Characterization of Electrodeposited CoSb Nanowires Used as Anode Materials in Batteries

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Our paper describes the fabrication of CoSb nanowires grown by electrochemical method using template synthesis. The electrodeposition was carried out bydouble pulse chronoamperometry using an aqueous electrolyte at two different temperatures (65 and 85°C) and two deposition times.Structural and morphological characterization (SEM, EDS, AFM) was performed. The results show that the CoSb nanowires were obtained with different morphologies and different Co:Sb ratio.

Keywords: electrodeposition, CoSbnanowires, morphology, SEM, AFM

Today is a huge worldwide demand for batteries, as energy supplies for the electrical automotive industry, household energy storage, different electronic instruments (computers, telephones, cameras etc.) [1]. On the other hand an important problem of the green energy sources is related to their discontinuous availability, e.g., solar energy available only during the day, wind energy only when wind is present, etc. In top of designing and developing a smart national energetic grid, able of handling this non-constant source of green energy, a crucial solution for storing the energy, when available, is represented by electrochemical batteries**.** If electric cars propelled by an electric motor, using electrical energy stored in batteries will replace gasoline and diesel vehicles, this will diminish considerably the emissions of greenhouse gases, avoiding in this way the global warming**.**

Intermetallic compounds, especially those of tin are very promising anode materials for Li batteries, and it seems that such structures are essential in the case of Mg.

The problem of materials suitable to be used in order to insert Li ions was extensively investigated during the last decade [1]. The conclusions of the most important studies in this field are summarized below.

From power/energy density point of view, *graphite* has been widely used as anode material for lithium batteries (LiBs) electrodes. The practical capacity of graphite is lower than 372 mAh g^{-1} which is not enough for the high technological demands in our days. Over a long cycling life, the capacity of graphite decrease in an alarming way. As an alternative of graphite other materials with high capacity have been investigated to solve the requirements of batteries such as Si (4200 $mAhg^{-1}$), Sn (980 mAh g^{-1}), or their oxides [2-6].

Silicon with high capacity of 4200 mAh g^{-1} was used in composites for anodes in LiBs [7]. But silicon has poor cycling performance because of its large volume expansion during intercalation of Li ions.

RuO_2 has a capacity of 1130 mAh $g^{-1}$when is used as anode for LiBs [8]. But RuO_2 is very expensive. It was used as additive to composites in supercapacitors and batteries [9]. A novel composite based on *Sn* was synthesized lately for use in LiBs as anode [10]. In theory the specific capacity of tin is 992 mAh g^{-1}, much higher than graphite. However, Sn confront with a big problem like volume contraction/expansion during the intercalation of Li^+. This disadvantage leads to the mechanical disintegration of the anode [11].

There are few data in the literature related to the co-deposition of cobalt and antimony. Co-deposition of cobalt and antimony from aqueous solutions, especially in citric-based solutions was made by direct current electrodeposition [12, 13].Antimony is more noble compared with cobalt and this fact determines the use of complex forming agents in order to shift the deposition potentials of antimony with cobalt closer [13].The behaviour of CoSb thin films growing from aqueous solution was systematically studied [14, 15] under various deposition conditions. Recently the CoSb electrodeposition was done from a new generation of ionic liquids using eutectic mixtures of quaternary ammonium salts (mostly choline chloride, ChCl) with amides, glycols or carboxylic acids [16-19].

An essential part of the challenge of the above battery is designing new nano-textured materials used in the negative electrodes of batteries [20-23]. In this paper we will introduce two types of new nanostructured anode materials as intermetallic compound nanostructures like CoSb, in order to increase the specific area of the electrode and to improve the battery performance by a facile ion insertion.

Our paper shows the fabrication of CoSb nanowires and CoSb nanomushrooms grown by electrochemical methods using template synthesis. Structural and morphological characterization (SEM, EDS, AFM) was performed.

Experimental part

The electrodeposition of CoSb nanowires (NWs) has been performed using electrolyte having the following composition [24]: 0.003 M Sb_2O_3 + 0.172 M $CoSO_4$x $7H_2O$+0.125 M $C_6H_7KO_7$ (potassium citrate monobasic) + 0.196 M $C_6H_8O_7$ (citric acid).

The use of citrate and citric acid is to increase the solubility of Sb_2O_3 by forming complexes and reduce the gap between the deposition potential of antimony and that of cobalt.

All reagents were purchased from Sigma-Aldrich. Deionized water (Milli Q l8-MΩ) was used for preparing solutions and for rinsing.

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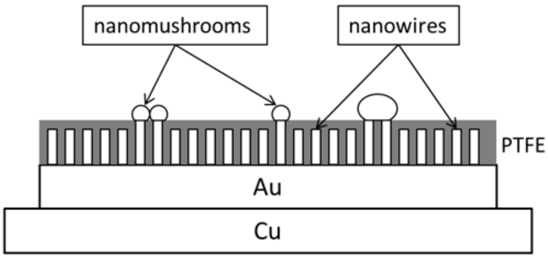

Fig. 1. Experimental setup for the working electrode

The pulsed electrodeposition of Co-Sb nanowires was carried out in a three-electrode cell in which a platinum spiral was used as auxiliary (counter) electrode and a saturated Ag/AgCl electrode was used as reference electrode.

For the working electrode, gold sputtered poly-tetrafluorethilene (PTFE) membranes (GE Water & Process Technologies, PA, USA) were used as a substrate for electro-deposition. The rough side of a 200 nm PTFE membrane was first sputtered with Au using a sputtering device for 5 min. A piece of double sided copper tape was then placed in contact with the Au-coated side of the membrane. Finally, the two pieces were sandwiched between two single sided plastic tapes exposing to the electrolyte an area of 0.198 cm^2Au with a pore density of approximate 10^6 pores/cm^2. A diagram of the set-up is shown in figure 1.

A VoltaLab 40 potentiostat/galvanostat equipment was employed to perform chronoamperometry investigations, for electrolytes temperatures of 65 and 85°C, in stationary conditions (table 1).

We will refer below to four samples, respectively: Co-Sb nanowires deposited at E_1=-1.1V and E_2=-0.7V for 7 minutes as sample 1, Co-Sb nanowires deposited at E_1 = -1.1V and E_2=-0.4V for 7 minutes as sample 2, Co-Sb alloy nanowires deposited at E_1=-1.1V and E_2=-0.7V for 3 min as sample 3 and Co-Sb alloy nanowires deposited at E_1 =-1.1V and E_2=-0.4V for 3 min as sample 4.

Surface morphology, structural and elemental analysis of electrodeposited coating, chemical composition of nanowires formed on the working electrode were studied using scanning electron microscopy (SEM) with Environmental Scanning Electron Microscope FEI/Phillips XL 30 ESEM at 0.7 Torr pressure.

The AFM measurements were performed using an A.P.E. Research A100-SGS atomic force microscope. All the AFM images (5x5μm) were obtained employing Contact Mode and a scan rate of 3μm/s. The raw images were analyzed using Gwyddion 2.20.

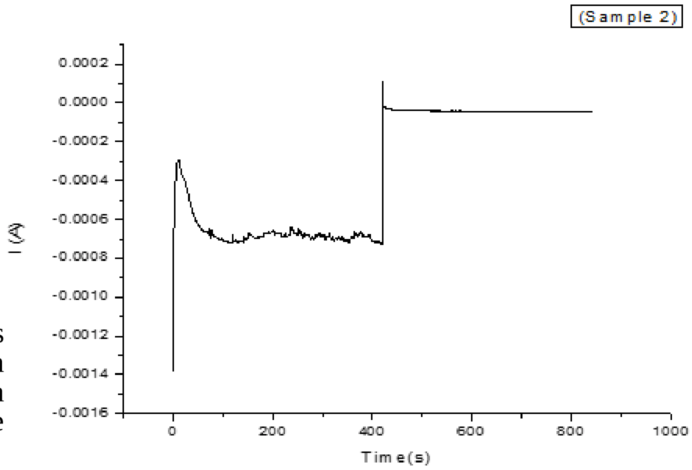

Fig. 2. Typical current-time plot recorded during the deposition of CoSb NWs (sample 2)

Results and discussions

Co-deposition of Co and Sb

Figure 2presents a typical deposition curve for samples obtained by fast chronoamperometric technique. A potentiostatic double pulse technique was performed in order to avoid grain size dispersion as a result of progressive nucleation and diffusion coupling [15, 16].

For sample 2, cathodic current increases slightly due to the formation of the nanowire nuclei in the membrane pores. It reaches a stationary state and the actual deposition of nanowires occurs.

The electrodeposition process of nanowires involves diffusion, adsorption and chemical reaction. For Co-Sb nanowires the deposition process could be described as follows [24]:

1) Diffusion and adsorption of $[(SbO)C_4H_4O_6^-]^-$ and Co^{2+} ions onto the Au electrode surface induced by the electric field applied between the two electrodes.

2) Adsorbed $[(SbO)C_4H_4O_6]^-$ and Co^{2+}species acquire electrons to form elemental Sb and Co according to the simultaneous process:

$$[(SbO)C_4H_4O_6]^- + 2H^+ + 3e^- = Sb(s) + H_2O + C_4H_4O_6^{2-}$$

$$Co^{2+} + 2e^- = Co(s)$$

3) Reduced Sb and Co atoms react with each other to form $CoSb_3$.

Morphology characterization of CoSb nanowires

A key issue in fabricating Co-Sb nanowires is to control the nanowire chemical composition in order to obtain a certain stoichiometry.

Table 1
EXPERIMENTAL CONDITIONS OF ELECTRODEPOSITION

Sample	First pulse		Second pulse		Temperature (°C)
	Potential, E_1(V)	Time, t_1(min)	Potential, E_2(V)	Time, t_2(min)	
Sample 1	-1.1	7	-0.7	7	65
Sample 2	-1.1	7	-0.4	7	85
Sample 3	-1.1	3	-0.7	3	65
Sample 4	-1.1	3	-0.4	3	85

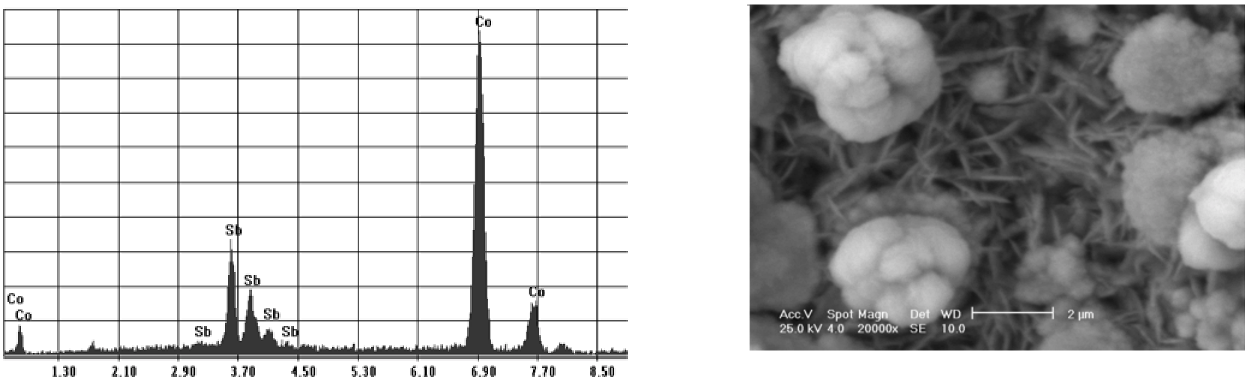

Fig. 3. EDS and SEM morphologies of nanowires electrodeposited (sample 1)

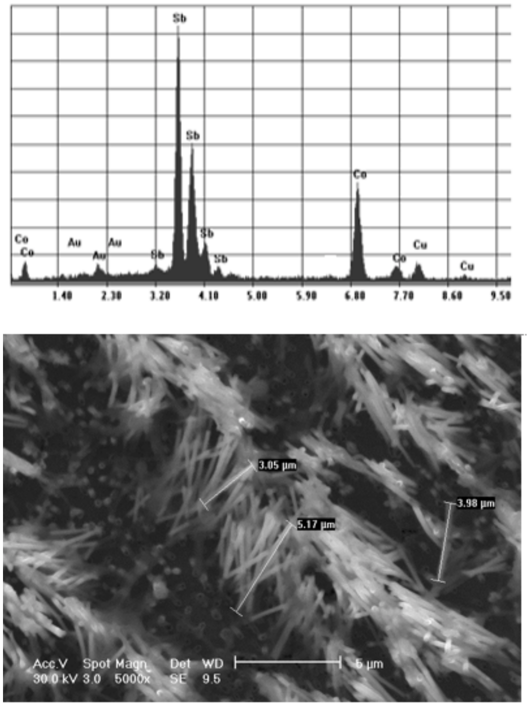

Fig. 4. EDS (top) and SEM (bottom) morphologies of nanowires electrodeposited (sample 2)

Figure 3 shows a representative Energy Dispersive Spectrometry (EDS) spectrum and SEM image for CoSb nanowires obtained. On the surface of the electrode appear a bundle of CoSb nanowires.

The nanowires obtained by chronoamperometric electrodeposition are straight and sturdy. We have obtained nanowires with an approximate diameter of 200 nm corresponding to the diameter of the pores. Overgrown nanowires present the typical mushrooms structures at the point where the nanowires reach the surface. The Co:Sb ratio is 1:3 according to EDS analysis.

For sample 2 (fig. 4) we have obtained a morphology specific for nanowires with a length between 3 and 6 µm, with a Co:Sb ratio of 1:2. The presence of Au and Cu in the scan is due to sample setting.

For sample 3 (fig. 5), the surface of the membrane is homogenous covered with nanowires. Nanomushroooms structures are missing. The length of nanowires is almost 3 µm. They are shorter than nanowires obtained for sample 1 and 2 because of the shorter time of electrodeposotion (3 mion compared to 7 min). The Co:Sb ratio is 1:1.5.

For sample 4, due to the short time of filling (3 min), the PTFE membrane is not entirely covered with nanowires. We can observe the pores of the membrane, only. But the EDS analysis has put in evidence a Co:Sb ratio of 1:3 (fig. 6) .

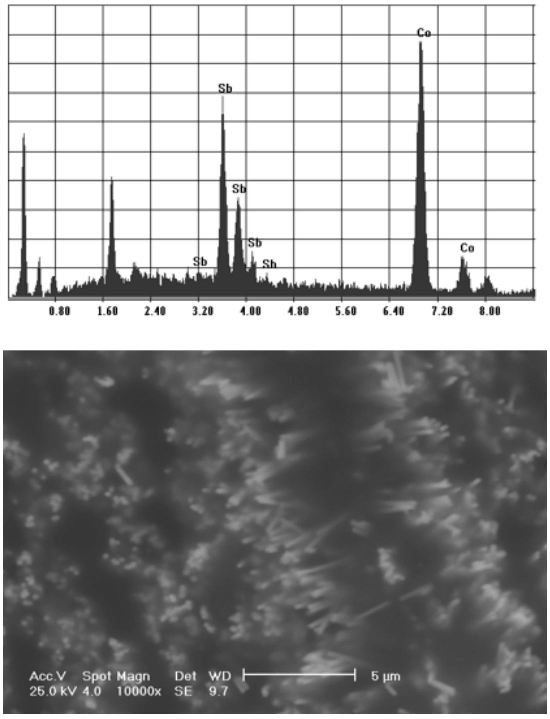

Fig. 5. EDS (top) and SEM (bottom) morphologies of nanowires electrodeposited (sample 3)

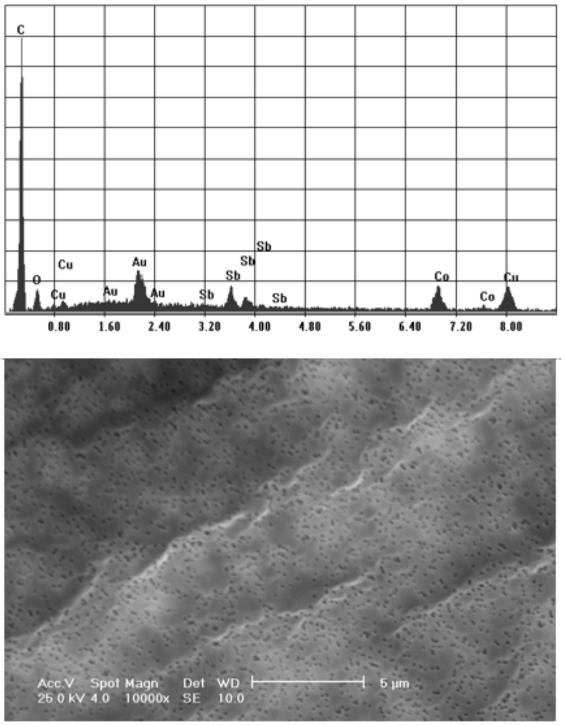

Fig. 6. EDS (top) and SEM (bottom) morphologies of nanowires electrodeposited (sample 4)

AFM imaging

Figure 7 shows the topographical features of the analyzed samples. For all the samples there was observed an overflowing of the CoSb from the matrix, forming different structures on the surface, which could affectthe overall thickness of the film and roughness parameters (table 2).

For Sample 1 the topographical image (fig. 7a) shows that the overflow of the CoSb from the matrix (nanomushrooms) hasformed two types of structures on the surface. The first type is composed of small, flat, domed structures with diameters of about 500 nm and heights lower than 100nm. The second type is formed when the smaller structures have merged, probably due to higher overflow rates, and have formed larger structures with ill-defined shape, but with heights reaching 250nm. Sample 1 has the lowest average roughness when compared to the other samples, leading to a generally flat surface.

Sample 2 (fig. 7b) has some notable differences when compared to Sample 1. Although there are present the same two types of structures on the surface, the slopes between them are more steep, forming ridges in some cases, hinting to a faster deposition speed. Thus, the small structures have more well defined boundaries, with diameters close to those of the pores of the matrix (200 nm) and heights between 50 and 75nm. However, on the surface are also present large shield like structures with almost vertical walls and heights close to 500nm. Sample 2 has the highest roughness value, given by the steep angles between the structures.

The surface of sample 3 (fig. 7c) is partially covered with structures formed by merging of the overflowed material. There are no clear boundaries between the smaller structures that form in this case a more compact layer over the matrix. The larger structures have lengths between 2 and 3μm and heights of 0.6 – 0.8μm. Given the low angles between the structures, the roughness value for this sample is relatively low.

The entire surface of Sample 4 is covered in structures given by the overflow of CoSb from the matrix. However in this case there is no clear distinction between larger and smaller structures, entire surface being composed of domed structures with diameters ranging between 150 and 300nm, with heights lower than 30nm.

Conclusions

We obtained CoSb nanowires with various Co:Sb ratios. The electrochemical deposition method paves the way for the creation of new technologies and nanomaterials with unique properties.

The obtained CoSb nanowires had approximate lengths between 3 and 6μm (depending on the electrodeposition time) and a diameter of about 200nm corresponding to thepore diameter of polymer membrane.

These materials can be used as nanostructured anodes in batteries, to improve their properties.

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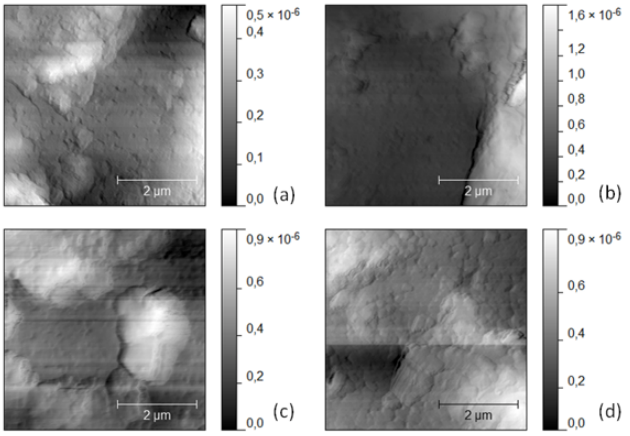

Fig. 7. AFM topographical images for a) sample 1, b) sample 2, c) sample 3, d) sample 4

Table 2

AVERAGE ROUGHNESS VALUES CALCULATED FOR THE CoSb SAMPLES

Sample	Average roughness (nm)
1	81.5
2	203.0
3	135.5
4	147.0

References

1. OWEN, J.R., Chem. Soc. Rev., 26, 1997, p. 259.
2. PARK, C. M., KIM, J.H., KIM, H., SOHN, H.J., Chem. Soc. Rev., 39, nr. 8, 2010, p. 3115.
3. BAUDRIN, E.,SUDANT, G.,CHENG, W.,DUNN, B.,TARASCON, J.M., Proc. Electrochem. Soc., 20, 2003, p. 335.
4. HUANG, S.Y.,KAVAN, L., EXNAR, I., GRATZEL, M., J. Electrochem. Soc., 142, 1995, L142.
5. NISHI, Y., J. Power Sources 100, nr.1–2, 2001, p.101.
6. LI, J.-L., DANIEL, C., WOOD, D, J. Power Sources, 196, nr.5, 2011, p. 2452.
7. SONG, T., XIA,J., LEE, J.H., LEE,D.H., KWON, M.S., CHOI, J.M., WU, J., DOO, S.K., CHANG, H., PARK, W.I., ZANG, D.S., KIM,H., HUANG,Y., HWANG, K.C., ROGERS, J.A., PAIK, U., Nano Lett., 10, nr.5, 2010, p.1710.
8. BALAYA, P., LI, H., KIENLE, L., MAIER, J., Adv. Funct. Mater., 13, nr. 8, 2003, p. 621.
9. WANG, Y.G., WANG, Z.D., XIA, Y.Y., Electrochim.Acta, 50, nr.28, 2005, p.5641.
10. ZHEN, W.,HAN, M., TAO, H., AISHUI, Y., J. Power Sources, 223, 2013, p. 50.
11. WANG, J., RAISTRICK, I.D., HUGGINS, R.A., J. Electrochem. Soc., 133, 1986, p. 457.
12. SADANA, Y.N., KUMAR, R., Surf. Technol., 11, 1980, p. 37.
13. NINEVA, S., DOBROVOLSKA, T.S., KRASTEV, I., ZastitaMaterijala, 52, 2011, p. 80.
14. CHENG, H., HNG, H.H., MA, J., XU, X.J., J. Mater. Res., 23, nr.11, 2008, p. 3013.
15. SANDMANN, G., DIETZ, H., PLIETH, W., J. Electroanal. Chem., 491,nr.1-2, 2000, p.78.
16. LIU, H., FAVIER, F., NG, K., ZACH, M., PENNER, R., Electrochim. Acta, 47, nr. 5, 2001, p.671.
17. CHENG, H., HNG, H.H., MA, J., Solid State Phenom.,136,2008, p. 75.
18. GOMEZ, E., COJOCARU, P., MAGAGNIN, L., VALLES, E., J. Electroanal. Chem., 658,2011, p. 18.
19. GOLGOVICI, F., COJOCARU, A., AGAPESCU, C., JIN, Y., NEDELCU, M., WANG, W., VISAN, T., Studia Univ. Babes-Bolyai, Chemia, 54,nr. 1, 2009, p. 175.
20. MARES, M.L., GOLGOVICI, F., VISAN, T., Chalcog. Lett., 10, nr. 8,2013, p. 259.
21.GOLGOVICI, F., MARES, M.L., COJOCARU, A., Rev. Chim.(Bucharest), **65**, no.1, 2014, p.98
22. POIZOT, P., LARUELLE, S., GRUGEON, S., DUPONT, L., TARASCON, J.M., Nature, 407, 2000, p. 496.
23. TARASCON, J.M., ARMAND, M., Nature, 414, 2001, p. 359.
24. VIDU, R., PRODANA, M., GOLGOVICI, F., NEGRU, A., BOJIN, D., ENACHESCU, M., Proceedings of the 37thARA, 2013,p. 576

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