Proceedings of the International Congress on Advances in Applied Physics and Materials Science, Antalya 2011

Sol–Gel Synthesis of Nanostructured SnO_2 Thin Film Anodes for Li-Ion Batteries

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Sol–gel technique was employed to prepare semiconductor tin dioxide (SnO_2) thin films. Comparatively, it gives an advantage over other techniques by its low reaction temperature, easy process and low cost. The effect of glycerin addition on the structure and preventing crack formation has been investigated. Scanning electron microscopy, atomic force microscopy, and X-ray diffraction analysis were performed to characterize nanostructured films.

PACS: 73.61.Jc, 82.45.Mp, 81.20.Fw, 82.47.Aa, 68.55.jm

1. Introduction

Lithium-ion batteries are one of the most popular types of rechargeable battery for portable electronics, with one of the best energy densities, and also the choice power source for electric and hybrid vehicles [1]. Lithium-ion batteries have a high energy density and are widely used in energy storage for electrical devices, such as mobile phones and notebook computers [2]. Tin dioxide is an *n*-type semiconductor material with wide optical band gap 3.6 eV and it has high mechanical and chemical stability [3, 4]. Tin and tin dioxide based materials are being used as active anode materials for rechargeable lithium batteries. Tin dioxide anodes have different discharge and charge mechanism compared with carbonaceous anodes. Therefore, these materials have attracted much attention due to their large reversible capacity [5].

Sol–gel technique is a useful method to prepare SnO_2 thin films. Comparatively, it gives a lot of advantages over other techniques by its low reaction temperature, easy process, and low cost. However, cracks on the thin films prepared by sol–gel technique exhibited adverse effects on response, so cracks on thin films prepared by this method are undesired. Therefore, glycerin was used as additive to prevent cracks [4]. Additionally, glycerin can be used as a template or pore forming agent [6, 7]. It is already known that glycerin has relatively high polarity, is highly viscous and is completely miscible in aqueous medium [8]. The use of the glycerin additive achieves the effect of enhancing thin film porosity and increasing solution viscosity [4]. Glycerin addition could improve obviously the quality of the thin film, and made it have a more smooth and homogeneous surface without deep fissure [9]. In this work, sol–gel method was applied to synthesize SnO_2 thin films. The effect of glycerin addition on the structure and preventing crack formation has been investigated.

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2. Experimental

The SnO_2 precursor solution was prepared from tin chloride by dissolving 0.2 M $SnCl_2{\cdot}2H_2O$ in 1:1, 2:1 and 4:1 volumetric ratio of absolute ethanol and glycerin mixtures. Obtained solutions were named as first, second and third sol. Then the solutions were stirred for 24 h at room temperature. At the end, transparent sols were obtained. The films were coated on glass substrates via spin coating method from transparent solutions at 3000 rpm. The coated films were dried at 100 °C in air. The above coating process was repeated so as to obtain the thickness of films required. The obtained films were precalcined at 400 °C and calcined in air up to 600 °C at a heating rate of 2 °C/min and left at the same temperature for 2 h.

The film surfaces were analyzed by scanning electron microscopy (SEM) (by JEOL-JSM 6060LV) and atomic force microscopy (AFM). AFM measurements were performed with a NTEGRA P9 (NTEGRA Prima) scanning probe system from NT-MTD, Moscow, Russia. Measurements were carried out in air with semicontact mode acquiring 256 pixel–256 pixel images. Thin film attachment equipped XRD analysis was performed with X-ray diffractometer (Rigaku D/MAX/2200/PC model device) using Cu K_α radiation (λ = 1.54050 Å) with 1°/ min scanning speed using a grazing angle of 5°. Phase analysis, nucleation and growth structures were investigated and the grain size of the resultant films was calculated. Resistivity measurement was performed using Lucas Pro-4 four points probe device.

3. Results and discussion

SEM micrographs of SnO_2 films obtained from first sol are given in Fig. 1. As can be seen in Fig. 1, the films coated with the first solution, prepared by dissolving 0.2 M $SnCl_2 \cdot 2H_2O$ in 1:1 volumetric ratio of ethanol and glycerin mixture, showed fine equiaxed grains and homogeneous distribution. The structure seems to have a

mesoporous nature with a homogeneous distribution of pores.

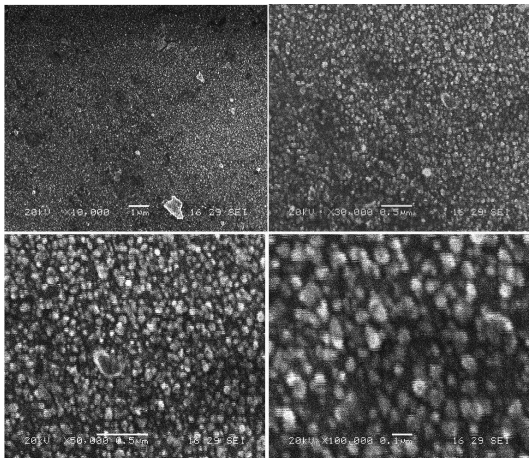

Fig. 1. SEM micrographs of SnO_2 films coated from 1st sol (1:1 ethanol/glycerin mixture containing 0.2 M $SnCl_2{\cdot}2H_2O$) at different magnifications.

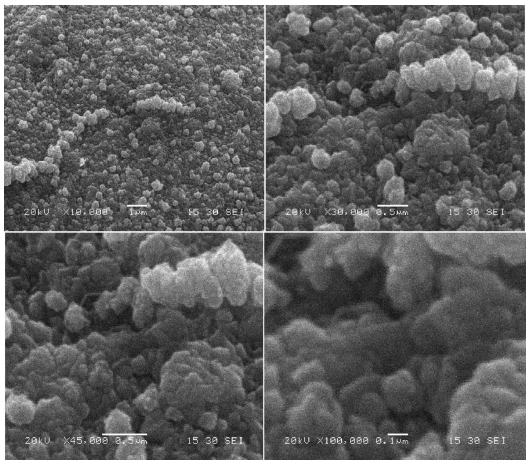

Fig. 2. SEM micrographs of SnO_2 films coated from 2nd sol (2:1 ethanol/glycerin mixture containing 0.2 M $SnCl_2{\cdot}2H_2O$) at different magnifications.

Figure 2 shows SEM image of the films coated from the second solution of 2:1 volumetric ratio of ethanol/glycerin mixture. When the ethanol ratio is increased, coarser equiaxed grains with high surface roughness are obtained. In high magnification SEM structure, some of the agglomerated grain groups are observed.

Figure 3 shows SEM image of the films coated from the third solution of 4:1 volumetric ratio of ethanol/glycerin mixture. Increasing the ethanol/glycerin ratio to 4:1, the agglomeration seems more pronounced and agglomerated groups are layered.

AFM investigations are well consistent with SEM structure. AFM micrographs of SnO_2 films obtained from all three solutions show mesoporous structure. In Fig. 4a, AFM images of SnO_2 film obtained from first

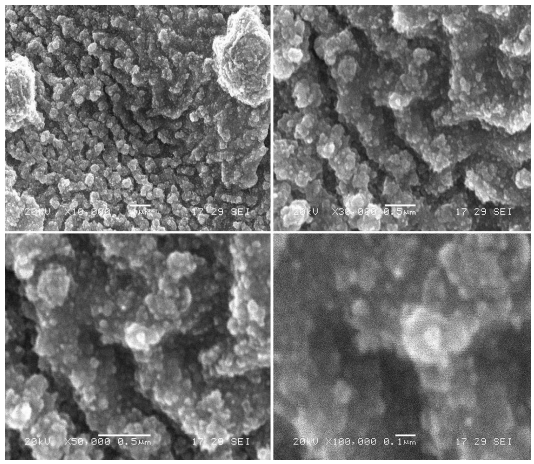

Fig. 3. SEM micrographs of SnO_2 films coated from 3rd sol (4:1 ethanol/glycerin containing 0.2 M $SnCl_2{\cdot}2H_2O$) at different magnifications.

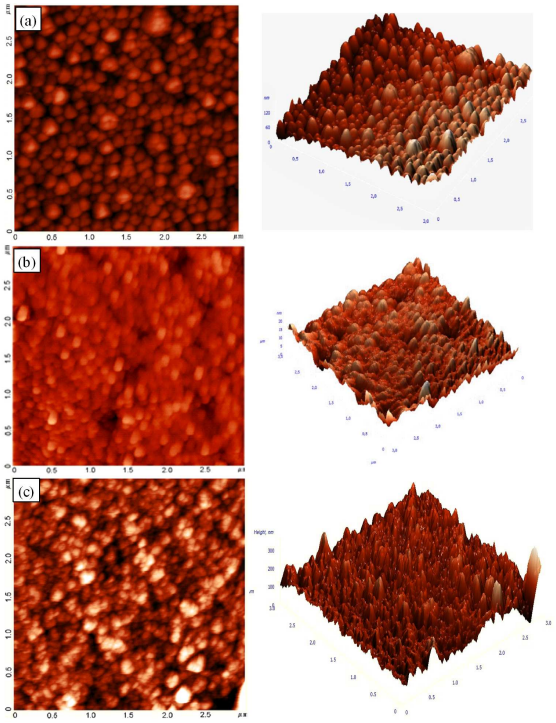

Fig. 4. AFM micrographs with 3D structures of SnO_2 films obtained from (a) 1st sol, (b) 2nd sol, (c) 3rd sol.

sol show homogeneous, spherical nanograins and mesoporous structure. The surface roughness is 120 nm. As can be seen from Fig. 4b, the film obtained from second sol possessed roughness lower than 20 nm. The resistivity of the film was measured only for the second film because of the proper surface structure and fewer cracks. The measured resistivity is 1.2×10^{-2} Ω cm. AFM micrographs of SnO_2 film obtained from third sol are given in Fig. 4c. Agglomerated small nanograins are observed similar to SEM image. The surface roughness was started to increase due to agglomeration of nanograins in a layered form. Due to rough and crack dense surfaces, we

could not measure reproducible resistivity for 1 and 3 solutions.

Scherrer's formula was used to determine the grain size of the SnO_2 coatings by using XRD data

$$t = \frac{K\lambda}{B\cos\theta_B}\,. \tag{1}$$

In this formula, t is the mean grain size of crystalline structure. λ is X-ray wavelength, B is full width at half maximum (FWHM) or integral breadth of XRD peak, and θ_B is the Bragg angle.

In Table, determined grain size of samples by Scherrer's formula can be seen. For the first sample maximum grain size was observed. Minimum grain size was obtained from the second sample which contained 2:1 volumetric ratio of ethanol/glycerin mixture.

TABLE

Grain size of SnO_2 particles obtained from sols.

Samples	1:1 ethanol /glycerin	2:1 ethanol /glycerin	4:1 ethanol /glycerin
grain size	33 nm	19 nm	25 nm

XRD analysis was performed to investigate the crystal structure of films. In Fig. 5, XRD results are given, and the results show that there is no significant preferential nucleation and growth by changing ethanol and glycerin ratios. The produced phase is mainly cassiterite type of SnO_2. The strongest peak for each case is the (110) plane in Fig. 5a–c. As can be seen from the XRD diagrams, the strongest peak (110) has broadest nature for 2nd solution. The broadest diffraction (110) peak of SnO_2, in Fig. 5b, suggests that the nanoparticles are very small in size. The similar effect of decreasing particle size on the peak broadening in tin oxide and tin oxide based nanocomposite materials was also proved by Lian et al. [10].

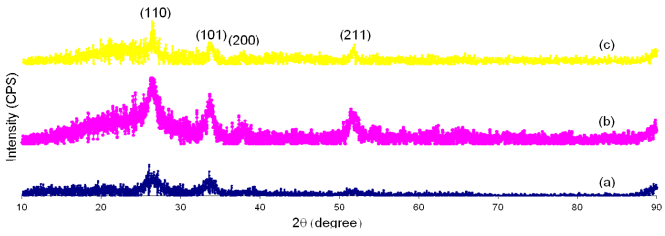

Fig. 5. XRD diffractograms of SnO_2 films obtained from (a) 1st sol, (b) 2nd sol, (c) 3rd sol.

4. Conclusions

SEM, AFM, and XRD results indicate that the films coated with second sol showed minimum grain size (19 nm), and high glycerin addition caused the growth of grain size (33 nm). In 1:1 and 4:1 ethanol/glycerin ratio, in first and third sol, grains were coarser. Results showed that an optimal volumetric ratio of ethanol and glycerin solution is 2:1. Reproducible resistivity values were observed in these films as 1.2×10^{-2} Ω cm. The results indicated that the mesoporous and nanocrystalline nature of the SnO_2 films obtained from optimized tin solution can be used for SnO_2 films for application of thin film electrodes such as sensors, solar cells and Li-ion batteries.

Acknowledgments

This work is supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the contract number 109M464. The authors thank the TÜBİTAK workers for their financial support.

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