

Influence of pH on the cathodic reduction of Sn(II) in sulfamic-fluoride solutions

Arūnas Lukinskas*,

Irena Savickaja,

Jurga Juodkazytė,

Aloyzas Sudavičius

*Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius,
Lithuania*

The influence of pH on cathodic reduction of Sn(II) in sulfamic-fluoride solutions was investigated using electrochemical and XPS techniques. Stable Sn(II) fluoride complexes were found to form in acid solutions with pH 1.0 and 2.5, and the reduction of these compounds was determined by diffusion and kinetic control. The surface of Sn electrode was active in these solutions. An increase in solution pH to 4.0 led to a slow settling of the equilibrium among various electroactive Sn(II) fluoride and hydroxofluoride complexes. An increase in temperature favoured the formation of mixed hydroxofluoride complexes. At pH = 4.0, the surface of Sn electrode interacted with solution components, and a layer of slightly soluble compounds was formed on the electrode surface, thus inhibiting the Sn(II) reduction process. The thickness of the passivating layer can exceed 40 nm, blocking the reduction of Sn(II) completely.

Key words: sulfamic-fluoride solutions, Sn electrode, Sn(II) fluoride complexes, cathodic process, passivation

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 interest shifted to Sn and its alloys. Numerous reports have been published concerning the effect of organic additives on the quality of Sn coatings as well as on the electrochemical process [2–6]. The properties of Sn coatings, such as solderability, depend on the conditions under which Sn coatings have been formed and kept since layers of different compounds can form on the surface. In air or aqueous solutions, tin surface is covered with a passivating layer of oxides and hydroxides, which determines the corrosion resistance of tin. The properties of this surface film depend on the solution pH and its ionic composition. M. Pourbaix [7] in the “tin-water” diagrams has defined three zones with a different electrode surface state. In acid and alkaline solutions tin corrodes, whereas at pH 3.5–9.0 the surface of tin is covered with a layer of slightly soluble oxides or hydroxides. However, if a solution contains ligands that can either form soluble compounds or precipitates with Sn(II) ions, or change the potential, E , of Sn electrode, the equilibrium changes. In Ref. [8], it has been demonstrated that in solutions with pH 4.2 the potential of a tin electrode

is determined by various equilibriums which depend on certain conditions. In oxygen-containing solutions, the potential of Sn electrode is conditioned by an equilibrium between $\text{Sn}(\text{OH})_2$ and $\text{Sn}(\text{OH})_4$, whereas in deaerated solutions $\text{Sn} \leftrightarrow \text{Sn}(\text{OH})_2$ the equilibrium is the potential-determining one. In acid solutions, E of Sn electrode is independent of pH, as it depends on the partial pressure of H_2 which is produced in the process of Sn dissolution.

The influence of passivating layers which form on the surface of Sn electrode becomes particularly evident upon the anodic polarization of the electrode. In the case of slightly acid and neutral solutions, a hindrance of the anodic process, related to the formation of passivating layer, occurs [9–14]. The passivating film is believed to be composed of Sn(II) and Sn(IV) hydroxides [9, 10], oxides [11, 12] or compounds of Sn oxygen species and solution components [13, 14]. Halogenide ions, depending on their concentration, can favor or hinder the passivation of the Sn electrode [14, 15].

The influence of passivating films on the electrochemical processes of various metals has been widely investigated by Prof. R. Višomirskis and co-workers [16].

Changes in the electrode surface state can be accompanied by changes in solution composition. In Sn(II) fluoride solutions, various complex compounds can be formed, depending on the ratio of Sn(II) and fluoride concentrations. According to Refs. [17, 18], only complexes of $[\text{SnF}_n]^{n-2}$ type are formed, where $n = 1-3$. Other authors [13, 14] claim that

* Corresponding author. E-mail: lukinsk@ktl.mii.lt

formation of mixed complexes $[\text{SnF}_3(\text{OH})]^{2-}$ is possible as the pH of the solution increases. Hydrolysis of Sn(II) fluoride complexes can also take place, yielding mixed compounds of Sn(II) and Sn(IV) or slightly soluble Sn_4OF_6 oxycomplexes [20]. An influence of the pH on the composition of depositing Sn(II) citrate complexes has been reported [21]. All the processes taking place in the solution or at the electrode / solution interface can influence the kinetics of electrochemical reactions in Sn(II) fluoride electrolytes.

The aim of the present study was to evaluate the influence of pH on the cathodic process in Sn(II) sulfamic-fluoride electrolytes.

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 the solutions was 1. The concentrate was used for 1–2 days.

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. A tin disk, surface area 1 cm², 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 backside of the electrode. A 15 cm² tin foil was used as a counter electrode. The surface of the electrode was polished, cleaned with a mixture of CaO and MgO, and then thoroughly washed with distilled water and electrolyte. Prior to each measurement, the electrode was kept in solution under open-circuit conditions for 45 s. The duration values indicated in the text should be added to the latter one. The potential of the Sn electrode was measured relative to a saturated AgCl reference electrode. Potentiodynamic voltammograms were generated on a PI-50-1-1 potentiostat (Belarus), using a PR-8 programmer (Belarus), and recorded with a H-307/1 xy-recorder (Russia). All potentials reported in this paper are given with respect to a normal hydrogen electrode.

Measurements taken under forced convection conditions were conducted using the rotating disc electrode technique. The rotating disc electrode was made of a tin cylinder pressed into a fluoroplastic frame. The area of the working electrode was 1 cm². The rotation rate was measured with a Ch3-33 frequency meter (Russia). The change of the potential in time was investigated by galvanostatically switching the current on. The current source was UIP-1 (Russia) with a sequentially connected resistance of 5 kΩ. Chronopotenti-

ograms were recorded with a H-307/1 xy-recorder and a C8-13 (Russia) oscillograph.

The composition of the surface compounds was investigated by XPS and Auger spectroscopies. The spectra were recorded with 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 analyser 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 account empirical sensitivity factors for each element [22]. The spectra recorded were compared to the standard spectra [23]. 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.

The pH-metric titration was performed as follows: 1 ml of electrolyte was diluted to a total volume of 10 ml and titrated with the solution of 0.1 M KOH + 0.1 M KSO₃NH₂.

RESULTS AND DISCUSSION

In an acidic medium up to pH 2, solutions of tin(II) salts are stable. As the pH increases, hydrolysis of tin salts begins and insoluble precipitates of SnO and Sn(OH)₂ are formed. Therefore, sulfamic-fluoride solutions in which stable Sn complexes form [24] were chosen for investigating the influence of pH on the tin deposition process. The measurements were performed in solutions with pH 1.0, 2.5 and 4.0. As it has already been mentioned, the solution pH can influence the state of Sn electrode surface due to the formation of a layer of slightly soluble compounds and changes in the composition of Sn(II) fluoride complexes.

INFLUENCE OF pH ON THE STATE OF Sn ELECTRODE SURFACE

When KF is added to the acid (pH 1.0) solution of tin sulfamate, the potential of the Sn electrode shifts towards more negative values, but the shape of voltammograms remains unchanged (Fig. 1). Partial complexing of Sn(II) ions does not produce any additional current waves in the voltammograms. This means that the Sn(II) fluoride complex is labile, and the discharge of complex ions does not require significant additional energy. Only at the KF concentration 0.5–1.0 M the limiting current i_{lim} decreases by ~10%. The transition time can be easily evaluated by means of galvanostatic switching. The product $i\sqrt{\tau}$ is constant, but it decreases with increasing the KF concentration (Fig. 2). This is most likely related to kinetic limitations occurring during the discharge of tin complexes.

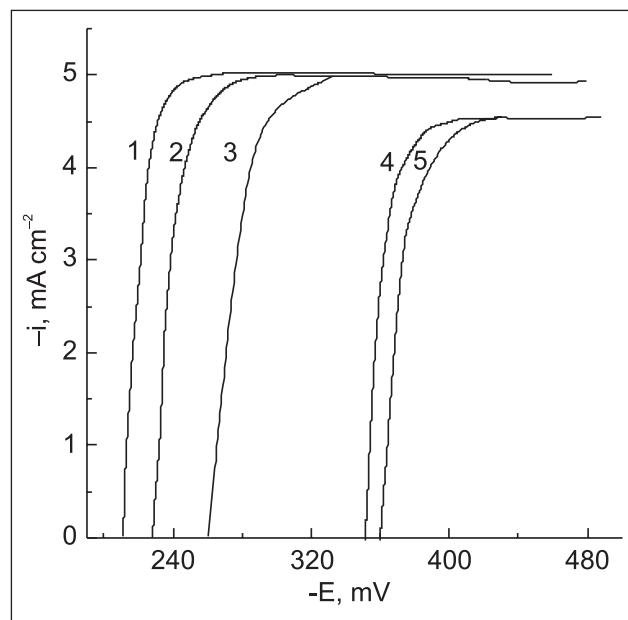


Fig. 1. Voltammograms of tin electrode in 0.05 M solution of $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.5 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KSO}_3\text{NH}_2$. Dependence on KF concentration (M): 1 - 0.0, 2 - 0.01, 3 - 0.1, 4 - 0.5, 5 - 1.0; $v = 1 \text{ mV s}^{-1}$, pH 1.0, $20 \text{ }^\circ\text{C}$

In the case of a rotating disc electrode, the rate of the cathodic process increases with increasing the rotation rate w (Fig. 3). The \sqrt{w} -dependence of i_{lim} is linear. The value of i_{lim} was evaluated at an overvoltage of 100 mV. As the concentration of KF increased, the rate of the cathodic process decreased.

An increase in the potential sweep rate leads to an increase in the cathodic limiting current (Fig. 4), but the linear dependence $i_{max} - \sqrt{v}$ is observed only in the range of lower v values. An increase in KF concentration results in a decrease of i_{max} . If the electrode is kept under open-circuit conditions in oxygen-containing solution for 1 hour, i_{max} increases by $\sim 5\%$. However, if after such treatment of the electrode the solution is mixed prior to measurements, no increase in the limiting current is observed. This means that the increase in i_{max} is the result of tin corrosion, which leads to an increase in the concentration of Sn ions at the electrode / solution interface. The linear dependence $i_{max} - \sqrt{v}$ at low w values and low potential sweep rates indicates that the cathodic process is diffusion-limited. The calculated value of the diffusion coefficient of Sn(II) ions ($6.0 \times 10^{-6} \text{ cm}^2/\text{s}$) is close to those determined in Sn(II) solutions in the absence of F^- ions. At higher w values and higher potential sweep rates, the calculated values of the diffusion coefficients decrease about 10-fold, suggesting that under these conditions either the cathodic process is influenced by kinetic limitations or a passivating surface layer is formed.

XPS analysis of a tin electrode surface kept in the solution for 1 hour has shown that the surface is oxidized and its uppermost layer contains a small amount (up to $\sim 2 \text{ at. } \%$) of

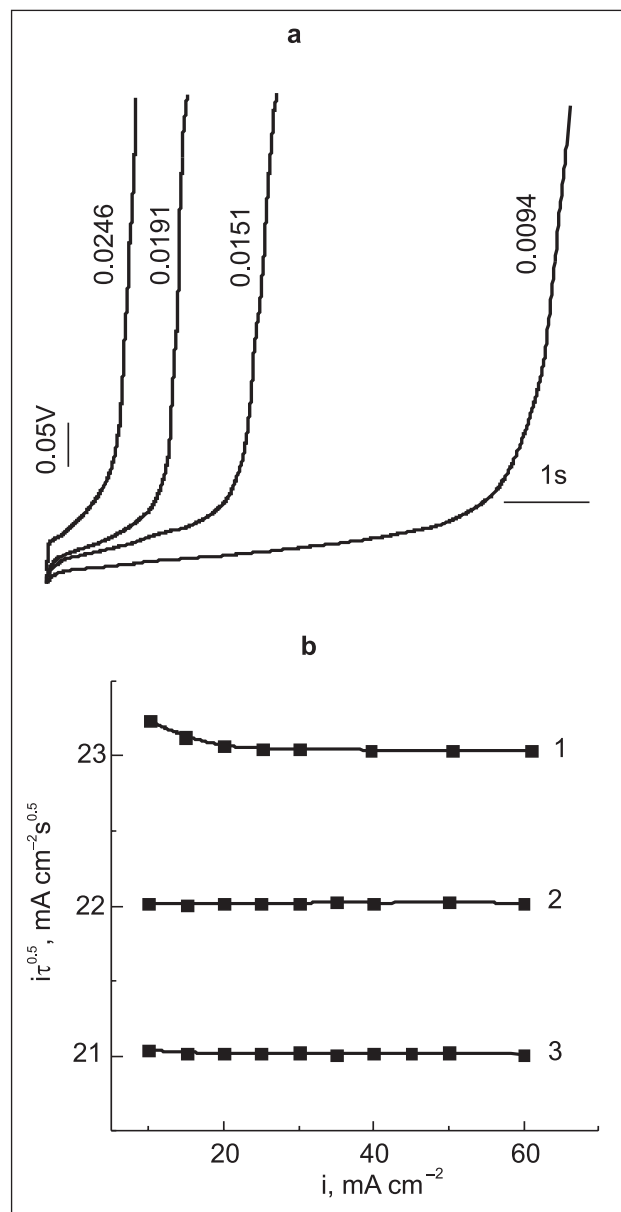


Fig. 2. a) Galvanostatic switching curves of Sn electrode in 0.05 M $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.5 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KF}$ solution. Current density values are indicated at the curves; b) current density dependence of $i\sqrt{\tau}$ at various KF concentrations (M): 1 - 0.0, 2 - 0.1, 3 - 0.5; pH 1.0, $20 \text{ }^\circ\text{C}$

compounds with F^- ions (Fig. 5a). After removal of a $\sim 0.6 \text{ nm}$ thick surface layer by means of argon etching, no fluorides are found. The amount of oxygen in the surface decreases with increasing the etching depth, and at a depth of about 2 nm only pure tin is found. Analogous surface oxide layers were found on a freshly prepared surface of a tin electrode which had been kept for one hour in a solution free of F^- ions. This means that a tin oxide layer forms on the electrode surface in the course of the electrode washing and preparation for analysis. These findings confirm the conclusion that in acid solutions a tin electrode surface is active and free of passivating surface layers, thus it cannot influence the rate of the cathodic process at higher values of w and v .

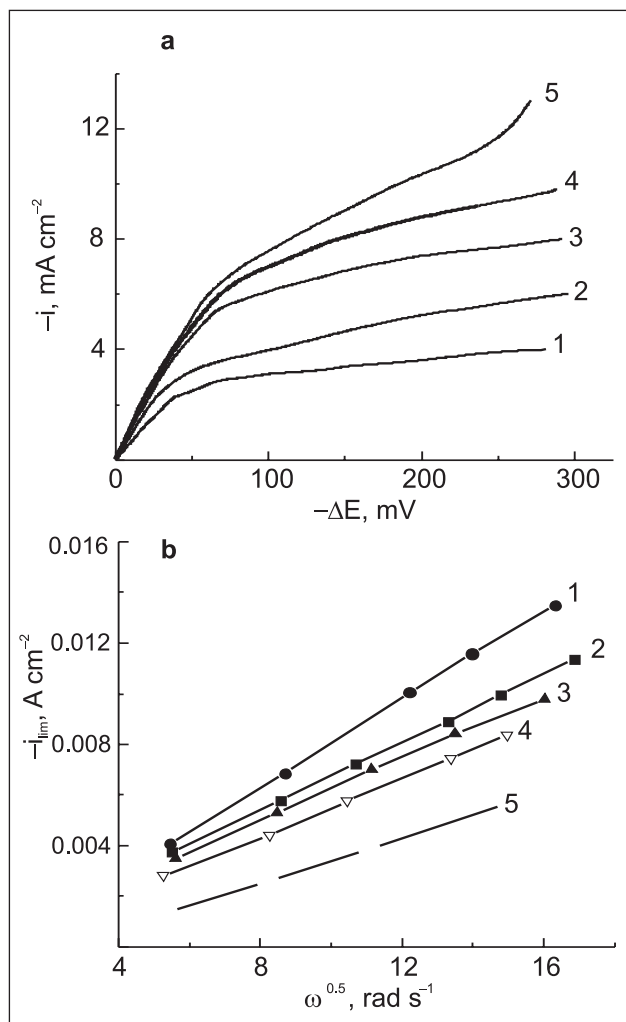


Fig. 3. a) Voltammograms of tin electrode in 0.01 M solution of $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.5 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KSO}_3\text{NH}_2 + 0.01 \text{ M KF}$, dependence on rotation rate w (rad s^{-1}): 1 – 31, 2 – 66, 3 – 120, 4 – 226, 5 – 249; b) w -dependence of limiting current at various KF concentrations (M): 1 – 0.0, 2 – 0.001, 3 – 0.002, 4 – 0.01, 5 – 0.15; pH 1.0, 20 °C

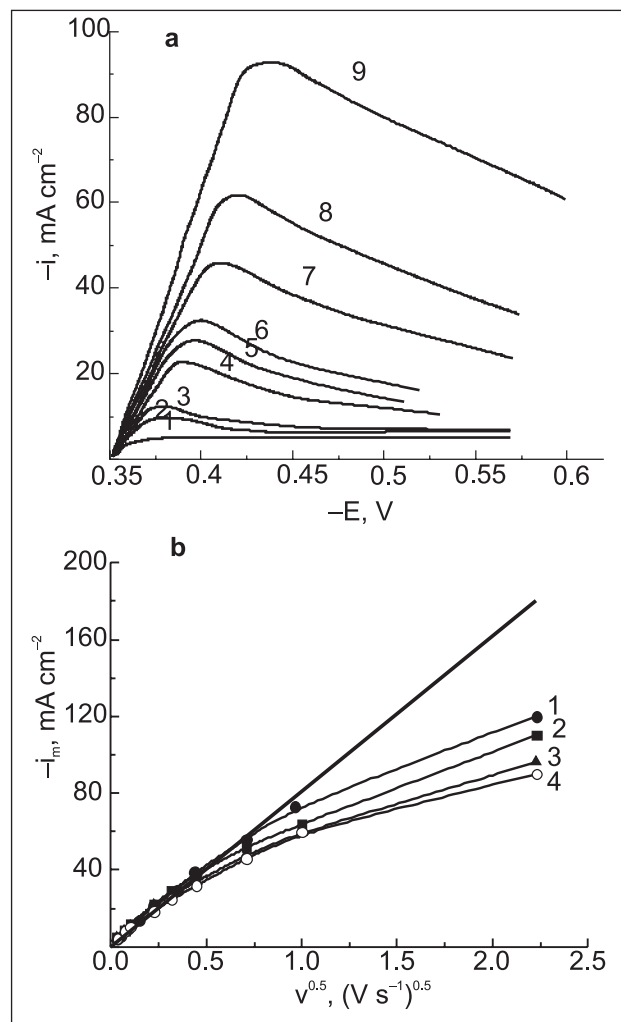


Fig. 4. a) Voltammograms of tin electrode in 0.05 M $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.5 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KSO}_3\text{NH}_2 + 0.5 \text{ M KF}$ recorded at different potential scan rates v (V s^{-1}): 1 – 0.001, 2 – 0.005, 3 – 0.01, 4 – 0.05, 5 – 0.1, 6 – 0.2, 7 – 0.5, 8 – 1.0, 9 – 5.0; b) v -dependence of peak current at various KF concentrations (M): 1 – 0.0, 2 – 0.1, 3 – 0.5, 4 – 1.0; pH 1.0, 20 °C

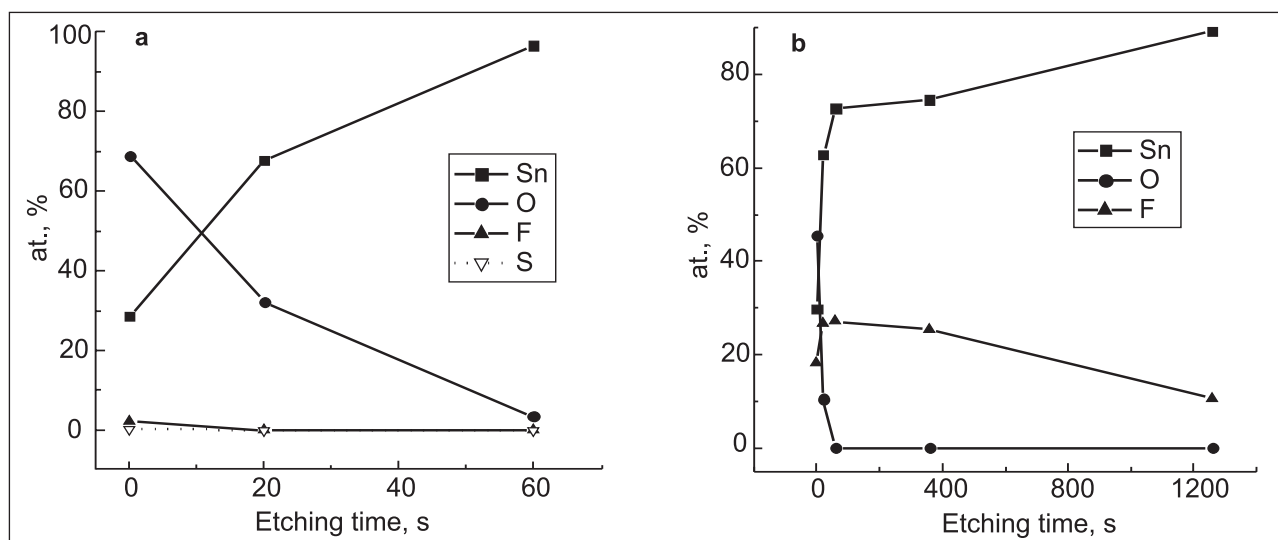


Fig. 5. Distribution of elements on tin electrode surface, kept for 1 hour in 0.05 M solutions of $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + \text{HSO}_3\text{NH}_2 + \text{KSO}_3\text{NH}_2 + 1.0 \text{ M KF}$ with pH 1.0 (a) and 4.0 (b); 20 °C. Argon etching rate 2 nm min^{-1}

Voltammetric measurements in solutions with pH 2.5 have shown that the rate of the cathodic process is almost the same as in solution with pH 1.0, however, the influence of F^- concentration is much greater than in the previous case. As one can see from the data presented in Fig. 6, an increase of F^- concentration up to 1 M leads to the disappearance of the current peak, whereas the dependence $i_{\max} - \sqrt{v}$ remains linear only in the range of lower v values. Chronopotentiograms recorded in the solutions with a lower fluoride concentration reveal a clearly pronounced transition time τ . An increase in fluoride concentration changes the character of chronopotentiograms. The initial potential leap increases, whereas τ becomes hardly discernable (Fig. 7). The dependence $i\sqrt{\tau} - i$ is linear only at lower concentrations of F^- ions. Keeping the electrode in the solution under open-circuit conditions for up to 1 h has almost no influence on

the cathodic process. These results suggest that in a solution with pH 2.5 the surface of the Sn electrode remains active like in a strongly acidic medium, whereas the rate of the cathodic process is determined mainly by kinetic limitations.

In a solution with pH 4.0, the situation is different. As one can see from Fig. 8, the longer the electrode is kept in the solution under open-circuit conditions, the lower is the cathodic current peak in the voltammograms. Eventually, this peak disappears and the character of the voltammograms changes. When the electrode is kept under open-circuit conditions for 10 min, a second cathodic current peak appears in the curves and eventually becomes larger than the first one. Stirring of the electrolyte prior to measurements has no influence on the phenomena described above. The possible explanation is that the active surface area of Sn electrode decreases due to formation of surface layers which hinder the cathodic process.

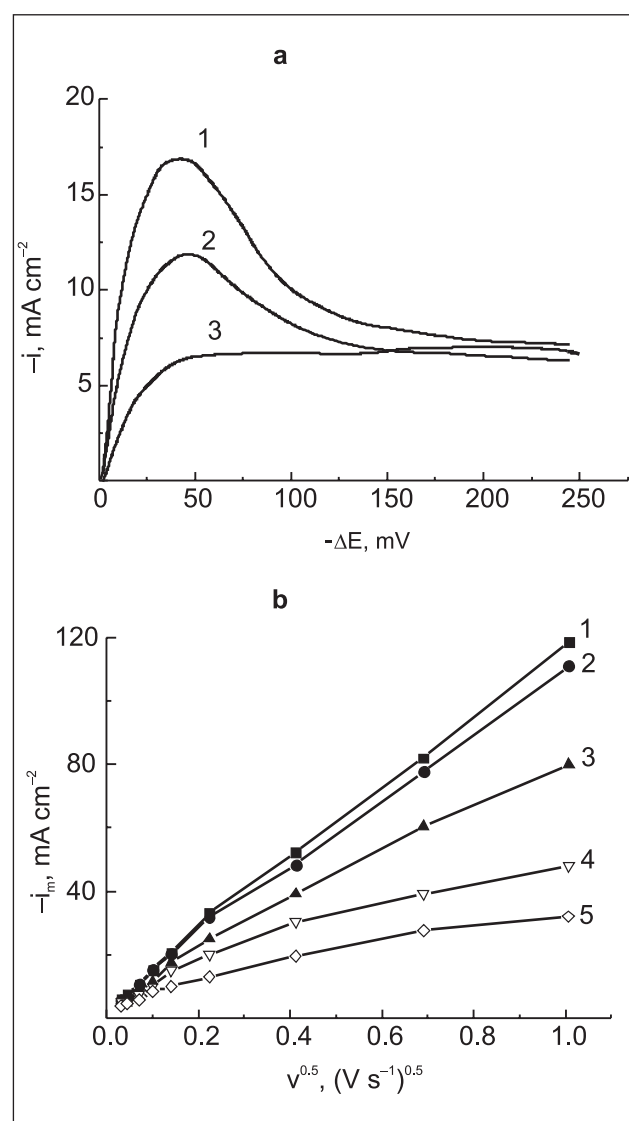


Fig. 6. a) Voltammograms of tin electrode in 0.05 M $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.3 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KSO}_3\text{NH}_2 + \text{KF}$; dependence on KF concentration (M): 1 – 0.15, 2 – 0.3, 3 – 1.0; $v = 20 \text{ mV s}^{-1}$; b) dependence of current peak on potential scan rate at KF concentration (M): 1 – 0.005, 2 – 0.015, 3 – 0.3, 4 – 0.5, 5 – 1.0; pH 2.5, 20 °C

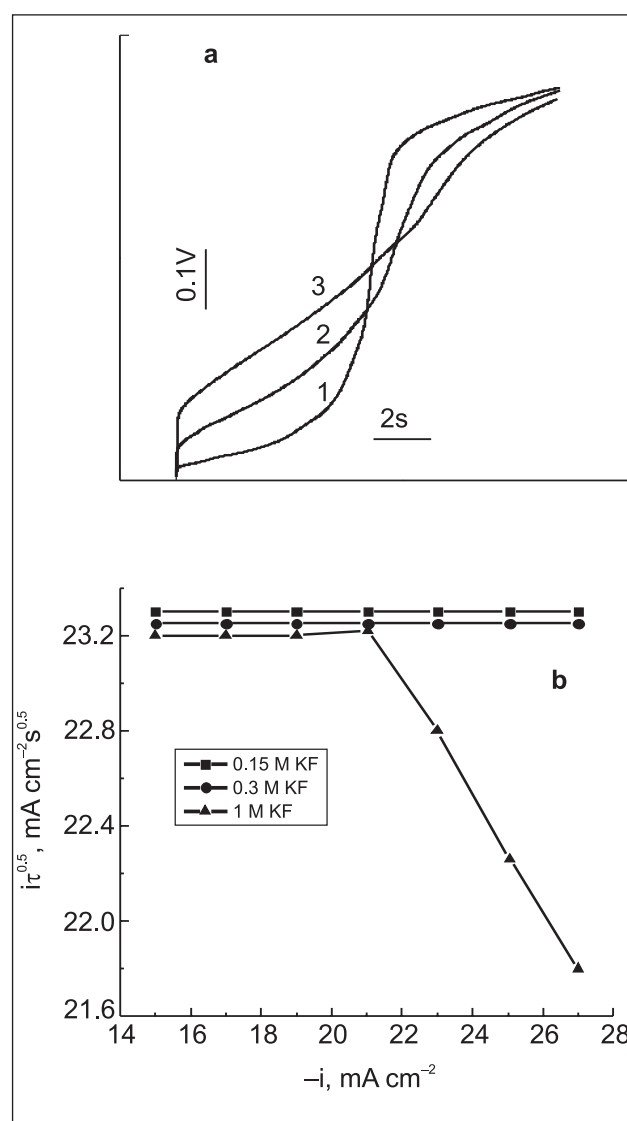


Fig. 7. a) Galvanostatic switching curves of Sn electrode in 0.05 M $\text{Sn}(\text{SO}_3\text{NH}_2)_2 + 0.3 \text{ M HSO}_3\text{NH}_2 + 0.1 \text{ M KSO}_3\text{NH}_2$ solution with various KF concentrations (M): 1 – 0.15, 2 – 0.3, 3 – 1, $l = 0.00965 \text{ A cm}^{-2}$; b) current density dependence of $i\sqrt{\tau}$ in the same solutions; pH 2.5, 20 °C

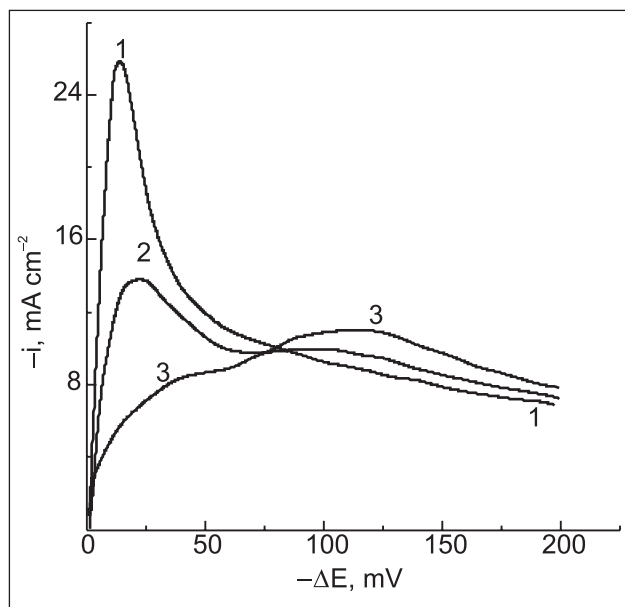


Fig. 8. Voltammograms of tin electrode in $0.05 \text{ M Sn(SO}_3\text{NH}_2)_2 + 0.1 \text{ M HSO}_3\text{NH}_2 + 0.5 \text{ M KSO}_3\text{NH}_2 + 0.5 \text{ M KF}$, dependence on duration of electrode aging in solution (min): 1 – 1.0, 2 – 5.0, 3 – 10; pH 4.0, 20°C

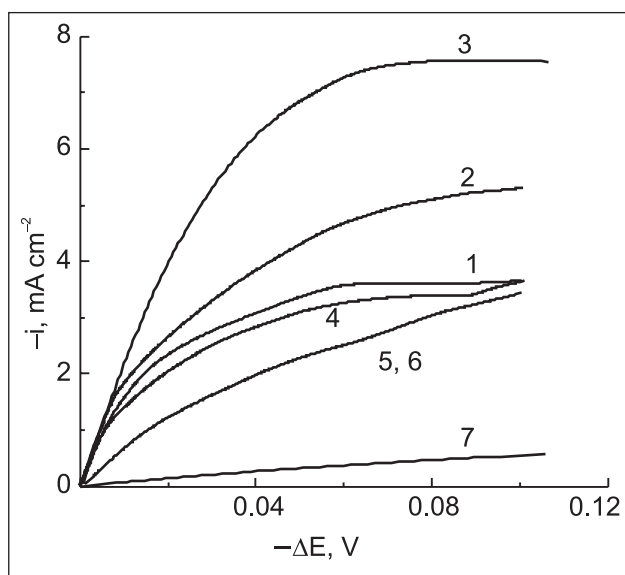


Fig. 9. Voltammograms of tin electrode in $0.05 \text{ M Sn(SO}_3\text{NH}_2)_2 + 0.1 \text{ M HSO}_3\text{NH}_2 + 0.5 \text{ M KSO}_3\text{NH}_2 + 0.5 \text{ M KF}$, dependence on temperature and duration of electrode aging in solution: 1, 6 – 20°C , 2 – 40°C , 3 – 60°C ; 1–3 – freshly prepared electrode, 4 – aging duration 0.5 h, 5 – aging duration 1.0 h, 6 – aging duration 24 h; pH 4.0, 20°C

The temperature-dependence of the cathodic process rate has confirmed the above assumption. One can see from Fig. 9 that an increase in temperature accelerates the cathodic process. However, if the electrode is kept under open-circuit conditions for 30 min, the rate of the cathodic process decreases significantly. When the electrode is kept under open-circuit conditions for 24 hours, the dependence $i-E$ has an ohmic character, whereas the electrochemical process is no longer

observed. Even the cathodic polarization of the electrode for 20 min at an overvoltage of 75 mV does not result in acceleration of the cathodic process. The surface of the Sn electrode is most likely covered with a passivating layer of insoluble compounds, which blocks the cathodic reduction of the Sn fluoride complex.

Chronopotentiograms recorded in the solution with pH 4.0 reveal a sudden initial potential leap which is not typical of diffusion-limited processes. The reproducibility of the transition time τ deteriorates. When the solution temperature is increased up to 60°C , τ becomes hardly definable, whereas its reproducibility becomes even worse. After keeping the electrode in the solution for 1 hour, τ cannot be defined at all.

The surface analysis of a Sn electrode kept for 1 hour in the solution of $0.05 \text{ M Sn(SO}_3\text{NH}_2)_2 + 0.1 \text{ M HSO}_3\text{NH}_2 + 0.5 \text{ M KSO}_3\text{NH}_2 + 1.0 \text{ M KF}$, pH 4.0, has shown that the electrode is covered with a thick layer of surface compounds containing Sn, F and O. The amount of oxygen in the surface layer decreases as the electrode is etched with Ar^+ ions, and after 60 s of argon etching only traces of O are found (Fig. 5b), whereas the amount of F starts to decrease at a significant rate only after more than 400 s of argon etching. Pure Sn is found only at a depth exceeding 40 nm. Analogous results have been obtained for an Sn coating deposited from such solution with pH 4.0.

The XPS results confirm and complement the conclusions drawn on the basis of electrochemical data that the surface state of Sn electrode in sulfamic-fluoride solution depends on the solution pH. As the pH increases up to 4.0, a film of insoluble compounds is formed on the Sn electrode surface, hindering or even blocking the cathodic process of Sn(II) reduction.

INFLUENCE OF pH ON THE COMPOSITION OF FLUORIDE COMPLEXES

In acid sulfamic-fluoride solutions, SnF^+ , SnF_2 or SnF_3^- complexes are formed depending on the ratio of F^- and Sn(II) concentrations. When this ratio is higher than 3.5, SnF_3^- complexes prevail in the solution [24]. Voltammetric measurements have shown that the same results are obtained irrespective of whether the solution is freshly prepared, aged for 24 hours or heated up to 65°C . This means that the composition of complexes in an acidic medium is stable.

As one can see in Fig. 10, in the case of solutions with pH 4.0, voltammetric results depend on the conditions of solution preparation, i. e. aging duration and temperature. Voltammograms recorded in a freshly prepared solution reveal one distinct current peak and a second one, considerably smaller. The latter becomes more distinct at higher potential scan rates. After heating the solution for 30 min at 65°C and cooling, the first peak decreases, whereas the second one increases. At a potential scan rate of 0.5 V/s , the second peak becomes larger than the first one. Voltammograms recorded

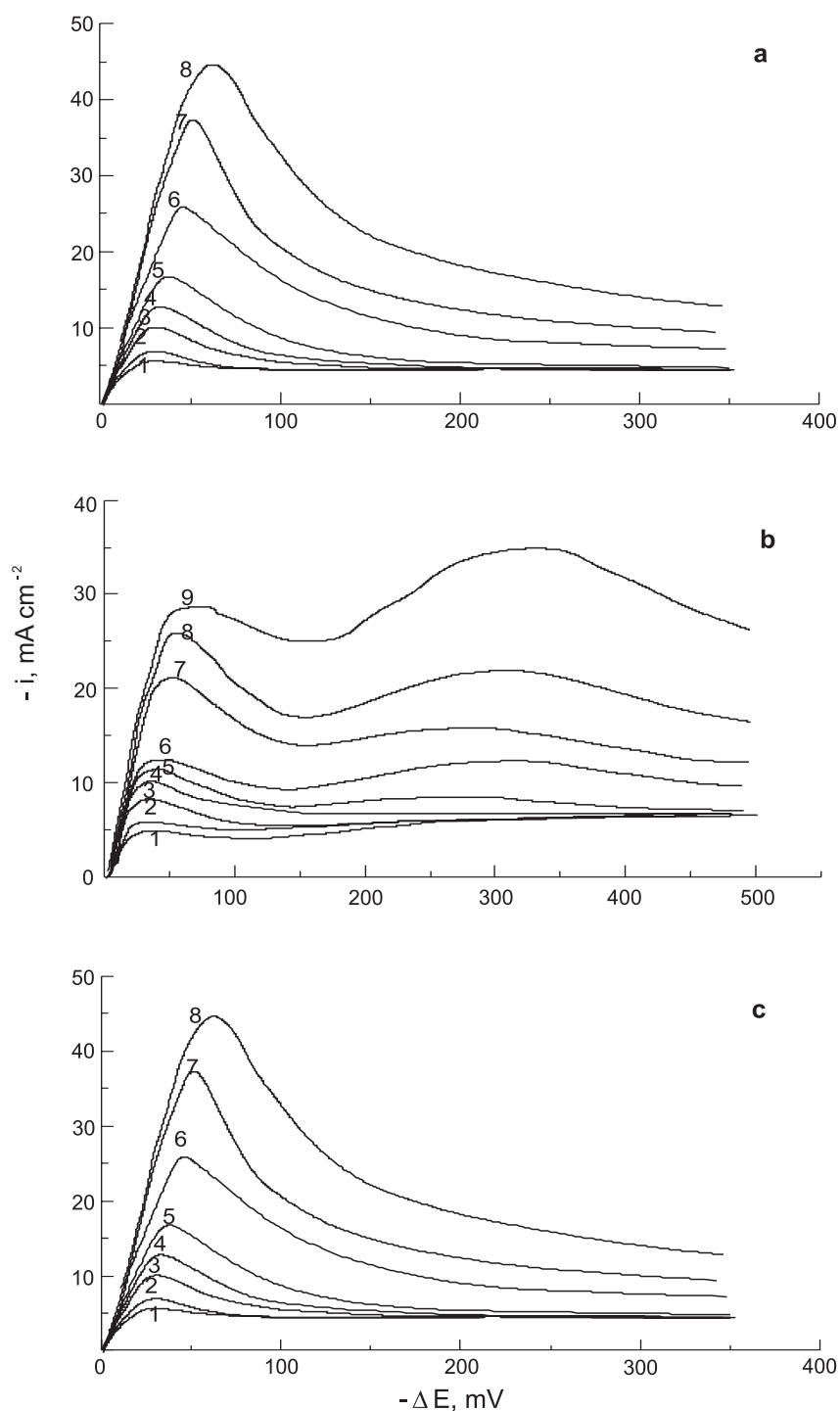


Fig. 10. Voltammograms of tin electrode in $0.05 \text{ M Sn(SO}_3\text{NH}_2)_2 + 0.1 \text{ M HSO}_3\text{NH}_2 + 0.5 \text{ M KSO}_3\text{NH}_2 + 0.5 \text{ M KF}$ recorded at different potential scan rates v (V s^{-1}): 1 – 0.001, 2 – 0.002, 3 – 0.005, 4 – 0.01, 5 – 0.02, 6 – 0.05, 7 – 0.1, 8 – 0.2, 9 – 0.5; in freshly prepared electrolyte (a); electrolyte heated for 30 min at 65°C and cooled (b), and electrolyte aged for 24 h (c); pH 4.0, 20°C

in the case of solution aged for 24 hours exhibit only one current peak. Analysis of the solution composition did not reveal any increase in Sn(IV) concentration. These findings suggest that in solutions with pH 4.0 a slow formation of a complex of different composition takes place. According to the literature [13, 14], formation of Sn(OH)F_2^- or Sn(OH)F_3^{2-}

is possible. Titration of the solution with pH 1.0 with $0.1 \text{ M KOH} + 0.1 \text{ M KSO}_3\text{NH}_2$ has shown that titration of sulfamic acid together with Sn(II) ions takes place, yielding Sn(OH)_2 precipitate (Fig. 11). Addition of KF into solution results in an additional wave, however, acid is titrated together with Sn(II) ions. If the solution is alkalinized to pH 4.0

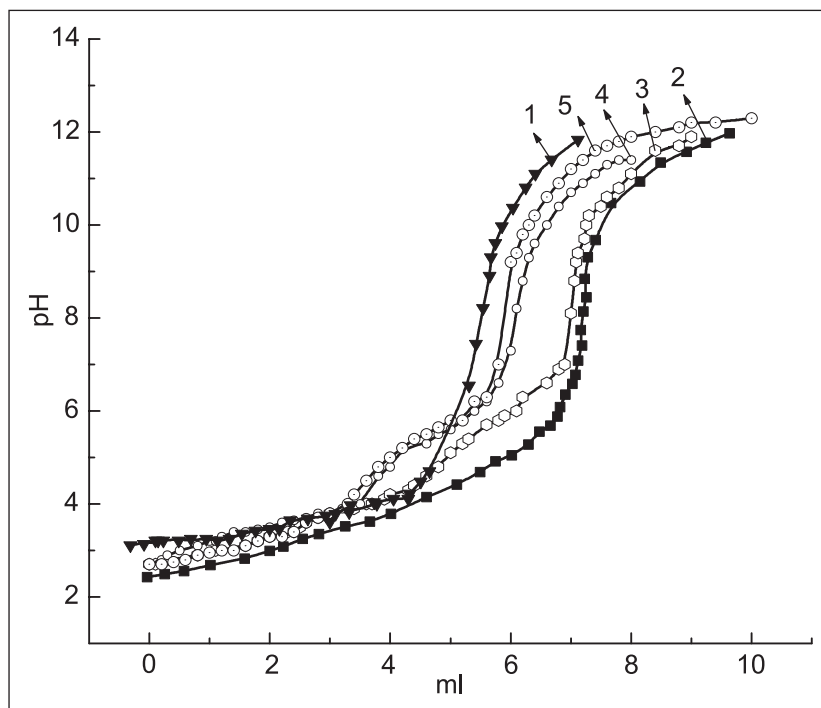


Fig. 11. Titration curves: 1 – 0.5 M HSO_3NH_2 + 0.1 M KSO_3NH_2 ; 2 – 1 + 0.5 M KF; 3–5 – 2 + 0.05 M $\text{Sn}(\text{SO}_3\text{NH}_2)_2$; titrant 0.1 M KOH + 0.1 M KSO_3NH_2 ; 3 – freshly prepared electrolyte, 4 – electrolyte with pH 4.0 heated for 30 min at 65 °C and cooled, 5 – electrolyte with pH 4.0 aged for 24 h; 20 °C

and kept for 24 hours or heated for 30 min at 65 °C, this additional wave becomes more pronounced, and only about half of Sn(II) ions are titrated. This means that one OH^- ion is consumed per one Sn(II) ion. Only a small amount of white precipitate is formed in the solution. We suggest that change in the dominating complex composition occurs in aged or heated solutions, resulting in the formation of $\text{Sn}(\text{OH})\text{F}_2^-$ or $\text{Sn}(\text{OH})\text{F}_3^{2-}$ complexes. This process most likely proceeds slowly till an equilibrium between various complexes in the solution is reached. Formation of various Sn(II) fluoride and hydroxofluoride complexes and their reduction processes are reflected in the voltammograms.

CONCLUSIONS

In acid sulfamic-fluoride solutions (pH 1.0–2.5) the tin electrode is active. The rate of the cathodic Sn(II) reduction process is determined mainly by diffusion phenomena. Increasing the KF concentration leads to an increased kinetic control of the cathodic process rate. When the solution is alkalized to pH 4.0, the interaction between electrode surface and solution components leads to the formation of a film of insoluble compounds on the tin surface. This surface film, containing Sn, O and F, hinders the discharge of Sn(II) ions. When the thickness of the passivating film reaches 40 nm, the reduction of Sn(II) ions is completely blocked. In the solution bulk, at pH 4.0, a slow equilibration among various complexes takes place, resulting in formation of hydroxofluoride complexes. This process is accelerated by temperature.

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Arūnas Lukinskas, Irena Savickaja, Jurga Juodkazytė,
Aloyzas Sudavičius

ELEKTROLITO pH ĮTAKA KATODINIAM PROCESUI Sn(II) SULFAMO-FLUORIDINIULOSE TIRPALULOSE

Santrauka

Elektrocheminiais ir rentgeno fotoelektronų spektroskopijos (RFS) metodais tirta Sn(II) sulfamo-fluoridinių tirpalų pH įtaka katodiniam procesui. Nustatyta, kad rūgščiuosiuose tirpaluose (pH 1,0 ir 2,5) susidaro stabilūs Sn(II) fluoridiniai kompleksai, kurių išsikrovimo procesą sąlygoja difuziniai bei kinetiniai reiškiniai. Sn elektrodo paviršius šiuose tirpaluose yra aktyvus. Pašarminus tirpalą iki pH 4,0 lėtai pasiekama pusiausvyra tarp įvairių elektroaktyvių Sn(II) fluoridinių ir hidroksfluoridinių kompleksų. Temperatūros didinimas skatina hidroksfluoridinių kompleksų susidarymą. Esant tirpalo pH 4,0, Sn elektrodo paviršius sąveikauja su tirpalo komponentais ir ant jo susidaro mažai tirpių junginių sluoksniai, kurie apsunkina Sn(II) redukcijos procesą. Tokios paviršinės plėvelės storis gali būti didesnis nei 40 nm ir visiškai stabdyti Sn(II) jonų redukcijos procesą.