Electro-deposition of Cobalt and Cobalt-Antimony from Non-Aqueous Media Containing Ethylene Glycol

FLORENTINA GOLGOVICI, MARIANA LILI MARES, ANCA COJOCARU*
Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 132 Calea Grivitei, Bucharest, Romania

Cobalt deposition and cobalt and antimony co-deposition were evidenced in two non-aqueous electrolytes, both with advantage of a larger electrochemical window: one with ethylene glycol as solvent and the other one a choline chloride based ionic liquid with ethylene glycol as the second component of eutectic mixture. Deposition of singular antimony was also studied in both media. Cyclic voltammetry and electrochemical impedance spectroscopy were used under various conditions (scan rate, ion concentration). A single pair of reduction/oxidation processes was evidenced in CV curves for individual deposition. In ionic liquids with both Co and Sb ions, a first process of Sb deposition occurs before Co + Sb co-deposition. Analyzing Nyquist and Bode spectra the differences between impedance behaviour at various cathodic polarization were observed.

Keywords: cobalt, cobalt-antimony compound, electro-deposition, ethylene glycol, choline chloride based ionic liquid

Cobalt attracted a great interest in view of applications in the production of alloys, sensors, heterogeneous catalysts, in energy storage and for magneto-optic recording media. Cobalt is one of the most typical ferromagnet and the microelectronic industry is a consumer of many kinds of magnetic thin films and nanostructures. Antimony as pure metallic (semimetallic) material is not often used in industry. However, its alloys and chemical compounds (semiconductors) have found broad applications in solar cells, humidity sensors and especially for thermoelectrical generators, thermopile sensors and microcrockers [1]. For instance, CoSb₃ (cobalt triantimonide) as films or nanowires is a compound with skutterudite type crystal-structure which has used recently to fill the voids in the CoSb₃ skutterudite structure in order to reduce the thermal conductivity and thus enhance the thermoelectric performances. These authors established that small quantities of Ce with In may be good partner with Yb to reduce the thermal conductivity.

An electrochemical study of cobalt electrodeposition onto a platinum electrode from an aqueous solution containing 10⁻² M CoCl₂ and 1 M NH₄Cl was carried out [5]. The voltammetric data clearly showed that a process of cobalt underpotential deposition (UPD) takes place during the application of potential in the less negative region. Formation of the cobalt adlayer involved the simultaneous presence of both adsorption and 2D nucleation processes. Zaraska et al. [6] successfully prepared antimony by galvanostatic electrodeposition from two electrolytes: one contains SbCl₅ (0.02 M) + citric acid (0.1 M) + sodium citrate (0.05 M) and the other contains 1.8 g/L and 7 g/L tartaric acid (in order to have 0.075 M antimonyl potassium tartrate). Bryngelsson et al. [7,8] reported the synthesis of Sb-based nanoscale coatings which were electrodeposited from tartrate solutions.

The literature data about the co-deposition of cobalt and antimony are very scarce. Direct current electrodeposition was used to co-deposit cobalt and antimony in aqueous solutions, especially in citric-based solutions [9,10]. The standard electrode potentials in aqueous solutions are as follows [10]: E°(Sb⁳⁺/Sb) = +0.212 V and E°(Co²⁺/Co) = -0.277. Thus, antimony is the nobler metal and this fact determines the use of complex forming agents in order to shift the deposition potentials of antimony with cobalt closer. The effects of agitation, temperature and citric acid content in the electrolyte on the composition and appearance of the alloy deposits, as well as the current efficiency of deposition are reported. Growth behaviour of Co–Sb alloy thin films was systematically studied [11,12] under various deposition conditions. Effects of deposition parameters on the microstructure, chemical, and phase composition of the deposited Co-Sb were also studied.

Based on the chemical composition of the deposits, it was established that the most successful electrolytes contained a 10:1 atomic ratio of cobalt(II) to antimony(III) [2].

Many research programmes have been developed to substitute cobalt electrodeposition from aqueous solutions which is accompanied by an intense hydrogen evolution and therefore has not always satisfactory current efficiency. Electrolytic media with organic solvents were tried to be used. Tseung and his coworkers [13] reported Co deposition from N,N-dimethylformamide (DMF) and confirmed the suggestion of Grzybowski and Pilarczyk [14] that the coordinated forms of CoCl₂ in DMF medium are [Co(DMF)₆]²⁺, [CoCl(DMF)₄]⁺ and [Co(DMF)₂]⁻ ionic species. The proposed mechanism [13] consisted in a

* email: a_cojocaru@chim.uptb.ro
was investigated in a nonaqueous solution of ethylene
mixture (1:2 mole ratio). We mention that a deposition
and the other one a choline chloride based ionic liquid with
non-aqueous solutions: one with ethylene glycol as solvent
present in this paper the preliminary results regarding cobalt
chloride with urea as hydrogen bond donor [28,29]. We
mention the possibility of electrodeposition of Sb as element from
ChCl-urea. Previously, we reported some results regarding
electrodepositing potentials for Co films prepared from
et al. [27] have shown the possibility to choose of
or carboxilic acids. In a study on vitreous carbon, Gomez
salts (mostly choline chloride,
liquids uses eutectic mixtures of quaternary ammonium
toxicological and purity issues. A new generation of ionic

shining in appearance with good adhesion to the platinum
deposition of various metals, since they have wide working
temperature range, wide electrochemical windows and
good thermal and chemical stability. The electrodeposition of
cobalt was first performed from ionic liquids based on
1-ethyl-3-methylimidazolium chloride (EMIC) [17,18].
Freyling [19] reported Co deposition from ionic liquids based
on 1-buthyl-methylimidazolium salts (AlCl3–
BPC ionic liquid for Co deposition onto Pt. They established
that a low concentration of electroactive species CoCl2-
and a high concentration of inactive species (tetrahedral
chlorocomplex) CoCl3- exist. The mechanism proposed was:

\[
\text{CoCl}_{\text{[x-1]}}^- + e \Leftrightarrow \text{CoCl}_{x}^{(x-1)} \text{(ads)} \quad (2)
\]

\[
\text{CoCl}^{(x-1)} \text{(ads)} \rightarrow \text{Co}^x \text{(ads)} + x \text{Cl}^- \text{(ads)} \quad (3)
\]

\[
\text{Co}^x \text{(ads)} + e \Leftrightarrow \text{Co} \quad (4)
\]

The Co electrodeposition procedure was used from 1-n-
buthyl-1-methylpyrrolidinium bis-trifluoromethyl sulfonyl
imide ([BMP][TFSO]) [21,22] or amide ([BMP][TFSA]) [21].
An, Yang and Su [23-25] have studied the electrodeposition of
Co from EMIC room temperature ionic liquid and from a
mixture of EMIC with ethylene glycol; they showed that
the cobalt coating from these media was uniform, dense,
shining in appearance with good adhesion to the platinum
substrate. Yang and Sun [26] prepared Sb from EMIM
chloride tetrafluoborate. However, electrolytes with
imidazolium derivatives have expensive costs and potentially
toxicological and purity issues. A new generation of ionic
liquids uses eutectic mixtures of quaternary ammonium
salts (mostly choline chloride, ChCl) with amidox, glycols
or carboxilic acids. In a study on vitreous carbon, Gomez
et al. [27] have shown the possibility to choose of
electrodepositing potentials for Co films prepared from
ChCl-urea. Previously, we reported some results regarding
the possibility of electrodeposition of Sb as element from
the same eutectic mixture (1:2 mole ratio) of choline
chloride with urea as hydrogen bond donor [28,29].
We present in this paper the preliminary results regarding
cobalt deposition and cobalt and antimony co-depositing in two
non-aqueous solutions: one with ethylene glycol as solvent
and the other one a choline chloride based ionic liquid with
ethylene glycol as the second component of eutectic
mixture (1:2 mole ratio). We mention that a deposition
process of CoSb as thermoelectric semiconductor films was
investigated in a nonaqueous solution of ethylene
glycol at 120°C in a recent paper [30]. From our knowledge
the deposition from ionic liquids of cobalt and cobalt-
antimony films is reported for the first time in literature.

Experimental part
Choline chloride (ChCl), ethylene glycol (EG), cobalt (II)
chloride hexahydrate, K2[Sb(tartrate)2]·3H2O (antimony
potassium tartrate trihydrate) and SbCl3 were used as
received. The electrolytes at 25°C containing ethylene
glycol as solvent were prepared by adding CoCl2, 6H2O or/
and K2[Sb(tartrate)2]·3H2O as precursors for Co(II) and
Sb(III) ions. ChCl-EG eutectic ionic liquid (1:2 molar ratio)
was obtained by mixing both reagents and heated at 90°C
for 30 min with permanent stirring. In this solvent, CoCl2,
6H2O and SbCl3 were then added at 60°C.

A computer driven Zahner elektrik IM6e potentiostat was
used in cyclic voltammety (5-1000 mVs-1 scan rates) and
electrochemical impedance spectroscopy EIS (10 mV dc
voltage, 200 kHz – 50 mHz frequency) experiments. The
conventional three-electrode cell contains a stationary
working electrode as a Pt foil (0.5 cm2) or disk (3 mm
diameter) and a platinum plate as auxiliary electrode. The
electrode potentials were measured in EG based solutions
against Ag/AgCl reference electrode, while in ChCl-EG ionic
liquids an Ag wire was a quasi-reference electrode.

Results and discussions

Studies in solutions with ethylene glycol as solvent
Cyclic voltammetry was first performed in order to
identify the electrodeposition processes of cobalt or
antrmony. Figure 1 shows cyclic voltammmograms obtained
in solutions of 264 mM CoCl2 and 540 mM CoCl2, with
ethylene glycol as solvent. When compared to the
voltammograms of the pure EG solvent (not shown here),
the presence of the Co(II) ions in solution gives rise to a
single pair of reduction and oxidation processes.

On the reduction branch of voltammograms the onset of
a first cathodic region attributed to underpotential
deposition (UPD) of cobalt is observed at around 0 V
potential for both cobalt ion concentrations. This UPD
process is a surface-limited reaction of Co atoms deposited
on the naked Pt substrate. Then a shoulder in the potential
range from -0.25 V up to -1.25, or even -1.5 V, is noticed,
with current densities increasing with the scan rate and
cobalt ion concentration. This part represents the massive
deposition of cobalt as multilayer and may be considered
as a mass-transport controlled process. Finally, at very
negative potentials the sudden increase of current is
certainly due to the involving of other reduction processes
which are probable the cathodic reduction of EG solvent
molecules together with hydrogen evolution as a result of
reduction of water introduced with cobalt chloride
hexahydrate.

Regarding the anodic branches of voltammograms, a
very distinct anodic peak of Co dissolution and stripping
from Pt is observed in the range from +0.5 V to +1.2 V.
Obviously, its peak potential and peak current are strongly
influenced by the scan rate and cathodic limit where the
scan is inversed. A supplementary anodic process which
begins at +1.3 V represents the oxidation of some
quantities of chloride ions (Cl-) which may be accompanied
with a further oxidation of Co(II) ions to Co(III) ionic species.

Figures 2 show the EIS curves obtained by polarization
with two different cathodic potential values, one where
the massive deposition of cobalt did not begin (-0.3 V)
and the other one where a significant deposition takes place
(at -1 V). Thus, the impedance results are interpreted in
relation with voltammetric results. The Nyquist diagram
shows the dependence of imaginary part of impedance
vs. real part of impedance in the shape of capacitive
semicircles with a drastically decrease of diameter; this
means a decrease of charge transfer resistance implying

\[
[\text{CoCl}_2,\text{DMF}]^- + 2 \text{e} \rightarrow \text{Co} + 3 \text{Cl}^- + \text{DMF}
\]

(rate determining step, rds)

\[
\text{CoCl}_{\text{[x-1]}}^- + \text{e} \Leftrightarrow \text{CoCl}_{x}^{(x-1)} \text{(ads)}
\]

\[
\text{CoCl}^{(x-1)} \text{(ads)} \rightarrow \text{Co}^x \text{(ads)} + x \text{Cl}^- \text{(ads)}
\]

\[
\text{Co}^x \text{(ads)} + \text{e} \Leftrightarrow \text{Co}
\]
an intense deposition rate at -1 V compared to -0.3 V. The Bode diagram represents simultaneously two dependences, namely impedance modulus vs. frequency and phase angle vs. frequency. This diagram shows a decrease of impedance modulus but also a change of negative phase angle from -20° to -5° proving the significant metallic character of Co deposit.

Figure 3 shows a family of CV curves exhibiting deposition and dissolution processes in solution containing EG + 50 mM Sb(III) ions. The precursor was antimony potassium tartrate. It can be seen during direct scan the cathodic shoulder representing the massive deposition of antimony which is continued with supplementary cathodic processes of EG reduction and hydrogen evolution. The main reduction of Sb(III) ions has limiting current densities increasing with scan rate, suggesting also a mass-transport control. In the inverse scans, in all cases an oxidation peak with Sb stripping from Pt surface occurred in the range from +1 V to +1.4 V.

As figure 4 shows, if the Pt electrode is polarized at two different potentials, EIS diagrams for the Sb/EG system indicate semicircles with decreased Nyquist diameter and also lowering of impedance modulus and maximum phase angle (from Bode graph). Although the data is somewhat dispersed, EIS results suggest a significant deposition of antimony at -1 V potential polarization.

As a preliminary investigation of solutions containing both cobalt and antimony ions we present in figures 5 comparative voltammograms recorded in solutions with different mole ratios between Co(II) and Sb(III) ions, namely 132 mM + 25 mM (fig. 5a) and 270 mM + 25 mM (fig. 5b), respectively. Of course, the shape of CV curves does not change significantly owing to predominance of
cobalt species against antimony species. In both cases the reduction limiting currents or even cathodic peaks may be attributed to direct CoSb deposition, with a location in the potential range from -0.8 V to -1.15 V, more positively for concentrated system in cobalt ions. The dependence of currents with scan rate and Co(II) concentration suggests a mass-transport controlled process. Some differences from curves recorded with singular ions consist in more positive potentials of shoulders of peaks, as well as a crossover during inverse scan which is characteristic of a nucleation control of CoSb deposition.

EIS diagrams (fig. 6) illustrate also the particular behaviour of Co and Sb simultaneous deposition, although the data are somewhat dispersed. Thus, Nyquist loops for -0.3V and -1V polarizations have quite similar diameter value, meaning a process that begins at more positive potentials than for single Co deposition and Bode phase angle is in the same region of -50° or even lower.

**Studies in choline chloride – ethylene glycol ionic liquid**

Figure 7 shows a family of CV curves exhibiting deposition and dissolution processes in choline chloride – ethylene glycol ionic liquid containing 8 mM Co(II) ions. On the cathodic scan the massive deposition of Co takes place as the current starts to rise significantly at around -0.9 V. A new increase of current at negative potentials (more than -1.6 V) was attributed to the cathodic process of ionic liquid species, probably the reduction of choline cation. An ill-defined, rather broad electrodeposition peak is noticed, followed on the inverse scan by another broad, dissolution peak on the anodic branch. Both cathodic and anodic peak currents increase with scan rate, suggesting diffusion control of this quite reversible process.

The EIS spectra of ChCl–EG + CoCl₂ system, presented in figure 8, were obtained at different potentials of Pt electrode corresponding to the following potential domains: before metal deposition, the onset of deposition, massive deposition showing cathodic peak. From Nyquist (fig. 8a) and Bode (fig. 8b) diagrams it can be found comparatively that the plots recorded at a starting potential of -0.6 V (more positive than the onset of Co(II) ion reduction) show only a capacitive semicircle behaviour, with the highest diameter of ca. 1800 Ωcm² and the largest
Bode phase angle, of -75°. By polarizing the Pt electrode from -0.8 V to -1 V in the range of the onset and massive deposition of metallic films, EIS spectra are similar to each other in shape, with a semicircle appearing in the high frequency domain and a straight line (a tail or a part of second semicircle) in the low frequency region. From these figures, it can be noticed that the experimental values of ohmic resistance of solution remained practically the same, of the order 1-2 Ohm cm². The inset of figure 8a shows details of the high frequency semicircle for Co deposition; this becomes smaller in diameter, suggesting a more intensive reaction process, reaches a minimum (value of 5 Ohm cm² at -1 V). The maximum Bode angles diminish from -50° (-0.8V) to -110° (-1.2V).

In figure 9 are presented the experimental results of cyclic voltammetry used for Pt electrode in ChCl-ethylene glycol eutectic with 9 mM SbCl₃ dissolved. The antimony started to deposit at +0.1V, and displayed an increasing current during the negative going scan, with a cathodic peak at 0 V ± 0.2 V. Only a single couple of reduction/oxidation peaks can be seen from figure 9, the electrochemical processes being assigned to massive deposition of Sb and its film stripping from Pt electrode, respectively.

Figures 10 (a,b) show Nyquist and Bode diagrams obtained at various electrode potentials, the temperature being 60°C. During the experimental procedure, the potential of the cathode was consecutively maintained at increasingly negative values: first at potentials where the reduction process does not start, then in the region of beginning the process, reaching the maximum cathodic current (-0.1 V ± -0.2 V) and, finally, in the region of massive metal deposition (-0.3 V). The Nyquist spectra show clearly capacitive semi-circles in the region of high frequencies. The gradually increase of the semi-circle diameter (diminution of the charge transfer resistance), if the electrode potential is more negative, indicates the decrease of electrodeposition current. The same behaviour by polarizing Pt electrode at various electrode potentials is evidenced in Bode diagrams. In figure 10b the phase angle at -0.1 V shows a single maximum around -65°, meaning a significant capacitive behaviour. For more negative potentials, this maximum shifts toward lower frequencies and remains at high negative values of phase angle.

The cyclic voltammetric behaviour of 4 mM CoCl₂ + 9 mM SbCl₃ and 8 mM CoCl₂ + 4 mM SbCl₃ solutions in ChCl-ethylene glycol is described in figures 11. The first reduction peak (at around -0.2 V) on cathodic branch of voltammograms may be associated with antimony deposition on naked platinum surface. The second cathodic peak (in the potential region from -0.85 V to -1.1 V) may be attributed to simultaneous deposition (co-deposition) of cobalt and antimony, with a current density much lower than cobalt deposition from solution containing single Co(II) ions (see the comparison made in fig. 12). By reverse scanning (in the anodic direction), on each voltammogram in figure 11 the first oxidation peak centered at +0.1 V ± +0.2 V is considered to be the preferential antimony dissolution from the deposited layers.

Further, the second anodic peak at +0.7 V is the oxidation of remaining cobalt from the cathodic deposit. A comparison between 4 mM CoCl₂ + 9 mM SbCl₃ system and 8 mM CoCl₂ + 4 mM SbCl₃, system both represented in figures 11, indicates that the first oxidation peak has a higher value of peak current for the system with higher antimony content in electrolyte; this may be a evidence of a higher antimony content in the corresponding cathodic deposit.

EIS results obtained from the same electrolytes containing either 4 mM CoCl₂ + 9 mM SbCl₃ or 8 mM CoCl₂ + 4 mM SbCl₃ confirm the voltammetric data. Thus, the semicircle at -0.1 V in Nyquist diagrams has the shortest
diameter due to the beginning of antimony deposition; next, the semicircle diameter increases by more Sb layers grown on Pt electrode and then decreases by polarizing from -0.2 V to more negative potentials. Starting from -0.8 V potential the CoSb semiconductor compound is formed with gradual decrease of semicircle diameter. The maximum phase angle follows the same order.

Conclusions
The results of applying cyclic voltammetry technique evidenced a single pair of reduction/oxidation processes for each medium containing ethylene glycol and a single kind of cobalt or antimony ions. In ionic liquids with both Co and Sb ions, a first process of Sb deposition occurs before Co + Sb co-deposition. Electrochemical impedance spectra confirmed theorder of cathodic processes by exhibiting the impedance behaviour (values of semicircle diameter, impedance modulus and maximum phase angle). The investigations demonstrate the possibility of CoSb deposition in both liquid media.

Acknowledgements: One of the authors recognizes financial support from the European Social Fund through POSDRU/107/1.3/S/76813 Project.

References

Manuscript received: 13.08.2013