements were carried out. Sn/SnO_2 coated stainless steel substrates were used as the working electrode in coin-type (CR2016) test cells. The energy storage capacity Sn/SnO_2 electrodes were determined depending on the oxidation time and $Sn:SnO_2$ ratio.

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1. Introduction

Lithium-ion batteries offer significant advantages in weight and energy density over other rechargeable batteries. They have proven to be ideal for small-scale portable electronic applications such as cellular phones and laptop computers. Emerging applications in implantable medical devices also take advantage of the high cycle life, light weight, and other benefits of Li-ion batteries [1]. Graphite is a standard anode material in Li-ion batteries as lithium can insert and deinsert during discharging and charging, respectively, with a theoretical specific capacity of 372 mAh g^{-1}. However, in order to meet the increasing demand for batteries with higher energy densities, it is essential to develop electrodes made from durable, nontoxic, and inexpensive materials with a high charge/discharge rate and a higher reversible capacity. Among Li-ion batteries anode materials, SnO_2-based materials have become one of the promising candidates, as SnO_2 has high theoretical capacity, the environmental friendliness of its raw material processing and low cost. In theory, SnO_2 exhibit a first discharge capacity of 1494 mAh g^{-1} and a reversible discharge capacity of 782 mAh g^{-1} [2].

In this study, tin/tinoxide (Sn/SnO_2) films were produced by thermal evaporation and plasma oxidation as anode materials for Li-ion batteries. Sn/SnO_2 coated on stainless steel substrates were used as working electrode in coin-type (CR2016) test cells. The ratio between metallic tin (Sn) and tinoxide (SnO_2) was controlled with plasma oxidation time and effects of the ratio were investigated on the morphological and electrochemical properties.

2. Experiment details

Thermal evaporation of metallic tin on the stainless steel substrates was performed in a multifunctional physical vapor deposition (PVD) unit equipped with thermal evaporation, dc and rf units. High purity metallic tin (99.999%) was placed in a Mo boat in the deposition chamber, which was evacuated to 10^{-4} Pa by a turbomolecular pump and then backfilled with argon to a pressure of 1 Pa to production of Sn films. Then, Sn/SnO_2 films were produced by RF plasma oxidation from the thermally evaporated pure Sn films. Before starting the plasma oxidation process, the chamber was evacuated to 10^{-4} Pa by a turbomolecular pump. The plasma oxidation of the Sn films were conducted using a high-purity oxygen (99.999%) and argon (99.9999%) gas mixture in ratio 1:1. Three different oxidation times of 30, 45, and 60 min were chosen for plasma oxidation. Total chamber pressure and RF power for each oxidation were kept constant at 1.6 Pa and 80 W. Figure 1 represents the methods of preparing of the Sn/SnO_2 films.

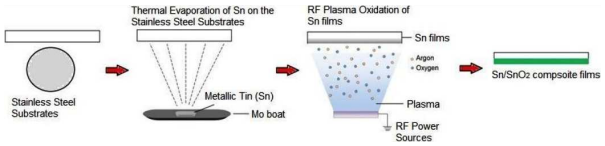

Fig. 1. Schematic representations of methods for preparing Sn/SnO_2 composite films.

An X-ray diffractometer (Rigaku D/MAX 2000), scanning electron microscopy SEM (JEOL 6060LV) and MTI BST8-MA Battery Analyzer were used for characterization of the composite films. Coin-type (CR2016) test cells were assembled in an argon-filled glove box, directly using the Sn/SnO_2 coated stainless steel substrates as the working electrode, a lithium metal foil as the counter electrode, a micro porous polypropylene (PP) membrane (Cellgard 2300) as the separator, and 1 M solution of LiPF6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by weight) as the electrolyte. The cells were charged and discharged between 0.1 V and 2.0 V at different current density.

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3. Results and discussion

The crystal structures of both the thermally evaporated and oxidized coating samples were determined using XRD with Cu K_α radiation. Figure 2 shows a typical XRD pattern for the pure tin (Sn) films evaporated onto the stainless steel substrates in an argon atmosphere at a pressure of 1.0 Pa (JCPDS file no. 01-086-2264 for powder Sn) and a SEM image. No obvious reflection peaks from impurities were detected, providing evidence of the high purity of the product. After thermal evaporation onto a stainless steel substrate, tin exhibits a crystalline microstructure with epitaxial grains as shown in Fig. 2b. The grain sizes have been calculated with Scherrer's formula. The calculated grain size of the tin film that was thermally evaporated in a 1.0 Pa Ar atmosphere is 34 nm.

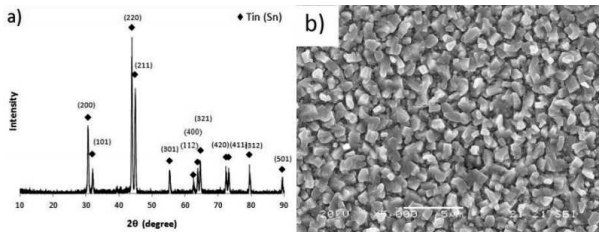

Fig. 2. (a) XRD pattern and (b) SEM image of pure tin (Sn) film evaporated at 1 Pa Ar.

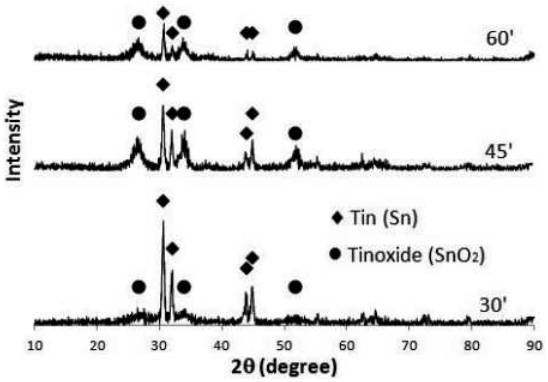

Fig. 3. XRD patterns of the tin and tin oxide (Sn/SnO_2) films.

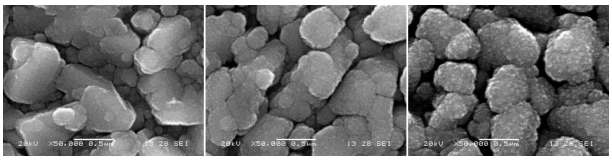

Fig. 4. SEM images of Sn/SnO_2 composite films produced by plasma oxidation for 30 min (a), 45 min (b) and 60 min (c) after thermal evaporation of Sn.

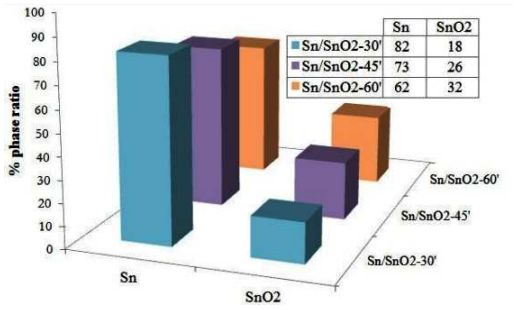

Fig. 5. % phase ratio of Sn/SnO_2 composite films.

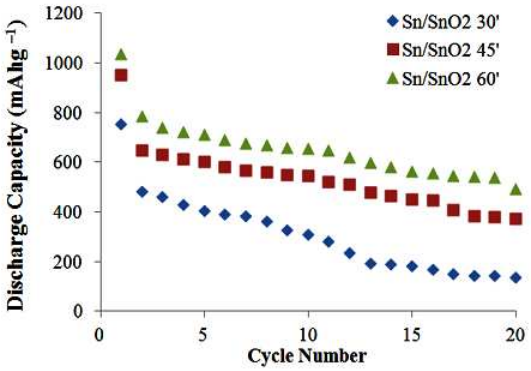

Fig. 6. Comparison of specific discharge capacities of Sn/SnO_2 composite films.

After the thermal evaporation process, the tin samples were subjected to a RF plasma oxidation process for three different oxidation times of 30, 45, and 60 min to produce Sn/SnO_2 nanocomposites films. The XRD patterns of the tin and tin oxide films produced for three different oxidation times of 30, 45, and 60 min are presented in Fig. 3. The films have a Sn and SnO_2 structure, which agrees well with the standard data files (Sn:JCPDS No. 01-089-2958 and SnO_2: JPDS No. 01-077-0447), and all of the films have a crystalline structure. Increasing oxidation time resulted in increasing intensity of SnO_2 peak while decreasing intensity of Sn peak.

The morphology of Sn/SnO_2 films produced at various plasma oxidation times from 30 min to 60 min were taken by SEM and displayed in Fig. 4. The particle shape was maintained to relatively round with the increasing plasma oxidation time [3].

For all Sn/SnO_2 composite films, quantitative phase analysis was performed in order to determine the relative phase amounts using the Rietveld refinement method with helping Rigaku software, as shown in Fig. 5. Increasing oxidation time resulted in increasing tin oxide percent and decreasing tin percent.

The discharge capacity vs. the number of cycles for cells made from Sn/SnO_2 films is shown in Fig. 6. The results show that the discharge specific capacity of the Sn/SnO_2 films increases with increasing amount of SnO_2

in the composite. Similar relationship between SnO_2 ratio and specific capacity values has been obtained by Sivashanmugam et al. [4]. Furthermore, the composites with a higher rate of SnO_2 exhibit a low capacity fade.

4. Conclusions

Crystalline pure tin (Sn) film with a grain size of 34 nm was thermally evaporated on the stainless steel substrates in 1 Pa Ar atmosphere. The tin films were subjected to RF plasma oxidation in $Ar+O_2$ atmospheres for three different times (30, 45, and 60 min) and Sn/SnO_2 nanocomposite films have been successfully obtained. According to RF plasma oxidation time, the ratios of $Sn:SnO_2$ are 82:18, 73:26 and 62:32. Sn/SnO_2 nanocomposite films were used as an electrode for Li-ion cells and discharge capacity values increase with increasing amount of SnO_2 in the composite.

Acknowledgments

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