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Ewa Rudnik, Grzegorz Chowaniec

Effect of organic additives on electrodeposition of tin from acid sulfate solution

Wpływ dodatków organicznych na katodowe osadzanie cyny z kwaśnego roztworu siarczanowego

Abstract

Basic electrochemical experiments on the kinetics of tin deposition from an acid sulfate solution containing organic additives were performed. The measurements showed that tin deposits with activation polarization in a narrow potential range. Organic additives like gelatin and β-naphtol inhibit the charge transfer stage of the cathodic reaction due to the formation of adsorption layers. In turn, the gluconate ions increase the rate of tin deposition due to the bonding of hydrogen ions and inhibiting hydrogen coevolution. This results in serious changes in the morphology of tin deposits from isolated polyhedron crystals (no additive) via rectangular plates (β-naphtol) and thin plates (sodium gluconate) to rounded grains (gelatin).

Keywords: electrolysis, gluconate, gelatin, β-naphtol, morphology

Streszczenie

Przeprowadzono podstawowe badania elektrochemiczne osadzania cyny z kwaśnego roztworu siarczanowego zawierającego dodatki organiczne. Pomiary wykazały, że cyna wydziela się w zakresie polaryzacji aktywacyjnej w stosunkowo wąskim przedziale potencjałów. Dodatki organiczne jak żelatyna i β-naftol hamują proces przeniesienia ładunku przez granicę faz wskutek tworzenia warstw adsorpcyjnych. Z kolei jony glukonianowe zwiększają szybkość osadzania cyny przez wiązanie jonów wodorowych i hamowanie współwydzielania wodoru. Powoduje to poważne zmiany morfologii osadów katodowych: od wielościennych kryształów cyny (brak dodatków), przez tworzenie prostokątnych ziaren płytkowych (β-naftol) i cienkich płytek (glukonian sodu), do ziaren o zaokrąglonych kształtach (żelatyna).

Słowa kluczowe: elektroliza, glukonian, żelatyna, β-naftol, morfologia

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Ewa Rudnik, Grzegorz Chowaniec: AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals, Krakow, Poland; erudnik@agh.edu.pl

1. Introduction

Tin is widely used in various industries due to its universal properties, such as its low viscosity in its liquid state, adhesion to metals, low melting point, high corrosion resistance, and non-toxicity. Tin coatings are obtained by means of two methods: immersing a coated surface in molten metal or electrodeposition from aqueous solutions. Electrolysis has many advantages over hot-dip galvanizing due to its more-even distribution of the coating on the substrate, reduced tin consumption, and production costs. Perspectives for tin demand in the fabrication of galvanic protective coatings are associated primarily with the development of novel commercial baths with environmentally friendly components giving smooth and uniform layers, thus preventing the formation of dendritic grains and whiskers [1]. The latter can grow on the finish surface after plating due to defects such as hydrogen or impurities incorporated into the metal lattice, residual stress, etc. [2].

The proper selection of an electrolytic bath for tin electrodeposition depends mainly on the shape and size of the object to be covered. Objects with complicated shapes and high requirements regarding the smoothness of the coating should be tinned in alkaline stannate baths, while acidic stannous baths are used when the requirements for the coating's smoothness are lower. Electrodeposition from acidic divalent tin solutions (chloride, sulfate, fluoroborate) is accompanied by low cathode polarization and consumes less electricity, but it usually produces loosely adherent and acicular deposits if no organic agents are present [3].

A review of the literature data has shown a variety of additives investigated for their potential application in tin electroplating [1]. Among them are grain refiners (e.g., aldehydes, thiourea, PEG decyl glucoside, gelatin, peptone) [4–7], brighteners (e.g., Triton X-100, formaldehyde) [5, 8, 9], levelling additives (e.g., sesame oil, aromatic carbonyl compounds) [10–12], and complexing compounds (e.g., citrate, gluconate, tartrate) [13–16] were examined. The influence of bath constituents on the course of the early stages of tin electrodeposition and the kinetics of Sn(II) ion reduction was also discussed in some papers [15–21], as it shows a great influence on the further growth of the metal layer. In turn, Sharma et al. [22] showed that the morphology of tin deposits can also be modified by the proper selection of current density, duty cycle, and frequency during pulsed current electrodeposition.

Although progress has been made in investigating the kinetics of tin deposition, there are still many unknown aspects regarding the mechanisms of action of organic agents. The type of additive may affect many process parameters such as increasing the cathode polarization, inhibiting the nucleation, or grain growth influencing the further morphology and adherence of the cathodic deposits. Therefore, the aim of this paper was to determine the influence of some organic compounds like gelatin, sodium gluconate, and β-naphtol on tin behavior during electrodeposition from an acidic sulfate solution.

2. Experimental

Tin was electrodeposited from solutions containing 50 mM $SnSO_4$ and 2 M H_2SO_4 in the absence or presence of 1 g/dm^3 of the additives (i.e., gelatin, β-naphtol, or sodium gluconate). Electrochemical measurements were carried out in a three-electrode cell using platinum plates (0.76 × 0.75 cm) as working and counter electrodes, while an Ag/AgCl/KCl(sat) electrode was used as a reference (all potentials are referred to this electrode). Before each experiment, the platinum electrodes were mechanically (2000-grit abrasive paper) and chemically (20% HCl, then ethanol) cleaned. A solution volume of 30 cm^3 was used in each electrochemical test. The voltammetric curves were registered at a potential scan rate of 10 mV/s. The first sweep was always performed from the initial potential of 0.2 V (Ag/AgCl) towards more-negative values. The nucleation of the tin was investigated using chronoamperometry realized at various constant potentials. A stripping analysis was performed immediately after potentiostatic tin deposition (for 40 s) at a fixed potential without removing the working electrode from the solution. Anodic stripping curves were registered from deposition potentials up to 0.2 V. Autolab potentiostat/galvanostat (PGSTAT30) controlled by a microcomputer was applied in all measurements. No bath agitation was used. The morphology of the layers was examined using a scanning electron microscope (Hitachi SU-70). The crystal structure of the deposits was analyzed by X-ray diffractometry (Rikagu MiniFlex diffractometer, $Cu_{K\alpha}$ radiation). All experiment were performed at room temperature.

3. Results and discussion

Three organic compounds were used as additives to the tin acidic solution. Gelatin is a translucent, colorless, and flavorless substance derived from the collagen obtained from various animal body parts (bones, cartilages, skin). It is an irreversibly hydrolyzed form of collagen, wherein the hydrolysis results in the reduction of protein fibrils into smaller peptides, which have broad molecular weight ranges. A gelatin colloid is often used as an inhibitor in the electrodeposition of metals; namely, copper [23], tin [7], silver [24], and zinc [25]. Sodium gluconate is a non-corrosive, non-toxic, biodegradable, and renewable additive to electroplating baths and can be successfully used for the electrodeposition of heavy metals and alloys [15, 16, 18, 26–28]. It shows excellent chelating power to many metals and can form stable complexes not only in alkaline and concentrated alkaline solutions but also in acidic electrolytes. β-naphtol (2-naphtol) is a colorless crystalline solid slightly soluble in water (1 g/dm^3 at 20°C) but well-soluble in ethanol. It is one of the first additives introduced for the improvement of tin electrodeposits and, despite its main disadvantage of being relatively easily oxidized under plating conditions, it is still used today [7, 29].

Figure 1 shows the influence of the organic agents on the course of the cyclic voltammetric (CV) curves registered in the $SnSO_4$-H_2SO_4 systems. For comparative purposes, a curve for a blank acid solution is also presented. For the latter case, only one cathodic reaction:

$$2H^+ + 2e \rightarrow H_2 \tag{1}$$

was observed on the platinum electrode below −0.25 V (vs. Ag/AgCl). This value was closed to the equilibrium potential of the hydrogen electrode immersed in 2M H_2SO_4 (−0.22 V vs. Ag/AgCl). No anodic peak was found in the reverse scan due to the removal of gas bubbles from the cathode surface.

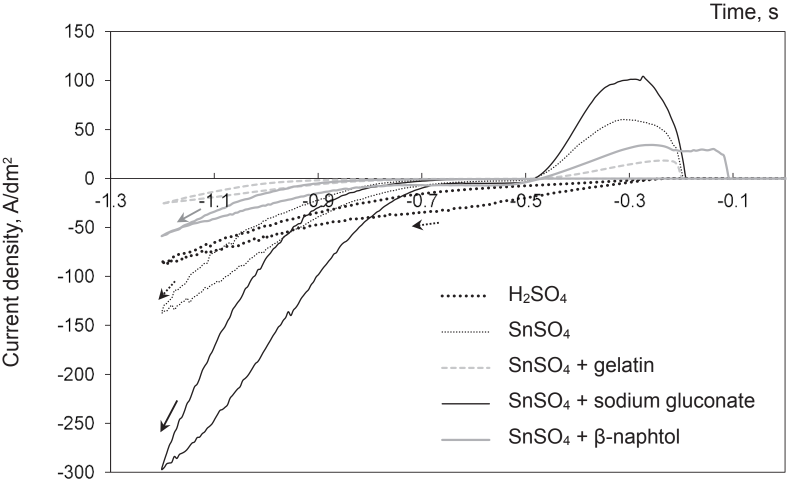

Fig. 1. Cyclic voltammetric curves registered on platinum electrode in acid $SnSO_4$ solutions in presence of organic additives

The course of the CV curves changed in the presence of Sn(II) ions. The reduction of metal ions:

$$Sn^{2+} + 2e \rightarrow Sn \tag{2}$$

occurred below −0.5 V, while the equilibrium potential of the Sn/Sn(II) electrode for 50 mM Sn(II) is −0.4 V (Ag/AgCl). Although the potential of the hydrogen electrode is more electropositive than that of the Sn/Sn(II) electrode, the dominant cathodic reaction is metal deposition. This is due to the fact that the hydrogen overpotential on the tin surface is much higher (about 0.8 V) than the overpotential for hydrogen evolution on platinum (about 0.1 V) [30]. In the potential range from −1.0 to −1.2 V, a simultaneous reduction of the tin and hydrogen ions takes place, resulting in higher total cathodic currents than in pure H_2SO_4.

The change of the sweep direction towards the higher potentials was accompanied by an enhanced deposition of the tin on the tin sublayer than on the platinum in the forward scan, as the nucleation and electrodeposition of the metal on the foreign substrate are more difficult and require higher overpotential than during deposition on the native metal surface. This resulted in higher cathodic currents in the reverse scan and a lack of the curve intersection corresponding to the nucleation potential. An intersection of the voltammetric branches was found at about –0.5 V. This crossover potential is usually consistent with the equilibrium value.

Above the potential of –0.5 V, an anode peak with a maximum at about –0.3 V was developed. It was associated with the oxidation of the previously deposited tin:

$$\mathrm{Sn} \rightarrow \mathrm{Sn}^{2+} + 2\mathrm{e} \tag{3}$$

Subsequent measurements were carried out in the presence of the additives. In all cases, the tin started to deposit at the same potential as in the $SnSO_4$ bath. Gelatin strongly inhibited the cathodic reaction, as evidenced by the low current densities even at potentials below –0.9 V. This can be related to the increase in solution viscosity and adsorption of the gelatin compounds on the cathode surface. This resulted in the slower transport of the tin ions to the cathode surface and hindered the reduction of the metal ions.

In the presence of β-naphthol, less shift in the deposition potential was observed as compared to the solution with gelatin, and higher cathodic currents were observed below –0.8 V. The process itself was slower than in the pure $SnSO_4$ bath, but it was not as strongly inhibited as in the case of the gelatin. This indicates that β-naphthol can also act via the adsorption mechanism, as it does not form any compounds with the tin ions.

The addition of sodium gluconate to the solution resulted in an increased rate of the cathodic reaction. Gluconate ions (Glu^-) can form complexes with the Sn(II) ions (Tab. 1); however, in an acid environment and at an insufficient concentration of the complexing agent (5 mM), the dominating species are the free metal ions and neutral sulfate complex (Fig. 2). However, sodium gluconate introduced into H_2SO_4 can dissociate:

$$\mathrm{GluNa} \rightarrow \mathrm{Glu}^- + \mathrm{Na}^+ \tag{4}$$

forming further weakly dissociated acid at the excess of hydrogen ions:

$$\mathrm{H}^+ + \mathrm{Glu}^- \rightarrow \mathrm{HGlu} \tag{5}$$

It seems that the bonding of the free hydrogen ions significantly inhibits the competitive reaction of the cathodic hydrogen evolution, enabling a more intensive reduction of the metal ions. This is confirmed by the very high anode peak developed in the reverse scan (Fig. 1), which shows that the tin was most-deposited in the presence of sodium gluconate.

Table 1. Stability constant of soluble species [31]

Species	**Logarithm of formation constant**
$SnOH^+$	−4.1
$Sn(OH)_2$	−7.8
$Sn(OH)_3^-$	−11.6
$SnSO_4$	1.29
$Sn(SO_4)_2^{2-}$	1.65
$SnGlu^+$	3.01
$SnGlu_2$	5.29
HSO_4^-	1.12
HGlu	3.56

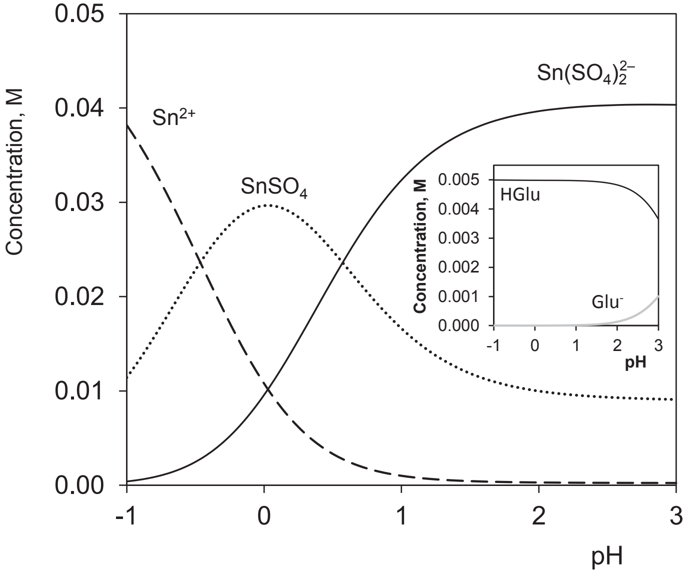

Fig. 2. Dominating tin species in Sn(II)-SO_4^{2-}-gluconate system. Equilibrium data calculated (Hyss2009) according to stability constants shown in Table 1 and for concentrations of components used in this study

The electrodeposition of the tin was further considered in terms of the rate-determining step. It is known that the process of metal deposition is accompanied by a polarization of the electrode originated from different rates of the intermediate stages of the electrode reaction. If the intermediate steps run consecutively, the total rate of the process is determined by the slowest one. If the charge transfer across the metal-electrolyte interface is the slowest step of the reduction of the metal ions, the activation polarization is described by the dependence of activation overvoltage η on current density *i* with the Tafel equation:

$$\eta = E_i - E_o = a + b\log i\,, \tag{6}$$

which is described for the cathodic reaction by a more detailed form:

$$\eta_C = \frac{2.3RT}{\alpha_C zF}\log i_o - \frac{2.3RT}{\alpha_C zF}\log i\,, \tag{7}$$

where:

i_o – exchange current density,
α_C – symmetry factor of energy barrier for cathodic reaction,
R – gaseous constant,
T – temperature.

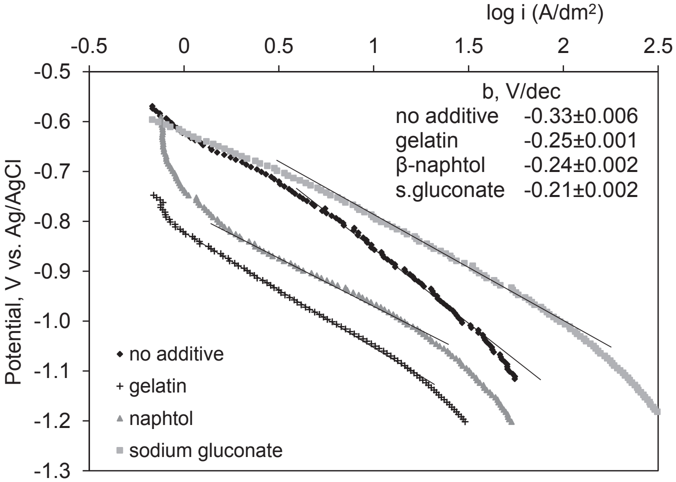

Fig. 3. Linear polarization curves for tin deposition plotted in the "Tafel coordination system" (the b values are given with the uncertainty calculated from the linear fitting procedure)

Figure 3 shows the cathodic polarization curves plotted in the log*i*-potential system for tin deposition. A linear dependence corresponding to the activation polarization was observed in a rather narrow potential range from about –0.7 V to about –1.1 V. The slopes of the straight lines changed from about 0.33 V/dec in the absence of the additives to 0.21–0.25 V/dec. The latter increased in the order of gluconate < β-naphtol < gelatin. The obtained values were quite similar to those reported in the literature for an acid stannous sulfate bath containing some nonionic additives [21]. The symmetry factors of the energy barrier were then calculated, giving the following series: no additive (0.089) < gelatin (0.118) < β-naphtol (0.123) < gluconate (0.141). The obtained results confirm the inhibiting effect of the additives on the formation of the tin grains. The high value of α_C for the gluconate ions indicates that the compound can also adsorb on the cathode surface during electrolysis. A similar effect was observed during the electrodeposition of manganese from slightly acidic gluconate solutions [26]. Thus, the rate-determining step for the electrodeposition of tin from acid stannous solutions that contain additives is most likely a charge transfer through a layer of adsorbed organic molecules. This layer of adsorbed organic molecules is reasonably complete in the range of the current densities in which Tafel linearity is maintained [21].

Adsorption mechanism of additive's action seems to be confirmed by modifications of the morphology of tin deposits (Fig. 4). In pure $SnSO_4$ bath coarse-grained and dendritic layers with polyhedron crystals were formed, while in the presence of organic agents the deposit's structure totally changed. Gelatin produced relatively compact fine-grained layers with rounded tin grains. In the presence of β-naphtol, tin formed flat rectangular plates, rather large in size and loose. The most fine-grained and compact deposits were formed in the gluconate-containing solutions and randomly placed, thin plates forming star-like structures were observed on the cathode surface.

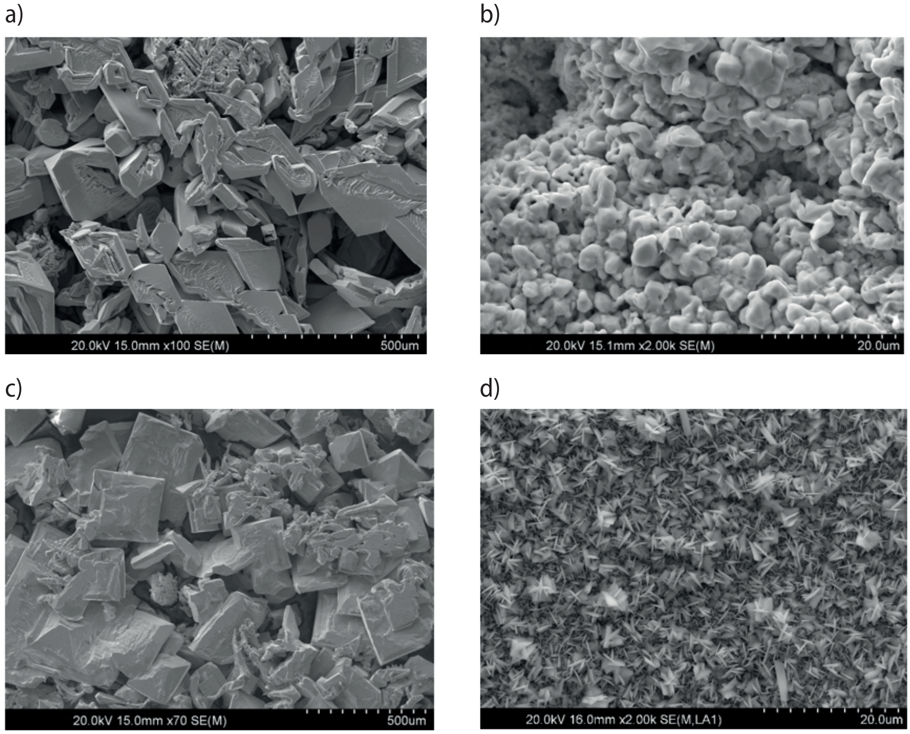

Fig. 4. Morphology of tin electrodeposits produced from acidic $SnSO_4$ bath: a) no additive; b) gelatin; c) β-naphtol; d) sodium gluconate. Deposition potential −0.8 V

Serious modification of the tin electrodeposits was not accompanied by the changes in the metal crystal lattice. In all cases, tin of tetragonal crystal system was produced as it is indicated by results of XRD analysis shown in Figure 5.

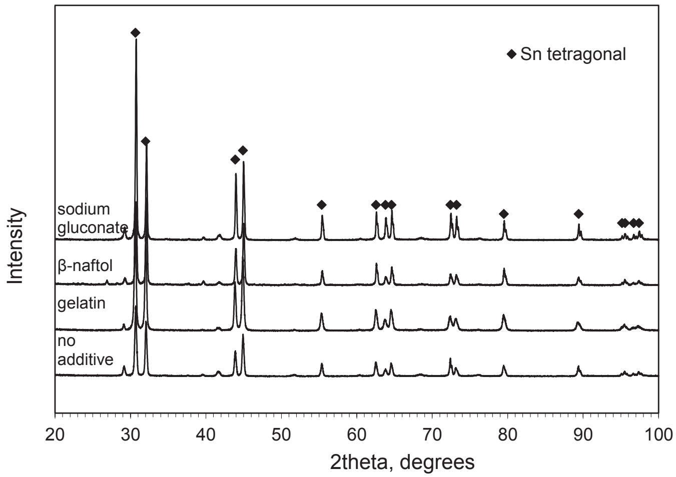

Fig. 5. X-ray diffraction data of tin deposited in the presence of additives

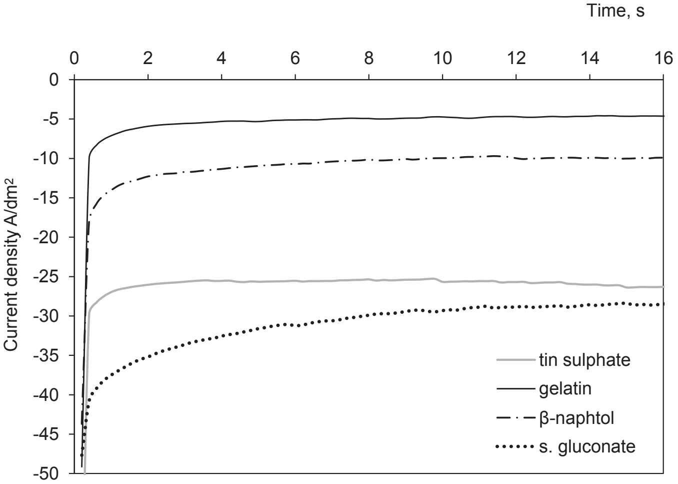

Fig. 6. Chronoamperometric curves registered during early stages of tin deposition at –0.9 V

Figure 6 demonstrates exemplary chronoamperometric curves describing early stages of tin deposition at constant potential. Independently on the deposition potential (in the range from –0.5 V to –1.1 V) transients showed sudden decrease in the current density to the constant value due to the charging of the double layer. Such course is characteristic for the cathodic process determined by the charge transfer [32]. No cathodic maximum typical for formation of metallic nuclei accompanied by diffusion-limited growth was observed. Increase in the deposition currents caused by a change in the bath composition is consistent with voltammetric data showing the strongest inhibiting effect on tin nucleation for gelatin and β-naphtol and enhanced deposition for sodium gluconate.

Figure 7 shows results of anodic stripping analysis. It was observed that development of the anodic response is dependent on the bath composition and deposition potential. In all cases, two series of anodic peaks were formed: one for the two higher deposition potentials (–0.5 and –0.6 V) and the second for the more-electronegative values. This corresponds to the dissolution of tin deposited directly on the platinum substrate (more electropositive potentials) or bulk tin deposited on the tin. Therefore, the anodic peaks can be attributed to the presence of fine or dendritic tin grains in the deposits, resulting in the shifting of the anodic peak towards the more-positive potentials. Intensive growth of the grains towards the bulk solution at the more-cathodic potentials can enhance the deposition of the metal due to the serious development of the cathode surface available for the reduction of the Sn^{2+} cations. This corresponds to the increased mass of the deposits and larger anodic peak. The strong inhibition of tin deposition in the presence of gelatin prevents the formation of dendritic grains; therefore, the smaller anodic responses involved the narrow range of the potentials.

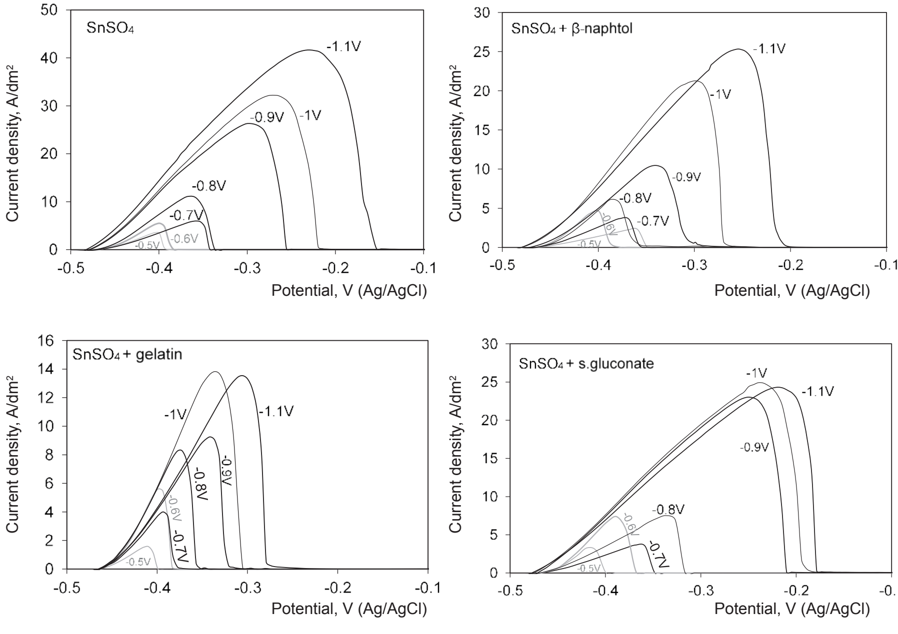

Fig. 7. Anodic stripping curves for tin deposition at various potentials for 40 s

4. Conclusions

Fundamental electrochemical experiments on the kinetics of tin deposition from an acid sulfate solution containing organic additives were performed. The measurements showed that tin deposits with activation polarization in a narrow potential range, but organic additives inhibit the charge transfer stage of the cathodic reaction due to the formation of the adsorption layers. This results in a serious change in the morphology of the tin from polyhedron crystals (no additive) via rectangular plates (β-naphtol) and thin plates (gluconate) to rounded grains (gelatin) but without changes in the crystal lattice.

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