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Investigation of electrochemical reduction of Sn(II) ions in acidic (pH 1) sulphamate–fluoride solutions

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The electrochemical reduction of Sn(II) ions in acidic (pH 1) sulphamate and sulphamate–fluoride solutions was investigated using voltammetric, chronopotentiometric, and rotating disc electrode techniques. In both solutions, the process of Sn(II) reduction was found to be reversible and mostly diffusion-controlled. The Sn(II) ion diffusion coefficient was $D = 6.1 \cdot 10^{-6}$ cm²/s.

In acidic sulphamate–fluoride solutions, the decomposition of Sn–fluoride complexes into Sn(II) ions and F^- ions precedes by the electrochemical reduction step.

The transfer reaction in acidic tin sulphamate and sulphamate–fluoride solutions proceeds in one step:

$$Sn^{2+} + 2e^- \rightleftarrows Sn.$$

The determined kinetic parameters of the ionization-reduction reaction in Sn(II) solutions (concentration 0.01 M–0.1 M) were: exchange current $i_0 = 0.0055–0.0100$ A/cm², cathodic and anodic transfer coefficients $\alpha \approx \beta \approx 0.5$, and the reaction rate constant $k_s = (1 \cdot 10^{-6}–10 \cdot 10^{-6})$ cm/s.

In both sulphamate and sulphamate–fluoride solutions, the electrochemical reduction of Sn(II) ions follows the same pattern which determines the identical properties of deposited Sn coatings.

Key words: sulphamate solution, Sn(II) ions, Sn(II) fluoride, diffusion, exchange current, polarization

INTRODUCTION

After the EU has adopted the WEEE (Waste Directive on Electronic and Electronic Components) directive which recommends banning lead-containing materials from electronics industry [1], the need for new lead-free solder materials has arisen. Several alternative lead-free solders have been proposed in the literature [2], but most of them can be formed only metallurgically. Electrochemical formation of solder materials is less material-demanding and, hence, is more desirable in electronics industry. One of the simplest alternatives would be pure Sn coatings that can be easily deposited from acidic Sn(II) solutions. Sn coatings deposited from unmodified Sn(II) solutions are coarse-grained, with needle-like crystals at higher current densities that poorly adhere to the base surface. Introduction of an organic additive to the system allows depositing bright fine-grained Sn coatings. Numerous reports have been published concerning the effect of organic additives on the quality of Sn coatings as well as on the electrochemical process [3–8]. The problem of whisker formation became rather keen in the latter case. It is known that the tendency of whisker formation is characteristic of bright Sn coatings with a field-orientated needle-like crystal structure formed by brighteners [9]. On the other hand, the coarse-grained mat tin coatings as well as fused Sn coatings are less inclined to form whiskers. It is also believed that the tendency of whisker formation is reduced in the case of tin alloys.

Fine-grained mat tin coatings can be deposited from solutions containing complexed ions. Over the past several decades, plating baths formulated with sulfamic (HSO_3NH_2) acid have become increasingly interesting for electroplating of Sn and its alloys. Sulphamic acid is highly soluble, biologically degradable, toxicologically safe, and also is less corrosive.

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Tin–fluoride complexes are known to be stable in acidic media [10, 11], so it was attempted to deposit Sn coatings from acidic sulphamate–fluoride solutions. Studies revealed that the quality of Sn coatings deposited from sulphamate–fluoride solutions was the same as in the case of unmodified Sn(II) solutions. To understand the nature of this rather surprising finding, it was attempted to clarify the electrochemical processes taking place in both unmodified and complexed Sn(II) systems.

The process of Sn(II) electroreduction from uncomplexed solutions has been extensively studied in acidic sulfate, chloride, and perchloride solutions on both solid and amalgam electrodes. The reported results were contradictory, irrespectively of the nature of the electrolyte or the electrode. Some authors have suggested that the electrochemical reduction or oxidation of Sn proceeds in one step, two electrons being simultaneous added or taken away [12–16]. Other studies have indicated that electrode processes proceed stepwise by addition or subtraction of a single electron. Most authors concluded that the transfer of the first electron is hindered [17–22], whereas Kozin [23] suggested that the transfer of the second electron is impeded. Yet other studies proposed that both electrons can be transferred either simultaneously or separately with comparable speeds, making it impossible to differentiate unmistakably between the two mechanisms [24–26]. Also, organic additives can influence the electrochemical process and affect the mechanism by hindering the transfer of the first or the second electron [22, 24].

There are only a few reports dealing with the elctroreduction of complexed Sn(II) ions in acidic media. Studies of Sn electrodeposition from acidic Sn(II)-citrate solutions [27] have suggested that, depending on pH, tin is electroreduced from different complexes, whereas no direct studies of the electroreduction step were attempted.

We could not find any reports on the processes taking place during Sn electrodeposition from acidic sulphamate or sulphamate–fluoride solutions. The goal of this study was, therefore, to investigate the factors influencing cathodic and anodic processes so as to understand the identical properties of Sn coatings formed from uncomplexed and complexed Sn solutions.

EXPERIMENTAL

All solutions were prepared using bidistilled water and either chemically pure or purissimus grade substances.

Tin sulphamate was prepared by neutralizing a freshly prepared tin hydroxide with sulphamic acid. Sn(II) hydroxide was precipitated by the reaction of $SnCl_2$ solution in concentrated hydrochloric acid with ammonium hydroxide. The precipitate was thoroughly washed, filtered and then neutralized with sulfamic acid. The pH of solutions was 1. The concentrate was used for 1–2 days. All measurements were conducted in electrolytes containing background solutions of 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2.

Polarization measurements. The dependence of the rate of electrode processes on the potential was studied using the potentiodynamic method. Measurements were conducted in an 80 ml rectangular thermostated cell made of acrylic glass. After each series of measurement, the solution was replaced, although no change in its concentration could be detected analytically. A tin disk with the surface area of 1 cm^2 was used as a working electrode. To avoid the ohmic potential drop due to solution resistance, the end of the Luggin capillary was brought to the level of the working surface of the electrode through the hole from the back side of the electrode. 15 cm^2 of tin foil was used as a counter electrode. Prior to each measurement, the surface of the electrode had been polished, cleaned with CaO and MgO mixture, and then thoroughly washed with distilled water and an electrolyte. The potential of the Sn electrode was measured relative to the saturated AgCl reference electrode. Potentiodynamic voltammetric curves were generated on a PI-50-1-1 potentiostat (Belarus), using a PR-8 programmator (Belarus) and recorded with an H-307/1 xy-recorder (Russia). All potentials reported in this paper are given in respect of a normal hydrogen electrode.

Measurements, taken under forced convection conditions, were conducted in diluted solutions to avoid the enlargement of the surface area due to the growth of needle-like crystallites on the electrode surface. The rotating disc electrode technique was used. The rotating disc electrode was made of a tin cylinder pressed into a fluoroplastic frame. The area of the working electrode was 1 cm^2. The rotation rate was measured with a Ch3-33 frequency meter (Russia). The change of the potential in time was investigated by galvanostatically switching on the current. The current source was UIP-1 (Russia) with the sequentially connected resistance of 5 kΩ. Chronopotentiograms were recorded with an H-307/1 xy-recorder and a C8-13 oscillograph (Russia). The current efficiency was measured gravimetrically using a copper coulometer.

The composition of surface compounds was investigated by XPS and Auger spectroscopies. The spectra were recorded using an ESCALAB MK II spectrometer (VG Scientific, UK) using Mg Kα radiation (1253.6 eV, pass energy of 20 eV). The spectrometer had a base pressure of 5×10^{-8} Torr in the analyzer chamber and 2×10^{-7} Torr in the sample preparation chamber where Ar^+ ion bombardment was performed. For sputter etching, the argon gas pressure was maintained at 6×10^{-5} Torr, and the ion gun was operated at 2 kV and 20 μA at a normal incidence. The quantitative elemental analysis was done by estimating peak areas and taking into consideration empirical sensitivity factors for each element [28]. The recorded spectra were compared to the standard spectra [29]. The binding energies were calibrated with respect to the C 1 s electron peak at 284.6 eV. No fewer than three spectra were recorded for each element. The maximum accuracy of the method was 0.1 at. %. A standard program was used for data processing.

RESULTS AND DISCUSSION

Electrochemical reduction of Sn(II) ions in acidic sulphamate solutions

As shown in our earlier publication, the potential of the Sn electrode in acidic sulphamate solutions is reversible, and no side reactions are taking place on the surface of the electrode [30].

Measurements of current efficiency have demonstrated that in sulphamate solutions Sn is deposited with a 100% efficiency up to the horizontal part of the polarization curve. This indicates that the limiting current i_l of the cathodic process is determined by the Sn(II) discharge process. As can be seen from Fig. 1, i_l increases with increasing the concentration of Sn(II) ions. An increase in $Sn(SO_3NH_2)_2$ concentration from 0.01 M to 0.1 M raises i_l more than 10-fold. A higher than expected raise of i_l might be due to the development of the electrode surface in more concentrated solutions. This dependence of i_l on the concentration of Sn(II) ions makes it possible to conclude that i_l is diffusion-controlled. To check this assumption, the galvanostatic switching on method was used. A well-pronounced transition time (τ) is observed in chronopotentiograms when the initial switch current is twice higher than i_l (Fig. 2a). The product of $i\sqrt{\tau}$ is constant and independent of the value of the current switched on (Fig. 2b). The product of $i\sqrt{\tau}$ is only dependent of the concentration of Sn(II)ions; this dependence is linear and passes the point of origin (Fig. 2c). All these facts show that the limiting current of the discharge of Sn(II) ions is diffusion-controlled; thus, $i\sqrt{\tau}$ can be employed to calculate

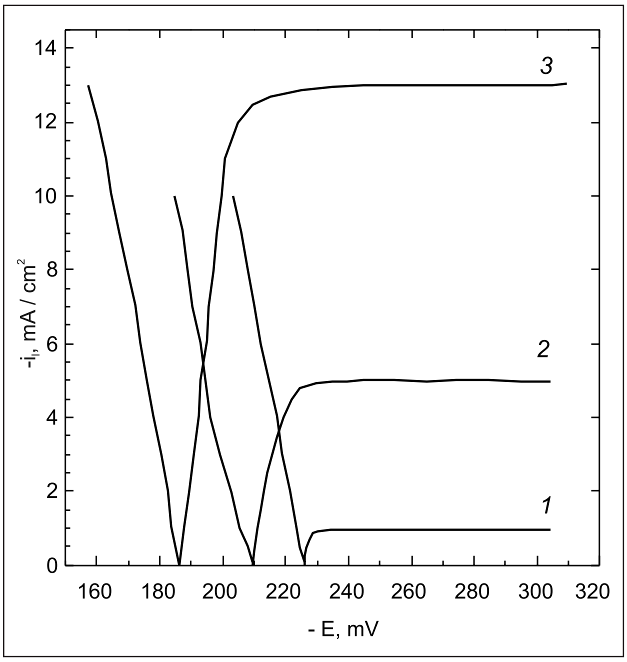

Fig. 1. Voltammograms of tin electrode in $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 solution. Dependence on Sn (II)(M) concentration: *1* – 0.01, *2* – 0.05, *3* – 0.1; $v = 1$ mV s^{-1}, pH = 1.0, $t = 20$ °C

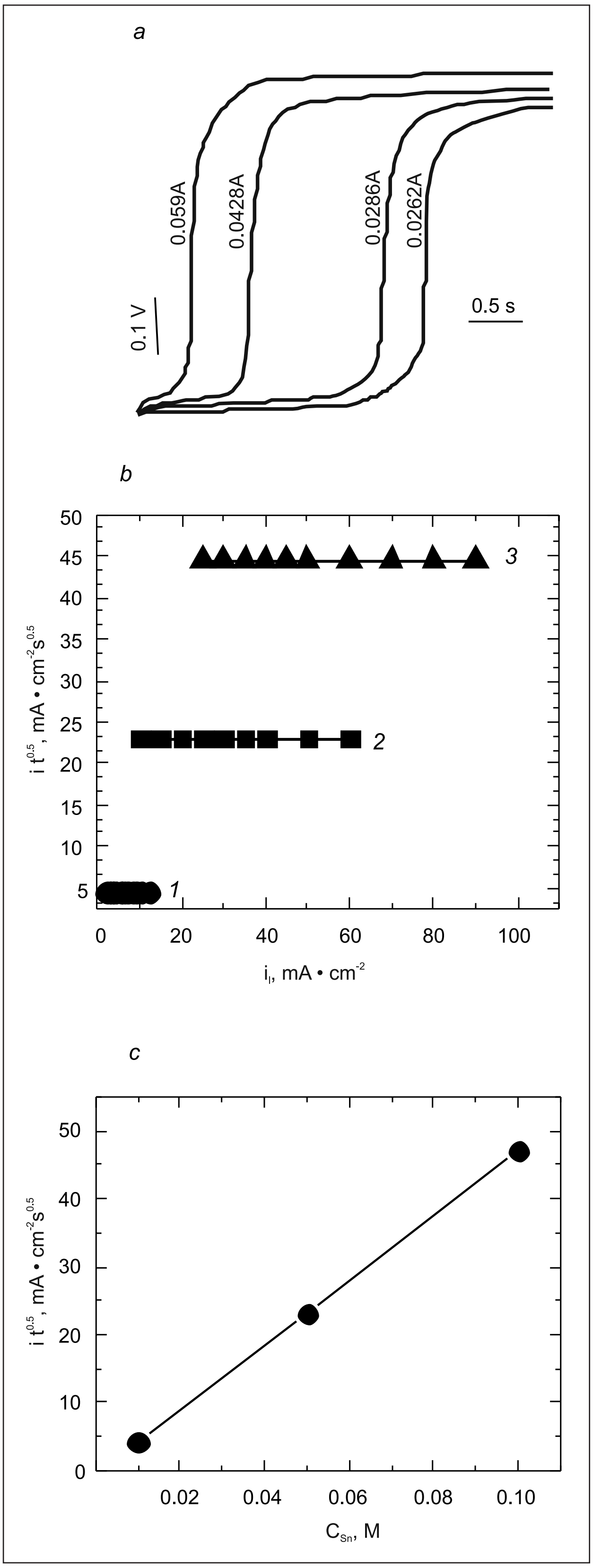

Fig. 2. *a* – galvanostatic switching curves of Sn electrode in 0.1 M $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 solution; current density values are indicated at the curves; *b* – current density dependence of $i\sqrt{\tau}$ at various Sn (II) concentrations (M): *1* – 0.01, *2* – 0.05, *3* – 0.1; *c* – dependence of $i\tau^{0.5}$ product on the concentration of Sn(II), pH = 1.0, $t = 20$ °C

the diffusion coefficient of Sn(II) ions according to Sand's equation [31]:

$$i\sqrt{\tau} = 0.5\, nF\, c\, \sqrt{\pi}\, \sqrt{D}, \qquad (1)$$

where n is the number of electrons transferred, F is Faraday's number (C/mol), c is the concentration of Sn(II) ions (mol/cm^3), and D is the diffusion coefficient (cm^2/s).

The calculated diffusion coefficient $D = 6.1 \pm \pm 0.1 \cdot 10^{-6}$ cm^2/s.

It is possible to judge about the nature of polarization in the system where only one type of ions are being discharged and no secondary processes are taking place by comparing the experimental data with those calculated from Eq. 2, which describes the change of diffusion polarization in time [32]:

$$\Delta E = \frac{2.3RT}{nF}\lg(1 - \frac{\sqrt{t}}{\tau}), \qquad (2)$$

where t is time (s) and τ is transition time (s).

As can be seen from Fig. 3, dependencies of η vs. lg $(1\text{-}\sqrt{t}/\tau)$ are linear with a slope of 30 ± 3 mV. We conclude that upon discharge of Sn(II) ions from sulphamate solutions, the limiting current and the cathodic polarization are predominantly diffusion-controlled.

The process of the discharge of Sn(II) ions is also studied by the rotating disc electrode (RDE) technique, i. e. under conditions of forced convection. The higher spinning rate of RDE raises the rate of the cathodic process. The dependence of i_l on $\sqrt{\omega}$ is linear (Fig. 4), which again proves the diffusion-controlled origin of i_l. The diffusion coefficient of Sn(II) is calculated according to equation [31]:

$$i_l = 0.61 nFcD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}, \qquad (3)$$

where ω is the angular velocity of *RDE* (rad/s) and ν is the kinematic viscosity of the solution (10^{-2} cm^2/s). The calculated D is $6.1 \pm 0.1 \cdot 10^{-6}$ cm^2/s.

It is possible to judge about the nature of the cathodic process from voltammetric measurements as well. Figure 5 shows that an increase in the potential sweep rate v leads to the appearance of a current maximum which increases with increasing the potential sweep rate. The current maximum dependence on $v^{1/2}$ at lower sweep rates is linear, and only at $v = 0.5$ V/s a deviation from the linear dependence is observed, which may be due to the limitation of slow charge transfer or to other kinetic limitations. For the revers-

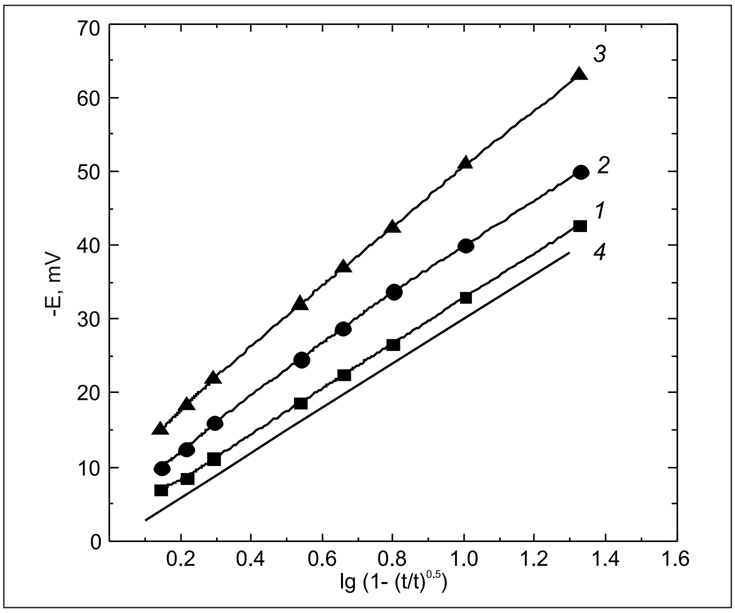

Fig. 3. Dependence of ΔE on lg(1-(t/τ)$^{0.5}$) at different concentrations of Sn(II) in Sn(SO$_3$NH$_2$)$_2$ + 0.3 M HSO$_3$NH$_2$ + 0.1 M KSO$_3$NH$_2$ solutions. *1* – 0.01 M, *2* – 0.05 M, *3* – 0.1 M, *4* – theoretical. pH = 1, t = 20 °C

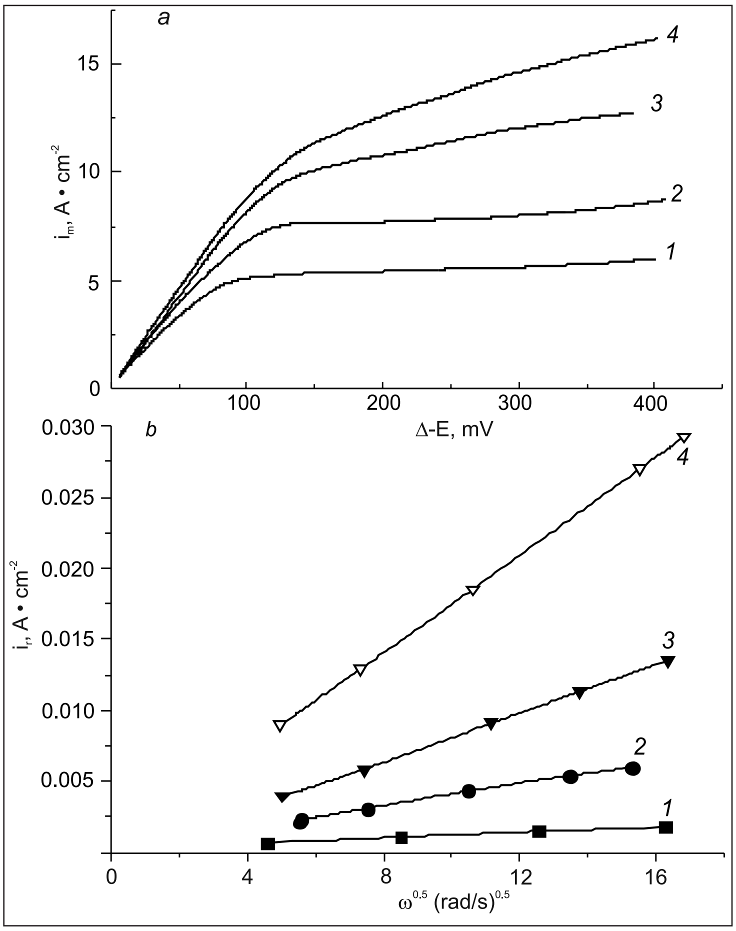

Fig. 4. *a* – voltammograms of tin electrode in solution of 0.01 M Sn(SO$_3$NH$_2$)$_2$ + 0.3 M HSO$_3$NH$_2$ + 0.1 M KSO$_3$NH$_2$, dependence on rotation rate w (rad s^{-1}): *1* – 24.3, *2* – 61.0, *3* – 138.8, *4* – 266.3–249; *b* – $w^{0.5}$-dependence of limiting current at various concentrations of Sn(II)(M): *1* – 0.001, *2* – 0.005, *3* – 0.01, *4* – 0.02, v = 10 mV/s; pH = 1.0, t = 20 °C

Table 1. **Calculated and experimental values of current maximum, i_m, as a function of the concentration of Sn(II) ions**

Concentration of Sn(II) ions, M	Sweep rate, V/s	i_m, A/cm^2	
		Calculated from Eq. 4	Experimental data
0.01	0.01	0.003	0.003
	0.05	0.006	0.006
	0.1	0.008	0.008
	0.5	0.019	0.018
0.05	0.01	0.013	0.012
	0.05	0.029	0.023
	0.5	0.051	0.056
0.1	0.01	0.027	0.025
	0.05	0.060	0.044
	0.1	0.085	0.056
	0.5	0.190	0.100

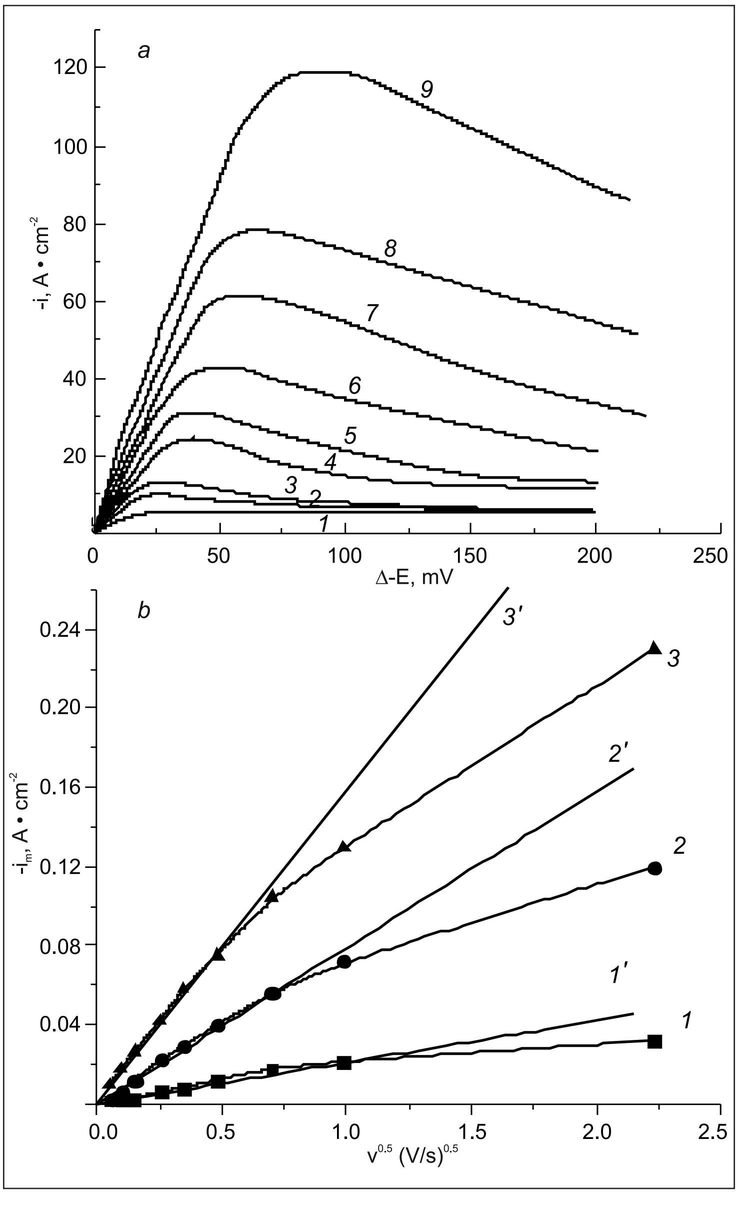

Fig. 5. *a* – voltammograms of tin electrode in 0.05 M $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 recorded at different potential scan rates $v^{0.5}$ (V s^{-1}): *1* – 0.001, *2* – 0.005, *3* – 0.01, *4* – 0.05, *5* – 0.1, *6* – 0.2, *7* – 0.5, *8* – 1.0, *9* – 5.0; *b* – *v*-dependence of peak current at various concentrations of Sn(II) (M): *1* – 0.01, *2* – 0.05, *3* – 0.1; *1'*, *2'*, *3'* are theoretical curves. pH = 1.0, *t* = 20 °C

ible process, the current maximum value can be calculated from Eq. 4 [31]:

$$i_m = 3.67\times10^5 n^{\frac{3}{2}} D^{\frac{1}{2}} c v^{\frac{1}{2}}. \quad (4)$$

The value of $D = 6.1 \cdot 10^{-6}$ cm^2/s, determined in our current work, was used to calculate the $i_{\max}$.

The values of the current maxima, estimated from Eq. 4, are close to experimental values (see Table 1), and only at higher sweep rates a discrepancy between the calculated and the experimental values is observed. It shows that the discharge of Sn(II) ions is reversible and the rate of the cathodic process is diffusion-limited only in specific experimental conditions.

When only stationary methods of investigation are employed, the cathodic process is mostly limited by diffusion. Introduction of either intensive agitation or fast measurement methods makes it possible to generate the conditions under which the charge transfer step becomes limiting. For this purpose, the galvanostatic switching on method was used to investigate the mechanism of electrode processes. The change of the electrode potential was monitored in the initial stages (up to 10 ms) when diffusive phenomena have little or no effect. Introduction of weak currents until the initial potential jump does not exceed 10 mV leads to a sharp initial potential jump which is little affected later on.

This shape of chronopotentiograms is typical of the Sn(II) solutions studied (Fig. 6). The dependences of *i* vs. ΔE are linear (up to overpotential of 10 mV) and pass through the point of origin (Fig. 7). The values of the exchange current are calculated from Eq. 5 [33]:

$$R_e = \frac{RT}{nFi_0}. \quad (5)$$

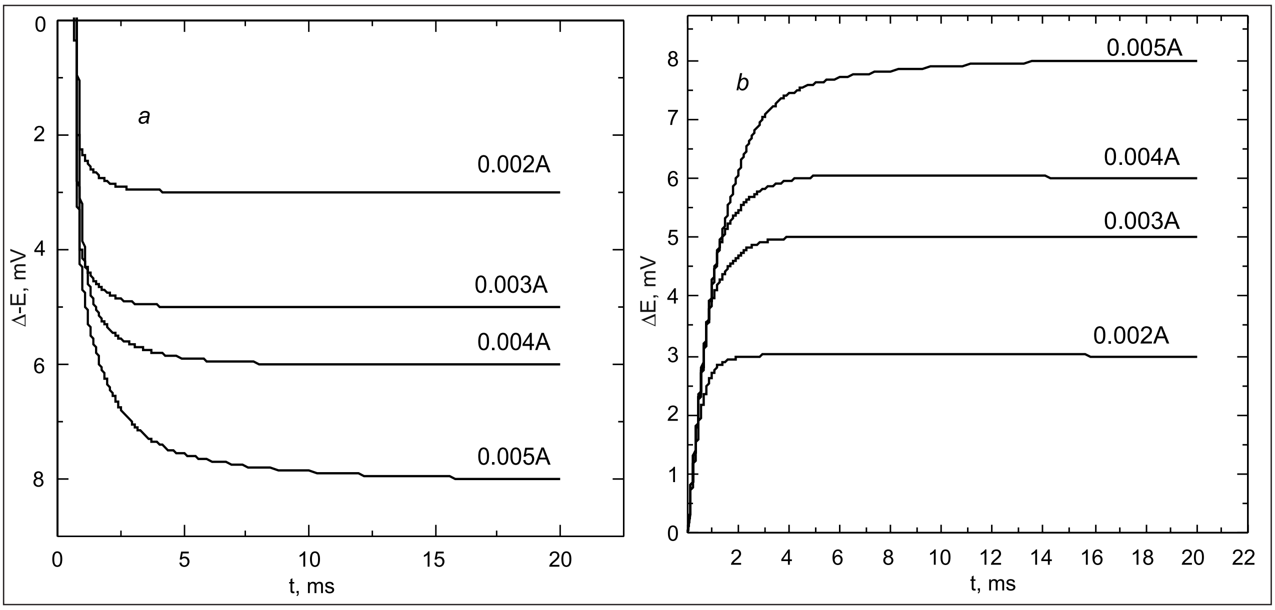

Fig. 6. Cathodic and anodic chronopotentiograms in 0.05 M $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 solution. Current density values are indicated next to curves. pH = 1, *t* = 20 °C

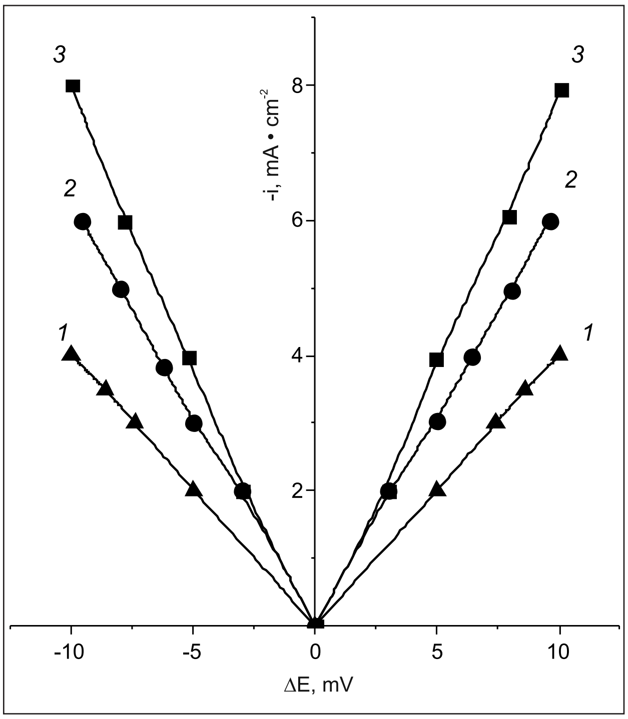

Fig. 7. Dependence of *i* vs. Δ*E* at different concentrations of Sn(II) in $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 solutions. *1* – 0.01 M, *2* – 0.05 M, *3* – 0.1 M. pH = 1, *t* = 20 °C

From the dependence of the exchange current vs. the concentration of Sn(II) ions, the transfer coefficients for both anodic and cathodic processes were calculated from Eq. 6 [33]:

$$\lg i_0 = \lg (nFk_s) + (1 - \alpha) \lg c_{Sn}. \qquad (6)$$

The calculated reaction transfer coefficients, exchange currents, and reaction rate constants are presented in Table 2.

The initial potential jump increases when higher currents are switched on. At very high values of the initial current, the transition time is reached. Semilogarithmic dependencies of *E* on lg (*i*) have no pronounced linear part from which it would be possible to calculate the parameters of the electrochemical reaction. In this case, the linear dependencies of *E* vs. lg (i_c), where $i_c = i / (1 - e^{(-nF/RT)\Delta E})$ were used. This formula allows estimating the influence of the reverse discharge-ionisation process on the overall reaction rate in the zone of low potentials (up to 120 mV). In this case, the linear dependence of Δ*E* vs. lg (i_c) was used [32]. As one can see from Fig. 8, linear dependences at the lowest values of polarization are observed in these coordinates, the cathodic and anodic dependences being symmetrical. The calculated reaction transfer coefficients, exchange currents, and reaction rate constants are presented in Table 3. As one can see from Tables 2 and 3, similar values of exchange currents are calculated using both methods, although these values are lower than those reported in the literature [12, 21]. The transfer coefficients α and β, as well as the calculated reaction rate constants are different for the two methods employed. The sum of the transfer coefficients is higher than 1 (1.3) in the first case, whereas it reaches only 0.9 in the second case. The reaction order (calculated from Eq. 7) is close to 1 in all cases, indicating that the electrochemical reaction with respect to Sn(II) ions is that of the first order:

$$z_0 = \frac{\partial \lg i_0}{\partial \lg c_{\mathrm{Sn}}} + \frac{\alpha \nu}{n} z. \qquad (7)$$

Table 2. **Kinetic parameters of ionization-reduction reaction, calculated from Eq. 5 and Eq. 6 in $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 + KF solutions, pH = 1, t = 20 °C**

Concentration of electrolytes		Kinetic parameters					
		Cathodic process			Anodic process		
$Sn(SO_3NH_2)_2$	KF	$i_o \cdot 10^3$ A/cm^2	α	$k_s \cdot 10^6$ cm/s	$i_o \cdot 10^3$ A/cm^2	β	$k_s \cdot 10^6$ cm/s
0.01	0	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2
0.01	0.01	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2
0.01	0.05	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2
0.01	0.1	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2
0.01	0.3	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2	5.2 ± 0.2	0.65 ± 0.01	1.5 ± 0.2
0.05	0	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.05	0.01	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.05	0.05	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.05	0.1	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.05	0.3	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	8.0 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.1	0	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.1	0.01	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.1	0.05	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.1	0.1	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
0.1	0.3	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2	10 ± 0.1	0.65 ± 0.01	1.3 ± 0.2
Average			0.65 ± 0.01	1.4 ± 0.2		0.65 ± 0.01	1.4 ± 0.2

Table 3. **Kinetic parameters of the ionization-reduction reaction, calculated Tafel's straights in $Sn(SO_3NH_2)_2$ + 0.3 M HSO_3NH_2 + 0.1 M KSO_3NH_2 + KF solutions, pH = 1, t = 20 °C**

Concentration of electrolytes		Kinetic parameters					
		Cathodic process			Anodic process		
$Sn(SO_3NH_2)_2$	KF	$i_o \cdot 10^3$ A/cm^2	α	$k_s \cdot 10^6$ cm/s	$i_o \cdot 10^3$ A/cm^2	β	$k_s \cdot 10^6$ cm/s
0.01	0	5.5 ± 0.2	0.44 ± 0.01	17 ± 0.2	5.3 ± 0.2	0.46 ± 0.01	14 ± 0.2
0.01	0.01	5.5 ± 0.2	0.44 ± 0.01	17 ± 0.2	5.3 ± 0.2	0.46 ± 0.01	14 ± 0.2
0.01	0.05	5.5 ± 0.2	0.44 ± 0.01	17 ± 0.2	5.3 ± 0.2	0.46 ± 0.01	14 ± 0.2
0.01	0.1	5.5 ± 0.2	0.44 ± 0.01	17 ± 0.2	5.3 ± 0.2	0.46 ± 0.01	14 ± 0.2
0.01	0.3	5.5 ± 0.2	0.44 ± 0.01	17 ± 0.2	5.3 ± 0.2	0.46 ± 0.01	14 ± 0.2
0.05	0	8.0 ± 0.1	0.47 ± 0.01	7.9 ± 0.2	8.8 ± 0.1	0.47 ± 0.01	8.7 ± 0.2
0.05	0.01	8.0 ± 0.1	0.47 ± 0.01	7.9 ± 0.2	8.8 ± 0.1	0.47 ± 0.01	8.7 ± 0.2
0.05	0.05	8.0 ± 0.1	0.47 ± 0.01	7.9 ± 0.2	8.8 ± 0.1	0.47 ± 0.01	8.7 ± 0.2
0.05	0.1	8.0 ± 0.1	0.47 ± 0.01	7.9 ± 0.2	8.8 ± 0.1	0.47 ± 0.01	8.7 ± 0.2
0.05	0.3	8.0 ± 0.1	0.47 ± 0.01	7.9 ± 0.2	8.8 ± 0.1	0.47 ± 0.01	8.7 ± 0.2
0.1	0	10 ± 0.1	0.46 ± 0.01	7.5 ± 0.2	10 ± 0.1	0.47 ± 0.01	6.8 ± 0.2
0.1	0.01	10 ± 0.1	0.46 ± 0.01	7.5 ± 0.2	10 ± 0.1	0.47 ± 0.01	6.8 ± 0.2
0.1	0.05	10 ± 0.1	0.46 ± 0.01	7.5 ± 0.2	10 ± 0.1	0.47 ± 0.01	6.8 ± 0.2
0.1	0.1	10 ± 0.1	0.46 ± 0.01	7.5 ± 0.2	10 ± 0.1	0.47 ± 0.01	6.8 ± 0.2
0.1	0.3	10 ± 0.1	0.46 ± 0.01	7.5 ± 0.2	10 ± 0.1	0.47 ± 0.01	6.8 ± 0.2
Average			0.46 ± 0.01	10.8 ± 0.1		0.47 ± 0.01	9.8 ± 0.1

Equal transfer coefficients and exchange currents for cathodic and anodic processes, as well as the fact that the cathodic and anodic parts of polarization curves are symmetrical, indicate that the process of the first loss of the electron and the process of the first assimilation of the electron are the same. This indicates that the overall reaction in sulphamate solutions (with pH = 1) coincides with the electrochemical transition reaction involving hydrated Sn(II) ions, which can add or take away two electrons:

$$Sn^{2+} + 2e^- \rightleftarrows Sn.$$

Analogous conclusions were also reached in the case of the electroreduction of Cd(II) ions from acidic sulfate sultions [34, 35].

The process of addition or loss of electrons should most likely be treated as an instant process, since it is impossible to distinguish between the transfer of the first and the second electrons.

Electrochemical reduction of Sn(II) ions in acidic sulphamate–fluoride solutions

Addition of potassium fluoride KF to the acidic solution of Sn–sulphamate leads to formation of Sn–fluoride complex ions [11]. Increase in the concentration of F^- ions leads to more negative values of E_0, whereas the nature and appearance of polarization curves remain unchanged. No new peaks associated with the electrodeposition of Sn from Sn–fluoride complexes are observed. As shown in our earlier work [36], the cathodic process in acidic sulphamate–fluoride solutions is of the same nature as in pure sulphamate solutions, only that kinetic limitations of the cathodic process are reached at higher F^- ion concentrations. The composition of the surface of the Sn electrode was examined by XPS. Mostly oxides and only minute amounts of *F*-containing species were found on the surface (Fig. 9). After the surface had been etched for 0.6 nm, the amount of oxygen-containing species was drastically reduced, whereas no *F*-containing species could be detected at all. Etching of 2 nm reveals pure metallic Sn. Oxygen-containing compounds are formed, most likely, after the sample has been exposed to water and air, suggesting that the surface of the Sn electrode in sulphamate–fluoride solutions is clean and active. This observation is also confirmed by the surface elemental analysis of a Sn electrode kept in fluoride-free solution (Fig. 9).

Examination of change of the initial potential in time by the galvanostatic switching-on method does not show any influence of F^- ions (up to 0.5 M) on the value of the initial potential jump. The calculated exchange currents and kinetic parameters are presented in Tables 2 and 3. The results indicate that the cathodic reaction is of a zero order in respect to F^- ions. We conclude, therefore, that in acidic sulphamate–fluoride solutions, complex SnF_n^{2-n} ions decompose near the electrode surface into constituents, and only hydrated Sn(II) ions are reduced. This explains the lack of peaks associated with the electrodeposition of Sn from Sn–fluoride complexes in the polarization curve diagrams as well as the kinetic limitations of the cathodic process. A higher concentration of F^- ions impedes the decomposition of fluoride complexes. We believe that the electrochemical reaction is the same as in the case of fluoride-free solutions. Hydrated Sn(II) are reduced

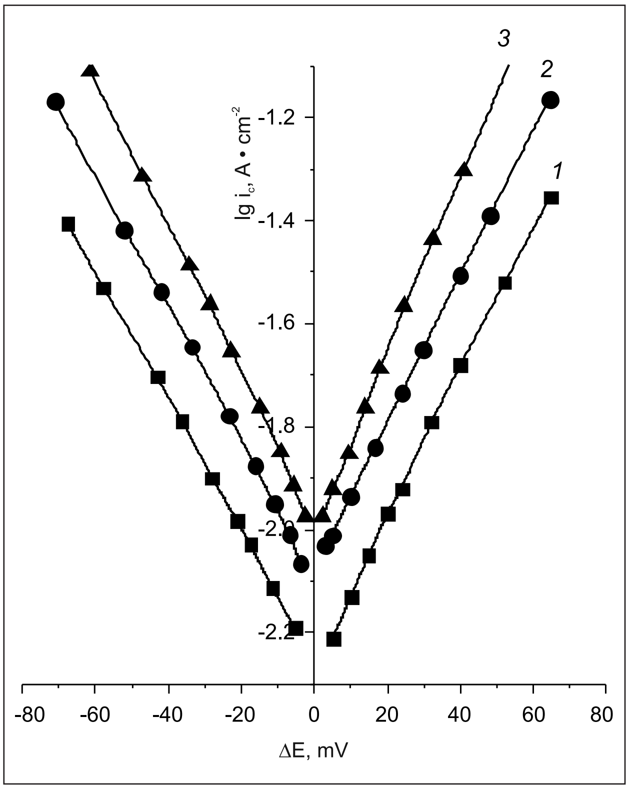

Fig. 8. Dependence of $\lg_{ic}$ vs. ΔE at different concentrations of Sn(II) in $Sn(SO_3NH_2)_2 + 0.3\ M\ HSO_3NH_2 + 0.1\ M\ KSO_3NH_2$ solutions. *1* – 0.01 M, *2* – 0.05 M, *3* – 0.1 M. pH = 1, *t* = 20 °C

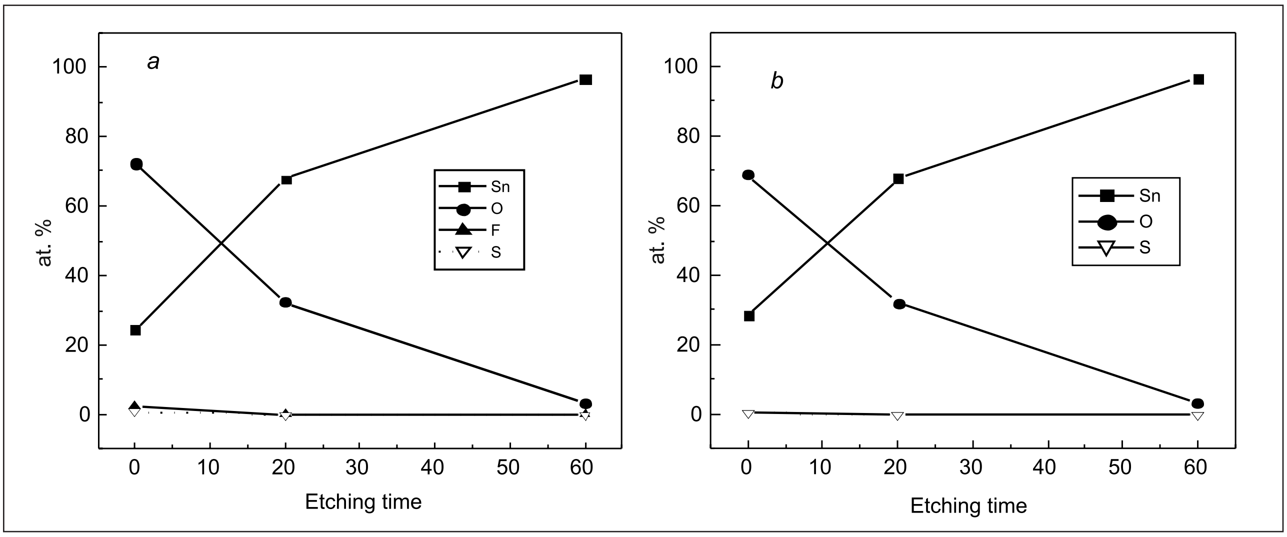

Fig. 9. Surface element distributition after the electrode had been kept for 1 hour in solutions: *a* – 0.05 M $Sn(SO_3NH_2)_2 + 0.3\ M\ HSO_3NH_2 + 0.1\ M\ KSO_3NH_2 + 1.0\ M\ KF$, *b* – 0.05 M $Sn(SO_3NH_2)_2 + 0.3\ M\ HSO_3NH_2 + 0.1\ M\ KSO_3NH_2$

on the surface of the electrode, and two-electron transfer is treated as a one-step reaction:

$$\mathrm{Sn}^{2+} + 2\mathrm{e}^{-} \rightleftarrows \mathrm{Sn}.$$

The transfer of the first and the second electrons is either simultaneous or proceeds at very similar rates and cannot be distinguished.

The obtained data explain the same appearance of Sn coatings deposited from sulphamate and sulphamate–fluoride solutions. Thus, sulphamate–fluoride solutions are not promising candidates for depositing pure Sn coatings for practical purposes.

CONCLUSIONS

1. The cathodic Sn(II) reduction process in acidic sulphamate and sulphamate–fluoride solutions (pH = 1) is reversible. The rate of the overall reaction is mostly diffusion-limited.

2. The kinetic parameters of the ionization-reduction reaction were determined to be as follows: $i_0 = 0.0055–0.0100$ A/cm^2 (the concentration of Sn(II) ions is 0.01–0.1 M);

$\alpha \approx \beta \approx 0.5$; $k_s = (1 \cdot 10^{-6}–10 \cdot 10^{-6})$ cm/s.

3. Close to the electrode, the decomposition of the $\mathrm{Sn}F_n^{2-n}$ complex ions into Sn(II) and F^- ions is taking place in acidic sulphamate–fluoride solutions.

4. Transfer reactions in acidic tin sulphamate and sulphamate–fluoride solutions are identical:

$$\mathrm{Sn}^{2+} + 2\mathrm{e}^{-} \rightleftarrows \mathrm{Sn}.$$

and, therefore, fluoride ions have no influence on the quality of deposited tin coatings.

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ELEKTROCHEMINĖS Sn(II) JONŲ REDUKCIJOS (pH 1) SULFAMO–FLUORIDINIUOSE TIRPALUOSE TYRIMAS

Santrauka

Elektrocheminė Sn(II) jonų redukcija rūgščiuose (pH 1) sulfamo ir sulfamo–fluoridiniuose tirpaluose buvo tirta voltamperometriškai, chronopotenciometriškai ir sukamo diskinio elektrodo metodu. Nustatyta, kad abiem atvejais Sn(II) jonų redukcijos procesas yra grįžtamas ir daugiausia sąlygotas difuzijos. Nustatytas Sn(II) difuzijos koeficientas $D = 6{,}1 \cdot 10^{-6}$ cm^2/s.

Rūgščiuose sulfamo–fluoridiniuose tirpaluose prieš elektrocheminę reakciją Sn fluoridiniai kompleksai skyla į Sn(II) ir F^- jonus.

Rūgščiuose alavo sulfamo ir sulfamo–fluoridiniuose tirpaluose elektrocheminė reakcija yra nestadijinė:

$Sn^{2+} + 2e \leftrightarrow Sn$.

Nustatyti kinetiniai oksidacijos–redukcijos reakcijos parametrai Sn(II) tirpaluose (koncentracija 0,01–0,1 M):

mainų srovė i_0 = 0,0055–0,01 A/cm^2, katodinis ir anodinis perėjimo koeficientai $\alpha \approx \beta \approx 0{,}5$, reakcijos greičio konstanta $k_s = (1 \cdot 10^{-6}–10 \cdot 10^{-6})$ cm/s.

Sulfamo ir sulfamo–fluoridiniuose tirpaluose elektrocheminė Sn(II) jonų redukcija vyksta vienodai, todėl ir nusodinamos vienodos kokybės Sn dangos.