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Short communication

Synthesis and characterization of nanocrystalline SnO_2 and fabrication of lithium cell using nano-SnO_2

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Abstract

Nanocrystalline tin oxide (SnO_2) materials are synthesized by a chemical precipitation method. The nanoparticles are of 5–20 nm in size, as calculated by using Scherrer's formula, and as observed by transmission electron microscopy (TEM). The electrical properties of the consolidated nano-structured SnO_2 are studied using an impedance spectroscopic technique. The SnO_2 particles are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), TEM and impedance spectroscopy. Electrochemical tests are performed using nanocrystalline SnO_2 as the negative electrode for a lithium cell. The results show that nanocrystalline SnO_2 materials can be used as an anode material for battery application.

Keywords: Impedance spectroscopy; Lithium cell; Nanocrystalline tin oxide; Transmission electron microscopy; X-ray diffraction

1. Introduction

Nanocrystalline materials with average grain size of less than 50 nm have attracted considerable scientific interest because of their peculiar structures and unusual physical and chemical properties [1]. The microstructure of nanocrystalline materials depends upon the method of preparation. Tin oxide, a stable and large band-gap semiconductor, has excellent photo-electronic properties and good sensitivity to gases [2–4]. It is well known for its application in gas sensors [5,6] and dye-based solar cells [7].

In recent years, there has been an increasing interest in the use of SnO_2 as the negative electrode for lithium batteries [8]. It appears that the basic process is lithium insertion into tin oxide, which forms a Li–Sn alloy in a matrix of Li_2O [9].

In the present work, we report the preparation of nanocrystalline SnO_2 material by chemical precipitation and the evaluation of its physico-chemical characteristics.

2. Experimental procedure

Nanocrystalline SnO_2 powders have been prepared by a chemical precipitation method. Tin chloride ($SnCl_2{\cdot}2H_2O$) 0.1 M was placed in aqueous medium in a flask fitted with a reflux condenser. The solution was hydrolyzed for 144 h and then neutralized with ammonia solution. The resulting precipitate was washed with distilled water and then dried. All the as-prepared samples were annealed at 600 and 900 °C. Powder X-ray diffraction (XRD) was carried out on all the samples with a Siefert X-ray diffractometer using Cu $K\alpha_1$ radiation and a quartz monochromator in the 2θ range 20–70° in steps of 0.02°. Instrumental broadening was estimated with a standard silicon sample and taken into account in the grain size estimation using Scherrer's formula [10]. The microstructure of the powder sample was characterized by means of transmission electron microscopy (TEM) with a JEOL 2000X instrument. The particle morphology of the as-prepared as well as annealed samples were characterized by scanning electron microscopy (SEM) with a JEOL JSM 840 A instrument.

Impedance measurements were performed on the as-prepared pellets with a Solartron SI 1260 impedance/gain phase analyzer in the frequency range 100 Hz to 1 MHz from 200 to 550 °C. Pellets of 8 mm diameter and 2.4 mm thickness were made by applying an uniaxial pressure of 0.57 GPa on the powder sample. Platinum was used as electrodes. Platinum paint was applied to both the surfaces of each pellet.

3. Preparation of SnO_2 electrode and cell assembly

The SnO_2 material prepared by chemical precipitation was sintered at 1000 °C for 6 h in order to enable the

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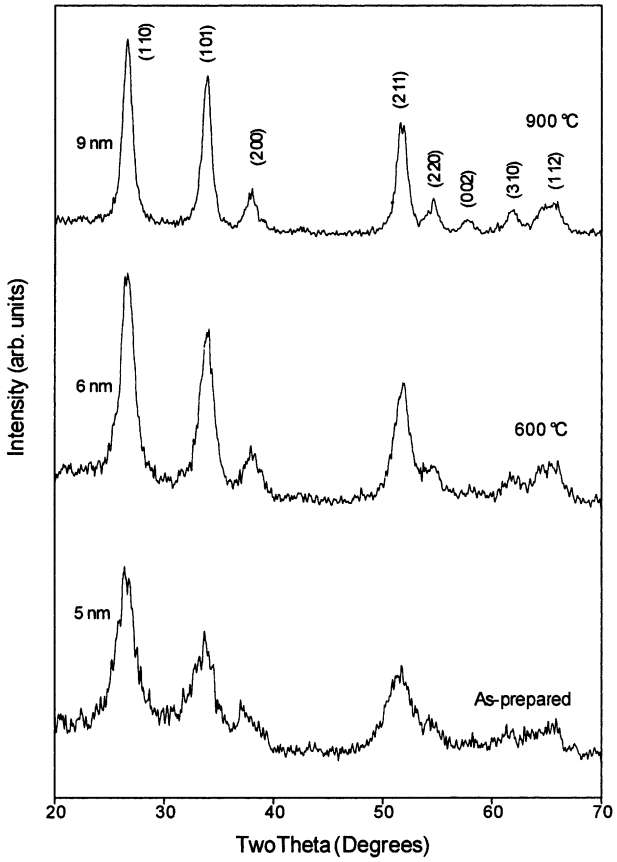

Fig. 1. XRD spectra of nanocrystalline SnO_2 powder annealed at different temperatures for 1 h.

material to undergo a solid-state reaction. Hence, a weight loss is observed after sintering. The product was ground to a fine powder in an agate mortar and mixed with 10 wt.% acetylene black and 5 wt.% PTFE (poly tetra fluro ethylene) as binder. The mixture was then pressed and pelletized. For electrochemical investigations, a laboratory test cell, Li/liquid electrolyte (PC:EC)/SnO_2 was fabricated. The electrolyte used was 50:50 mixture by volume of ethylene carbonate (EC) and propylene carbonate (PC). The cell was properly insulated and measurements were carried out under high vacuum conditions.

4. Results and discussion

The XRD spectra of an as-prepared SnO_2 sample and annealed samples at 600 or 900 °C are shown in Fig. 1. All samples showed the tetragonal phase of SnO_2. It is also observed that broadening of the peak decreases with increase of annealing temperature. At the same time, the peak intensity increases with annealing temperature. The average grain size, measured from the XRD line width, is found to increase from 5 nm for the as-prepared powder, to 9 nm on annealing the powder at 900 °C for 1 h. The XRD profile for the as-prepared sample show asymmetry which

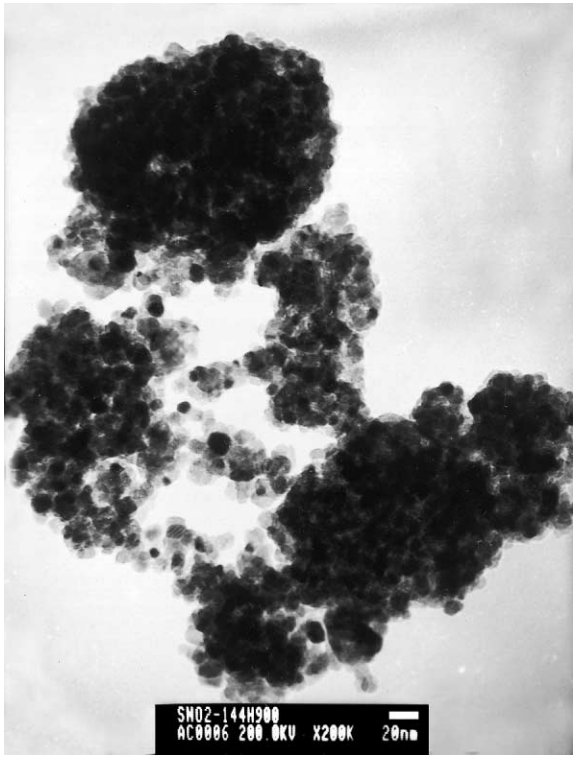

Fig. 2. TEM micrograph of SnO_2 powder annealed at 900 °C.

may be due to lattice strain [11]. The lattice strain is reduced when the sample is annealed above 600 °C.

A TEM image of the SnO_2 material annealed at 900 °C for 1 h is presented in Fig. 2. The average grain size of the annealed sample is in the range of 20 nm. The fine particles are more or less spherical in shape and each particle is found to be an aggregate of very small crystallites.

Scanning electron micrographs of an as-prepared and annealed sample of SnO_2 are shown in Fig. 3. All the particles are almost spherical in shape. The as-prepared sample consists of particles of smaller size compared with those of the annealed sample.

The complex impedance spectra (Z'' plotted against Z') for as-prepared nanocrystalline SnO_2 held at 250–450 °C are shown in Fig. 4. In the temperature range between 250–300 °C, the grain and grain boundary resistances are resolved into two overlapped semicircles. The two semicircular arcs are attributed to different relaxation processes in the grains and grain boundaries. As the measuring temperature increases, the high frequency part of the semicircle merges with the low frequency part. Hence, above 350 °C, only one semicircle is observed and corresponds to grain boundary polarization. At higher temperatures, the impedance spectra display a typical depressed semicircular arc behavior. The single semicircle results from the grain and grain boundary having identical time constants. The arcs are highly depressed which is due to the distribution of relaxation time [12]. Hence, the semicircle in the spectra is the combination of a constant-phase element (CPE) in series

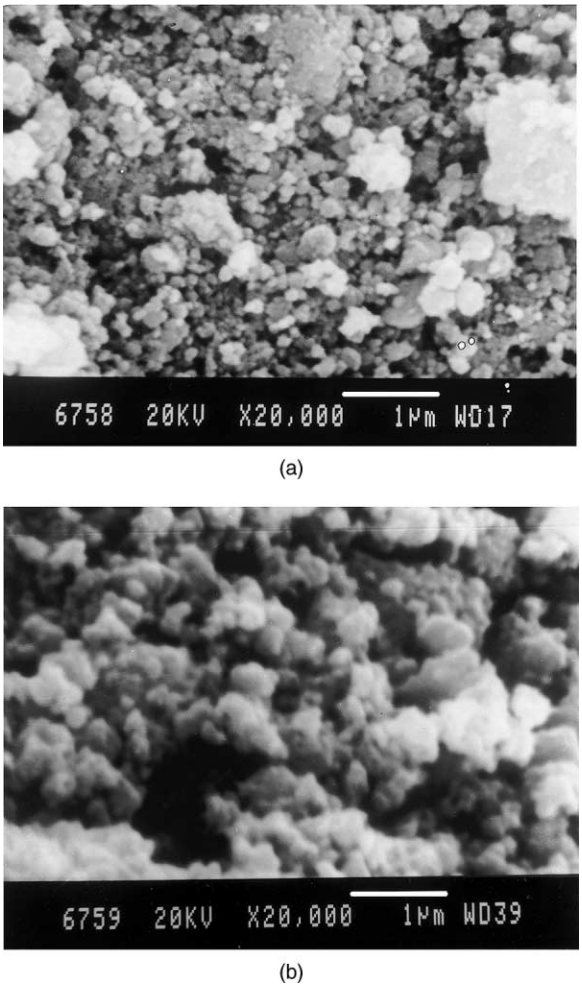

Fig. 3. SEM micrographs of SnO_2 powder: (a) as-prepared, (b) annealed at 900 °C.

with a parallel combination of resistance and capacitance. This is mainly due to the domination of the grain boundary polarization effect than the bulk effect as the temperature is increased.

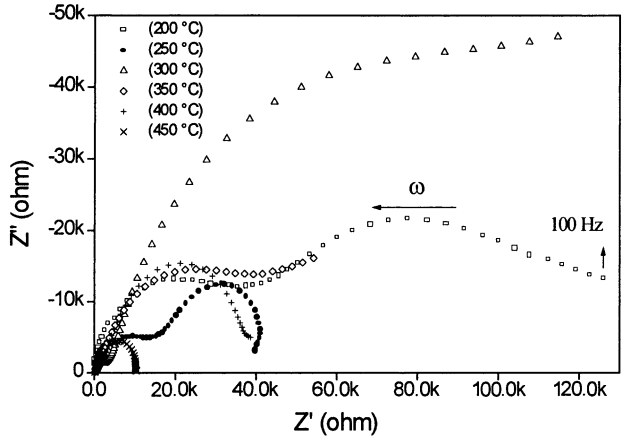

Fig. 4. Complex impedance spectra of SnO_2 (as-prepared) at different temperatures.

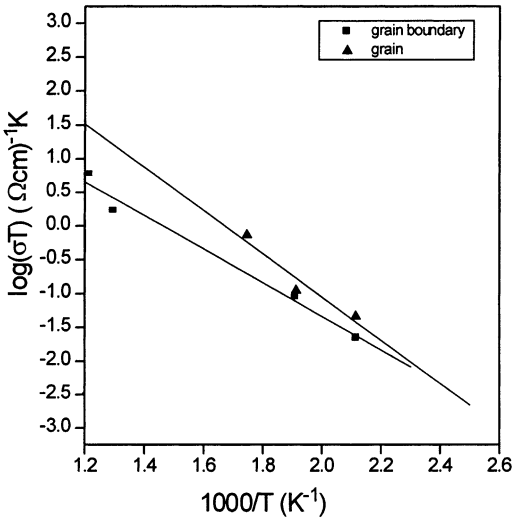

Fig. 5. Arrhenius plot for as-prepared SnO_2 compacted pellet.

The variation in conductivity with temperature for the as-prepared nanocrystalline SnO_2 is plotted as Arrhenius plots in Fig. 5 for the grain and grain boundary components. The activation energy for the grain (0.6 eV) is higher than that for the grain boundary (0.48 eV). The surface atoms will have a higher diffusion coefficient in the nanocrystalline state than in the bulk grains and, therefore, the grain boundaries are expected to exhibit higher conductivity. In the present case, however, the observed inferior conductivity in the grain boundaries may be due to discontinuous grain boundaries and the porosity of the material.

5. Discharge characteristics

The average discharge characteristics of a lithium insertion electrode made from chemically prepared nanocrystalline SnO_2 particles, acetylene black and a binder are shown in Fig. 6. The cell was discharged at 25 μA. The electrode chosen for the test was EC:PC, which is commonly used for Li-ion batteries. The electrochemical reactions of the discharge of the cell are:

$$SnO_2 + 2Li \rightarrow SnO + Li_2O \quad (1)$$

$$SnO + 2Li \rightarrow Sn + Li_2O. \quad (2)$$

In an assembled condition, i.e. Li/PC:EC/SnO_2, gives an open-circuit voltage (OCV) of 3.06 V.

The specific energy can be calculated by

$$\text{energy density} = \text{power density} \times \text{hours of service} \quad (3)$$

$$\text{i.e. Wh kg}^{-1} = \text{W kg}^{-1}\,\text{h} = (\text{AVh})\,\text{kg}^{-1}. \quad (4)$$

The specific energy of the system is 240 Wh kg^{-1}. Hence, it is clear that the crystallinity of the SnO_2 nanoparticles increases the accessibility of the active mass to lithium ions, as well as electrons. Thus, its conversion to Li_2O and Li–Sn alloy by cathodic polarization is more complete in the

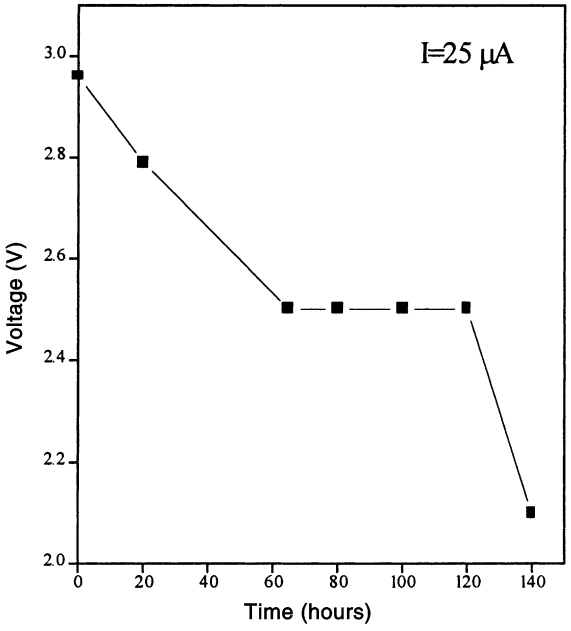

Fig. 6. Discharge characteristics of SnO_2 based Li-ion cell.

nanocrystalline form than amorphous state. This result suggests that nanocrystalline SnO_2 can be used as negative-electrode material for batteries of high specific energy.

6. Conclusions

In this work, a chemical precipitation method is used for the preparation of nanocrystalline SnO_2 particles. A preliminary electrochemical test was performed for studying the behavior of electrodes containing nanocrystalline SnO_2 as the active mass in a Li-ion battery. These tests indicate that nanocrystalline SnO_2 particles have promising capacity and good stability in repeated lithiation/de-lithiation processes. Good performance of these materials may be due to optimization of the heat treatment and solution composition. Hence, this study demonstrates that nanocrystalline SnO_2 particles prepared by a chemical precipitation method can be used as a viable electrode material for batteries of high specific energy.

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