

# Tin/tin oxide thin film electrodes for lithium-ion batteries

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## Abstract

Amorphous and crystallized tin-based composite oxide (TCO) thin layers were elaborated by radio frequency (r.f.) sputtering from a Sn/SnB<sub>0.6</sub>P<sub>0.4</sub>O<sub>2.9</sub> target. Chemical, physical and electrochemical properties of these thin film electrodes are presented. The electrochemical behavior depends on several parameters including the nature of the metallic sub-layer acting as the current collector. Partially crystallized thin film-based electrodes deposited on an Au sub-layer and containing high amount of metallic tin were found to present a very interesting specific capacity (550 mAh/g) associated to promising cyclability. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Tin/tin oxide; Thin film; Electrodes; Li-ion batteries

## 1. Introduction

Much attention has been focussed on lithium-ion batteries because the promising applications due to their high specific energy and energy density. Currently, a conventional anode material based on carbonaceous compounds is used, but the recent announcement by Fuji Photo Co [1] of an amorphous tin-based composite oxide (TCO) as an anodic material renewed interest in the lithium alloys electrodes. Indeed, the TCO-based anodes have a capacity density four times higher than carbon-based negative electrodes.

Basically, the TCO-based electrode is working — following the electrochemical reduction of SnO — on the formation of Li–Sn alloys with an ultimate Li<sub>22</sub>Sn<sub>5</sub> composition according to the equilibrium phase diagram. So, after the first charge (uptake of Li ions), the electrode is like a micro-composite containing a fine dispersion of Li–Sn alloys in the vitreous matrix, the reversible reaction being mainly based on the alloying/de-alloying process [2–6].

The amorphous matrix which is not involved in the electrochemical process exhibits a large number of vacant sites minimizing the volume change of the electrode. Moreover, the inactive component may act as a glue reducing the aggregation rate of the metallic particles during cycling [7].

This paper will discuss the thin film concept applied to the elaboration of electrodes from a composite target

(Sn/SnB<sub>0.6</sub>P<sub>0.4</sub>O<sub>2.9</sub>). The first objective was to obtain full glassy thin film-based electrodes with interesting electrochemical properties previously announced with bulk TCO's materials [1]. The second objective was to increase the tin amount and as a consequence the specific capacity while keeping up the coexistence with the wrapping glassy matrix.

## 2. Experimental

The glassy target elaboration was already described [8]. Tin disks were pasted onto its surface (~20 cm<sup>2</sup>) in order to obtain a composite target offering a metallic tin/vitreous matrix area ratio close to 30%.

Thin films were obtained by radio frequency (r.f.) sputtering under an argon plasma. Depending on the sputtering conditions, especially the power, amorphous or crystallized thin films were obtained. XRD diffraction (Seifert  $\theta$ - $\theta$  diffractometer with Cu K $\alpha$  radiation) was used to check out the samples. SEM (Cambridge 360) associated to EDX allows the thickness and the semi-quantitative composition of the thin film to be obtained. The tin oxidation state into the thin layers were determined by means of XPS (Surface Science Instruments) and electrical conductivity was investigated by complex impedance spectroscopy (HP4192A Impedance Analyzer).

Galvanostatic charge/discharge curves were obtained by means of a scanning potentiostat (EGG/PAR362) using the sputter deposited film as the working electrode and a lithium disk as both the counter and reference electrodes. The

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electrolyte (1 M  $\text{LiPF}_6\text{-EC-PC-3DMC}$ ) was supported by a porous glass fiber disk. All electrochemical measurements were carried out in an argon filled dry box where  $\text{H}_2\text{O}$  content was kept below 1 ppm.

### 3. Results and discussion

#### 3.1. Physical and chemical characterization of the thin films

Obtaining amorphous and more or less crystallized forms of the sputter deposited thin films is strongly depending on the experimental conditions; the higher the power value, the larger the amount of metallic tin in the deposit. Consequently, diffraction peaks belonging to tin metal were observed in XRD patterns. On the other hand, with lower power values, the deposits remained amorphous.

The conductivity values of the thin films deposited under high power (70 W) were close to  $2 \times 10^{-1}$  S/cm, a mid-value between the bulk glassy matrix ( $10^{-7}$  S/cm) and metallic tin ( $10^5$  S/cm). Although a chemical semi-quantitative analysis of the thin layers may be investigated by the EDX, an accurate coulombic capacity can only be obtained if the different oxidation states of tin are well determined. In this way, the XPS allows to separate and provide the relative amount of each oxidation state from  $\text{Sn}^0$  to  $\text{Sn}^{\text{II}}$  and  $\text{Sn}^{\text{IV}}$ . Depending on the sputtering conditions, the spectra were quite different as shown in Fig. 1. It may be difficult to distinguish  $\text{Sn}^{\text{II}}$  versus  $\text{Sn}^{\text{IV}}$  but, using a  $\text{SnO}$  bulk sample as a reference allow to mainly confirm the presence of  $\text{Sn}^{\text{II}}$  in the thin film elaborated under low power (30 W). In the same spectrum, the small peak observed at 484.6 eV proved out that  $\text{Sn}^0$  was also a minor component ( $\sim 3$  at.%) of this thin film. Contrariwise, the relative amount of  $\text{Sn}^0$  was greatly enhanced ( $\sim 31$  at.%) in the thin film elaborated under high power evidencing different deposition rates between metallic tin disks and vitreous matrix during the sputtering process.

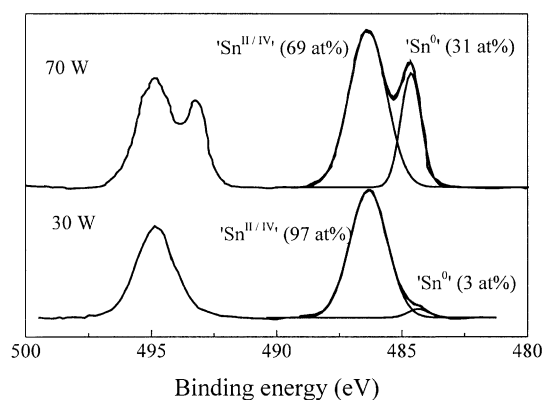


Fig. 1. XPS spectra of sputtered thin films elaborated under low (30 W) and high (70 W) power.

In conclusion, r.f. sputtering using a composite target appears to be a very convenient tool to obtain more or less tin loaded thin films, but the reproducibility of thin layers (adherence, composition, etc.) requires very well controlled sputtering conditions.

#### 3.2. Electrochemical behavior

The objective of this study was to improve the specific capacity of the thin film electrodes based on the TCO material by increasing the total tin amount while keeping a good cyclability. Sputter deposited thin films were elaborated on different substrates ( $1 \text{ cm}^2$ ) at two different power rates giving rise to amorphous or partially crystallized layers. Thin film electrodes were cycled between 1.2 and 0.1 V versus lithium at  $200 \mu\text{A}/\text{cm}^2$ . The coulombic capacity of the electrodes was calculated knowing the formula weight (XPS), the thickness (SEM) and assumed densities, i.e.  $3.7$  and  $4 \text{ g}/\text{cm}^3$  for amorphous or partially crystallized layers, respectively. Stainless steel substrates were first used and after five cycles, the specific capacity of the electrodes deposited under 30 W (thickness  $\approx 1 \mu\text{m}$ ) was close to  $200 \text{ mAh}/\text{g}$  while the other electrodes elaborated under 70 W (thickness  $\approx 3 \mu\text{m}$ ) were already poorly reversible. This latter result may be due to the bad adherence of the thin layer after lithium uptake. As a consequence, “cracking and crumbling” probably occur and electrode fails very fast. Nevertheless, the large specific capacity observed during the second cycle ( $580 \text{ mAh}/\text{g}$ ) with the highly tin loaded electrode was an interesting indication. First of all, the tin was confirmed as the only active electrochemical component of the material and secondly, our new approach had to be developed in a view to stabilize the deposit. In this way, trials of overlaying the stainless steel substrates with sputtered thin films of chromium or gold were achieved. Chromium metal is well known as an adhesive enhancer and gold as a very good electric collector. Moreover, gold was also chosen because the possibility to form alloys either with lithium or tin. Considering this aspect, one can say that chromium is belonging to substrates which show no alloying reaction contrary to gold that alloys with lithium and tin. As a matter of fact, the electrochemical behavior of these thin films samples was different from the one previously observed with stainless steel substrates. After five cycles, the remaining specific capacity of the thin film electrodes were two and three times larger and close to  $460$  and  $620 \text{ mAh}/\text{g}$  on chromium (thickness  $\approx 0.5 \mu\text{m}$ ) and gold (thickness  $\approx 0.3 \mu\text{m}$ ) sub-layers, respectively. Trying to explain the results obtained with the gold substrate, we suggested that during sputtering process the tin atoms may have enough energy to interact with the sub-layer and give rise to a pseudo sub-Au/Sn-based multiphase layer [9]. During the lithium alloying reaction, the tin atoms will react first but at the end of the process, lithium may partially alloy with Au/Sn-based phases in the interphase domain. In this way, we believe that the gold sub-layer may buffer the

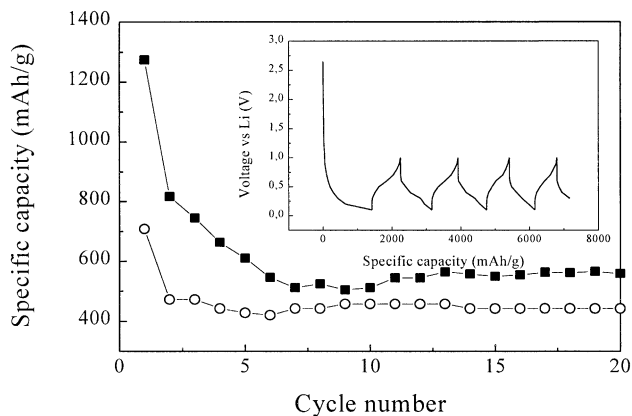


Fig. 2. Specific capacity vs. cycle number of thin film electrodes elaborated under 70 W ((■): gold sub-layer, (○): chromium sub-layer). The insert shows the first four charge/discharge curves on gold sub-layer. Current density:  $200 \mu\text{A}/\text{cm}^2$ ; voltage window: 1–0.1 V vs. Li.

volume expansion, improves the adhesiveness in the boundary domain and finally may be involved in the overall coulombic capacity. It is well known that cyclability of TCO bulk materials is greatly depending on parameters including the vitreous matrix/Sn ratio, size of tin particles, tin aggregation as well as cycling conditions (e.g. voltage window) [10]. Considering that the sputtering process gives rise to very well dispersed fine tin particles limiting the aggregation rate, the major effect allowing to keep up the cyclability seems to be a limitation in the voltage range. So, thin film electrodes elaborated under 70 W on a previously sputter deposited gold layer were cycled in the 1–0.1 V range versus Li since a high cut off voltage is detrimental to the matrix [10]. Moreover, according to [11] the Li–Sn alloying/de-alloying process occurs in the 0.66–0.38 V range versus Li (at equilibrium) and there is a net benefit to use a reduced voltage window in order to improve the cyclability. In these conditions, specific capacities only calculated with respect to the mass of the tin/tin oxide and close to 440 and 550 mAh/g were obtained on Cr and Au sub-layers, respectively (Fig. 2).

#### 4. Conclusion

Tin/tin oxide-based thin films were sputter deposited under argon plasma. Depending on the conditions process, amorphous or partially crystallized thin layers were obtained and characterized. Highly tin loaded thin film electrodes deposited on gold or chromium sub-layers exhibit very interesting electrochemical properties partly linked to the nature of the sub-layer. A 550 mAh/g specific capacity, i.e. a  $2200 \text{ mAh}/\text{cm}^3$  capacity density over 20 cycles was obtained, evidencing the interest of such thin films for micro-batteries applications.

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