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Electrochemical evaluation of nanocrystalline Zn-doped tin oxides as anodes for lithium ion microbatteries

Morteza Torabi, S.K. Sadrnezhaad*

Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

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ABSTRACT

Nanocrystalline tin oxides were synthesized using electron beam evaporation (e-beam) and further heat treatment. X-ray diffraction (XRD) revealed that as-deposited samples were amorphous SnO. Heat treatment of the as-deposited thin films at 250 °C for 2 h and 500 °C for 10 h led to the formation of romarchite SnO and tetragonal SnO_2, respectively. Scanning electron microscopy (SEM) showed a compact morphology of the coatings. Elemental mapping of the films also represented homogeneous distribution of the zinc atoms in the SnO_2 structure. Atomic force microscopy (AFM) images demonstrated a fine and smooth surface of the e-beam evaporated films for the SnO samples, and rough topography for the SnO_2. Doping led to the formation of finer and more uniform surface morphology. Anodic behavior of the thin film during charge/discharge process showed that specific capacity of the pure SnO_2 increased from 502 to 903 $\mu Ah\,cm^{-2}\,\mu m^{-1}$ for nanocrystalline Zn-doped SnO_2. Moreover, specific capacity of the doped film enhanced to 137.6 that is, higher than 69.5 $\mu Ah\,cm^{-2}\,\mu m^{-1}$ for the pure SnO_2. XRD results also show that Zn doping decreased Sn clustering during cycling.

1. Introduction

Rechargeable thin-film lithium ion batteries served much attention recently due to their applications in microelectronics such as smart cards, medical devices and integrated circuits [1,2]. A thin-film microbattery is made up of a cathode, a solid electrolyte and an anode. Lithium metal was used as anode in rechargeable lithium ion batteries. Lithium metal has low melting point and is reactive to the air and water that make lithium inappropriate for integration with micro-devices. Therefore, replacing the lithium anode with other stable thin-film materials would be welcome. Many alloys and composites, such as Ni–Sn, Cu–Sn, Si–Sn, N–Sn, Zr–Sn, Sn–Zr–Ag [3–6] or metal oxides such as SnO_2 [7] were introduced and tested as anodes for Li-ion microbatteries.

Tin oxide based materials have been proposed as alternative anode materials for lithium ion batteries due to their high energy densities and stable capacity retention [8–10]. Because of formation of Li_2O in the first cyclic loading, SnO_2-based materials have displayed unusual electrochemical behavior. Li_2O formation and capacity fading caused by volume changing would be controlled using nanotechnology or doping process [11–13]. Therefore, nanocrstalline Zn-doped SnO_2 can also be suggested as a promising anode material. The particle size of the nanocrystalline Zn-doped SnO_2 is small enough to increase the active surface of the particles and materials efficiency. Furthermore, it would excel the kinetic of the lithium intercalation/deintercalation process in the lithium ion batteries [14].

In this study, synthesis of the Zn-doped SnO_2 using electron beam evaporation was investigated. Nanocrystalline Zn-doped SnO_2 was evaluated electrochemically as possible anode materials for Li-ion thin-film batteries.

2. Experimental

Nanocrystalline Zn-doped tin oxides were prepared using e-beam evaporation method. During this process, copper thin layer was firstly deposited with thickness of about 50 nm onto a 1 cm × 1 cm glass. Zn-doped tin oxides source was prepared by cold pressing (10MPa) of SnO_2 and 1 wt% ZnO powders (Merck, Germany). Prior to each deposition, vacuum was applied in the chamber until the pressure equal to 10^{-5} Pa. Then, pre-evaporating has systematically been achieved in order to clean the source surface. Two different heat treatments were applied to the as-deposited thin films. In the first, thin layers were put into the crucible in the air for 2 h at 250 °C. In the other heat treatment, the as-deposited samples were oxidized for 10 h at 500 °C.

The morphology of the Zn-doped tin oxide thin films were studied using scanning electron microscopy (SEM, VEGA, TESCAN) equipped with energy dispersive X-ray (EDX) analysis which was used for compositional analysis of the nanocrystalline Zn-doped

* Corresponding author. Tel.: +98 261 6210009; fax: +98 261 6201888.
E-mail address: sadrnezh@sharif.edu (S.K. Sadrnezhaad).

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