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SYNTHESIS, CORROSION AND ELECTROCATALYTIC PROPERTIES OF TIN-COBALT ALLOY COATINGS.

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Tin-cobalt alloy coatings with a tin content of 5–85 wt.% were synthesized from a polyligand citrate-chloride electrolyte. The surface morphology and composition of tin-cobalt alloy coatings depending on the conditions of their production were studied using EDS and XRD methods. The dynamics of changes in the parameters of the equivalent impedance circuit on tin-cobalt alloy coatings in 0.1 $mol·l^{-1}$ KOH solution is determined by the process of formation of a cobalt (II) hydroxide layer on the coating surface. The parameters of corrosion resistance and electrocatalytic activity of the coatings in the reaction of hydrogen evolution were calculated from the stationary voltammetry dependences. The corrosion currents on tin-cobalt alloy coatings with a tin content of 33–85 wt.% are about 10^{-6}–10^{-8} $A·cm^{-2}$. An inverse dependence of the hydrogen evolution overvoltage on tin-cobalt alloy coatings on the corrosion current was established.

Key words: electrodeposition, tin-cobalt alloy, citrate-chloride electrolyte, corrosion resistance, electrocatalytic activity.

INTRODUCTION. Electrolytic coatings of tin-cobalt alloy are promising anode materials for lithium-ion batteries (LIB) due to their high specific capacity and stability during cycling [1–3]. Cobalt serves as a kind of buffer, contributing to an increase in the mechanical strength of tin during cycling in LIB. In addition, tin-based alloy coatings are currently being studied as electrocatalysts for reactions of hydrogen ion [4–7] and nitrate ion [8, 9] reduction, oxygen evolution [7], and selective reduction of carbon dioxide to formate ions [10, 11].

One of the most effective and controlled methods of applying coatings with metals and alloys, allowing to influence their morphology, structure and functional properties, is electrolytic deposition from aqueous solutions of complex compounds. Correctly selected ligands allow to influence purposefully the inhibition of the electrode process, the composition of electrochemically active complexes

(EAC), the mechanism of the process, and, consequently, the morphology, structure and functional properties of the resulting coatings with metals and alloys [12–14].

For deposition of tin-cobalt alloy coatings, we selected a polyligand citrate-chloride electrolyte, in which the formation of electrochemically active complexes (EAC) and deposition of tin (II) into the alloy is limited by the dissociation of electrochemically inactive complexes (EIC) $[SncitCl_2]^{3-}$, and this allows us to control the chemical composition of the alloy by selecting the ratio of the electrolyte components and the deposition conditions. In a polyligand citrate-chloride electrolyte at pH 4-6, tin (II) ions, in contrast to the citrate electrolyte, exist in the form of the EIC of the composition $[SncitCl_2]^{3-}$ [15], while cobalt (II) ions exist in the form of the EAC of the composition $[CoH_2cit]^+$ and [CoHcit] [14]. Precipitation of tin (II) and cobalt (II) ions from the monoligand citrate electrolyte in this pH region is limited by mixed kinetics [16]. The precipitation of tin(II) ions into a tin-cobalt alloy from a polyligand citrate-chloride electrolyte at pH 4-6, in contrast to a citrate electrolyte, is limited not by mixed kinetics, but by a preceding chemical reaction of dissociation of polyligand electrochemically inactive complexes $[SncitCl_2]^{3-}$:

$$[SncitCl_2]^{3-} \leftrightarrow [Sncit]^- + 2Cl^-. \qquad (1)$$

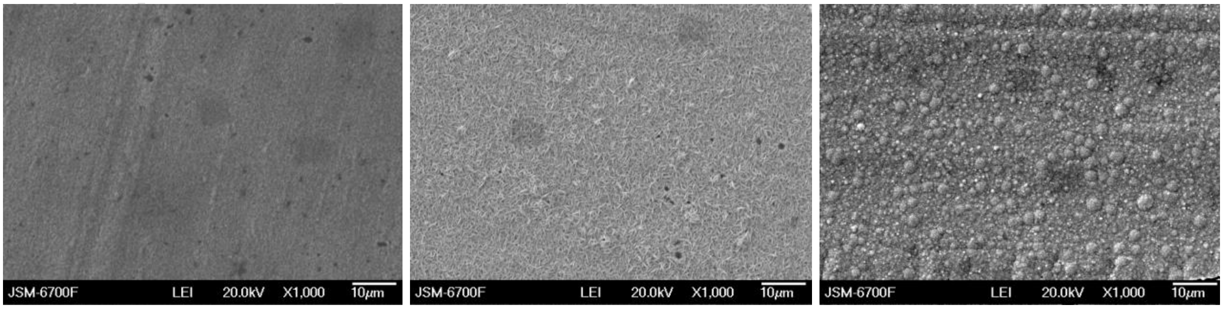
The presence of electrochemically inactive $[SncitCl_2]^{3-}$ complexes in the citrate-chloride electrolyte is an additional factor that allows us to influence the composition, morphology, structure and functional properties of the resulting tin-cobalt alloy coatings, primarily their porosity and corrosion resistance. The presence of citric acid in the proposed citrate-chloride electrolyte allows increasing the buffer capacity and stability of the electrolyte during its long-term operation. This work is devoted to the development of a process for applying functional tin-cobalt alloy coatings from a complex citrate-chloride electrolyte for various functional purposes, as well as studying their morphology, phase, chemical composition, corrosion resistance and electrocatalytic activity in the reaction of hydrogen evolution in an alkaline medium.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Tin-cobalt alloy coatings were applied to copper foil (S = 2 cm^2) from a citrate-chloride electrolyte of the following composition, mol·l^{-1}: $SnCl_2·2H_2O$ – 0.05; $CoSO_4·7H_2O$ – 0.10; $Na_3C_6H_5O_7$ – 0.30; $C_6H_8O_7·H_2O$ – 0.05; $Na_2SO_4·10H_2O$ – 0.50; pH 4.6 in a thermostatic cell at a direct current density of 1-30 mA·cm^{-2} and a temperature of 40 ^{0}C. A platinum plate (S = 12 cm^2) was used as the anode. Analytical grade reagents were used to prepare the electrolyte. The surface of the copper substrate was pre-degreased with Vienna lime and activated according to the method [17]. The electrolysis parameters were set using a PI-50-1 potentiostat and a PR-8 programmer. To obtain good quality coatings, the citrate-chloride electrolyte was pre-treated at a current density 0.5 mA·cm^{-2} for 4 hours.

The structural characteristics of the coatings were studied by X-ray phase analysis using a DRON-2UM setup with CuKα radiation in the angle range from 10 to 85 degrees with a recording step of 0.04 degrees at an exposure time of 3 sec. The chemical composition of the tin-cobalt alloy coatings was determined using the atomic absorption method. The corrosion properties of the tin-cobalt alloy coatings were studied in a 0.1 mol·l^{-1} KOH solution at 20 ^{0}C.

The electrochemical impedance spectra and current-voltage dependencies were obtained using the AUTOLAB system with GPES4.7 software in the frequency range from 0.1 Hz to 100 kHz and voltage amplitude of 10 mV. A saturated silver chloride electrode was used as a reference electrode. Platinum served as an auxiliary electrode. The value of the active resistance of the coatings R_z was calculated using the built-in program "Find circle". The parameters of the electrocatalytic activity of tin-cobalt alloy coatings in the of hydrogen evolution reaction were calculated from the linear sections of the lg $j - \eta$ dependences. The polarization value was calculated relative to the hydrogen electrode based on the potential of the $2H^+/H_2$ pair, which in a 0.1 mol·l^{-1} KOH solution is 0.75 V (pH = 12.7).

Micrographs of the surface of tin-cobalt alloy coatings obtained from a citrate-chloride electrolyte are shown in Fig. 1. At a current density of up to 3.0 mA·cm^{-2}, as can be seen from Fig. 1a, fine-crystalline coatings are deposited that are well bonded to the substrate. The tin-cobalt alloys coatings are well formed, densely packed, fairly uniform, and are close in appearance to smooth coatings. With an increase in current density, a scaly structure of the deposit is observed, and at higher current densities (from 20 mA·cm^{-2} and higher), crystalline coatings are deposited, consisting of spherulites with particle sizes 1–5 μm.



a b c

Fig. 1. Microstructure of the surface of tin-cobalt alloy coatings obtained from citrate-chloride electrolyte at a current density, mA·cm^{-2}: 3.0 (a); 12.0 (b); 30.0 (c), temperature of 40 ^{0}C, stirring speed of 400 rpm, electrolysis time of 20 min.

The tin content in tin-cobalt alloy coatings obtained from citrate-chloride electrolyte depends on the parameters of their deposition and varies in the range of 5–85%. The X-ray diffraction pattern of the tin-cobalt alloy coating (Fig. 2) contains several diffraction peaks. It should be noted that the number of peaks and their position in the X-ray diffraction pattern does not depend on the conditions of coating production. Electrolysis parameters affect only the magnitude of the diffraction peaks and the properties of the resulting coatings. Peaks characteristic of the tin-cobalt alloy are observed at 2θ deviation angles of 32 and 45 degrees. These peaks indicate the presence of an amorphous or incompletely formed crystalline phase in the tin-cobalt alloy and do not allow one to determine a specific phase. In addition to the peaks corresponding to the tin-cobalt alloy, there are peaks that, by their position, can be attributed to metallic tin. The presence of a peak corresponding to metallic copper is due to its use as a substrate when applying coatings with a tin-cobalt alloy from a citrate-chloride electrolyte.

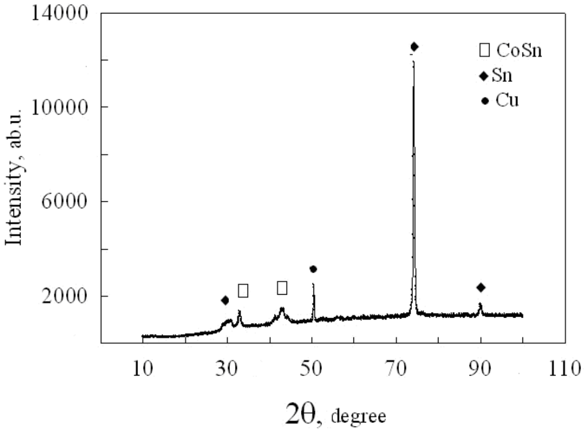


Fig. 2. X-ray diffraction pattern of a tin-cobalt alloy coating obtained from a citrate-chloride electrolyte at a current density of 4.0 mA cm^{-2}, 40 ^{0}C and an electrolysis duration of 60 min.

According to the phase diagram [18, 19], tin forms intermetallic compounds with cobalt of the following composition: CoSn, Co_2Sn and Co_3Sn_2. The Co_3Sn_2 compound consists of two phases Co_2Sn + α-CoSn or Co_2Sn + β-CoSn. It should be noted that tin-cobalt alloy coatings, which are a single-phase intermetallic compound of the CoSn composition, can only be obtained by the electrolytic method from complex electrolytes. According to the results of chemical analysis of the obtained coatings, with an increase in the current density, the ratio of cobalt to tin in the alloy changes from 1:2 to 2:1, which may indicate a change in the composition of the intermetallic compounds of the alloy from $CoSn_2$ to CoSn, Co_3Sn_2 and further to Co_2Sn, which is consistent with the data of [2, 20]. The impedance spectra of tin-cobalt alloy coatings with a content of 66.7 at. % tin, obtained from a citrate-chloride electrolyte at a current density of 3.0 mA·cm^{-2}, from the holding time in a 0.1 mol·l^{-1} KOH solution, are shown in Fig. 3.

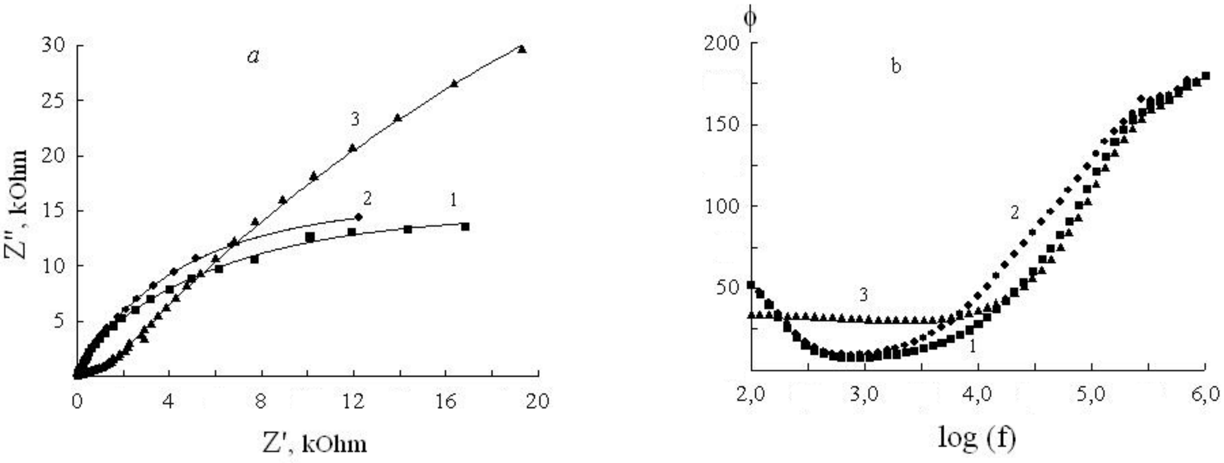
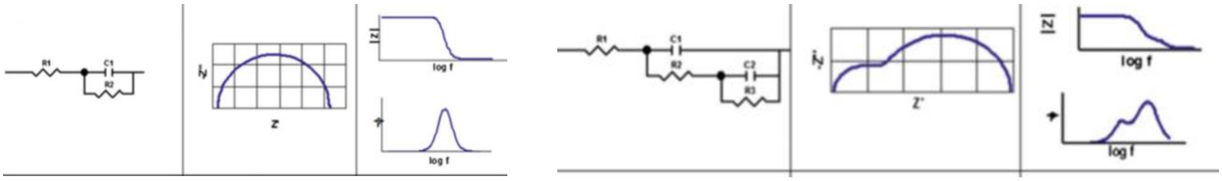


Fig. 3. Nyquist (a) and Bode (b) plots for tin-cobalt alloy samples containing 66.7 at.% tin versus holding time, min.: 20 (*1*), 40 (*2*) and 60 (*3*) in 0.1 mol·l^{-1} KOH solution.

When comparing the obtained dependencies with the diagnostic ones shown in Fig. 4 [21, 22], it can be concluded that an oxide-hydroxide layer of cobalt (II) has formed on the film surface. After a sufficiently long holding time (60 min.) of the sample in a 0.1 mol·l^{-1} KOH solution the electrical parameters of the coating (resistance and capacity) remain constant.



a b

Fig. 4. Equivalent impedance circuits of tin-cobalt alloy coatings and Nyquist and Bode diagnostic dependences when the coatings are kept in a 0.1 mol l^{-1} KOH solution for 20 (a) and 60 (b) min.

On samples of tin-cobalt alloy with a tin content of 33.3 at. %, obtained at a deposition current density of 7.5 mA·cm^{-2}, the Nyquist and Bode dependences have a similar character. In this case, only the numerical values of the parameters of the equivalent impedance circuit change: the contribution of the hydroxide layer resistance to the total corrosion resistance of such films is insignificant (< 5%). Based on the equality of the values of the stationary electrode potentials of reactions (2) and (3), we can write the reactions:

$$Sn = Sn^{2+} + e^-,$$
$$E_2 = -0.136 + 0.0291 \lg [Sn^{2+}], \qquad (2)$$

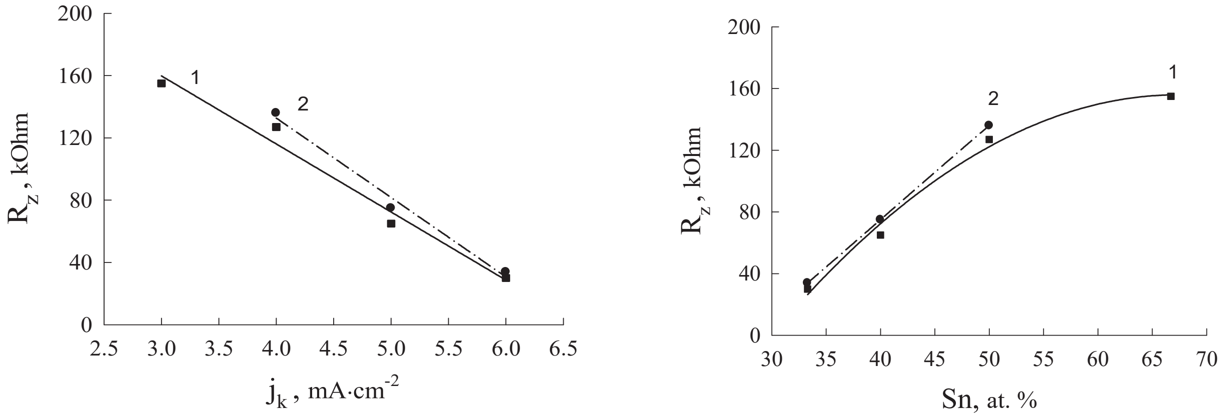
$$Co = Co^{2+} + e^-,$$
$$E_3 = -0.277 + 0.0291 \lg [Co^{2+}], \qquad (3)$$

which can occur on the surface of a tin-cobalt alloy in a 0.1 mol·L^{-1} KOH solution (pH 12.7), it can be shown that under these conditions, corrosion of the tin-cobalt alloy coating occurs due to the dissolution of cobalt, since the value of lg ([Sn^{2+}]/[Co^{2+}]) is equal to −4.85, that is, in the studied solution the concentration of ions [Co^{2+}] >> [Sn^{2+}]. According to the Pourbaix diagram of the cobalt – water and tin – water systems [23], in the range of values of stationary electrode potentials E_2 and E_3, equal to, depending on the tin content in the tin-cobalt alloy, −0.02 −0.08 V and −0.23 −0.34 V (table) in a 0.1 mol·l^{-1} KOH solution (pH 12.7), a stable hydroxide film consisting of cobalt hydroxide $Co(OH)_2$ is formed on the surface of the coatings. The dissolution of cobalt with the formation of hydroxide $Co(OH)_2$ most likely occurs by an electrochemical mechanism according to the reaction:

$$Co + 2H_2O = Co(OH)_2 + 2H^+ + 2e^-,$$
$$E_4 = 0.095 - 0.0581pH \qquad (4)$$

The steady-state electrode potential of reaction (4) under these conditions (pH 12.7) is −0.643 V. The formation of a poorly soluble compound of hydroxide $Co(OH)_2$ (SE(solubility equilibrium) = 2.5 10^{-16}) on the surface of the tin-cobalt alloy leads to passivation of the coating surface and, consequently, to stabilization of the steady-state potential of the electrode. Tin in the tin-cobalt alloy in 0.1 mol·l^{-1} KOH solution (pH 12.7) is practically insoluble. The resulting hydrogen ions are then reduced on tin. It can be assumed that the processes of formation and growth over time of the hydroxide layer of cobalt (II) on the alloy surface are accompanied by changes in other characteristics of the coatings, such as, the resistance of the coating, the capacity of the double electric layer and the value of the specific surface. The dependence of the coating resistance measured by impedance spectroscopy on the current density of its production and the holding time in a 0.1 mol·l^{-1} KOH solution is shown in Fig. 5a, from which it is evident that the coating corrosion resistance decreases with increasing current density and depends insignificantly on the holding time of the sample in the solution. At the same time, the coating corrosion resistance R_z increases with increasing tin content in the alloy (Fig. 5b) and is practically independent of the holding time in a 0.1 mol·l^{-1} KOH solution. Obviously, such a dependence of the coating corrosion resistance R_z on the current density is due to a decrease in the tin content in the coating with increasing current density.

Holding tin-cobalt alloy coatings in an alkaline electrolyte leads to an increase in the corrosion resistance of the electrode. This is accompanied by a shift in the steady-state potential to more positive values.



a b

Fig. 5. Dependence of corrosion resistance of tin-cobalt alloy coatings on current density (a) and tin content in the alloy (b); holding time in 0.1 mol·l^{-1} KOH solution, min.: 20 (1), 40 (2).

Table 1.

Electrocatalytic and corrosion characteristics of tin-cobalt alloys.

Sn, at.%	E_{st}, V	$\eta_{j=10}$, V	R_Z, kOhm	lgj_{corr}, A·cm^{-2}
66.7	-0.34	1.4	150	-7.35
40.0	-0.36	0.8	71	-6.15
33.3	-0.23	0.6	46	-5.78

The corrosion current of tin-cobalt alloy coatings decreases from $1.6\cdot10^{-6}$ to $4.5\cdot10^{-8}$ A·cm^{-2} as the tin content increases, while the overvoltage of hydrogen ion reduction increases. Thus, an increase in the cobalt content leads to an increase in the electrocatalytic properties of the alloy in the hydrogen evolution reaction, and an increase in the tin content leads to an improvement in the corrosion properties of the alloy.

CONCLUSIONS. Tin-cobalt alloy coatings were synthesized from a polyligand citrate-chloride electrolyte with a tin content of 5-85 wt. Since the deposition of tin (II) into a tin-cobalt alloy from a citrate-chloride electrolyte is limited by the preceding chemical reaction of dissociation of polyligand electrochemically inactive complexes $[\mathrm{SncitCl}_2]^{3-}$, which makes it possible to influence the chemical composition and functional properties of the resulting coatings by selecting the ratio of the electrolyte components and the deposition conditions. The surface morphology was studied using EDS and XRD methods, and the phase composition of the tin-cobalt alloy coatings was determined depending on the conditions of their preparation. It was found that with an increase in current density, the phase composition of the coating's changes. An increase in the tin content in the alloy improves the quality of the coatings, increases their corrosion resistance and reduces the electrocatalytic activity in the reaction of hydrogen ion reduction in an alkaline medium. The dynamics of the change in the parameters of the equivalent impedance circuit on tin-cobalt alloy coatings in 0.1 mol l^{-1} KOH solution was studied, which is associated with the formation of a hydroxide layer on the coating surface. The corrosion current decreases with increasing tin content in the alloy. It was found that the overvoltage of hydrogen evolution is lower, the higher the corrosion current, which can be a criterion for assessing the catalytic activity of the electrode.

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СИНТЕЗ, КОРОЗІЙНІ ТА ЕЛЕКТРОКАТАЛІТИЧНІ ВЛАСТИВОСТІ ПОКРИТТІВ СПЛАВОМ ОЛОВО – КОБАЛЬТ

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Синтезовано покриття сплаву олово – кобальт із полілігандного цитратно-хлоридного електроліту. Вміст олова в покриттях сплаву олово – кобальт залежить від параметрів їхнього осадження і змінюється в широкому діапазоні від 5.0 до 85.0 мас. %. Осадження олова (II) у сплав олово – кобальт із цитратно-хлоридного електроліту лімітується попередньою хімічною реакцією дисоціації полілігандних електрохімічно неактивних комплексів $[\mathrm{SncitCl}_2]^{3--}$, що дозволяє шляхом вибору співвідношення компонентів електроліту та умов осадження впливати на хімічний склад і функціональні властивості одержуваних покриттів. Методами *EDS* і *XRD* досліджено морфологію поверхні, встановлено хімічний та фазовий склад покриттів олово – кобальт залежно від умов їхнього отримання. Збільшення вмісту олова в сплаві покращує якість покриттів, підвищує їхній корозійний опір і зменшує електрокаталітичну активність у реакції відновлення іонів водню в лужному середовищі.

Вивчено динаміку зміни параметрів еквівалентної схеми імпедансу на покриттях сплавом олово – кобальт зі вмістом 33.3, 40.0 і 66.7 ат. % олова в 0.1 моль·л$^{-1}$ розчині KOH. Показано, що динаміка зумовлена утворенням гідроксидного шару кобальту (II) на поверхні покриттів. Методом імпедансної спектроскопії підтверджено утворення гідроксидного шару на поверхні покриттів у лужному середовищі. Виходячи з рівності значень стандартних електродних потенціалів олова (II) та кобальту (II) у водних розчинах, показано, що за цих умов корозія покриття сплаву олово – кобальт відбувається внаслідок розчинення кобальту з утворенням на поверхні сплаву стійкої плівки гідроксиду кобальту $Co(OH)_2$. Із вольт-амперних залежностей розраховано показники корозійної стійкості та електрокаталітичної активності покриттів у реакції відновлення іонів водню в лужному середовищі. Показано, що витримка покриттів у 0.1 моль·л$^{-1}$ розчині KOH призводить до збільшення їхнього корозійного опору й зменшення струму корозії. При підвищенні вмісту олова в сплаві струм корозії зменшується від $3{\cdot}10^{-6}$ до $1{\cdot}10^{-8}$ А·см$^{-2}$. Перенапруга реакції виділення водню при струмі реакції 10 мА·см$^{-2}$ зростає з підвищенням вмісту олова в сплаві від 0.6 В до 1.4 В. Встановлено антибатну залежність перенапруги виділення водню на покриттях сплаву олово – кобальт від струму корозії. Перенапруга тим менша, що більший струм корозії.

Ключові слова: електроосадження, олово-кобальтовий сплав, цитратно-хлоридний електроліт, корозійна стійкість, електрокаталітична активність.

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