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Effect of Sn-doping on the electrochemical behaviour of TiO_2 nanotubes as potential negative electrode materials for 3D Li-ion micro batteries

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HIGHLIGHTS

- ► Sn-doped TiO_2 nanotubes were fabricated by anodization of sputtered Ti–Sn thin films.
- ► The Sn-doped TiO_2nts can be used as anodes for 3D Li-ion micro batteries.
- ► The electrochemical performance of Sn-doped TiO_2nts was better than simple TiO_2nts.
- ► The improved performance is related to enhanced lithium diffusivity with Sn doping.
- ► This synthesis approach is extendable for Fe/Sb/Nb-doping of TiO_2 nanotubes.

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ABSTRACT

Self-organized Sn-doped TiO_2 nanotubes were fabricated by anodization of co-sputtered Ti–Sn thin films in a glycerol electrolyte containing NH_4F. The Sn-doped TiO_2nts were studied in terms of composition, morphology and structure by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and ^{119}Sn Mössbauer spectroscopy. The electrochemical behaviour of the Sn-doped TiO_2nts was evaluated in Li test cells as a possible negative electrode for 3D Li-ion micro batteries. The Sn-doped TiO_2nts delivered much higher capacity values compared to simple TiO_2nts. The outstanding electrochemical behaviour is proposed to be related to the enhanced lithium diffusivity evidenced with Cottrell plots, and the rutile-type structure imparted with the Sn doping.

1. Introduction

The advent of modern microelectronic devices challenges scientists to investigate high-performance micro batteries. All-solid-state (thin-film) micro batteries are integrated into microelectronic circuit boards to deliver low energy to various devices such as hearing aids, medical implants, remote sensors, RFID tags etc [1–3].

To date, these micro batteries are based on a parallel (or pseudo-parallel) or a sandwich configuration of planar electrodes separated by a solid electrolyte. This planar configuration leads to relatively low volumetric energy and power densities. However, the miniaturization of recent electronic devices requires higher volumetric energy densities in addition to size diminution (on the order of 0.1 cm^3). In this context, the development of three-dimensional (3D) thin-film micro batteries represents a viable alternative [4,5]. The 3D design will ensure that anode and cathode materials have (active) surface areas exposed in three dimensions – exploiting the out-of-plane dimension instead of just the conventional in-plane surface. Nano-structuration of electrode materials is one of the most promising approaches to realize this 3D paradigm of micro batteries [6]. Not only is the reduction of the areal footprint crucial, new and highly performing anode, cathode and electrolyte materials are also imperative for high performance and low manufacturing cost.

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Actually, the negative electrode material of thin-film micro batteries is of a great concern. Almost all thin-film micro batteries utilize metallic lithium anode that has a low melting point and a strong reactivity. Furthermore, an expensive packaging technology is always required due to the lithium anode [7,8]. Recently, significant attempts are being made to fully adopt the "Li-ion" or the "rocking-chair" concept in the design of lithium-based micro batteries [1,9]. This implies combining cathode materials such as $LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$ [10–12] with the wide range of possible anode materials proven to react reversibly with lithium either by insertion [13,14], alloying [9,15–18] or conversion [19–22]. Cathode materials such as V_2O_5 and TiO_xS_y are of considerable interest particularly with a lithiated anode material to maintain the 'Li-ion' concept [8,23–25]. Among all the potential anode materials, TiO_2 nanotubes (TiO_2nts) possess a spectacular characteristic for the design of 3D Li-ion micro batteries [26,27]. Besides the self-organized (3D) nano-architecture, TiO_2 nanotubes exhibit very good capacity retention particularly at moderately high kinetic rates [13,14,27–29]. As TiO_2 (anatase or rutile) effectively inserts only 0.5 Li^+ per formula unit, corresponding to a theoretical capacity of 168 mAh g^{-1} [14,30,31], interest has risen recently to improve the overall performance of TiO_2 nanotubes for the design of high-performance 3D Li-ion micro batteries. TiO_2 being a semiconductor, selective doping by aliovalent or homovalent substitution of Ti affects the intrinsic electrical properties to some extent.

In this work, TiO_2 nanotubes were doped with Sn^{4+} by potentiostatic anodization of Ti–Sn thin films which were produced by co-sputtering of titanium and tin targets. X-ray diffraction, X-ray photoelectron spectroscopy and ^{119}Sn Mössbauer spectroscopy were employed to help ascertain the quality of the doping operation. The effects of Sn^{4+} doping on the morphology and the electronic properties of TiO_2 nanotubes were investigated. Finally, the impact of Sn^{4+} doping on the electrochemical behaviour of TiO_2 nanotubes as anodes for 3D Li-ion micro batteries was evaluated in lithium test cells.

2. Experiment

Metallic targets (Ti and Sn, 99.9% pure) were supplied by Sigma–Aldrich. For the co-sputtering, the Ti and Sn targets were cut into the right proportions (considering the sputtering rates of Ti and Sn in relation to the anticipated thin film composition), cleaned and assembled in a target holder with the aid of a silver paste. The target, after drying overnight at room temperature, was inserted into the PVD chamber. Silicon substrates (p-type Si with a resistivity of 1–10 Ω cm [WaferWorld, Inc.]) were cut to size along the (100) crystallographic plane and cleaned by sonicating sequentially in acetone, isopropanol, and methanol for 10 min each. The native oxide layer was then removed by dipping the Si wafers in a solution of 1 wt% HF for 1 min, followed by rinsing with distilled water and drying with compressed air. The cleaned Si substrates were immediately inserted into the PVD chamber which was subsequently evacuated until a low residual pressure was reached (10^{-6} mbar).

Thin films (Ti or Ti–Sn) of ~1.5 μm thickness were deposited by cathodic sputtering onto the mirror-polished Si wafers. The substrates were constantly rotated (360°) during the deposition to ensure a uniform thin film composition. An ultrapure Ar atmosphere was maintained inside the chamber at a pressure of 6×10^{-4} mbar during the deposition, with a current of 150 mA. For the Ti–Sn thin film, Ti was first deposited for 30 min to obtain a barrier layer on the silicon substrate for galvanostatic experiments. Anodization experiments were carried out by applying a constant voltage of 40 V during 1.5 h in a conventional two electrode cell using an EG&G PARSTAT 2273 potentiostat/galvanostat. The thin films (Ti or Ti–Sn) were the working electrodes while a platinum foil served as a counter electrode. The electrodes were separated by a distance of 3 cm and the electrolyte was a solution of 88.7 wt% glycerol, 1.3 wt% NH_4F and 10 wt% H_2O.

Optional thermal treatments at 450 °C were performed in air during 3 h. X-ray-diffraction studies were carried-out at room temperature with a step-time of 10 s and step-size of 0.02° using a Siemens D5000 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Scanning Electron Microscope (SEM) images were recorded with a Philips XL-30 FEG SEM. Mott–Schottky analysis was carried out in a 0.1 M Na_2SO_4 solution using an Ag/AgCl reference electrode, a platinum foil counter electrode and the nanotubes as working electrodes. The potential was changed in 0.1 V voltage steps and the impedance was determined at 30 Hz fixed frequency with 10 mV a.c. amplitude using an EG&G PARSTAT 2273 potentiostat/galvanostat.

^{119}Sn room temperature Mössbauer spectra were recorded in the constant acceleration mode and Conversion Electron Mössbauer Spectroscopy (CEMS) geometry. A specific helium-flow counter was used for the detection of conversion electrons. The γ-ray source consisted of $Ba^{119m}SnO_3$ with a nominal activity of 7 mCi. The hyperfine parameters, isomer shift (δ) and quadrupole splitting (Δ), were determined by fitting appropriate Lorentzian lines to the experimental data. The quality of the fit was controlled by the usual χ^2-test. All isomer shifts for Sn are given relative to $BaSnO_3$ at room temperature.

XPS measurements were carried out with a Kratos Axis Ultra spectrometer, using focused monochromatized Al Kα radiation ($h\nu = 1486.6$ eV). The XPS spectrometer was directly connected to an argon dry box through a transfer chamber, to avoid moisture/air exposure of the samples. The analysed area of the samples was 300 μm × 700 μm. Peaks were recorded with a constant pass energy of 20 eV. The pressure in the analysis chamber was around 5×10^{-8} Pa. Short acquisition time spectra were recorded before and after each normal experiment to check that the samples did not suffer from degradation under the X-ray beam during measurements. Peak assignments were made with respect to experimental reference compounds, namely bulk anatase and/or rutile TiO_2. The binding energy scale was calibrated from hydrocarbon contamination using the C1s peak at 285.0 eV. Core peaks were analysed using a non-linear Shirley-type background. The peak positions and areas were optimized by a weighted least-square fitting method using 70% Gaussian and 30% Lorentzian line-shapes. Quantification was performed on the basis of Scofield's relative sensitivity factors.

For the electrochemical measurements, two-electrode Swagelok-type cells were assembled in a glove-box filled with purified argon in which moisture and oxygen contents were less than 2 ppm. The galvanostatic experiments were then carried out with the prepared Li/$LiPF_6$ (EC:DEC)/W_E (Working electrode) cells using a VersaSTAT 3 potentiostat/galvanostat. The electrolyte supplied by Merck was embedded in a Whatman glass microfiber, which acts as a separator. It is remarkable to note that additives such as poly(vinyl difluoride) that is a binding agent, and carbon black (conductive agent) were not utilized. For the discharge/charge, a constant current density of 70 μA cm^{-2} (1C) was applied to the assembled cells in the $1.0 \le U/V \le 2.6$ voltage range. Additionally, cyclic voltammetry was carried out with the VersaSTAT 3 potentiostat/galvanostat in the $0.65 \le U/V \le 3$ voltage range at a scan rate of 0.1 mV s^{-1}.

3. Results and discussion

3.1. Morphology, composition and structure

Fig. 1 shows the current transients recorded during the anodization of Ti and Ti–Sn thin films in an electrolyte consisting of 88.7 wt% glycerol, 1.3 wt% NH_4F and 10 wt% H_2O. It can clearly be