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THE EFFECT OF ELECTRODEPOSITION CONDITIONS ON MORPHOLOGY AND COMPOSITION OF SN-SNSB DEPOSITS

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Sn-SnSb films were electrochemically deposited on the Cu and Cu/Au substrates by simple galvanostatic electrodeposition from a chloride-based solution. Dense, adherent and quite homogeneous deposits were obtained and the effect of current density on morphology and composition of as synthesized materials was investigated. It was found that with increasing current density the size of particles decreases and deposits become smoother and more homogeneous. Moreover, antimony content in the deposit decreases with increasing current density independently of the type of substrate. Both, Sn and SnSb metallic compound phases were identified in the samples by XRD analysis.

Keywords: *antimony, tin, electrodeposition*

Since 1990, lithium ion batteries have become the most popular power source for portable devices such as lap-top computers, cellular phones or even medical devices [1]. At present, mainly carbon based materials are used as anodes of lithium ion cells, but considerable attention is focused on alternative anode materials that can replace graphitic carbon and improve battery characteristics [2]. Very promising candidates for anodes are metallic or intermetallic electrodes which could form alloys with lithium e.g., Sn, Sb or Si-based materials [3-5]. A big advantage of this kind of materials is a relatively high specific capacity much higher than offered by conventional graphite anode (372 mAh g^{-1}). For example, metallic tin can react with lithium and form an alloy with the composition of $Li_{4.4}Sn$ that corresponds to the theoretical capacity of 993 mAh g^{-1}. Unfortunately, high volume changes during lithiation-delithiation processes often result in a significant capacity decay due to the cracking of the alloy grains and lost of the electric contact with a current collector [5]. Several strategies have been already proposed to overcome this problem. One of them is to use multicomponent instead of single-component materials. Usually, one of the components is less active towards lithium and buffers the volume changes during cycling. Very interesting examples of such kind of materials were proposed recently [6-9]. The authors prepared Sn-SnSb thin films by electrodeposition on the Cu planar substrate [7] and three-dimensional copper collectors [8]. It is obvious that the morphology and composition of such kind of deposits strongly depend on electrodeposition conditions.

Formulation of the problem

In this communication we present some results on the influence of current density on morphology and composition of Sn-Sb layers electrochemically deposited on Cu and Au surfaces.

Objects and the methods of the investigation

A schematic representation of the experimental procedure is shown in figure 1. Copper plates were used as starting materials (Fig. 1 A).

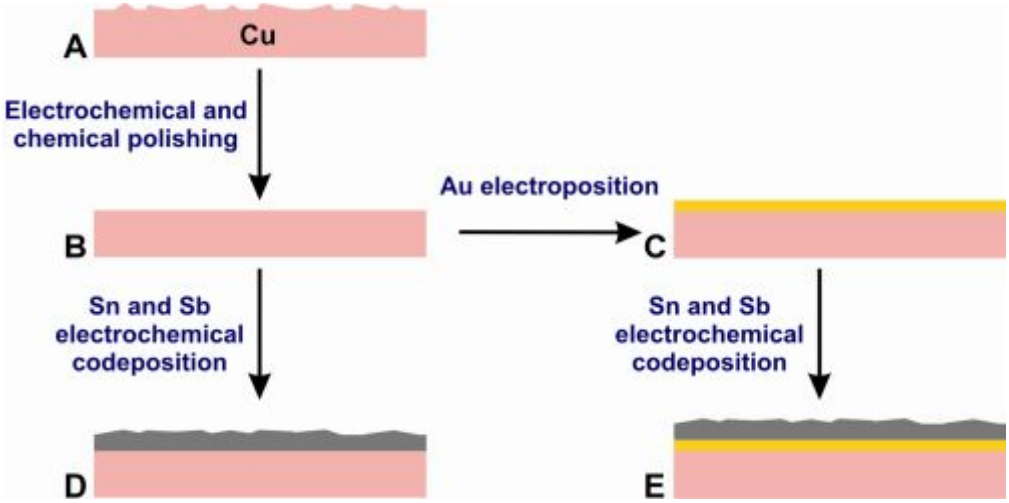

Fig. 1. **Schematic representation of the experimental procedure**

At first, Cu plates were electrochemically polished in a mixture of 250 cm^3 85 wt.% H_3PO_4 and 100 cm^3 H_2O under a constant current density of 80 mA/cm^2 for 1 min at room temperature. After that, a working surface of the electrode (0.5 cm^2) was selected by insulating of the rest of the Cu plate with an acid resistant paint. Just before electrodeposition, chemical polishing was carried out in a 0.5 M H_2SO_4 solution for 1 min in order to remove a native oxide layer (Fig. 1B). During the next step, a thin Au layer was electrodeposited on some Cu plates from commercially available solution Auruna® 5000 (7 g Au/dm^3) under the constant current density of 2 mA/cm^3 for 60 s (figure 1C). Finally, Sn and Sb were galvanostatically codeposited on Cu and Cu/Au surfaces from the electrolyte containing $SnCl_2 \cdot 2H_2O$ (30 g/dm^3), $SbCl_3$ (1.8 g/dm^3), $Na_4P_2O_7 \cdot 10H_2O$ (115 g/dm^3), tartrate acid (7 g/dm^3) and gelatin (0.4 g/dm^3). Different constant current densities ranging from 1 to 4 mA/cm^3 were applied and the temperature of the electrolyte was kept at 45 °C. All experiments were carried out in a simple three-electrode cell powered by a Reference 3000 potentiostat (Gamry Instruments) with the Cu plate as a working electrode and Pt plates as both counter and reference electrodes. Alter electrodeposition, samples were rinsed with

water then with ethanol and dried. The morphology of deposits was investigated by a field-emission scanning electron microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7) and the composition was confirmed by EDS and XRD analyses. The XRD patterns were obtained using a Rigaku Mini Flex II Desktop X-ray diffractometer with monochromatic Cu Kα radiation (λ = 1.54056 Å, U = 30 kV, I = 15 mA, 2θ: 20 º to 100 º and a step size 0.5 º per 1 min).

Results and discussion

Current density usually considerably affects the morphology and composition of deposits. Herein the effect of current density was investigated in the range from 1 mA/cm^2 to 4 mA/cm^2. The obtained deposits were dense, adherent and quite homogeneous. Moreover, the surface coverage was quite satisfactory independently of the electrodeposition conditions and kind of the substrate. SEM images of deposits obtained on Cu substrates at different current densities are shown in Fig. 2. When the current density of 1 mA/cm^2 was applied for the electrodeposition, a metallic film consists of spherical particles ranging from several hundreds of nm to over 2 μm (Fig. 2A). It can be seen that with increasing current density the size of particles decreases and deposits become smoother and more homogeneous (Fig. 2B and 2C). In general, the same tendency was observed for films deposited on the Au surface

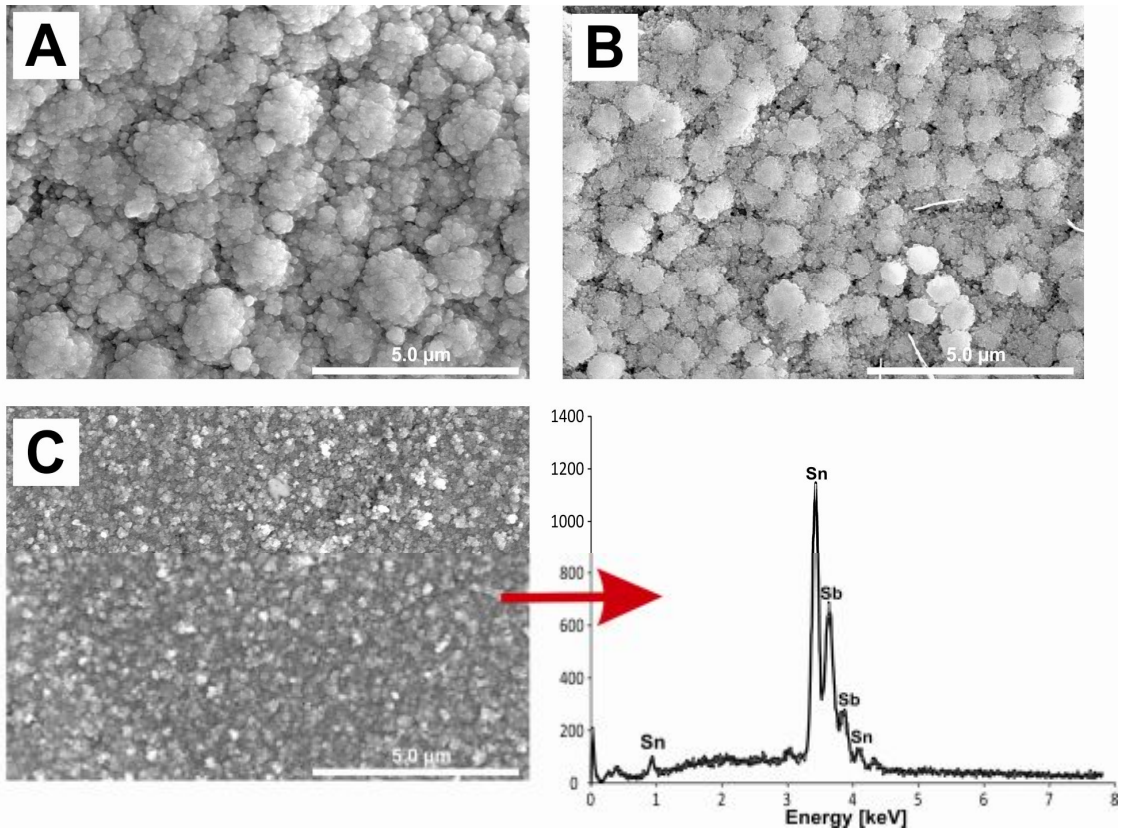

Fig. 2. **FE-SEM images of the Sn-SnSb deposits on Cu substrate obtained by electrodeposition under constant current densities of 1 mA/cm^2 (A), 2 mA/cm^2 (B) and 4 mA/cm^2 (C) together with the EDS spectrum of the sample C**

(Fig. 3), but in this case, particle sizes were a little bit smaller than those observed in deposits formed on Cu substrates under the same electrodeposition conditions (compare Fig. 2A and 3A or 2C and 3B). The chemical composition of samples, electrodeposited under different conditions, was inspected by energy dispersive spectroscopy (EDS). The EDS spectrum for the film deposited at the current density of 4 mA/cm^2 is shown in Fig. 2. As can be seen, strong peaks of Sn and Sb appear in the spectrum. A weak peak of oxygen present at about 0.5 keV, can be attributed to the insignificant oxidation of the surface. Moreover, a lack of Cu

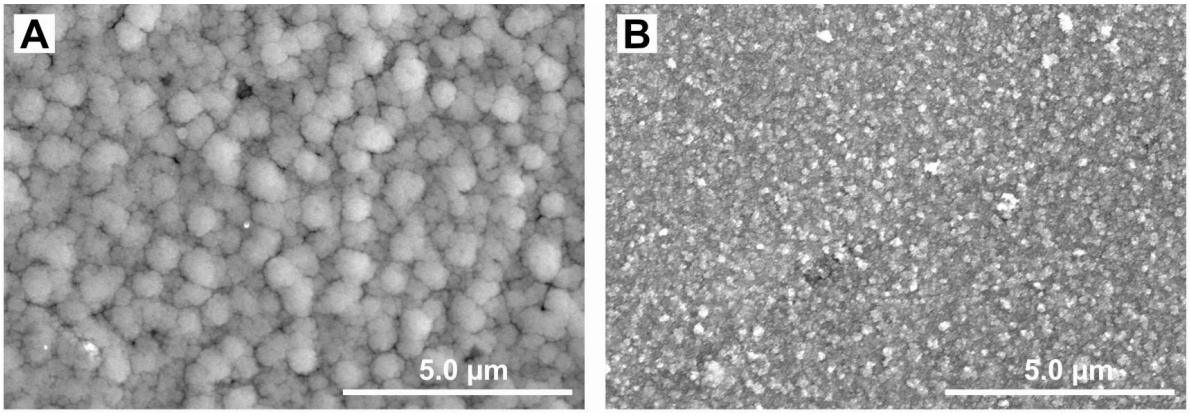

Fig. 3. **FE-SEM images of Sn-SnSb deposits on the Cu/Au substrate obtained by the electrodeposition under constant current densities of 1 mA/cm^2 (A) and 2 mA/cm^2 (B)**

peaks indicates that the substrate was completely covered by the deposit.

Tin and antimony contents in the deposits were estimated from the EDS analyses in order to investigate the effect of current density on the composition of fabricated films. The results are collected in Table 1. It can be seen that the antimony content in deposits decreases with increasing current density independently of the type of substrate.

Table 1

Sn and Sb content in the deposits obtained under different current densities estimated from the EDS analyses

Substrate	1 mA/cm^2		2 mA/cm^2		4 mA/cm^{-2}	
	Sn (% at.)	Sb (% at.)	Sn (% at.)	Sb (% at.)	Sn (% at.)	Sb (% at.)
Cu	71	29	78	22	86	14
Cu/Au	74	26	80	20	85	15

The crystal structure and phase composition of alloy deposits were studied by X-ray diffraction (XRD). A typical example of the XRD pattern recorded for the isolated metallic layer is shown in Fig.4. As can be seen from figure 4, such a material is composed of Sn and SnSb, and both phases seem to have a relatively high degree of crystallinity. These results are in excellent agreement with those obtained by Zhang et al., for deposits obtained from citrate based electrolyte [7]. It is believed that this kind of films can be promising anode materials for high-performance lithium-ion batteries.

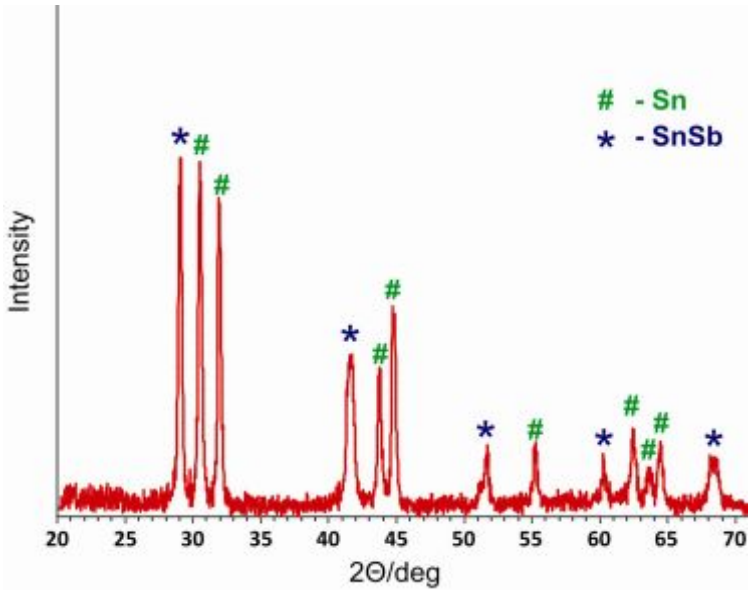

Fig. 4. **XRD patterns of a Sn–SnSb composite film**

Conclusions

The main conclusions from this study are as follows:

1. Sn-SnSb films can be easily deposited on Cu and Au surfaces by the simply galvanostatic DC electrodeposition.
2. The prepared material consists of Sn and SnSb metallic compound.
3. For increasing current density applied for electrodeposition, the morphology of as obtained deposits becomes more uniform and smoother.
4. An antimony content in deposited films decreases with increasing current density.

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Вплив умов електроосадження на морфологію та склад Sn-SnSb осадів.

Sn-SnSb плівки були осаджені електрохімічно на Cu та Cu/Au субстрати простим гальваностатичним методом з хлоридних розчинів. Були отримані щільні, міцні та достатньо гомогенні покриття та досліджений вплив густини струму на морфологію та склад синтезованих матеріалів. Було показано, що з підвищенням густини струму розмір частинок зменшується і осади стають більш гладкими та гомогенними. Крім того, з підвищенням густини струму вміст сурми в осаді зменшується незалежно від типу субстрату. Наявність металевих фаз Sn та SnSb в зразках була ідентифікована методом рентгенівського аналізу.

Ключові слова: *сурма, олово, електроосадження.*

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Влияние условий электроосаждения на морфологию и состав Sn-SnSb осадков.

Sn-SnSb пленки были осаждены электрохимически на Cu и Cu/Au субстраты простым гальваностатическим методом из хлоридных растворов. Были получены плотные, прочные и достаточно гомогенные покрытия и исследовано влияние плотности тока на морфологию и состав синтезированных материалов. Было показано, что с повышением плотности тока размер частиц уменьшается и осадки становятся более гладкими и гомогенными. Кроме того, с повышением плотности тока содержание сурьмы в осадке уменьшается независимо от типа субстрата. Наличие металлических фаз Sn и SnSb в образцах была идентифицирована методом рентгеновского анализа.

***Ключевые слова**: сурьма, олово, электроосаждение.*